PHOSPHINE-SUPPORTED ORGANO MANGANESE COMPLEXES
CHEMISTRY OF MANGANESE COMPLEXES CONTAINING METAL–CARBON, METAL–SILICON, AND METAL–HYDRIDE LINKAGES

By

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TITLE: Chemistry of Manganese Complexes Containing Metal–Carbon, Metal–Silicon, and Metal–Hydride Linkages

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Lay Abstract

The focus of this work is the synthesis and investigation of manganese-containing complexes with Mn–P, Mn–C, Mn–H, and/or Mn–Si linkages. Many of these complexes feature unusual bonding motifs, including the first group 7 complexes bearing an unstabilized silylene (:SiR₂) ligand and the first 1st row transition metal complexes bearing an unstabilized silene (R₂Si=CR₂) ligand. Variable temperature Nuclear Magnetic Resonance (NMR) spectroscopy and X-ray crystallography were employed to investigate the structures of these complexes, while Density Functional Theory (DFT) calculations and trapping experiments were employed to understand the mechanisms for various unusual chemical transformations. Some of the complexes were evaluated for activity towards catalytic hydrosilylation of ethylene. This work provides valuable insights to unusual metal–ligand bonding motifs and reactions, and as such contributes to the fundamental understanding of organometallic chemistry.
Abstract

The solid state structures and the physical, solution magnetic, solid state magnetic, and spectroscopic (NMR and UV/Vis) properties of a range of oxygen- and nitrogen-free dialkylmanganese(II) complexes are reported, and the solution reactivity of these complexes towards H₂ and ZnEt₂ is described. The dialkyl compounds investigated are [{Mn(μ-CH₂SiMe₃)₂}∞] (1), [{Mn(CH₂CMe₃)(μ-CH₂CMe₃)₂}₂{Mn(μ-CH₂CMe₃)₂Mn}] (2), [Mn(CH₂SiMe₃)₂(dmpe)] (3) (dmpe = 1,2-bis(dimethylphosphino)ethane), [{Mn(CH₂CMe₃)₂(μ-dmpe)}₂] (4), [{Mn(CH₂SiMe₃)(μ-CH₂SiMe₃)}₂(μ-dmpe)] (5), [{Mn(CH₂CMe₃)(μ-CH₂CMe₃)}₂(μ-dmpe)] (6), [{Mn(CH₂SiMe₃)(μ-CH₂SiMe₃)]₂(μ-dmpm)] (7) (dmpm = bis(dimethylphosphino)methane), and [{Mn(CH₂CMe₃)(μ-CH₂CMe₃)}₂(μ-dmpm)] (8). Syntheses for 1-4 have previously been published, but the solid state structures and most properties of 2-4 had not been described. Compounds 5 and 6, with a 1:2 dmpe:Mn ratio, were prepared by reaction of 3 and 4 with base-free 1 and 2, respectively. Compounds 7 and 8 were accessed by reaction of 1 and 2 with 0.5 or more equivalents of dmpm per manganese atom. An X-ray structure of 2 revealed a tetrametallic structure with two terminal and six bridging alkyl groups. In the solid state, bis(phosphine)-coordinated 3-8 adopted three distinct structural types: (a) monometallic [LMnR₂], (b) dimetaltic [R₂Mn(μ-L)₂MnR₂], and (c) dimetaltic [{RMn(μ-R)}₂(μ-L)] (L = dmpe or dmpm). Compound 3 exhibited particularly desirable properties for an ALD or CVD precursor, melting at 62-63 °C, subliming at 60 °C (5 mTorr), and showing negligible decomposition after 24 h at 120 °C. Comparison of variable temperature solution and solid state magnetic data provided insight into the solution structures of 2-8. Solution reactions of 1-8 with H₂ yielded manganese metal, demonstrating the thermodynamic feasibility of the key reaction steps required for manganese(II) dialkyl complexes to serve, in combination with H₂, as precursors for metal ALD or pulsed-CVD. By contrast, the solution reactions of 1-8 with ZnEt₂ yielded a zinc-manganese alloy with an approximate 1:1 Zn:Mn ratio.
Wilkinson’s manganese(I) ethylene hydride complex *trans*-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) can react as a source of a low-coordinate manganese(I) ethyl complex. This is illustrated in the reactivity of 10 towards a variety of reagents in this work (*vide infra*). The proposed low-coordinate intermediate, [(dmpe)$_2$MnEt] (13), was not observed spectroscopically, but could be trapped using isonitrile ligands; reaction of 10 with CNR (R = 'Bu, o-xylyl) afforded the manganese(I) ethyl complexes [(dmpe)$_2$MnEt(CNR)] (14a: R = 'Bu, 14b: R = o-xylyl). Ethyl complex 14a did not react further with CN'Bu at 80 °C. By contrast, complex 14b reacted with excess o-xylyl isonitrile to form 1,1 insertion products, including the iminoacyl complex [(dmpe)Mn(CNXyl)$_3$]{C(=NXyl)CEt(=NXyl)} (15, Xyl = o-xylyl). Complexes 14a-b and 15, as well as previously reported 10, were crystallographically characterized, and DFT calculations were employed to probe the accessibility of *cis* ethylene hydride and ethyl isomers of 10.

Reaction of the ethylene hydride complex *trans*-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with H$_2$SiEt$_2$ at 20 °C afforded the silylene hydride [(dmpe)$_2$MnH(=SiEt$_2$)] (16$^{\text{Et2}}$) as the *trans* isomer. By contrast, reaction of 10 with H$_2$SiPh$_2$ at 60 °C afforded [(dmpe)$_2$MnH(=SiPh$_2$)] (16$^{\text{Ph2}}$) as a mixture of the *cis* (major) and *trans* (minor) isomers, featuring a Mn–H–Si interaction in the former. The reaction to form 16$^{\text{Ph2}}$ also yielded [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (18$^{\text{Ph2}}$); [(dmpe)$_2$MnH$_2$(SiHR$_2$)] {R = Et (18$^{\text{Et2}}$) and Ph (18$^{\text{Ph2}}$)} were accessed cleanly by reaction of 16$^{\text{R2}}$ with H$_2$. Both 16$^{\text{Et2}}$ and 16$^{\text{Ph2}}$ engaged in unique reactivity with ethylene, generating the silene hydride complexes *cis*-[(dmpe)$_2$MnH(R$_2$Si=CHMe)] {R = Et (19$^{\text{Et2}}$) and Ph (19$^{\text{Ph2}}$)}. Compounds *trans*-16$^{\text{Et2}}$, *cis*-16$^{\text{Ph2}}$, and 19$^{\text{Ph2}}$ were crystallographically characterized, and bonding in 16$^{\text{Et2}}$ and 19$^{\text{Et2}}$ was probed computationally.

*trans*-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) reacted with primary hydrosilanes H$_3$SiR (R = Ph, 'Bu) at 60 °C to afford ethane and the manganese disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] (20$^{\text{Ph}}$: R = Ph, 20$^{\text{Bu}}$: R = 'Bu). 20$^R$ reacted with ethylene to form silene hydride complexes [(dmpe)$_2$MnH(RHSi=CHMe)] (19$^{\text{Ph,H}}$: R = Ph, 19$^{\text{Bu,H}}$: R =
Compounds \(19^{R,H}\) reacted with a second equivalent of ethylene to generate \([(\text{dmpe})_2\text{MnH(ReSi=CHMe)}]\) \(19^{\text{Ph,Et}}\): \(R = \text{Ph}\), \(19^{\text{Bu,Et}}\): \(R = "\text{Bu}\)\), resulting from apparent ethylene insertion into the silene Si–H bond. Furthermore, in the absence of ethylene, silene complex \(19^{\text{Bu,H}}\) slowly isomerized to the silylene hydride complex \([(\text{dmpe})_2\text{MnH(=SiEt}^n\text{Bu)}]\) \(16^{\text{Bu,Et}}\). Reactions of \(20^R\) with ethylene likely proceed via low-coordinate silyl \([(\text{dmpe})_2\text{Mn(SiH}_2\text{R})]\) \(17^{\text{Ph}}\): \(R = \text{Ph}\), \(17^{\text{Bu}}\): \(R = "\text{Bu}\)\) or silylene-hydride \([(\text{dmpe})_2\text{MnH(=SiHR)}]\) \(16^{\text{Ph,H}}\): \(R = \text{Ph}\), \(16^{\text{Bu,H}}\): \(R = "\text{Bu}\)\) intermediates accessed from \(20^R\) by \(\text{H}_3\text{SiR}\) elimination. DFT calculations and high temperature NMR spectra support the accessibility of these intermediates, and reactions of \(20^R\) with isonitriles or \(N\)-heterocyclic carbenes yielded the silyl isonitrile complexes \([(\text{dmpe})_2\text{Mn(SiH}_2\text{R})(\text{CN}R')]\) \(21a-d\): \(R = \text{Ph or "Bu; R'} = o\text{-xylyl or 'Bu}, and \(\text{NHC}\)-stabilized silylene-hydride complexes \([(\text{dmpe})_2\text{MnH(=SiHR(NHC)}]\) \(22a-d\): \(R = \text{Ph or "Bu; NHC = 1,3-diisopropylidazolin-2-ylidene or 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene), respectively, all of which were crystallographically characterized.

Manganese silyl dihydride complexes \([(\text{dmpe})_2\text{MnH}_2(\text{SiHR}_2)]\) \(R = \text{Ph (18}^{\text{Ph2}}\) or Et \(18^{\text{Et2}}\)\) and \([(\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{R})]\) \(R = \text{Ph (18}^{\text{Ph}}\) or "Bu \(18^{\text{Bu}}\)\) were generated by exposure of silylene hydride complexes, \([(\text{dmpe})_2\text{MnH(=SiR}_2)]\) \(16^{\text{R2}}\), and disilyl hydride complexes, \([(\text{dmpe})_2\text{MnH(SiH}_2\text{R}_2)]\) \(20^R\), respectively, to \(\text{H}_2\) at room temperature. In solution, \(18^R\) and \(18^{\text{R2}}\) exist as an equilibrium mixture of a \textit{central} isomer with a meridional H–Si–H arrangement of the silyl and hydride ligands \{this isomer may be considered to contain an \(\eta^3\)-coordinated silicate (\(\text{H}_2\text{SiR}_3\)) anion\}, and a \textit{transH}Si isomer with \textit{trans}-disposed hydride and nonclassical hydrosilane ligands (the latter is the result of significant but incomplete hydrosilane oxidative addition). Additionally, DFT calculations indicate the thermodynamic accessibility of \textit{lateralH} and \textit{transH} isomers with \textit{cis}- and \textit{trans}-disposed silyl and dihydrogen ligands, respectively. Compounds \(18^{\text{Ph2}}\) and \(18^{\text{Ph}}\) crystallized as the \textit{central} isomer, whereas \(18^{\text{Bu}}\) crystallized as the \textit{transH}Si isomer. Bonding in the \textit{central} and \textit{transH}Si isomers of \(18^R\) and \(18^{\text{R2}}\) was further investigated through \(^{29}\text{Si}\	ext{edited}^{1}\text{H–}^{1}\text{H COSY solution NMR experiments to determine both the sign and magnitude of }J_{29\text{Si},1\text{H}}\) coupling (negative and positive values of \(J_{29\text{Si},1\text{H}}\)
are indicative of dominant 1-bond and 2-bond coupling, respectively). These experiments afforded $J_{29Si,1H}$ coupling constants of $-47$ Hz for $\eta^3-(H_2SiR_3)$ in the central isomer of $18^{E12}$ (calcd. $-40$ to $-47$ for $18^R$ and $18^{R2}$), $-38$ to $-54$ Hz for $\eta^2-(R_3Si-\cdots H)$ in the transHSi isomer of $18^R$ and $18^{R2}$ (calcd. $-26$ to $-47$ Hz), and $5$ to $9$ Hz for the terminal manganese hydride ligand in the transHSi isomer of $18^{E12}$, $18^{Ph}$, and $18^{Bu}$ (calcd. $12$ to $14$ Hz for $18^R$ and $18^{R2}$), experimentally supporting the nonclassical nature of bonding in the central and transHSi isomers.

Exposure of disilyl hydride complexes $20^R$ to diisopropylcarbodiimide $\{C(N^{i}Pr)_2\}$ afforded manganese(I) amidinylsilyl complexes $[(\text{dmpe})_2Mn{\kappa^2-SiHR(N^{i}PrCHN^{i}Pr)}]$ ($R = \text{Ph}$ ($25^{Ph,H}$) or $\text{Bu}$ ($25^{Bu,H}$}). DFT calculations and analysis of XRD bond metrics suggest that the structure of $25^{R,H}$ involves a contribution from a resonance structure featuring a neutral base-stabilized silylene and an anionic amido donor on manganese. Reactions of $20^R$, as well as the silylene hydride complex $16^{E12}$, with CO yielded the manganese(I) formate complex $\text{trans-}[(\text{dmpe})_2Mn(CO)(\kappa^1-O_2CH)]$ ($26$), with a polysiloxane byproduct. Compound $26$ was found to undergo reversible CO elimination at room temperature, and was only stable under an atmosphere of CO$_2$. Complexes $25^{R,H}$ and $26$ were crystallographically characterized.

Silyl, silylene, and silene complexes in this work were accessed via reactions of $[(\text{dmpe})_2MnH(C_2H_4)]$ ($10$) with hydrosilanes, in some cases followed by ethylene. Therefore, ethylene (C$_2$H$_4$ and C$_2$D$_4$) hydrosilylation was investigated using $[(\text{dmpe})_2MnH(C_2H_4)]$ ($10$) as a pre-catalyst, resulting in stepwise conversion of primary to secondary to tertiary hydrosilanes. Various catalytically active manganese-containing species were observed during catalysis, including silylene and silene complexes, and a catalytic cycle is proposed. The proposed catalytic cycle is unusual due to the involvement of silylene hydride and silene hydride complexes, potentially as on-cycle species.

The reaction of $[(\text{dmpe})_2MnH(C_2H_4)]$ ($10$) with H$_2$ at 60 °C afforded ethane and the dihydrogen hydride complex $[(\text{dmpe})_2MnH(H_2)]$ ($11$), which has previously been
prepared by an alternative route. Complex 10 reacted with hydroborane reagents 9-BBN or HBMes₂ at 60 °C to afford EtBR₂ and Mn(I) borohydride complexes [(dmpe)₂Mn(μ-H)₂BR₂] (29: R₂ = C₈H₁₄, 30: R = Mes); two intermediates were observed in each of these reactions. Deuterium labelling experiments using the deuterated hydroborane DBMes₂ suggest that this reaction proceeds via the 5-coordinate ethyl isomer of 10; [(dmpe)₂MnEt] (13). By contrast, exposure of 10 to BH₃·NMe₃ required a higher temperature (90 °C) to yield [(dmpe)₂Mn(μ-H)₂BH₂] (28), and ethylene was formed as the reaction byproduct; this reaction presumably proceeded by ethylene substitution. Deuterium incorporation into both the MnH and BH environments of 28 was observed under an atmosphere of D₂ at 90 °C. Reactions of 10 with free dmpe yielded ethylene and a mixture of [{(dmpe)₂MnH}₂(μ-dmpe)] (31) and [(dmpe)₂MnH(κ¹-dmpe)] (32), which could be isolated by washing/recrystallization or sublimation, respectively. Similar reactivity was observed between 10 and HPPh₂, which afforded ethylene and [(dmpe)₂MnH(HPPh₂)] (33) at 90 °C. Exposure of 10 to HSnPh₃ yielded the manganese(II) stannyl hydride complex [(dmpe)₂MnH(SnPh₃)] (34) along with ethylene and, presumably, additional unidentified products. However, the mechanism for formation of 34 is unclear, it could not be isolated in pure form due to decomposition to form various species including SnPh₄, and the mechanism of the decomposition process remains obscure. Previously reported complex 11, along with new complexes 28-31 and 33-34, were crystallographically characterized.

This work provides valuable insights to unusual metal–ligand bonding motifs and reactions, and as such contributes to the fundamental understanding of organometallic chemistry.
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Let me Rephrase That – C. Montgomery Burns
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(trans-10)

(11)

14a: R = ‘Bu
14b: R = o-xylyl

15

16^{Ph_2}: R = R' = Ph
16^{Et_2}: R = R' = Et
16^{Ph,H}: R = Ph, R' = H
16^{Bu,H}: R = "Bu, R' = H
16^{Bu,Et}: R = "Bu, R' = Et

18^{Ph_2}: R = R' = Ph
18^{Et_2}: R = R' = Et
18^{Ph}: R = Ph, R' = H
18^{Bu}: R = "Bu, R' = H
18^{Ph,Et}: R = Ph, R' = Et
18^{Bu,Et}: R = "Bu, R' = Et

additional isomers calculated
19\textsubscript{\textit{Ph}:} \( R = R' = \text{Ph} \)
19\textsubscript{Et}: \( R = R' = \text{Et} \)
19\textsubscript{Ph,H}: \( R = \text{Ph}, R' = \text{H} \)
19\textsubscript{Bu,H}: \( R = \text{"Bu}, R' = \text{H} \)
19\textsubscript{Ph,Et}: \( R = \text{Ph}, R' = \text{Et} \)
19\textsubscript{Bu,Et}: \( R = \text{"Bu}, R' = \text{Et} \)

20\textsubscript{Ph}: \( R = \text{Ph} \)
20\textsubscript{Bu}: \( R = \text{"Bu} \)

21a: \( R = \text{Ph}, R' = \text{o-xylyl} \)
21b: \( R = \text{"Bu}, R' = \text{o-xylyl} \)
21c: \( R = \text{Ph}, R' = \text{Bu} \)
21d: \( R = \text{"Bu}, R' = \text{Bu} \)

22a: \( R = \text{Ph}, R' = \text{\textit{i-Pr}} \text{NHC} \)
22b: \( R = \text{"Bu}, R' = \text{\textit{i-Pr}} \text{NHC} \)
22c: \( R = \text{Ph}, R' = \text{Me} \text{NHC} \)
22d: \( R = \text{"Bu}, R' = \text{Me} \text{NHC} \)

25\textsubscript{Ph,H}: \( R = \text{Ph} \)
25\textsubscript{Bu,H}: \( R = \text{"Bu} \)

26: \( \text{Mn} \)
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Key Intermediates Calculated by DFT

- (cis-10)
- (12)
- (13)
- (17R)
- (23R)
- (24R)

additional isomers calculated
List of Abbreviations, Acronyms, and Symbols

General (acronyms)

CIF – Crystallographic Information File
CMOS – complementary metal-oxide semiconductor
CSD – Cambridge Structural Database
DRAM – dynamic random-access memory
ESI – electronic supporting information
HOMO – highest occupied molecular orbital
LPV – low pressure/vacuum
LUMO – lowest unoccupied molecular orbital
MIM – metal-insulator-metal
MOS – metal-oxide-semiconductor
m.p. – melting point
NIR – near-infrared
n.o. – not observed
OA – oxidative addition
o.d. – outer diameter
RE – reductive elimination
SG – special glass
T – temperature
TFEL – thin-film electroluminescent

TIP – temperature independent paramagnetism

UHAR – ultrahigh aspect ratio

UHV – ultra-high vacuum

UV – ultraviolet (radiation)

u. p. – unidentified product

**General (symbols)**

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<tr>
<th>Symbol</th>
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<tr>
<td>$\kappa^n$</td>
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*a Symbols related to DFT, IR spectroscopy, NMR spectroscopy, UV/Vis spectroscopy, and magnetism are listed below (the latter is listed under ‘SQUID’).*
‡ – transition state

**Units**

Å – angstrom

A (mA) – ampere (milliampere)

atm – standard atmosphere

BM – Bohr magneton

°C – degrees Celsius

deg or ° – degree

g (mg) – gram (milligram)

h – hour

Hz (MHz) – hertz (megahertz)

J (kJ) – Joule (kilojoule)

K – Kelvin

L (mL) – litre (millilitre)

m (nm, μm, mm, cm) – metre (nanometre, micrometre, millimetre, centimetre)

mol (mmol) – mole (millimole)

mol% – mole percent

M (μM, mM) – molarity (micromolarity, millimolarity)

Oe – oersted

ppm – parts per million

lx
s (ms) – second (millisecond)

Torr (mTorr) – torr (millitorr)

V (kV) – volts (kilovolts)

W (kW) – Watts (kilowatts)

**Equipment and Techniques (abbreviations, acronyms, and symbols)**

ALD – Atomic Layer Deposition

Anal. – combustion elemental analysis results

CVD – Chemical Vapour Deposition

DFT – Density Functional Theory

$\Delta \rho_n$ – deformation density

$\psi_n$ – wavefunction

ADF – Amsterdam Density Functional

BSSE – basis set superposition error

D3-BJ – Grimme’s D3 dispersion correction method with Becke-Johnson damping

DZP – double-$\zeta$ basis set with one polarization function

ETS-NOCV – extended transition state method for energy decomposition analysis with natural orbitals for chemical valence

GUI – graphical user interphase

NBO – natural bond order

NOCV – natural orbitals for chemical valence
PBE – Perdew-Burke-Ernzerhof exchange and correlation functional

PBE0 – hybrid Perdew-Burke-Ernzerhof exchange and correlation functional

SCF – self-consistent field

TZ2P – triple-ζ basis set with two polarization functions

TZ2P-J – triple-ζ basis set with two polarization functions with additional steep basis functions

ZORA – scalar zeroth-order regular approximation for relativistic effects

ZPE – zero point energy

EPR – electron paramagnetic resonance (spectroscopy)

FT-IR – Fourier-transform infrared (spectroscopy)

IR – infrared (spectroscopy)

ν(XY) – frequency of the stretch vibration arising from atoms X and Y

NMR – nuclear magnetic resonance (spectroscopy)

app. – apparent

br. – broad

d – doublet

m – multiplet

p – pentet

q – quartet

s – singlet
sat. – satellite
t – triplet
v. – very
δ – chemical shift

\( J_{x,y} \) – coupling constant between nuclei \( x \) and \( y \), where the number of bonds is not specified

\( nJ_{x,y} \) – \( n \)-bond coupling constant between nuclei \( x \) and \( y \)

1D – one dimensional

2D – two dimensional

COSY – correlation spectroscopy

uDEFT – uniform driven equilibrium Fourier transform

DEPTq – distortionless enhancement by polarization transfer including the detection of quaternary nuclei

DOSY – diffusion ordered spectroscopy

dqf – double quantum filter

EXSY – exchange spectroscopy

FID – free induction decay

HMBC – heteronuclear multiple bond correlation

HMQC – heteronuclear multiple quantum coherence

HSQC – heteronuclear single quantum coherence

INEPT – insensitive nuclei enhanced by polarization transfer
NOE – nuclear Overhauser effect

NOESY – nuclear Overhauser effect spectroscopy

ns – number of scans

$T_1$ relaxation – spin-lattice relaxation

$td1\text{ eff}$ – size of FID utilized for the $2^{nd}$ dimension in a 2D NMR experiment

$td2\text{ eff}$ – size of FID utilized for the $1^{st}$ dimension in a 2D NMR experiment

TOCSY – total correlation spectroscopy

PEALD – plasma enhanced atomic layer deposition

PVD – physical vapour deposition

PXRD – powder X-ray diffraction

SQUID – superconducting quantum interference device

MPMS: Magnetic Properties Measurement System

$\mu_B$ – effective magnetic moment

$J$ – exchange coupling constant (for antiferromagnetic coupling)

$\rho$ – fraction paramagnetic impurity

$\chi$ – magnetic susceptibility

$100R$ – Measure of goodness of fit ($R = \left[(\sum\chi_{obs}-\chi_{calc})^2/(\sum\chi_{obs})^2\right]^{1/2}$)

$\theta$ – Weiss temperature or Weiss-like temperature correction

UV/Vis – ultraviolet and visible (Spectroscopy)
$\lambda_{\text{max}}$ – wavelength of maximum intensity

Vis – visible spectroscopy

XPS – X-ray photoelectron spectroscopy

XRD – X-ray diffraction

CCD – charge coupled device

**Chemical species (compounds, ligands, and substituents)**

acac – acetylacetonate

Ad – adamantyl

AMD – amidinate

Ar – aryl

  Dipp – 2,6-diisopropylphenyl

  Dur – duryl (2,3,5,6-tetramethylphenyl)

  $i$ – ipso

  $m$ – meta

  Mes – mesityl

  Naph – naphthyl

  $o$ – ortho

  $p$ – para

  Ph – phenyl

  tol – tolyl (methylphenyl)
Trip – 2,4,6-triisopropylphenyl

xyl – xylyl

9-BBN – borabicyclo(3.3.1)nonane

bipy – 2,2’ bipyridine

Bis(phosphines)

dope – 1,2-bis(diethylphosphino)ethane

dfpe – 1,2-bis(ferrocenylphosphino)ethane

dmpe – 1,2-bis(dimethylphosphino)ethane

dmpm – 1,2-bis(dimethylphosphino)methane

dmpp – 1,2-bis(dimethylphosphino)propane

dppe – 1,2-bis(diphenylphosphino)ethane

dppm – 1,2-bis(diphenylphosphino)methane

dtbpm – 1,2-bis(di-tert-butylphosphino)methane

Butyl groups

"Bu – n-butyl (n = normal)

‘Bu – tert-butyl

C_x – specific carbon label

C_{br} – carbon bridging between two metal atoms

C_{term} – carbon bound to a single metal atom

COD – 1,5-cyclooctadiene
Cp – cyclopentadienyl

\[ \text{Cp}^* \rightarrow \text{C}_5\text{Me}_5 \]

\[ \text{Cp}^+ \rightarrow \text{C}_5\text{H}_2(\text{tBu})_3 \]

\[ \text{Cl}^5\text{Cp} \rightarrow \text{C}_5\text{Cl}_5 \]

\[ \text{Et}^5\text{Cp} \rightarrow \text{C}_5\text{H}_4\text{Et} \]

\[ \text{Et}^5\text{Cp} \rightarrow \text{C}_5\text{Et}_5 \]

\[ \text{EtMe}^4\text{Cp} \rightarrow \text{C}_5\text{Me}_4\text{Et} \]

\[ \text{Me}^6\text{Cp} \rightarrow \text{C}_5\text{H}_4\text{Me} \]

\[ \text{Me}^3\text{SiCp} \rightarrow \text{C}_5\text{H}_4(\text{SiMe}_3) \]

\[ \text{Me}^3\text{SiMeCp} \rightarrow \text{C}_5\text{H}_3\text{Me}(\text{SiMe}_3) \]

\[ \text{tBu}^5\text{Cp} \rightarrow \text{C}_5\text{H}_4(\text{tBu}) \]

Cy – cyclohexyl

DIBAL – diisobutylaluminum hydride

DME – 1,2-dimethoxyethane

dpm – dipivaloylmethanate

Et – ethyl

hex – 1-hexyl

hfac – hexafluoroacetylacetonate

L – general neutral ligand

LA – Lewis acid
Me – methyl

NHC – $N$-heterocyclic carbene

$^\text{iPr}$NHC – 1,3-diisopropylimidazolin-2-ylidene

$^\text{Me}$NHC – 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene

NHSi– $N$-heterocyclic silylene

pmdeta – pentamethyldiethylenetriamine

Propyl groups

$^\text{iPr}$ – $iso$-propyl

$^\text{nPr}$ – $n$-propyl ($n$ = normal)

Py – pyridinyl

R – general anionic organic substituent (typically an H, CR$_3$ or SiR$_3$ group)

tfac – trifluoroacetylacetonate

THF – tetrahydrofuran

TMEDA – N,N,N′,N′-tetramethylethylenediamine

Tp – hydrotris(pyrazolyl)borate, {HB(pz)$_3$}$^-$

Xyl – $o$-xylyl, 2,6-dimethylphenyl
Declaration of Academic Achievement

Dr. David J. H. Emslie was responsible for the synthesis and obtaining an X-ray crystal structure of dineopentylmanganese(II) (2). Dr. Preeti Chadha, as postdoctoral fellow in the Emslie group, was responsible for the synthesis and obtaining X-ray crystal structures of complexes \[\{(\mu\text{-dmpe})\text{Mn(CH}_2\text{CMe}_3)_2\}\] (4), \[\{(\mu\text{-dmpe})\text{Mn(CH}_2\text{CMe}_2)(\mu\text{-CH}_2\text{CMe}_3)\}\] (6), and \[\{(\mu\text{-dmpm})\text{Mn(CH}_2\text{CMe}_3)(\mu\text{-CH}_2\text{CMe}_3)\}\] (8) (for complex 8, one of two different structures was obtained by Dr. Chadha, and the other by the author). Dr. Hilary Jenkins (of the McMaster Analytical X-ray Diffraction Facility) was responsible for XRD crystal mounting, data acquisition, refinement, and structure solution for \[\{(\mu\text{-dmpe})\text{Mn(CH}_2\text{SiMe}_3)(\mu\text{-CH}_2\text{SiMe}_3)\}\] (5) and \[\{(\mu\text{-dmpm})\text{Mn(CH}_2\text{SiMe}_3)(\mu\text{-CH}_2\text{SiMe}_3)\}\] (7). Dr. James Britten (of the McMaster Analytical X-ray Diffraction Facility) was responsible for XRD refinement and structure solution for \[(\text{dmpe})\text{Mn(CNXyl)}_3\{\text{C(=NXyl)CEt(=NXyl)}\}\] (15), and Fang Yuan (a graduate student in the Mozharivskyj group at McMaster University) was responsible for XRD crystal mounting and data acquisition for \[(\text{dmpe})_2\text{MnEt(CNXyl)}\] (14b), \[(\text{dmpe})\text{Mn(CNXyl)}_3\{\text{C(=NXyl)CEt(=NXyl)}\}\] (15), \[(\text{dmpe})_2\text{MnH\{SiH}_n\text{Bu(}^{i}\text{PrNHC)\}}\] (22b), and \[(\text{dmpe})_2\text{MnH\{SiPh(MeNHC)\}}\] (22c). Dr. Paul Dube was responsible, in combination with the author, for obtaining SQUID data on complexes 2-8. Megan Fair was responsible for running combustion elemental analysis when carried out in-house. Dr. Allen Pauric was responsible for obtaining T1 relaxation times and attempting DOSY NMR measurements for \[\{(\mu\text{-dmpe})\text{Mn(CH}_2\text{CMe}_3)_2\}\] (4). Dr. Rana Sodhi (of Surface Interface Ontario) was responsible for obtaining XPS. Dr. Bob Berno created the pulse program for \[^{29}\text{Si_edited} \text{^1H-}^1\text{H COSY NMR spectroscopy. All other results were obtained by Jeffrey S. Price.}\]
Chapter 1:

Introduction

1.1 – Introductory Remarks

This thesis includes the synthesis of volatile manganese alkyl complexes as potential Atomic Layer Deposition (ALD) precursors, the synthesis and reactivity of manganese alkyl, hydride and silyl complexes (which could be potential Chemical Vapour Deposition (CVD) precursors), the synthesis of silylene and silene complexes, and manganese-catalyzed ethylene hydrosilylation. Therefore, the introduction is divided into the following topics:

1.2 – CVD and ALD Using Manganese Precursors

1.3 – Manganese Alkyl Complexes

1.4 – Manganese Hydride Complexes

1.5 – Manganese Silyl Complexes

1.6 – Silylene Complexes of Transition Metals

1.7 – Silene Complexes of Transition Metals

1.2 – CVD and ALD Using Manganese Precursors

Portions of this section have been reprinted (adapted) with permission from Emslie, D. J. H.; Chadha, P.; Price, J. S. Metal ALD and Pulsed CVD: Fundamental Reactions and Links with Solution Chemistry, Coord. Chem. Rev. 2013, 257, 3282-3296 (Copyright 2013 Elsevier B.V.), and Price, J. S.; Chadha, P.; Emslie, D. J. H. Base-Free and Bisphosphine Ligand Dialkylmanganese(II) Complexes as Precursors for Manganese Metal Deposition, Organometallics 2016, 35, 168-180 (Copyright 2016 American Chemical Society).
1.2.1 – Scope of Section

This section provides an introduction to the thin film deposition techniques of Chemical Vapour Deposition (CVD) and Atomic Layer Deposition (ALD), with a particular focus on deposition of elemental manganese. A review of thermal CVD and ALD using manganese-containing precursors is provided. Plasma enhanced CVD and ALD are beyond the scope. Nucleation issues are an important consideration in developing CVD or ALD reaction chemistry, but are also beyond the scope.

1.2.2 – Introductory Remarks on CVD and ALD

Deposition of thin films is an important area in materials science. Many different types of materials can be deposited as thin films including nitrides, carbides, oxides, and pure metals. Research in this field is often focused on applications related to microelectronics, and being able to prepare high quality thin films with a specific thickness is important as advances in this area are often driven by shrinking the size of the critical features (e.g. transistors and memory cells) in technological devices (e.g. microprocessors and memory). The breadth of research involved in thin film deposition is highlighted by the existence of dedicated peer-reviewed journals such as Thin Solid Films and Chemical Vapor Deposition.

While a variety of methods exist for depositing thin films (including wet chemical deposition, electrochemical deposition, and physical vapour deposition), the processes of Chemical Vapour Deposition (CVD) and Atomic Layer Deposition (ALD) are of particular interest in materials chemistry as methods to deposit films with predictable thicknesses and composition. Introductions to these techniques are provided in sections 1.2.3 and 1.2.4, respectively.

In CVD and ALD, particularly challenging targets are thin films of pure, elemental metals (which are often required for diffusion barriers, electronic contacts, resistors, interconnects, electrodes, reflective coatings, or protective coatings (those resistant to oxidation, corrosion, or abrasion)). For many metals, thermal CVD and ALD
processes have yet to be conceived. Furthermore, many of the existing methods for metal CVD or ALD suffer from limitations which preclude industrial applications, including poor physical properties and significant contamination (especially by carbon).\textsuperscript{1} Therefore, it is incumbent upon synthetic chemists to develop chemistry to enable new approaches in metal CVD and/or ALD.\textsuperscript{3}

1.2.3 – Introduction to Chemical Vapour Deposition (CVD)

Chemical Vapour Deposition (CVD) is a method for depositing thin films by decomposition of vapours of a volatile precursor at the surface of a heated substrate, where all by-products are volatile. CVD normally requires a carrier gas (usually inert, but sometimes a reactive gas) both to bring the precursor into the reactor, and to remove the volatile by-products from the reactor. Normally, a large excess of precursor is continuously allowed to flow over the substrate, and as time passes the deposited film becomes thicker (thus, the duration of precursor exposure, and the amount of precursor that reaches each point on the substrate surface, controls the film thickness). A variety of texts have been written which provide excellent overviews of the CVD process and its applications.\textsuperscript{4} While a variety of modifications of CVD exist, this introduction is focused exclusively on thermal CVD. This technique is generally utilized for deposition of thin films 0.1-10 μm in thickness, with thickness controlled by the vapour pressure, gas-flow rate, and deposition temperature, in addition to the duration of deposition (\textit{vide supra}). Some advantages of CVD are the potential to produce films of high density, purity, uniformity, reproducibility of thickness, and conformality (relative to non-vapour phase deposition techniques, but not relative to ALD; \textit{vide infra}). Other advantages are relatively low temperatures required for deposition, an easily adjustable deposition rate, good adhesion to a substrate, and high deposition rates.\textsuperscript{5}

Metal hydride complexes are one class of CVD precursor that has been investigated for deposition of elemental metals.\textsuperscript{6} The driving force for metal reduction in these complexes is often reductive elimination (sometimes bimolecular) of H\textsubscript{2}. A significant amount of work has been reported on Al\textsubscript{(s)} deposition\textsuperscript{7} from various amine
adducts of alane \((R_3N\cdot AlH_3)\)^8 or aluminaborane \(\{R_3N\cdot AlH_2(BH_4)\}\).^9 Al\(_\text{(s)}\) deposition by CVD has also been reported from alkyl hydride compounds such as Me\(_2\)AlH, though only under an atmosphere of H\(_2\).^10 Similarly, W\(_\text{(s)}\) deposition has been reported from mixed hydrocarbyl-hydride complexes \([\text{Cp}_2\text{WH}_2]\)^11 and \([\text{MeCp}_2\text{WH}_2]\)^12 under an atmosphere of H\(_2\).

1.2.4 – Introduction to Atomic Layer Deposition (ALD)

For many years, Physical Vapour Deposition (PVD) and CVD (vide supra) have been central techniques for the deposition of thin metal films with a broad range of applications. However, the directional nature of these methods can lead to difficulties in: (a) obtaining ultra-thin films of uniform thickness, and (b) deposition of conformal films within nano-scale high aspect ratio features (e.g. trenches or vias), and these difficulties are becoming increasingly significant in the microelectronics industry as a result of rapidly decreasing device (e.g. transistor or memory cell) dimensions. Furthermore, CVD suffers from: (a) the potential for particle formation due to reactions occurring in the vapour phase rather than on the substrate surface, (b) in the case of solid precursors, dependence of film growth rate on precursor particle size, and (c) unavailability of precursors for deposition of certain materials, including many of the transition metals.\(^{13,14}\)

Atomic Layer Deposition (ALD), sometimes referred to as Atomic Layer Epitaxy (ALE), is a technique related to CVD which largely overcomes the limitations outlined above, although the overall deposition rate is generally much lower than that of CVD. In ALD, a volatile metal precursor is employed, as in CVD, but in this case, the substrate temperature and precursor thermal stability are such that the precursor does not undergo thermal decomposition upon contact with the substrate. Instead, deposition is achieved by repeated alternating self-terminating surface-based reactions between a metal precursor and a co-reactant, at least one of which is adsorbed (through chemisorption or physisorption) on the substrate surface.\(^{13-17}\) In thermal ALD, the co-reactant is a ‘stable’ entity (e.g. H\(_2\), H\(_2\)O, O\(_2\) or O\(_3\)), while in plasma-enhanced ALD (PEALD), the co-reactant is plasma-generated (e.g. H, O or N atoms). Potential drawbacks of PEALD are that it
introduces additional complexity to an ALD reactor, exposure to plasma-generated ions and UV-radiation can cause damage to the substrate and/or the growing film, and conformal deposition inside high aspect ratio features is difficult; this is especially the case for metal deposition using hydrogen plasma, since hydrogen radicals have particularly high recombination rates on most metal surfaces. On the other hand, a major advantage of PEALD is that it can be used to deposit a range of materials at low temperature, due to the high reactivity of species such as atomic hydrogen, oxygen and nitrogen. In this thesis, only thermal ALD will be discussed, and from herein the term ALD is used to mean thermal ALD unless otherwise specified.

The reactions in ALD are designed to yield only volatile byproducts, and these byproducts, as well as excess metal precursor / co-reactant, are removed in inert gas purge steps between metal precursor and co-reactant pulses. The defining characteristic of ALD is that the metal precursor and the co-reactant are adsorbed and/or react with the surface in a self-limiting fashion. Therefore, so long as sufficient vapour doses of the metal precursor and co-reactant are delivered to ensure maximum surface coverage and complete reaction, the thickness of the deposited film will depend only on the number of precursor/purge/co-reactant/purge cycles, and the film will grow conformally on all exposed surfaces on which nucleation can occur, including the surfaces of high aspect-ratio features. If self-limiting behaviour cannot be achieved, the overall process is termed pulsed-CVD.

Although ALD offers advantages not conferred by pulsed-CVD, in both cases, the use of a metal precursor and a co-reactant provides access to a broader range of deposition chemistries than CVD involving thermal decomposition of a single metal precursor. Consequently, both ALD and pulsed-CVD provide the potential for deposition of materials that are inaccessible using single precursor CVD, as well as enhanced potential for the development of deposition reactions capable of operating at low temperature.
1.2.5 – Requirements for CVD and/or ALD Precursors

Both CVD and ALD rely upon delivery of a metal-containing precursor molecule to the surface of a substrate in the vapour phase, followed by reactivity (thermal decomposition or reaction with a co-reactant) to generate the desired material and volatile byproducts which are readily eliminated from the growing film. Consequently, ALD and CVD place strict requirements on the physical and chemical properties of metal precursors and co-reactants. In particular, metal precursors and (for ALD) co-reactants should exhibit:

- Volatility such that the precursor can be delivered below the temperature required for film deposition (for solid precursors used with an ALD reactor operating under non-UHV conditions, typical vapour pressures at the delivery temperature are in the 0.01 to 10 Torr range, preferably at least 0.1 Torr). It is also preferable that the precursor (and, for ALD, co-reactant) are sufficiently volatile to allow low-temperature ALD/CVD if the reactivity between the precursor, the co-reactant (for ALD), and the substrate is such that this can be achieved.

- For ALD, sufficiently high thermal stability and reactivity to ensure that ALD can be achieved at temperatures below the onset of CVD (the larger the ALD window, the better). A similar criterion will in some cases apply to pulsed-CVD.

- Long-term thermal stability at the temperature of the delivery bubbler.

- ALD/CVD reactivity that yields only volatile byproducts.

- Surface reactivity which allows adsorption and film growth on both the substrate material (in initial stages of film deposition) and the growing film material.

- Scaleable syntheses with reasonable overall yields.

- Low melting points are also desirable, since the use of liquid precursors helps to avoid particle incorporation, and to ensure uniformity in the amount of precursor and co-reactant delivered in each pulse (for solids, the amount of precursor or co-
reactant delivered in each pulse can depend on average particle size, which can vary significantly as precursor / co-reactant is consumed). With respect to the latter point, use of liquid precursors and co-reactants is less critical for ALD than for CVD, since film thickness will depend only on the number of reaction cycles, providing that sufficiently long precursor and co-reactant pulses are employed.

These requirements unavoidably curtail the complexity of ALD and CVD precursors and (for ALD) co-reactants. However, by the same token, the development of new ALD reactivity that is compatible with precursors and co-reactants that meet the above criteria presents a substantial and interesting challenge. This is especially the case for more difficult targets (e.g. metals currently inaccessible by ALD or low temperature ALD reactivities), and in many cases the development of new ALD or CVD reactivity must go hand in hand with the design of new precursors able to meet the requirements of the target reactivity.

1.2.6 – A Brief Introduction to Deposition of Elemental Metals by ALD or Pulsed-CVD

Relative to metal oxide and metal nitride ALD, examples of thermal ALD for metal deposition are far less common. In fact, as illustrated graphically in Figure 1.1, thermal ALD of metals has thus far mainly been achieved for the least electropositive transition metals: the noble metals, 1st row congeners of the noble metals, rhenium, the group 6 elements molybdenum and tungsten. The only group 3-5 transition metal to have been deposited by ALD is titanium.
Figure 1.1: Periodic table, not including hydrogen, halogens and noble gases, highlighting metals that have been deposited by thermal ALD or pulsed-CVD (only reports in peer-reviewed literature are included). Metals that have been deposited by ALD are enclosed by solid black boxes.\textsuperscript{b} Metals (or alloys) that have been deposited only by pulsed-CVD are enclosed by dashed black boxes. Atomic numbers are shown above the atom symbols and Pauling electronegativities are shown below (for values with two decimal places, the oxidation state is: I for groups 1 and 11, II for groups 2, 4-10 and 12, III for groups 3 and 13, and IV for group 14).\textsuperscript{21} Non-metals (including semi-metals) and elements without significant natural abundance are shown in white. The remaining elements are shaded.

\textsuperscript{b} References for elemental metal ALD of most of the elementals highlighted in Figure 1.1 can be found in ref. 19a. Since the publication of this review (in 2013), ALD processes have been reported for deposition of Al\textsubscript{(s)},\textsuperscript{19b} Ti\textsubscript{(s)},\textsuperscript{19c} Re\textsubscript{(s)},\textsuperscript{19d} Ag\textsubscript{(s)},\textsuperscript{19e} Au\textsubscript{(s)},\textsuperscript{19f} and Sn\textsubscript{(s)}.\textsuperscript{19g} In addition, Winter et al. has reported ALD-like deposition of elemental Cr\textsubscript{(s)} and Mn\textsubscript{(s)}, though this process only proceeded on Ru substrates and stopped after the substrate was completely covered.\textsuperscript{20}
From the above discussion, it follows that a major challenge in ALD is the development of suitable reaction chemistry for deposition of metals not yet accessed by ALD. However, even for metals that have previously been accessed by ALD, various features of the precursors, the deposition process, and/or the resulting films may prevent commercial application. These include: (a) difficulties in precursor scale-up, (b) insufficient precursor or co-reactant thermal stability, (c) an ALD temperature that is too high to be compatible with the desired substrate (temperatures of 200-400 °C are common), (d) an ALD temperature that causes agglomeration of thin metal films, (e) deposition of metal films containing impurities at levels that are unacceptable for the target application, (f) impractical or complex and costly deposition conditions (e.g. those involving extremely long pulse or purge durations, an unacceptably low growth rate, a very narrow ALD temperature window, injection of the precursor or co-reactant as a solution, or UHV deposition conditions), (g) an unacceptably long induction period prior to the onset of self-limiting film growth, (h) film growth that does not lead to continuous films at low film thicknesses (island growth), (i) film morphologies that do not provide the desired physical properties and performance, (j) poor adhesion between the deposited film and the underlying substrate, and (k) deposition of films that do not have the desired crystalline phase, crystal orientation, or level of crystallinity. Which of these potential limitations are relevant will depend on the metal being deposited and the target application.

Limitations (b)-(e) above can be related fairly directly to precursor, co-reactant and reaction byproduct volatility/thermal stability, and the reaction pathways occurring at the surface. By contrast, limitations (g-k) will be substrate specific and are less directly linked to the fundamental classes of chemical reaction involved in metal deposition. The development of new ALD methods that overcome limitations such as those outlined above is clearly an important goal, although in the case of substrate-specific behaviour, the development of multiple fundamentally different reaction chemistries, each with a different substrate scope, may be required. New ALD reaction chemistries that allow for straightforward and controlled addition of specific impurities via an ALD mechanism
may also be of interest. Furthermore, substrate-selective ALD/pulsed-CVD of metals (e.g. deposition on Pd and/or Pt rather than an glass, silica or a metal oxide surface,\textsuperscript{23,24} on H-terminated Si rather than OH-terminated SiO\textsubscript{2},\textsuperscript{25} or on substrates patterned with self-assembled polymer monolayers)\textsuperscript{26,27,28} is an active field of research with its own deposition chemistry requirements.

Metals deposited by ALD have a broad range of potential applications in the fields of microelectronics (microprocessors, memory devices etc.), flat panel displays, fuel-cells, solar cells, and catalysis.\textsuperscript{13,17} In the area of microelectronics, various potential applications of ALD metal films have been cited in the literature. These include:\textsuperscript{17} rear electrode materials for inverted TFEL devices or plugs for the UHAR contacts of advanced DRAM (Mo, W),\textsuperscript{29} positive channel MOS gate electrodes (Re, Ru, Rh, Ir, Pd, Pt),\textsuperscript{27} electrode materials in MIM capacitors for future DRAM (Ru, Ir),\textsuperscript{14,30} nanocrystals for non-volatile nanocrystal memory (W, Ru, Pd, Au),\textsuperscript{17} diffusion barriers, adhesion layers or seed layers for copper deposition (Ru, Os, Rh and others),\textsuperscript{30,31} precursors to CoSi\textsubscript{2}, NiSi or PtSi source and drain materials to replace TiSi\textsubscript{2} in MOS devices (generated by annealing Co, Ni or Pt metal films on silicon substrates),\textsuperscript{25,32,33} gate materials for CMOS devices (Pt),\textsuperscript{33} and interconnect wiring (Cu or Ag).\textsuperscript{34}

Elemental metals with low electronegativity pose a particular challenge, in that metal precursors usually contain the metal in a positive oxidation state, and reduction to the zero oxidation state becomes increasingly difficult as the metal becomes more electropositive (i.e. the potential for M\textsuperscript{x+}→M\textsuperscript{0} reduction becomes increasingly negative). In this regard, manganese is an interesting target for elemental ALD, given that it has an electronegativity of 1.55 (Pauling scale), which is higher than that of gr. 3-4 metals, but lower than that of gr. 8-11 metals. Manganese is also the only gr. 7-11 metal (not including radioactive Tc) for which thin film deposition of the elemental metal by ALD has not been reported (\textit{vide supra}). One of the most discussed applications of manganese in metal thin film deposition chemistry is formation of a diffusion barrier between silica and copper in microelectronics.\textsuperscript{35} These barriers (composed of manganese oxide, silicide,
and/or silicate) can be ‘self-formed’ by migration of Mn(0) from a deposited Cu/Mn alloy into the silica substrate,\(^\text{36}\) or from initial Mn(0) deposition onto a silica surface.\(^\text{37}\) While CVD of elemental manganese has been reported to form films of varying quality from a number of precursors (see section 1.2.7), no ALD method has yet been reported to produce high quality films of Mn(0); section 1.2.8.

Neutral homoleptic metal alkyl complexes are intriguing potential precursors for electropositive metal ALD because (a) the high reactivity of polar metal–alkyl bonds may provide access to low temperature reaction pathways for elemental metal deposition,\(^c\) (b) the metal-nitrogen and metal-oxygen bonds typically encountered in coordination complexes can be avoided, precluding metal oxide or nitride formation, and (c) the expected byproducts in reactions with hydride sources (alkanes; see Chapter 2) are highly unreactive and volatile (and therefore should be easily eliminated from the growing film).

Transition metal alkyl complexes have rarely been used as precursors for pulsed-CVD or ALD, although notable exceptions are \([\text{PtMe}_2(\text{COD})]\),\(^{39}\) and \([\text{MeCpPtMe}_3]\).\(^{40}\) Chapter 2 of this thesis will investigate the potential for neutral homoleptic alkylmanganese complexes, and Lewis base adducts thereof, to act as precursors in Mn\(_{(s)}\) deposition.

1.2.7 – Chemical Vapour Deposition Using Mn-containing Precursors

To our knowledge the first report of CVD using a manganese-containing precursor involved the deposition of Mn silicides MnSi and Mn\(_2\)Si\(_3\) (the deposited film contained a mixture of both) by Aylett and Colquhoun in 1977 from the volatile precursor \([(\text{CO})_5\text{Mn(SiH}_3\text{)}]\) (a in Figure 1.2).\(^{41}\) Manganese silicide (with varying Mn : Si stoichiometries) could also be deposited from CVD of \([\{(\text{OC})_5\text{Mn}\}_2(\mu-\text{SiH}_2)\] (b in Figure 1.2)\(^{42}\) or \([(\text{OC})_5\text{Mn(SiCl}_3\text{)}]\) (c in Figure 1.2)\(^{43,44}\) at temperatures ranging from 300-700 °C. Thin films of other manganese-containing species have been prepared from CVD using single-source precursors, including MnGe\(_{x(s)}\) (from

\(\text{c} \) Alkyl complexes of more electropositive metals are typically more reactivity towards \(\sigma\)-bond metathesis reactions; see ref. 38.
[(OC)$_3$Mn$_2$Ge{$\kappa^2$-CH$_2$(CMC)(CMC)CH$_2$})]; d in Figure 1.2, MnGa$_{(s)}$ (from [(OC)$_3$MnGaH$_2$(NMe$_3$)]; e in Figure 1.2, MnIn$_{(s)}$ (from [(OC)$_3$MnIn{$\kappa^2$-(CH)$_2$}{$\eta^2$}NMe$_2$$_2$)]; f in Figure 1.2, and MnF$_2$$_{(s)}$ (from [(TMEDA)Mn(hfac)$_2$]; g in Figure 1.2).

Figure 1.2: Single-source precursors used for CVD of Mn-containing thin films (not including elemental manganese).

In addition to using single-source precursors, Mn-containing thin films have also been deposited by simultaneous decomposition of multiple precursors, one of which is a volatile Mn-containing complex. Complexes used as Mn sources include [MeMn(CO)$_5$] (for MnSe$_{(s)}$, Cd$_{(1-x)}$Mn$_{x}$Te$_{(s)}$, Hf$_{1-x-y}$Cd$_x$Mn$_y$Te$_{(s)}$, or MnAs$_{(s)}$, a in Figure 1.3), [CpMn(CO)$_3$] (for MnS$_{(s)}$, b in Figure 1.3), [MeCpMn(CO)$_3$] (for Cd$_{(1-x)}$Mn$_{x}$Te$_{(s)}$; c in Figure 1.3), [Mn(acac)$_2$] (for Mn$_2$Zn$_{(1-x)}$Fe$_2$O$_{(4s)}$; d in Figure 1.3), [Mn(dpm)$_3$] (for LaMnO$_{(3s)}$ or PrMnO$_{(3s)}$; e in Figure 1.3), and [Mn{(PrN)$_2$C$_6$Bu}$_2$] (for Mn$_4$N or MnCu$_x$; f in Figure 1.3). CVD using Mn-containing precursors has also been used to
dope various films with Mn, including ZnE₆ (E = S, Se) \{using \[^{Me}CpMn(CO)₃\] (d in Figure 1.3)\}⁵⁶ or [Cp₂Mn] (g in Figure 1.3))\}⁵⁷ or AlN₆ \{using \[^{Me}Cp₂Mn\] (h in Figure 1.3)\}.⁵⁸

\[ \text{Figure 1.3: Precursors used for CVD of Mn-containing thin films (not including oxides or elemental manganese) by simultaneous decomposition of multiple precursors or decomposition of Mn-containing precursors in the presence of a reactive gas.} \]

However, the most common manganese-containing thin film to have been deposited by CVD are oxides, usually formed by decomposition of a Mn-containing species in the presence of O₂ (either reagent-grade or air) or water. Examples of Mn-sources for these processes include \[^{\text{\textsuperscript{Me}}CpMn(CO)₃\}]\_₂ (a in Figure 1.4),⁵⁹ [ArMn(CO)₃] (Ar = \(^{\text{\textsuperscript{Bu}}}\text{Cp}, \text{Cp}^\ast\); b and c in Figure 1.4),⁶⁰ [(η⁵-C₆H₇)Mn(CO)₃] (d in Figure 1.4), [Mn(acac)₃] (e in Figure 1.4),⁶¹ [Mn(dpm)₃] (f in Figure 1.4),⁶²,⁶³ [(TMEDA)Mn(hfac)₂] \{g in Figure 1.4; in the absence of O₂, MnF₂(s) deposition was observed: \textit{vide supra}\}⁶⁴,⁶⁵ and [(TMEDA)Mn(tfac)₂] (h in Figure 1.4).⁶⁵,⁶⁶ As well, CVD using Si-containing precursors \[^{\text{\textsuperscript{Me}}S\text{I}}CpMn(CO)₃\] (i in Figure 1.4), \[^{\text{\textsuperscript{Me}}S\text{I},\text{Me}}CpMn(CO)₃\] (j in Figure 1.4),⁶⁰ or [(Mn\{N(2-Py)(SiMe₃)₁₂\}] (k in Figure 1.4)⁶⁷ in the presence of O₂ has been shown to produce thin films composed of both manganese silicate and oxide. Manganese oxide is also commonly observed during deposition of Mn(0) on silica substrates in the absence of O₂ (\textit{vide infra}).
In 1997, decades after it was used as a source of Mn dopants by CVD (vide supra), $\left[\text{MeCpMn(CO)}_3\right]$ (a in Figure 1.5) was shown to deposit films (in the presence or absence of $\text{H}_2$) of elemental Mn$_{(s)}$ by CVD. In the last ten years, elemental Mn$_{(s)}$ has been deposited by CVD using $\left[\text{Mn}\left\{\text{R}N}_2\text{C}''\text{Bu}\right\}_2\right]$ (b in Figure 1.5), $\text{bis}[1-\text{(tert-butyramid)}]-2\text{-dimethylaminoethane-}N,N''\text{manganese}$ (c in Figure 1.5), or $\left[\text{EtCp}_2\text{Mn}\right]$ (d in Figure 1.5), in each case in the presence of H$_2$ (deposition using $\left[\text{Mn}\left\{\text{RN}_2\text{CR}'\right\}_2\right]$ was also successful in the absence of $\text{H}_2$). When deposited on silica, a layer of oxide, silicide, and/or silicate was observed between the substrate and Mn$_{(s)}$ film, due to diffusion of Mn atoms into the silica; this layer blocked further migration of Mn atoms into the bulk silica. Attempts to deposit Mn$_{(s)}$ by CVD using $\left[\{\text{Mn(CO)}_5\}_2\right]$ yielded films composed only of oxide, though it is unclear if the oxygen content is residual from the precursor, substrate, or incidental oxidation of Mn(0). It is also notable that exposure of $\left[\text{EtCp}_2\text{Mn}\right]$ to a silica substrate at temperatures lower than the onset of Mn$_{(s)}$ CVD ($<500~\text{°C}$) yielded manganese oxide, potentially due to reactions with the silica.

Figure 1.4: Mn-containing precursors used for CVD of manganese oxides (pink box; oxides and silicates) in the presence of oxygen or water.
substrate as opposed to decomposition.\(^{73}\) It is worth noting that in 1994, Dossi et al. reported a process which was described as CVD of elemental manganese using \([\{\text{Mn(CO)}_5\}_2]\), but didn’t involve decomposition at the solid/vapour interphase. Instead, it involved initial sublimation of intact precursors, which were then heated to cause decomposition (with no Mn-containing vapour remaining). In addition, the presence of Mn\(_{(s)}\) was inferred from H\(_2\) evolution (from the putative reaction of Mn\((0)\) with residual water), and the films were not directly characterized.\(^{74}\)

\[\text{Figure 1.5: Precursors used for CVD of elemental manganese.}\]

1.2.8 – Atomic Layer Deposition (ALD) of Manganese-containing Films

To our knowledge, the first report of ALD of a manganese-containing film was the deposition of manganese oxide from \([\text{Mn(dpm)}_3]\) (a in Figure 1.6) and ozone in 2003 by Kjakshus et al.\(^{75}\) Interestingly, different oxides were observed at different temperature ranges; MnO\(_2(s)\) for deposition between 140 and 230 °C, with Mn\(_3O_4(s)\) deposition at higher temperatures. Reports on ALD of manganese oxides (of varying stoichiometries) have dominated the literature of Mn-containing films formed from ALD. The majority of these reports involve the same precursor combination as Kjakshus’ initial report (\([\text{Mn(dpm)}_3]\) with ozone).\(^{75,76}\) Ozone is also used as a co-reactant for ALD of manganese oxide using \([\{\text{Mn(CO)}_5\}_2]\) (b in Figure 1.6)\(^{77}\) or \([\text{MeCpMn(CO)}_3]\) (c in Figure 1.6).\(^{78}\) Manganese oxide ALD has also been reported with water as the co-reactant and either \([\{\text{EtCp}]_2\text{Mn}\) (d in Figure 1.6)\(^{79}\) or \([\text{Mn(tBu-MeAMD)}_2]\) (e in Figure 1.6)\(^{80}\) as the Mn-containing precursor. In addition, Qin and Zaera have reported ALD of manganese oxide using \([\text{MeCpMn(CO)}_3]\) (c in Figure 1.6) and N\(_2\)O, though with only three ALD cycles.\(^{81}\) Thin films of polymetallic oxides (where one of the metals is Mn) have also been
deposited by ALD, using cycles of three reagents; (a) a Mn-containing species, (b) another metal-containing precursor, and (c) an oxygen-containing co-reactant. These films include $M'Mn_3O_3$ ($M'$ = Y, La, Sm, Tb, Yb, Lu), $(Mn,Co)_3O_4$, $Li_xMn_2O_4$, and $Ti_xMn_4O$. Mn-containing precursors and oxygen-containing co-reactants used in these reports are the same as those used for manganese oxide deposition.

Figure 1.6: Mn-containing reagents used for ALD of manganese oxide.

Only a handful of ALD processes have been reported for manganese-containing films that aren’t oxides. For example, in 2014 the Winter group reported deposition of a Mn/Cu alloy using $[Mn_2('BuNCHC('Bu)(Me)O)]_4$ (a in Figure 1.7) as the Mn-containing precursor, with $[Cu(OCHMeCH_2NMe_2)_2]$ and BH$_3$(NHMe$_2$) as co-reactants. In 2016, Ahvenniemi and Karppinen reported the deposition of a ‘hybrid’ film with Mn ions separated by rigid organic backbones {using $[Mn(dpm)]_3$ (b in Figure 1.7) as the manganese-containing precursor and terephthalic acid as the co-reactant}. The same year, the Winter group reported ALD of a manganese borate $Mn_3(BO_3)_2$ using $[MnTp_2]$ (c in Figure 1.7) and ozone, and the Georgy group reported ALD of MnF$_2$ using $[{^1}EtCp_2Mn]$ (d in Figure 1.7) and HF.
Figure 1.7: Mn-containing precursors used for ALD of Mn-containing thin films (aside from oxides).

No successful methods for Mn\(_{(s)}\) ALD have yet been reported. However, the Winter and Zaera groups have reported preliminary results suggesting potential routes for ALD of elemental manganese (Scheme 1.1). First, the Winter group reported ALD using the Mn(II) \(\alpha\)-imino alkoxide dimer \([\{\text{Mn(Me}^\text{Bu}^\text{t}^\text{BuCOCN}^\text{t}^\text{Bu})(\mu-\text{Me}^\text{Bu}^\text{t}^\text{BuCOCN}^\text{t}^\text{Bu})\}_2]\) as a Mn-containing precursors and BH\(_3\)(NHMe\(_2\)) as a reducing co-reactant, which produced a manganese oxide film (presumably due to initial deposition of Mn\(_{(s)}\) followed by oxidation upon exposure to air).\(^\text{20}\) However, this deposition was only observed on Ru substrates, and following complete coverage of the substrate, film growth ceased. This was hypothesized to be due to Ru-catalyzed conversion of the borane co-reactant to a more reactive species. Second, the Zaera group conducted and ALD experiment with \([\text{Me}^\text{CpMn(CO)}_3]\) and H\(_2\), though only 3 ALD cycles were carried out and Si/SiO\(_2\) was used as a substrate (which leads to Mn(0) conversion to manganese silicide and manganese oxide; \textit{vide supra}). While this experiment did not afford Mn metal, the
authors suggested that elemental manganese deposition should be possible on an alternative substrate, or using an alternative reducing agent.\textsuperscript{81}

\textbf{Scheme 1.1:} Potential ALD processes for elemental manganese deposition proposed by the (a) Winter and (b) Zaera groups, based on preliminary results (Mn\textsubscript{(s)} was not observed in either case).
1.3 – Manganese Alkyl Complexes

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1.3.1 – Scope of Section

The aim of this section is to provide an overview of the synthesis and structure of neutral homoleptic base-free dialkylmanganese(II) complexes, and their adducts with Lewis bases. A particular focus is given to adducts of Mn(CH₂EMe₃)₂ (E = C, Si) and complexes of dmpe. An overview of dialkylmanganese(II) complex reactivity is also provided. Spectroscopic and magnetic characterization of these complexes is beyond the scope of this section. A brief overview is also given of neutral homoleptic polyalkyl manganese complexes of manganese(III) and (IV), and their Lewis base adducts.

1.3.2 – Alkyl Complexes for Transition Metal ALD

Alkyl complexes, which feature the simplest hydrocarbyl ligands, are among the most studied species in organometallic chemistry. Homoleptic alkyl complexes, where all ligands are identical, are of particular interest in that their reactivity is completely dependent on reactions of alkyl ligands. While homoleptic metal alkyl complexes have been known since the discovery of ZnEt₂ in 1849, the development of stable transition metal examples only began in the 1970s with the introduction of bulky ligands which lack β-hydrogen atoms. Employment of such ligands imparts stability by preventing β-hydride elimination (Scheme 1.2), one of the most common decomposition pathways for transition metal alkyl complexes. Despite the reversibility of this process, the resulting alkene and hydride ligands are prone to further, irreversible reactions. For example, C–H bond-forming reductive elimination from mixed alkyl hydride products is kinetically much more favourable than C–C bond-forming reductive elimination from homoleptic precursors.
1.3.3 – Homoleptic Neutral Dialkylmanganese(II) Complexes

The first neutral homoleptic dialkylmanganese(II) complex, MnMe₂, was reported by Clauss and von Beermann over a half century ago. However, the structure of this compound, which explodes under the influence of shock or friction, remains unknown. In the 1970s, Wilkinson et al. prepared homoleptic trimethylsilylmethyl (–CH₂SiMe₃), neopentyl (–CH₂CMe₃), neophyl (–CH₂CMe₂Ph),¹⁵,⁶ and 1-adamantylmethyl¹⁷ manganese(II) complexes, which all displayed much greater thermal stability than MnMe₂ due to increased steric bulk. X-ray crystal structures were reported for the trimethylsilylmethyl and neophyl complexes, which are polymeric and dimeric, respectively (a and c in Figure 1.8).¹⁶,⁹⁸ However, only limited structural data, and no CIF files, were reported; X-ray crystal structures of both complexes were later reported by the Mulvey⁹⁹ and Cámpora¹⁰¹ groups {the original CIF files were later submitted to the CSD as a communication, though the data quality was poor}.¹⁰¹ As well, Wilkinson noted that Mn(CH₂CMe₃)₂ is a tetramer in the solid state, citing a personal communication from M. B. Hursthouse and P. Raithby⁹⁸ (the CIF was also later submitted to the CSD as a communication, though the quality is also poor; b in Figure 1.8).¹⁰¹ In addition, gas-phase electron diffraction has determined that Mn(CH₂CMe₃)₂ is monomeric in the gas-phase.¹⁰²

**Scheme 1.2:** Decomposition pathways via β-hydride elimination from homoleptic transition metal alkyl complexes. For clarity, the simplest β-hydride-containing ligand (Et) is used in place of a generic alkyl ligand.
More recently, neutral homoleptic dialkylmanganese(II) complexes with tris(trimethylsilyl)methyl\(^{103}\) or 2-pyrrolidinyl ligands\(^{104}\) have also been crystallographically characterized (d and e, respectively, in Figure 1.8), and a gas-phase electron diffraction structure was obtained for \([\text{Mn} \{\text{CH} \{\text{SiMe}_3\}_2\}]\).\(^{105}\) These three examples (with extremely bulky alkyl groups) are isostructural monomers with \textit{trans} disposed alkyl ligands (C–Mn–C = 180°).\(^{103,105}\) Additionally, it should be noted that homoleptic dialkylmanganese(II) complexes with benzyl\(^{100}\) or –\(\text{C(SiMe}_3\)\(_2\)\(\text{SiMe}_2\)NMe\(_2\)\)\(^{106}\) ligands have been prepared, but not structurally characterized (though the former was inferred to be polymeric based on low solubility). All stable examples of base-free neutral dialkylmanganese(II) complexes lack β-hydrides, so are not susceptible to the common alkyl decomposition pathway of β-hydride elimination.

Two neutral homoleptic dialkylmanganese(II) complexes with pendent amine groups have also been reported; \([\text{Mn}(\text{o-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2]\) (f in Figure 1.8)\(^{107}\) and \([\text{Mn}(\text{o-CH(SiMe}_3\)\(_2\)\(\text{C}_6\text{H}_4\text{NMe}_2)_2]\) (g in Figure 1.8).\(^{108}\) These complexes feature coordination of the pendent amine donors to the metal centres. While the first of these complexes is a dimer in the solid state, with three of the four amine donors coordinated to
the metal centers, the bulkier analogue is monometallic, with coordination of both amine donors to the metal centre.

Many neutral dialkylmanganese(II) complexes were prepared by the reaction of MnCl$_2$ with Grignard reagents or dialkylmagnesium species (a in Scheme 1.3). By contrast, reactions of MnCl$_2$ with alkyllithium reagents often resulted in tetraalkylmanganese(II) dianions; several of these have been isolated, even with ligands for which the neutral MnR$_2$ complexes are unstable. However, for some very bulky ligands, {o-CH$_2$C$_6$H$_4$NMe$_2$, o-CH(SiMe$_3$)$_2$C$_6$H$_4$NMe$_2$, 1-adamantylmethyl, –CH(SiMe$_3$)$_2$, and –C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)} neutral MnR$_2$ species could also be prepared from the reaction of an alkyllithium precursor with MnX$_2$ (X = Cl, Br, I); presumably steric congestion limits further alkylation (b in Scheme 1.3). In addition, one example (e in Figure 1.8) was prepared by the reaction of H$_2$ with a bis(carbene) complex (c in Scheme 1.3).

**Scheme 1.3:** Synthetic routes for neutral dialkylmanganese(II) complexes.

X-ray crystallography is a mainstay characterization technique in organometallic chemistry, and is commonly used to investigate the structures of dialkylmanganese(II) complexes in the solid state (Table 1.1). The monometallic complexes feature Mn–C distances of 2.102(4)-2.136(4) Å. However, the polymetallic examples feature two (polymeric complexes) or three (dimeric complexes) sets of Mn–C distances. For dimeric

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In the following discussion, the original structures of neophyl, neosilyl, and neopentyl complexes, and [Mn(o-CH$_2$C$_6$H$_4$NMe$_2$)$_2$], are excluded due to low data quality.
complexes, the shortest Mn–C distance involves the terminal alkyl ligand (2.118(2) Å), and is consistent with the distances observed in monometallic species. The metal centres in polymetallic complexes are bridged by two alkyl ligands, and each metal is involved in one shorter (2.2023(17)-2.255(2) Å) and one longer (2.327(2)-2.4358(17) Å) Mn–C distance, both of which are longer than the Mn–C\textsubscript{terminal} distance in mono- and di-metallic complexes. Furthermore, short Mn–Mn distances (< 2.9 Å) are observed in the polymetallic species, potentially allowing for metal–metal interactions.

**Table 1.1:** Selected Mn–Mn and Mn–C distances (Å) for neutral dialky lmanganese(II) complexes obtained by X-ray crystallography (br = bridging, term = terminal). Letters are those in Figure 1.8.

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(Mn–Mn)</th>
<th>d(Mn–C\textsubscript{br}) \hspace{1cm} (shorter)</th>
<th>d(Mn–C\textsubscript{br}) \hspace{1cm} (longer)</th>
<th>d(Mn–C\textsubscript{term})</th>
<th>Structure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.682(2)-3.149(2)</td>
<td>2.116(6)-2.265(8)</td>
<td>2.365(7)-2.480(9)</td>
<td>–</td>
<td>polymer Wilkinson (1976/2012)\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>2.8874(5)-2.8897(5)</td>
<td>2.2023(17)-2.2039(17)</td>
<td>2.4203(17)-2.4358(17)</td>
<td>–</td>
<td>polymer Mulvey (2009)\textsuperscript{99}</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>2.706(6)-2.733(6)</td>
<td>2.21(1)-2.26(1)</td>
<td>2.34(1)-2.44(1)</td>
<td>2.10(1)</td>
<td>tetramer Wilkinson (1976/2012)\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>2.718(3)</td>
<td>2.257(9)</td>
<td>2.331(9)</td>
<td>2.15(1)</td>
<td>dimer Wilkinson (1976/2012)\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>2.7286(6)</td>
<td>2.255(2)</td>
<td>2.327(2)</td>
<td>2.118(2)</td>
<td>dimer Cámpora (2010)\textsuperscript{100}</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.102(4)</td>
<td>monomer Sullivan (1985)\textsuperscript{103}</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.106(2)</td>
<td>monomer Dittrich (2013)\textsuperscript{104}</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>2.810(3)</td>
<td>2.30-2.31</td>
<td>2.30-2.38</td>
<td>2.14-2.18</td>
<td>dimer Manzer (1977)\textsuperscript{107}</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.131(4)-2.136(4)</td>
<td>monomer Liu (2008)\textsuperscript{108}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Wilkinson first reported these complexes in 1976,\textsuperscript{95} but only provided limited structural data. The CIF was deposited in the Cambridge Structural Database in 2012.\textsuperscript{101}
By contrast, NMR spectroscopy, which is one of the most utilized methods for investigating the structures of organometallic complexes in the solution state, is not normally used for dialkylmanganese(II) complexes, which are paramagnetic (high spin d^5), and therefore produce spectra with extremely broad peaks and widely dispersed chemical shifts. However, given the presence of unpaired electrons, EPR spectroscopy and magnetic measurements are commonly used characterization tools. Additional tools which are sometimes used to characterize dialkylmanganese(II) complexes include IR spectroscopy, photoelectron spectroscopy, and mass spectrometry.

1.3.4 – Lewis Base Adducts of Neutral Dialkylmanganese(II) Complexes

Dialkylmanganese(II) complexes have been coordinated to a wide variety of Lewis bases including PMe_3, PEt_3, PMe_2Ph, PMePh_2, PCy_3, dmpe, pyridine, 2,2'-bipyridine (bipy), TMEDA (N,N,N',N'-tetramethylethylenediamine), a bidentate diimine ligand {N,N'-bis(mesitylmethylene)-1,2-cyclohexanediamine}, sparteine, THF, iPr_2NC(O)CH_2Ph, 1,4-dioxane, and a carbene \{1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene\}, although many of these complexes have not yet been structurally characterized. Additionally, dialkylmanganese(II) complexes with o-phenylenedimethylene \{o-C_6H_4(CH_2)_2\} and methyl groups have been structurally characterized, but only with neutral supporting co-ligands. In general, these adducts are prepared by exposure of base-free dialkylmanganese(II) complexes to free Lewis bases, generation of the base-free dialkylmanganese(II) complexes in the presence of free Lewis bases, or substitution of another neutral ligand in a dialkylmanganese(II) complex.

Given the focus on neopentyl (–CH_2CMMe_3) and neosilyl (–CH_2SiMe_3) complexes in this work (see Chapter 2), a comprehensive overview of their adducts with Lewis bases is included here. In Wilkinson’s report of the first stable dialkylmanganese(II) complexes, it was suggested that Lewis base coordination should break up the oligomeric nature of the base-free complexes (the earliest examples were polymeric, tetrameric, or
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dimeric in the solid state; vide supra). This has a significant effect on the physical properties; for example, the first reported adduct of Mn(CH₂SiMe₃)₂ (with TMEDA) sublimed at a temperature 70 °C lower than the base-free complex and is significantly more soluble in non-coordinating solvents.⁹⁶

Concurrent with the first reports of stable base-free dialkylmanganese(II) complexes (vide supra), the Wilkinson group also reported adducts of Mn(CH₂EMe₃)₂ (E = C, Si) with monodentate (pyridine) or bidentate (N,N'-dimethylpiperazine or TMEDA) amines.⁹⁵,⁹⁶ It was observed that these adducts contain either 2 equivalents of a monodentate amine, or 1 equivalent of a bidentate amine. However, no crystal structures were obtained at that time. A few years later, the same group reported adducts of various dialkylmanganese(II) complexes with a series of monodentate phosphines (PR₃; R₃ = Me₂Ph, MePh₂, Ph₃, (OMe)₃, (SiMe₃)₃, Cy₃, Me₃, Et₃)¹¹⁰,¹¹² as well as a bidentate phosphine (dmpe).¹¹¹ In all cases, 1:1 adducts were formed, though EPR studies have shown that in solution, 1:1 PMe₃ adducts are in an equilibrium with a small amount of the 1:2 MnR₂:PMe₃ adduct, formed by ligand redistribution (addition of excess free phosphine allowed in-situ characterization of pure 1:2 adducts).¹¹² While the monodentate phosphine adducts proved to be susceptible to phosphine loss, adducts of bidentate phosphines were significantly more stable under vacuum.¹¹¹

X-ray crystal structures have been obtained for a series of Lewis base adducts of Mn(CH₂SiMe₃)₂ (Figure 1.9). In the solid state, the 1:1 adducts of Mn(CH₂SiMe₃)₂ with PMe₃,¹¹⁰ PMePh₂,¹¹⁰,¹¹² THF (two isostructural structures have been reported),¹⁰⁰,¹¹⁷ or pyridine⁹⁹ form dimers with two terminal and two bridging alkyl groups, and one neutral donor located on each metal centre (a-c and f in Figure 1.9). A similar dimetalllic core was observed in the adduct containing half an equivalent of 1,4-dioxane per Mn centre (i in Figure 1.9).⁹⁹ In each case, the Mn–Mn distances (2.7715(8)-2.828(1) Å; Table 1.2) are shorter than those in base-free [\{Mn(CH₂SiMe₃)₂\}∞] (2.8874(5)-2.8897(5) Å). Furthermore, these polymetallic adducts contain three significantly different Mn–C distances involving each metal; short (2.111(3)-2.128(3) Å) Mn–Cterminal distances,
slightly longer (2.193(5)-2.218(3) Å) bridging Mn–C distances, and significantly longer (2.346(2)-2.389(5) Å) bridging Mn–C distances (Table 1.2). Relative to the two sets of bridging Mn–C distances in base-free \([\{\text{Mn(CH}_2\text{SiMe}_3)_2\}_\infty]\), the shorter set in these adducts is similar (2.2023(17)-2.2039(17) Å), but the longer set is significantly shorter (2.4203(17)-2.4358(17) Å).

**Figure 1.9:** Lewis base adducts of Mn(CH\(_2\)EMe\(_3\))\(_2\) (E = C, Si) for which X-ray crystal structures were obtained.

The other adducts of Mn(CH\(_2\)SiMe\(_3\))\(_2\) involve monometallic environments at Mn. These include 1:1 adducts with bidentate TMEDA,\(^99\) sparteine,\(^116\) or 1,4-dioxane (in this structure, the two donors are attached to different well-separated Mn atoms) moieties\(^99\) (d, e, or h in Figure 1.9), and the adduct with two equivalents of pyridine (g in Figure 1.9),\(^100\) which all feature tetrahedral donor coordination at manganese. The 5-coordinate
1:1 adducts with tridentate bis(imine) pyridine or tris(pyridine) moieties (j-m in Figure 1.9) adopted a related edge-capped tetrahedral environment at manganese, with coordination of all three N donors. Finally, a solid-state structure was obtained for an NHC adduct (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; n in Figure 1.9), which is unique (for complexes if Figure 1.9) in that it yields a 3-coordinate trigonal planar environment at Mn, presumably due to the extreme steric bulk of the neutral donor. In all these monometallic structures, the Mn–C distances range from 2.129(1)-2.220(7) Å (Table 1.2); the fact that many of these are longer than the Mn–C_{terminal} distances in dimetallic adducts could be due to the presence of extremely bulky neutral ligands.

In contrast to the neosilyl complexes, only two crystal structures have been obtained for Lewis base adducts of Mn(CH$_2$CMe$_3$)$_2$ (Figure 1.9, Table 1.3). One of these was a PMe$_3$ adduct (o in Figure 1.9) isostructural to the neosilyl PMe$_3$ analogue (a in Figure 1.9). The Mn–Mn distance in the PMe$_3$ adduct of Mn(CH$_2$CMe$_3$)$_2$ (2.772(1) Å) is significantly longer than in the neosilyl analogue (2.718(3) Å), due to the reduced steric profile of CH$_2$SiMe$_3$ vs. CH$_2$CMe$_3$ ligands (resulting from longer C–Si vs. C–C bonds). In addition, an adduct was obtained with a bidentate diimine ligand (p in Figure 1.9), for which the crystal structure revealed a monometallic species. The Mn–C bonds in this structure (2.141(6)-2.165(6) Å) are consistent with those observed in monometallic adducts of Mn(CH$_2$SiMe$_3$)$_2$ (vide supra).
Table 1.2: Selected distances (Å) for adducts of Mn(CH₂SiMe₃)₂ obtained by X-ray crystallography. L indicates the neutral ligand. n_L and n_Mn are the number of neutral ligands and metal centres in one molecule. Letters correspond to structures in Figure 1.9.

<table>
<thead>
<tr>
<th>L (complex)</th>
<th>n_L/n_Mn</th>
<th>Mn-Mn</th>
<th>Mn-C₁</th>
<th>Mn-C₂</th>
<th>Mn-termination</th>
<th>Mn-L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe₃ (a)</td>
<td>2/2</td>
<td>2.772(1)</td>
<td>2.208(3)</td>
<td>2.369(5)</td>
<td>2.111(3)</td>
<td>2.650(1)</td>
<td>Wilkinson (1982)⁹⁹⁹</td>
</tr>
<tr>
<td>PMePh₂ (b)</td>
<td>2/2</td>
<td>2.828(1)</td>
<td>2.193(5)</td>
<td>2.389(5)</td>
<td>2.117(5)</td>
<td>2.684(1)</td>
<td>Wilkinson (1983)¹¹²</td>
</tr>
<tr>
<td>THF (c)</td>
<td>2/2</td>
<td>2.790(2)</td>
<td>2.214(3)</td>
<td>2.376(3)</td>
<td>2.128(3)</td>
<td>2.188(4)</td>
<td>Gambarotta/Thompson (2003)¹¹⁷</td>
</tr>
<tr>
<td>THF (c)</td>
<td>2/2</td>
<td>2.7792(11)</td>
<td>2.203(4)</td>
<td>2.352(4)</td>
<td>2.127(4)</td>
<td>2.184(4)</td>
<td>Cámara (2010)¹⁰⁰</td>
</tr>
<tr>
<td>TMEDA (d)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.1379(15)</td>
<td>2.3284(12)</td>
</tr>
<tr>
<td>Sparteine (e)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.158(2)-2.297(2)-2.165(2)</td>
<td>Chirik (2004)¹¹⁶</td>
</tr>
<tr>
<td>Pyridine (f)</td>
<td>2/2</td>
<td>2.7927(5)</td>
<td>2.1991(18)</td>
<td>2.3711(7)</td>
<td>2.124(2)</td>
<td>2.2251(14)</td>
<td>Cámara (2010)¹⁰⁰</td>
</tr>
<tr>
<td>Pyridine (g)</td>
<td>2/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.143(3)-2.260(3)-2.150(4)</td>
<td>Mulvey (2009)⁹⁹⁹</td>
</tr>
<tr>
<td>1,4-dioxane (h)</td>
<td>1:1ᵇ</td>
<td>7.296³</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.1385(12)</td>
<td>2.2611(9)</td>
</tr>
<tr>
<td>1,4-dioxane (i)</td>
<td>1:2ᵇ</td>
<td>7.2774(8), 2.1991(18)</td>
<td>2.3711(7)</td>
<td>2.124(2)</td>
<td>2.2251(14)</td>
<td>2.133(2)-2.2279(17)-2.169(2)</td>
<td>Cámara (2010)¹²³</td>
</tr>
<tr>
<td>Bis(imine)-pyridine (j)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.133(2)-2.2279(17)-2.4181(12)</td>
<td>Zhang/Zheng (2016)¹²⁴</td>
</tr>
<tr>
<td>Tris(py) (k)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.172(3)-2.279(3)</td>
<td>Zhang/Zheng (2016)¹²⁴</td>
</tr>
<tr>
<td>Tris(py) (l)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.161(3)-2.270(2)</td>
<td>Zhang/Zheng (2016)¹²⁴</td>
</tr>
<tr>
<td>Tris(py) (m)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.166(2)-2.274(2)</td>
<td>Zhang/Zheng (2016)¹²⁴</td>
</tr>
<tr>
<td>IPr (n)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.129(1)</td>
<td>2.236(2)</td>
</tr>
</tbody>
</table>

a. Bond metrics in the paper and CIF are slightly different, though within the margin of error; values in Table 1.2 are from the CIF.
b. A ratio is provided because these complexes are polymeric.
c. This range corresponds to Mn centers separated by a bridging ligand, with no Mn–Mn interaction.
Table 1.3: Selected distances (Å) for adducts of Mn(CH$_2$CMe$_3$)$_2$ obtained by X-ray crystallography. L indicates the neutral ligand. $n_L$ and $n_{Mn}$ are the number of neutral ligands and metal centres in one molecule. Letters correspond to structures in Figure 1.9.

<table>
<thead>
<tr>
<th>L (complex)</th>
<th>$n_L/n_{Mn}$</th>
<th>Mn-Mn</th>
<th>Mn-C$_{br1}$</th>
<th>Mn-C$_{br2}$</th>
<th>Mn-C$_{term}$</th>
<th>Mn-L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMe$_3$ (o)</td>
<td>2/2</td>
<td>2.718(3)</td>
<td>2.23(2), 2.31(2)</td>
<td>2.44(2), 2.45(2)</td>
<td>2.14(3), 2.19(3)</td>
<td>2.67(1)</td>
<td>Wilkinson (1983)</td>
</tr>
<tr>
<td>Diimine (p)</td>
<td>1/1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.141(6)-2.165(6)</td>
<td>2.279(4)-2.344(4)</td>
<td>Copéret (2002)</td>
</tr>
</tbody>
</table>

While no bis(phosphine) adducts of Mn(CH$_2$EMe$_3$)$_2$ (E = C, Si) have been structurally characterized, X-ray crystal structures have been obtained for dmpe adducts of MnR$_2$ ($R_2 = \{\sigma-(CH$_2$)$_2$C$_6$H$_4\}$, Cy$_2$, or $\{CH(SiMe$_3$)$_2\}$)$_2$; Figure 1.10). In each case, a different number of dmpe equivalents were observed in the adduct. [(dmpe)$_2$Mn{$\sigma$-(CH$_2$)$_2$C$_6$H$_4$}] (a in Figure 1.10) is a monomer with two chelating dmpe ligands; the ability of Mn to assume an octahedral environment is presumably due to the small steric footprint of the single chelating dialkyl ligand (C–Mn–C = 84.7(2)°). By contrast, [{Mn(Cy)(μ-Cy)}$_2$(μ-dmpe)] (b in Figure 1.10), contains half an equivalent of dmpe per metal centre, and a structure similar to dimetallic monodentate phosphine complexes (a-b in Figure 1.9), but where the two P donors are tethered together by an ethylene bridge. The final example, [(dmpe)Mn{CH(SiMe$_3$)$_2$}]$_2$ (c in Figure 1.10), is a 1:1 adduct where the environment about Mn is distorted tetrahedral, and a very obtuse C–Mn–C angle of 141.4(7)° is presumably due to the presence of extremely bulky alkyl ligands.

Figure 1.10: Structurally characterized dmpe adducts of neutral MnR$_2$ complexes.
While allyl ligands normally interact in an $\eta^3$-fashion, $\eta^1$-coordinated allyl ligands can be considered as alkyl groups with a pendent alkene moiety. In 2012, the Hanusa group reported the synthesis and X-ray crystal structures for a pair of Lewis base adducts of neutral bis($\eta^1$-allyl)manganese(II) complexes where the hydrocarbyl substituents are, like alkyl ligands, $\sigma$-donors; [(TMEDA)Mn{C(H)(SiMe$_3$)C(H)=C(SiMe$_3$)$_2$}]$_2$ and [(THF)$_2$Mn{C(H)(SiMe$_3$)C(H)=C(H)(SiMe$_3$)$_2$}]$_2$ (a and b, respectively, in Figure 1.11). Both adducts are monomers with a tetrahedral environment at Mn, and feature Mn–C distances (2.174(2)-2.189(3) Å) similar to those of monometallic neutral dialkylmanganese(II) adducts listed in Tables 1.2-1.3 (2.129(1)-2.220(7) Å).

**Figure 1.11:** Structurally characterized neutral bis($\eta^1$-allyl)manganese(II) complexes.

### 1.3.5 – Selected Reactions of Neutral Dialkylmanganese(II) Complexes (Homoleptic and Lewis Base Adducts)

Dialkylmanganese(II) complexes are prone to decomposition, even in the absence of $\beta$-hydrides. As well, they are highly air- and moisture sensitive. In some cases, the products of thermal decomposition or exposure to H$_2$O or O$_2$ have been identified. For example, dineophylmanganese(II) decomposes via C$_{\text{ortho}}$–H bond oxidative addition (followed by C$_{\alpha}$–H bond-forming reductive elimination involving an intact alkyl ligand). Wilkinson suggested that exposure of dialkylmanganese(II) complexes to small amount of O$_2$ results in oxidation to neutral tetraalkylmanganese(IV) complexes. However, an excess of O$_2$ yields insoluble manganese oxides. Cámpora et al. has reported the products of the reaction of a 1:1 bipy adduct of Mn(CH$_2$SiMe$_3$)$_2$ (which was not structurally characterized) with a quarter equivalent of oxygen to form a tetrametallic
mixed valence manganese(II/III) complex with two oxo ligands, each bridging between three Mn atoms (two with two alkyl groups, and two with one alkyl group and bipy).\textsuperscript{100}

Surprisingly, exposure of the phosphine adducts \[\{\text{(Me}_3\text{P})\text{Mn(CH}_2\text{SiEMe}_3\text{)}_2\}\_2\] (E = C, Si) to dihydrogen did not result in any reaction at room temperature.\textsuperscript{112} However, proton sources such as alcohols and pyrroles have been shown to cleanly protonate off alkyl groups from dialkylmanganese(II) complexes, with concurrent installation of new anionic ligands.\textsuperscript{114,117} As well, alkyl ligands have been shown to be prone to 1,2-insertion across the C=N bonds in imine\textsuperscript{115} or isocyanide\textsuperscript{126} adducts of dineopentylmanganese(II). Furthermore, a series of tris(pyridine) adducts of Mn(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2} have displayed activity towards catalytic hydroboration, presumably via initial \(\sigma\)-bond metathesis (or oxidative addition followed by reductive elimination) to form a manganese(II) hydride or boryl complex.\textsuperscript{124}

1.3.6 – Homoleptic Neutral Tri- and Tetra- Alkylmanganese Complexes and their Lewis Base Adducts

While the majority of reported neutral homoleptic alkylmanganese complexes are divalent, a small number of stable tetraalkylmanganese(IV) analogues have also been prepared. In 1972, Bower and Tennent reported Mn(1-norbornyl)\textsubscript{4} (a in Figure 1.12),\textsuperscript{127} which is stable to \(\beta\)-hydride elimination because, as Bredt’s rule states, generation of double bonds at the bridgehead position of a small ring system is disfavoured.\textsuperscript{128} This complex is prepared from the reaction of MnCl\textsubscript{2} and excess alkyl lithium, and presumably involves disproportionation of a transient dialkylmanganese(II) species. Then, in 1983, Wilkinson et al. reported the stable base-free tetraalkylmanganese(IV) complexes \([\text{MnR}_4]\) (R = CH\textsubscript{2}SiMe\textsubscript{3}, CH\textsubscript{2}CMe\textsubscript{3}) (b-c in Figure 1.12) and phosphine adducts of \([\text{MnMe}_4]\) (d-e in Figure 1.12) via disproportionation of a transient Mn(III) intermediate; an X-ray crystal structure was obtained for the dmpe adduct revealing octahedral coordination of the four alkyl and two phosphate donors.\textsuperscript{129}
The Marks group has recently reported an X-ray crystal structure of \([(\text{TMEDA})\text{MnMe}_3]\) (g in Figure 1.12), the single known Lewis base adduct of a neutral homoleptic trialkylmanganese(III) complex.\(^{122}\) However, this complex was unstable and underwent spontaneous disproportionation to Mn(II) and Mn(IV) complexes over hours (in solution) or days (in the solid state). The resulting TMEDA adduct of \(\text{MnMe}_4\) (f in Figure 1.12) was unstable, but was characterized by Evans magnetic measurements.

**Figure 1.12:** Reported neutral homoleptic tri- and tetra- alkylmanganese complexes.
1.4 – Manganese Hydride Complexes

1.4.1 – Scope of Section

The aim of this section is to provide an overview of the synthesis, structure, characterization, and reactivity of manganese hydride complexes, and $\sigma$-H$_2$ complexes of manganese are also discussed. Given the vast size of this field, this review is not comprehensive. While many bi- and tri-metallic complexes have been reported with bridging hydrides, this review will cover only complexes with terminal hydride ligands. As well, manganese hydride complexes with silyl, silylene, or silene co-ligands are covered separately in sections 1.5, 1.6, and 1.7, respectively, and Mn(I) borohydride complexes are discussed in Chapter 3. Complexes where the hydride interacts with co-ligands (for example, boryl groups) are also beyond the scope of this section.

1.4.2 – Manganese(I) Hydride Carbonyl Complexes

While the earliest reports on manganese hydrides involved ill-defined homoleptic species, the first stable molecular manganese hydride complex, [(OC)$_5$MnH] (synthesized by protonation of the [(OC)$_5$Mn]$^-$ anion), was reported by Hieber and Wagner in 1957. Though initial characterization was limited, subsequent X-ray and neutron crystal structures determined that this species features an octahedral environment with the hydride ligand occupying one of the six coordination sites. Over the past half century, the chemistry of manganese hydride complexes has been dominated by complexes which, like [(OC)$_5$MnH], are (a) monovalent, (b) octahedral at the metal centre, (c) feature carbonyl co-ligands, and (d) neutral. Structurally characterized examples of these complexes feature a wide variety of co-ligands, including monodentate phosphines, bidentate bis(phosphine) ligands, isonitriles, a Ga carbenoid, a bidentate P–C$_{\text{NHC}}$ ligand, tetradentate neutral P-N-P pincer ligands, a tridentate neutral P-N-N pincer ligand, and $\eta^6$-hexamethylbenzene. To date, all CO-containing manganese hydride complexes to be structurally characterized (either neutral or ionic) have been monovalent.
Many Mn(I) carbonyl complexes have been prepared in a similar manner to [(OC)$_3$MnH] (exposure of the conjugate base to an acid; a in Scheme 1.4).$^{145,155}$ Other pathways include addition of a hydride (e.g. NaH, LiAlH$_4$, or NaBEt$_3$H) to a Mn(I) halide complex (b in Scheme 1.4)$^{141,149,153}$ or Mn(I) cation (c in Scheme 1.4),$^{142}$ homolysis of [{Mn(CO)$_5$}]$_2$ in the presence of a source of hydrogen atoms (d in Scheme 1.4; the hydrogen source is sometimes the solvent),$^{135,138,156-158}$ and thermal decomposition of a Mn formyl complex (e in Scheme 1.4; the eliminated CO ligand may be incorporated into the resulting manganese hydride complex).$^{137}$ As well, $\alpha$-hydride elimination from a gallyl ligand has been observed to yield a manganese hydride with a gallylene ligand (f in Scheme 1.4).$^{146}$ Of course, manganese hydride complexes can also be prepared by manipulation of other manganese hydride complexes (where the hydride ligand is not directly involved in the reactions). Examples of this include co-ligand substitution$^{140}$ and deprotonation of a co-ligand.$^{143}$
Scheme 1.4: Selected synthetic pathways (not involving H$_2$ as a reagent) for the preparation of Mn(I) hydride carbonyl complexes.

Additional synthetic pathways for forming Mn(I) hydride complexes with carbonyl co-ligands involve H$_2$ addition to complexes with multidentate ligands (Scheme 1.5). These reactions involve protonation either at a site on the multidentate ligand distant from the metal centre (a in Scheme 1.5; these reactions were often driven by aromatization within the multidentate ligand)\textsuperscript{144,147,148} or at an amido anion to generate an amine donor (b in Scheme 1.5).\textsuperscript{152,159} In some cases, primary alcohols substituted for H$_2$ as the hydride source (with production of an aldehyde byproduct).
Scheme 1.5: Synthesis of CO-containing manganese(I) hydride complexes using H₂.

In 2004, McGrady et al. reported an X-ray crystal structure of $[^{\text{Me}}\text{Cp(OC)}_2\text{MnH}]^-$, which is (to date) the only example of an anionic Mn(I) hydride complex to have been structurally characterized in the solid state\cite{160} (this complex was first observed spectroscopically a decade earlier by Schubert\cite{161}, and a very similar complex, $[^\text{Cp(OC)}_2\text{MnH}]^-$, was isolated by Cooper et al. as early as 1988).\cite{162} As well, X-ray crystal structures have been reported for a pair of cationic Mn(I) hydride complexes prepared by heterolytic H₂ cleavage; these complexes are octahedral with two bis(phosphine) ligands (one of which contains a pendent ammonium group) forming an equatorial plane, and trans-disposed carbonyl and hydride ligands.\cite{143,163}

1.4.3 – CO-Free Manganese Hydride Complexes

The first CO-free manganese complex to be reported was $[(\text{F}_3\text{P})_3\text{MnH}]$ (a in Figure 1.13) in 1968, which is electronically similar to $[(\text{OC})_5\text{MnH}]$\cite{164} (subsequent
reports provided detailed spectroscopic analysis for this complex). In 1970, Das and Rao reported a series of anionic Mn(IV) complexes with halide and pyridine-based ligands, though with limited characterization (b in Figure 1.13). Starting in the 1980s, a series of examples featuring monodentate phosphine co-ligands were reported; $[^\text{Me}\text{Cp}(\text{ON})(\text{PPh}_3)\text{MnH}]$ (c in Figure 1.13), $[(\text{Me}_3\text{P})_2\text{MnH}(\eta^6-C_6\text{H}_6)]$ (d in Figure 1.13), and $[(\text{R}_3\text{P})_2(\text{ON})_2\text{MnH}]$ (e in Figure 1.13; an X-ray crystal structure was obtained for R = Me). As well, in 2004 Roddick et al. observed the Mn(III) dihydride complex $[\text{Cp}(\text{dfepe})\text{MnH}_2]$ (f in Figure 1.13) in an equilibrium with the σ-dihydrogen species.

Figure 1.13: CO-free terminal manganese hydride complexes.
In the early 1980s, Girolami and Wilkinson reported the synthesis of a pair of dmpe Mn(I) complexes; [(dmpe)$_2$MnHL] (L = ethylene, H$_2$; g and h in Figure 1.13).$^{120,172}$ Lithiation of the ethylene complex resulted in abstraction of hydrogen atoms on the bis(phosphine) co-ligands to form [(Me$_2$PCH$_2$CH$_2$PMeCH$_2$)$_2$MnH(C$_2$H$_4$)$_2$Li$_4$(OEt)$_2$] (i in Figure 1.14), which was the first CO-free manganese hydride complex to be structurally characterized.$^{120}$ In 1992, the Jones group investigated the reactions of Wilkinson’s [(dmpe)$_2$MnH(H$_2$)] with a variety of nucleophiles (CO, N$_2$, ethylene, 1-pentene and isonitriles), and observed substitution of the dihydrogen ligand in each case (g, j, and k in Figure 1.13); crystal structures were obtained for the o-xylyl isonitrile and $\eta^1$-dinitrogen analogues.$^{173}$ To provide additional insight into the bonding environment of the H$_2$ and N$_2$ adducts, Jones also prepared the depe analogues [(depe)$_2$MnHL] (L = H$_2$, N$_2$; l in Figure 1.13).$^{173}$ More recently, H$_2$ substitution from [(dmpe)$_2$MnH(H$_2$)] has also been employed in the synthesis of the chlorostannyldene-hydride complex [(dmpe)$_2$MnH{≡SnCl(2,6-Mes$_2$C$_6$H$_3$)}], and abstraction of the halide produced the stannylidyne-hydride anion [(dmpe)$_2$MnH{≡Sn(2,6-Mes$_2$C$_6$H$_3$)}]$^–$; X-ray crystal structures were reported for both complexes (m and n, respectively, in Figure 1.13).$^{174}$ Only a couple of additional carbonyl-free Mn complexes with terminal hydride ligands have been structurally characterized; in 2012, a Mn cluster containing a MnH$_6$ core (o in Figure 1.13) was reported by Neese and Walter et al.,$^{175}$ and in 2017, Baik and Trovitch et al. reported the crystal structure of a Mn(I) hydride complex with a pentadentate P–N–N–N–P ligand (p in Figure 1.13).$^{176}$

Seven synthetic pathways have been used to prepare the complexes outlined in Figure 1.13. Most commonly, CO-free manganese hydride complexes were prepared by the reaction of other manganese hydride complexes, where the hydride ligand was not directly involved in the reactions {used for the synthesis of a, g, i, j, k, l (where L = N$_2$), m, and n in Figure 1.13}. Other pathways involve i) protonation (by a solvent) of a transient Mn(IV) complex generated by halogenation of pyridine-based adducts of Mn(II) dihalides (used for the synthesis of b in Figure 1.13), ii) exposure of a manganese halide to a hydride-source (used for the syntheses of c, e, o, and p in Figure 1.13), iii) co-
condensation of elemental manganese with benzene and phosphines (used for the synthesis of d in Figure 1.13; the source of the hydride atom is unclear), iv) substitution of a neutral ligand with H$_2$ followed by oxidative addition of the H–H bond across the metal centre (used for the synthesis of f in Figure 1.13), v) β-hydride elimination from a transient manganese ethyl complex (used for the synthesis of g in Figure 1.13), and vi) reaction of a Mn(I) aluminate complex with water {used for the syntheses of h and l (where L = H$_2$) in Figure 1.13},

1.4.4 – Selected Characterization Methods for Manganese Hydride Complexes

Given that carbonyl groups are common co-ligands in manganese hydride complexes (*vide supra*), IR spectroscopy is commonly utilized to measure C≡O frequencies (which provides insight about the electronic environment at the metal centre). In complexes with nitrosyl co-ligands, the N=O stretch in the IR spectrum is also normally reported. Notably, the M–H stretch is not normally reported.

The majority of manganese hydride complexes, unlike homoleptic alkyl complexes (see section 1.3), are diamagnetic. Mn(I) is d$^6$, so a low-spin octahedral structure (most manganese hydride complexes are monovalent and octahedral; *vide supra*) would have only paired d electrons. Because of this, NMR spectroscopy is generally used to characterize these complexes. The hydride ligand gives rise to a diagnostically low frequency (negative) signal in $^1$H NMR spectroscopy, providing a key handle for characterizing such complexes.$^{177}$ Furthermore, many hydride complexes feature phosphine co-ligands, so $^{31}$P NMR spectroscopy is a common characterization tool ($^{31}$P is 100% naturally abundant and has a spin of $\frac{1}{2}$). It is notable that NMR signals for spin $\frac{1}{2}$ nuclei (e.g. $^1$H or $^{31}$P) close to a quadrupolar metal centre may be broadened due to very short $T_2$ relaxation times. However, for octahedral manganese complexes ($^{55}$Mn = 100% abundance, I = 5/2, Q = $4.0\times10^{-29}$ m$^2$), substantial signal broadening is not typically observed, presumably due to a small electric field gradient at the metal nucleus.$^{109}$
Like most organometallic species, analysis of the solid state structure is of great interest in that it provides an unambiguous description of the bonding environment. However, X-ray crystallography suffers from some limitations in the analysis of hydride complexes. Specifically, given the low electron density around a hydride ligand, the hydrogen atoms are often not located, and when they are located the M–H distances are inaccurate. It is important to note that even when the hydride ligand is not directly located from the difference map, its location can often be inferred from the arrangement of co-ligands on the metal centre. To get around these problems, neutron crystal structures are sometimes obtained, where hydrogen atoms could be accurately located. However, use of neutron crystallography is often limited by expense, access, and requirement for large crystal sizes. Neutron structures have been obtained for \([(\text{OC})_3\text{MnH}]\) and \([(\text{OC})_4(\text{Ph}_3\text{P})\text{MnH}]\), and reveal Mn–H distances of 1.573(2)-1.601(16) Å.

### 1.4.5 – Selected Stoichiometric Reactions of Manganese Hydride Complexes

A vast number of reactions of manganese hydride complexes have been reported, so a complete list of their reactions is beyond the scope of this review. However, we will briefly provide an overview of some key classes of reported stoichiometric reactions (focusing only on those for which the hydride ligand is directly involved). Reactions where such species are implicated in catalytic cycles have been reported, including dehydrogenative coupling of alcohols with amines, and hydrogenation of \(\text{CO}_2\). However, further discussion of catalytic reactions is beyond the scope of this review.

Many manganese hydride reactions can be described in terms of acid/base chemistry. Most transition metal ‘hydride’ complexes are amphoteric, where the \(\text{MH}\) moiety could act either as a acid (proton) or base (hydride). Neutral manganese hydride complexes react with weak acids to produce \(\text{H}_2\), and the resulting Mn-containing species either obtains a new anionic ligand or becomes cationic (a and b, respectively, in Scheme 1.6). Examples the former are the reaction of \([(\text{OC})_3\text{MnH}]\) with \(\text{CF}_3\text{SO}_3\text{H}\) to yield \([(\text{OC})_3\text{Mn}({\text{O}_3\text{SCF}_3})]\), and the reactions of \([(\text{Et}_3\text{P})_2(\text{ON})_2\text{MnH}]\) with alcohols to form

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\(^{4}\) References in section 1.4.5 provide examples for each reaction.
[(Et$_3$P)$_2$(ON)$_2$Mn(OR)].$^{170}$ An example of the latter is the reaction of [(OC)$_3$(R$_3$P)$_2$MnH] with HPF$_6$ in acetonitrile (to generate [(OC)$_3$(R$_3$P)$_2$Mn(NCMe)][PF$_6$] with concomitant H$_2$ elimination).$^{157}$ Manganese hydride complexes have been observed to act as weak Brønsted-Lowry acids (c in Scheme 1.6). For example, [(OC)$_5$MnH] has a pK$_a$ of 7.1 in water$^{182}$ or 15.1 in acetonitrile.$^{183}$ In fact, exposure of Mn(I) hydride complexes to alkyllithium reagents can abstract the hydride ligand as a proton (forming a Mn-containing anion and an alkane byproduct; d in Scheme 1.6).$^{184}$

\[
\text{(b) } [\text{Mn}]^{+} + \text{A}^{-} \quad \xrightarrow{\text{HA}} \quad \text{H} \quad \xrightarrow{\text{A}} \quad [\text{Mn}]^{-} + \text{H}^{+}
\]

\[
\text{(a)} \quad \text{H} \quad \text{A} \quad \xrightarrow{\text{HLi}} \quad \text{R} \quad \text{Li}^{-} [\text{Mn}]^{-}
\]

**Scheme 1.6:** Acid/base reactivity of manganese hydride complexes.

Much of the chemistry involving hydride ligands involves insertion into the Mn–H bond to yield new anionic σ-donor ligands. For example, many reactions of carbonyl-containing manganese hydride complexes proceed by initial 1,1-insertion of CO into the Mn–H ligand to form a transient formyl intermediate (a in Scheme 1.7).$^{185}$ As well, 1,2-insertion reactivity has been observed between manganese hydride complexes and alkenes (to generate alkyl complexes$^{186}$ or result in H/D exchange with deuterated alkenes,$^{187}$ via irreversible or reversible 1,2-insertion of an alkene into the Mn–H bond, respectively), alkynes,$^{170}$ or CO$_2$ (b-d in Scheme 1.7).$^{150,152,170}$ Insertion of heteroatoms such as S (from a propylene sulfide reagent) into the Mn–H bond has also been observed (e in Scheme 1.7).$^{188}$
Scheme 1.7: Insertion reactivity of manganese hydride complexes.

Another set of reactions observed in manganese hydride complexes involve hydrogen/halogen exchange. For example, \([(OC)_{5-n}(R_3P)_nMnH]\) \((n = 0, 1)\) reacts with CCl\(_4\) or XP(CF\(_3\))\(_2\) \((X = Cl, Br, \text{ or I})\) to form \([(OC)_2MnX]\) and CHCl\(_3\) or HP(CF\(_3\))\(_2\) \((a\ \text{in Scheme 1.8})\).\(^{134,189}\) Also, \([(OC)_3(R_3P)_2MnH]\) undergoes H/X exchange with X\(_2\) \((X = Br, I)\) \((b\ \text{in Scheme 1.8})\).\(^{156}\)

Scheme 1.8: Halogenation of manganese hydride complexes. X = halogen.

In aromatic or donating solvents, reactions of the manganese(I) hydride complex \([(OC)_5MnH]\) with various metal alkyl or acyl complexes (of Mn, Re, Co, or Fe) have
resulted in bimolecular C–H bond-forming reductive elimination, usually yielding a bimetallic Mn–M complex (in some cases, subsequent decomposition resulted in a different complex being observed); Scheme 1.9. The byproducts of this reaction were normally the expected protonated ‘R’ groups (alkanes or aldehydes, respectively), though in some cases reactions involving alkyl complexes yielded an aldehyde byproduct (the expected product if there is initial 1,1-insertion of a carbonyl co-ligand into the Mn–C<sub>alkyl</sub> bond to form an acyl group prior to reductive elimination). As well, reactions involving manganese alkyl or aryl complexes with [(OC)<sub>5</sub>MnH] in alkane solvents yielded bimetallic η<sup>1</sup>-aldehyde complexes (where the aldehyde byproduct does not dissociate from the transition metal coordination sphere).\(^{185}\)

![Scheme 1.9: Bimolecular reductive elimination reactivity of manganese hydride complexes. R = alkyl or acyl.](image)

1.4.6 – σ-H<sub>2</sub> Complexes of Mn

σ-H<sub>2</sub> complexes feature neutral ligands formed upon side-on coordination of dihydrogen to a transition metal centre.\(^{191,192}\) If this ligand then undergoes oxidative addition, the result would be a dihydride complex. The first examples of σ-dihydrogen complexes were reported by Kubas in 1984.\(^{193}\) Structurally, these complexes can be differentiated from dihydride species by short H–H distances (≤1.2 Å).\(^{191}\) Spectroscopically, the H–H distance can be estimated by measuring the \(^1\)H–\(^2\)H NMR coupling constant of a partially deuterated analogue,\(^{93}\) solid-state NMR spectroscopy (based on large dipolar coupling between the two H atoms in dihydrogen ligands),\(^{194}\) and T<sub>1</sub> solution-state NMR measurements.\(^{195}\) Also, determination of the oxidation state (for example, by electrochemical methods), has been used to infer whether the ‘H<sub>2</sub>’ moiety is a single neutral H<sub>2</sub> ligand or two anionic hydride ligands.\(^{173}\) It is notable that the NMR
chemical shifts of the H₂ environments in σ-H₂ complexes are in the same low-frequency range as the MH environment in hydride complexes.¹⁹¹

In 1985, Girolami and Wilkinson reported the ‘Mn(III) trihydride complex’ [(dmpe)₂MnH₃].¹²⁰ However, Jones has subsequently shown (by T₁ NMR measurement and electrochemistry) that this complex, as well as its depe analogue, is better described as a trans-Mn(I) dihydrogen-hydride complex (with rapid exchange between the dihydrogen and MnH environments); a and b in Figure 1.14.¹⁷³ A similar series of reports has involved [Cp(OC)₂Mn(H₂)], which was first prepared in 1988¹⁶² but not recognized as a σ-H₂ complex until the next year (c in Figure 1.14).¹⁹⁶ However, [Cp(OC)₂Mn(H₂)], as well as Cp* and Et₅Cp analogues of this complex (d and e in Figure 1.14),¹⁹⁷ were only characterized by IR spectroscopy and were thermally unstable. [(OC)₄Mn(H₂)X] (X = Cl, Br; f and g in Figure 1.14) complexes have been observed in Ar matrices.¹⁹⁸ As well, in 2004 Roddick et al. observed the σ-H₂ complex [Cp(dfepe)Mn(H₂)] (h in Figure 1.14) in equilibrium with the Mn(III) dihydride complex [Cp(dfepe)MnH₂] (vide supra).¹⁷¹ Various stable cationic H₂ Mn complexes have been spectroscopically observed, including [(R₃P)₅-n(OC)ₙMn(H₂)]⁺ {R₃ = OEt₃, Ph(OEt)₂, Ph₂(OEt), Cy₃, (OCH₂C)₃Me, n = 3, 2, 1; i-o in Figure 1.14, not all combinations were observed}¹⁹⁹,²⁰⁰ and [(OC)(PP₁)(PP₂)Mn(H₂)]⁺ (PP = dppe, dppm, PNMe₃P, PNPh₃, PN₅BuP, P₂Ph₂N₂Bn; p-t in Figure 1.14).¹⁴¹ The only two examples of manganese σ-H₂ complexes for which an X-ray crystal structure has been obtained are [(L)₂(OC)Mn(H₂)]⁺ (L = dppe, depe; u and v in Figure 1.14), though the dihydrogen atom locations proved unstable to refinement.²⁰¹ All reported Mn σ-H₂ complexes are monovalent, and have been prepared by i) the reaction of a manganese aluminate complex with water, ii) protonation of a hydride complex, iii) substitution of a neutral ligand by H₂, or iv) coordination of H₂ to a vacant coordination site.
Figure 1.14: $\sigma$-H$_2$ complexes of Mn.
1.5 – Manganese Silyl Complexes

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1.5.1 – Scope of Section

The aim of this section is to provide an overview of monometallic manganese silyl complexes, with a particular focus on complexes with hydride co-ligands (including classical silyl hydride, nonclassical hydrosilane, and classical hydrosilane complexes). Also included is a brief introduction to ‘nonclassical’ hydrosilane complexes, where silyl and hydride ligands feature significant Si–H interligand interactions. This section will focus on synthesis, structures, and characterization; reactivity is beyond the scope. For silyl complexes lacking hydride co-ligands, only those with structural characterization are included (for silyl hydride/hydrosilane complexes, a comprehensive review is provided).

1.5.2 – Early Manganese Silyl Complexes

Transition metal complexes with silyl ligands are extremely common in organometallic chemistry. As expected for heavy analogues of alkyl ligands, bonding involving silyl groups is dominated by σ-donation from a formally anionic SiR₃ group (although σ-donation is weaker than in alkyl ligands with identical substituents). However, unlike alkyl ligands, significant π-backdonation (into a Si–R σ*-orbital) is also pertinent.¹²

The first manganese silyl complex \{[(OC)₅Mn(SiPh₃)]\} (a in Figure 1.15), reported in 1966 by Graham et al., was prepared by the reaction of HSiPh₃ and half an equivalent of [(OC)₅MnMn(CO)₅] with concurrent H₂ elimination.²⁰³ While initially this complex was characterized only by IR spectroscopy and elemental analysis, an X-ray
crystal structure was later reported. The first manganese silyl complex to be crystallographically characterized, [(OC)₃Mn(SiMe₃)] (b in Figure 1.15), was reported two years later by Hamilton and Corey. Another set of milestones were reached in 1971 with the syntheses of the first manganese silyl hydride complexes [Cp(OC)₂MnH(SiCl₃)], [McCp(OC)₂MnH(SiPh₃)], and [Cp(OC)₂MnH(SiPh₃)] (c-e in Figure 1.15) by the Graham group, followed 10 years later by the first reported X-ray crystal structure ([McCp(OC)₂MnH(SiFPh₂)]; f in Figure 1.15) by Schubert et al. Despite the fact that manganese is the third most abundant transition metal in the Earth’s crust, only 22 monometallic manganese silyl complexes have been structurally characterized (a tiny fraction of the total number of transition metal silyl complexes).

![Early manganese silyl complexes](image)

**Figure 1.15:** Early manganese silyl complexes.

### 1.5.3 – Structurally Characterized Hydride-free Mn(I) Silyl Complexes

A handful of manganese(I) silyl complexes which lack hydride co-ligands have been structurally characterized (Figure 1.16). In all of these cases, the environment about the metal centre is octahedral, and at least three of the co-ligands are carbonyls. When a phosphine co-ligand is also present, the PR₃ ligand is located *trans* to the silyl group (c and h in Figure 1.16). By contrast, in [(OC)₃(CNAR₁Dipp₂)₂Mn(SiCl₂Me)] (f in Figure 1.16), the extreme steric bulk of the two isonitrile co-ligands forces those to be *trans* to each other (and, by extension, the silyl ligand is *trans* to a CO ligand).

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*In 1971, Graham cites a manuscript in preparation as having determined the structure of [Cp(OC)₂MnH(SiPh₃)] by X-ray crystallography. However, no such structure has been deposited in the CSD, or to our knowledge published. Various bonding metrics were later published by Corriu et al, citing a PhD thesis.*
Figure 1.16: Structurally characterized Mn(I) silyl complexes lacking hydride co-ligands.

Common routes for accessing hydride-free manganese(I) silyl complexes are summarized in Scheme 1.10. These include the pathway used in the seminal synthesis of [(OC)₅Mn(SiPh₃)] (vide supra); the reaction of bimetallic Mn(0) complexes with two equivalents of a hydrosilane (a in Scheme 1.10). This reaction was proposed to proceed via oxidative addition of the H–Si bond across the Mn–Mn bond, initially yielding a single equivalent of the manganese (I) silyl product and a manganese(I) hydride byproduct; a second equivalent of HSiR₃ could then react with the hydride byproduct to generate a second equivalent of the Mn(I) silyl complex with H₂ elimination. In fact, the second half of this mechanism (reaction of a hydrosilane with a Mn(I) hydride complex; b in Scheme 1.10) is another commonly used pathway to access Mn(I) silyl complexes. The final commonly used synthetic route to Mn(I) silyl complexes involves the reaction of a halosilane with an alkali metal salt of a manganese(I) anion (c in Scheme 1.10).

References in the following paragraph are for syntheses of complexes in Figure 1.16 via the identified route.
Scheme 1.10: Selected synthetic routes to hydride-free manganese(I) silyl complexes.

Given that all examples of hydride-free Mn(I) silyl complexes feature carbonyl co-ligands (vide supra), IR spectroscopy is a commonly utilized characterization tool because the carbonyl C≡O bond vibrations are highly dependent on the electronic environment at the metal centre. As well, the diamagnetic nature of these complexes has allowed them to be characterized in the solution state by NMR spectroscopy. In particular, $^{29}$Si NMR spectroscopy ($^{29}$Si is 4.70% abundant, with I = ½) provides a diagnostic NMR handle; for the hydride-free silyl complexes in Figure 1.16 for which $^{29}$Si NMR chemical shifts have been located, the MnSi environments range from –43.2 to 59.13 ppm (Table 1.4). This extremely wide range appears to be highly dependent on the nature of the substituents on Si. Of course, X-ray crystallography is another commonly employed method for investigating the structure of silyl complexes, and Mn–Si distances for hydride-free Mn(I) silyl complexes range from 2.342(2)-2.564(6) Å (Table 1.4).
Table 1.4: $^{29}$Si NMR chemical shifts and solid-state Mn–Si distances for hydride-free Mn(I) silyl complexes for which X-ray crystal structures have been reported. Reference column refers to the report where a crystal structure was obtained (not where the complex was first synthesized). Letters correspond to those in Figure 1.16.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{29}$Si NMR (MnSi) δ (ppm)</th>
<th>d(Mn–Si) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(OC)$_5$Mn(SiMe$_3$)] (a)</td>
<td>10.98$^{219}$</td>
<td>2.498(5)</td>
<td>Hamilton and Corey (1968)$^{205}$</td>
</tr>
<tr>
<td>[(OC)$_3$Mn{Si(SiMe$_3$)$_3$}] (b)</td>
<td>–</td>
<td>2.564(6)</td>
<td>Simpson (1973)$^{220}$</td>
</tr>
<tr>
<td>[(OC)$_4$(Ph$_3$P)Mn{Si(SiMe$_3$)$_3$}] (c)</td>
<td>–</td>
<td>2.453(4)</td>
<td>Simpson (1976)$^{214}$</td>
</tr>
<tr>
<td>[(OC)$_3$Mn(SiPh$_3$)] (d)</td>
<td>17.9$^{221}$</td>
<td>2.504(6)</td>
<td>Butler (1997)$^{204}$</td>
</tr>
<tr>
<td>[(OC)$_3$Mn(SiCl$_3$)] (e)</td>
<td>59.13$^{44}$</td>
<td>2.352(2)</td>
<td>Jin (2008)$^{43}$</td>
</tr>
<tr>
<td>[(OC)$_3$(CNR$_2$)$_2$Mn(SiCl$_2$Me)] (f)</td>
<td>–</td>
<td>2.342(2)-2.346(2)</td>
<td>Figueroa (2011)$^{145}$</td>
</tr>
<tr>
<td>[(OC)$_3$Mn(SiMe[κ$^2$-(SiMe$_3$)$_2$]) (g)</td>
<td>–21.5$^{217}$-43.2$^{218}$</td>
<td>2.537(1)</td>
<td>Roewer (2017)$^{218}$</td>
</tr>
<tr>
<td>[(OC)$_4$(Ph$_3$P)Mn(SiHPh$_2$)] (h)</td>
<td>–24.5$^{215}$</td>
<td>2.410(1)</td>
<td>Wang (2018)$^{215}$</td>
</tr>
</tbody>
</table>

1.5.4 – Structurally Characterized Mn(II) and Mn(III) Hydride-free Silyl Complexes

Relative to Mn(I) silyl complexes, even fewer hydride-free manganese silyl complexes have been reported for other oxidation states. In fact, X-ray crystal structures have only been reported for two Mn(II) examples (both Lewis base adducts of [Mn{Si(SiMe$_3$)$_3$}]$_2$; a and b in Figure 1.17) and one Mn(III) example ([MeCp(OC)$_2$Mn(SiCl$_3$)$_2$]; c in Figure 1.17). The divalent complexes were both prepared by THF substitution from [(THF)$_2$Mn{Si(SiMe$_3$)$_3$}]$_2$ (which was itself characterized by IR spectroscopy, elemental analysis, and magnetic measurements)$^{222}$ Both of these divalent complexes are tetrahedral at the Mn centre, and contain Mn–Si distances of 2.642(3)-2.662(6) Å which are significantly longer than those for Mn(I) analogues (vide supra)$^{222}$ By contrast, the trivalent example (formed as a byproduct in the synthesis of [MeCp(OC)$_2$MnH(SiCl$_3$)]) features a Mn–Si distance of 2.320(2) Å, which is shorter than those observed in Mn(I) complexes (vide supra)$^{223}$ Mn(II) complexes are paramagnetic,
and therefore NMR spectra are not generally obtained for these complexes. In addition, no NMR data was reported for $[^\text{MeCp(OC)}]_2\text{Mn(SiCl}_3\text{)}_2$.

**Figure 1.17:** Structurally characterized hydride-free Mn(II) and Mn(III) silyl complexes.

1.5.5 Introduction to ‘Nonclassical’ Hydrosilane Complexes of Transition Metals

Transition metal hydrosilane complexes are a class of sigma complex important in many chemical transformations, especially those involving formation of Si–C bonds.\textsuperscript{208,224-230} Isolated examples of hydrosilane complexes are far less common than related dihydrogen complexes, despite the fact that the first hydrosilane complex was reported by Graham et al. in 1969,\textsuperscript{231} 15 years before Kubas’ report of the first H\textsubscript{2} complex.\textsuperscript{193} Upon oxidative addition of the Si–H bond, classical silyl hydride complexes (with two separate 2c-2e bonds, as opposed to a single 3c-2e bond) are formed. However, as early as 1971, Graham reported a monometallic silyl hydride complex with significant interligand Si–H bonding.\textsuperscript{207} These “nonclassical” hydrosilane complexes have been the subject of a number of reviews,\textsuperscript{232-234} and from a molecular orbital perspective, they are typically described using a modification of the Dewar-Chatt-Duncanson bonding model, with concomitant σ donation and π backdonation to/from the metal (Figure 1.18). A
variety of terms have been employed to describe these intermediate complexes, and comprehensive studies by a number of groups, including those of Nikonov, Sabo-Etienne, and Scherer, have shown that a continuum exists between classical hydrosilane and classical silyl hydride complexes along the oxidative addition/reductive elimination reaction coordinate, with progressively weakening Si–H interactions indicative of a greater degree of oxidative addition. Nonclassical hydrosilane complexes therefore provide snapshots along the oxidative addition pathway, which is one of the most important classes of organometallic reaction.

**Figure 1.18:** Top; From left to right, structures of classical hydrosilane, nonclassical hydrosilane, and classical silyl hydride complexes. Bottom; Dewar-Chatt-Duncanson model of σ donation and π backdonation from/to a hydrosilane ligand.

Analyses of nonclassical hydrosilane complexes have naturally focused on the strength of the Si–H interaction, from which the degree of oxidative addition can be

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A variety of terms have been used to describe Si–H interactions in nonclassical hydrosilane complexes, including stretched σ-bonding or Si–H bonding (ref 226), interligand hypervalent interactions (IHI; refs. 236 and 237), secondary interactions between silicon and hydrogen atoms (SISHA; ref. 234), and α-agostic interactions (ref. 235). Complexes featuring interligand Si–H interactions are sometimes referred to as hybrids between σ-hydrosilane and silyl hydride complexes (ref. 238), or complexes featuring incomplete (or arrested) oxidative addition. The latter are sometimes divided further into asymmetric oxidative addition products (ASOAPs, typically featuring significant Si–H interactions and negative $J_{\text{Si,H}}$ coupling constant), and symmetric oxidative addition products (SOAPs, featuring weak residual Si–H interactions and positive $J_{\text{Si,H}}$ coupling constants); refs. 239-241.
inferred. These strengths have often been determined computationally, while experimental studies have primarily involved solid-state structural determination of the Si–H distance. However, care must be taken when discussing Si–H distances determined by X-ray crystallography, due to difficulties associated with accurately locating hydrogen atoms from the difference map. More importantly, it has been observed that significant changes in the degree of oxidative addition (based on $J_{\text{Si,H}}$ coupling constants; vide infra) may only yield very small changes in the Si–H distance, and Si–H distances below the sum of the van der Waals radii may be steric in origin, so do not necessarily imply Si–H bonding. Furthermore, there is no intuitive boundary to define nonclassical hydrosilane complexes with respect to either classical hydrosilane or classical silyl hydride complexes, and different Si–H distance ranges have been suggested to correspond to these intermediate complexes. The lower end of this range is often considered to be 1.8 Å, while distances of 2.1 and 2.4 Å have been proposed by Nikonov and Sabo-Etienne respectively to correspond to the upper limit.

Spectroscopically, $^1$H and $^{29}$Si NMR chemical shifts are not especially useful to evaluate the extent of hydrosilane oxidative addition, given that similar ranges of values are observed for classical hydrosilane, classical silyl hydride, and nonclassical hydrosilane complexes. By contrast, $^{29}$Si–$^1$H NMR coupling constants ($J_{\text{Si,H}}$) can be used as a sensitive tool to measure the nature of interligand Si–H interactions. However, it is important to recognize that 1-bond Si–H coupling has a negative sign, whereas 2-bond Si–H coupling has a positive sign, so $J_{\text{Si,H}}$ passes through zero on the continuum from a classical hydrosilane to a classical silyl hydride complex, and proper placement of a complex along this continuum requires knowledge both of the magnitude and sign of $J_{\text{Si,H}}$.

The magnitude of $J_{\text{Si,H}}$ can typically be obtained via 1D $^1$H or $^{29}$Si NMR spectroscopy, but measurement of the sign is more difficult. One method used in the literature is spin tickling, but individual multiplet signals must be well-resolved, and its
analysis is not conceptually straightforward. Recently, Scherer reported an alternative spectroscopic method for determining the sign (and magnitude) of $J_{\text{Si,H}}$ in silyl hydride/hydrosilane complexes where the silicon centre also features a terminal Si–H bond. This method relies upon 2D $^1$H–$^1$H COSY data, using the negative coupling constants of the terminal Si–H bond as an internal reference to definitely determine the sign of $J_{\text{Si,H}}$ from the orientation of $^{29}$Si satellites associated with a cross-peak of interest. While there is still some debate, $J_{\text{Si,H}}$ values ranging from 0 to –70 Hz are commonly considered to indicate activated Si–H bonds in nonclassical silyl hydride complexes (with values more negative than –70 Hz indicative of classical hydrosilane complexes and positive values indicative of classical silyl hydride complexes).

A range of transition metal complexes have also been isolated containing a silyl group accompanied by more than one hydride ligand. The generic term ‘silyl dihydride’ is frequently used to describe complexes with one SiR$_3$ and two hydride moieties interacting with a metal centre, regardless of the extent of any interligand Si–H interaction(s). Within this class of complexes, a variety of examples have been observed where a single silyl ligand simultaneously interacts with multiple hydride ligands. In 1989, Crabtree et al. first proposed such a complex as a potential intermediate in the dynamic exchange between the terminal metal hydride and bridging hydrosilyl environments in [(Ph$_3$P)$_2$IrH$_2$(η$^2$-HSiEt$_3$)]$^+$. Then, in 1990, the same group reported the first examples of transition metal (Re) complexes featuring multiple (four or two) hydride ligands interacting with a single silyl ligand (Figure 1.19, a and b), though the hydride atoms were not crystallographically located. Five years later, Klabunde and Radonovich et al. reported X-ray crystal structures for a pair of chromium disilyl dihydride complexes with short distances between one of the silyl ligands and two neighboring hydride ligands (1.75(7) and 1.60(6) Å for one, 1.66(4) and 1.87(4) Å for the other; c in Figure 1.19), though the authors stopped short of stating that two Si–H interactions were present due to significant errors in the bond distances and potential involvement of the second silyl ligand in the bonding scheme. Then, in 1999, Sabo-Etienne and Chaudret reported a Ru complex featuring a silyl ligand with two adjacent
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hydride co-ligands (d in Figure 1.19), with short Si–H distances of 1.72(3) and 1.83(3) Å determined by X-ray diffraction. Over the past two decades, approximately a dozen crystallographically characterized monometallic transition metal silyl dihydride complexes have been reported to feature interactions between a silyl ligand and two hydride ligands, and are often referred to as silicate (H₂SiR₃⁻) complexes. However, no examples involving manganese have yet been reported. These complexes highlight the potential for silicon hypervalency in transition metal complexes, and are of interest as models in the heterolytic splitting of hydrosilanes on metal centres.

Figure 1.19: Early examples of complexes reported to involve multiple Si–H interactions to the same silicon centre.

1.5.6 – Silyl Hydride/hydrosilane Complexes of Manganese

A wide variety of classical silyl hydride, nonclassical hydrosilane, and classical hydrosilane complexes (collectively referred to herein as silyl hydride/hydrosilane complexes) have been reported for manganese. To our knowledge, all reported examples involve varying degrees of oxidative addition to a Mn(I) centre, to the extent that classical silyl hydride examples could be considered complexes of Mn(III). Photoelectron spectroscopy is sometimes employed to determine if the metal centre could be best described as mono- or tri-valent. However, it is of note that the overall electron count is unaffected by the extent of oxidative addition (i.e. both 6-coordinate Mn(I) and 7-coordinate Mn(III) complexes are 18-electron species). As well, DFT calculations have often been employed to gain a greater understanding of the bonding environment at the metal centre. It is also notable that the vast majority of Mn silyl hydride/hydrosilane complexes are neutral, with the exception of anionic [(OC)₄MnH(SiPh₃)]⁻ and cationic [(OC)₃{MeC(CH₂O)₃P}₂MnH(SiR₃)]⁺.

55
The vast majority of reported silyl hydride/hydrosilane complexes of Mn contain carbonyl co-ligands and are diamagnetic. Because of this, IR and NMR spectroscopy are commonly used characterization tools. Nearly all reported examples have been characterized by IR spectroscopy because the electronic environment at the metal centre has a significant effect on the C≡O vibration. In fact, many manganese silyl hydride/hydrosilane complexes have been analyzed by IR spectroscopy with no corroborating spectroscopic or structural data; [(OC)4MnH(SiPh3)]−, [Cp(OC)2MnH(SiRPh2)] (R = Ph207 or H277), [MeCp(OC)2MnH(SiRPh2)] (R = Cl, Br, I280 or Me281), and [Tp(OC)2MnH(SiEt3)].282

NMR analysis of manganese silyl hydride/hydrosilane complexes has mainly focused on three parameters. The most common NMR handle to be reported is the MnH environment in the 1H NMR spectrum, which gives rise to a low frequency environment (–5.21 to –16.81 ppm; Table 1.5) characteristic of a metal hydride. In a significant subset of examples, the 29Si NMR chemical shift was also reported, and these values (–2.62 to 60.7 ppm; Table 1.5) are consistent with hydride-free Mn(I) silyl complexes (vide supra). 29Si–1H coupling constants involving the adjacent MnSi and MnH moieties (which are important for identifying classical silyl hydride vs. nonclassical hydrosilane vs. classical hydrosilane complexes; vide supra) have been reported to range in magnitude from 20 to 69 Hz (aside from [MeCp(OC)(Me3P)MnH(SiCl3)], all JSi,H have a magnitude greater than 40 Hz; Table 1.5). For a handful of cases, the signs of these coupling constants were measured or calculated to be negative (in no cases were positive coupling constants measured or calculated). These coupling constants are consistent with (or indicative of, for complexes where the sign of JSi,H has been determined) significant Si···H interactions associated with nonclassical hydrosilane ligands (vide supra).
Table 1.5: Selected NMR data for silyl hydride/hydrosilane complexes of Mn. References refer to the first reported synthesis, and when NMR data was obtained following the initial report, references for that are in the pertinent box. For clarity, all chemical formulae are given as the classical silyl hydride isomer. If no sign is explicitly given, $J_{\text{Si,H}}$ values are magnitudes. NMR values are from the first report (in some cases, later publications included slightly different data, often due to use of an alternative solvent). Empty boxes indicate that no data was reported.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H NMR (MnH) $\delta$ (ppm)</th>
<th>$^{29}$Si NMR (MnSi) $\delta$ (ppm)</th>
<th>$J_{\text{Si,H}}$ (Hz) expt. ${\text{calcd.}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp(OC)$_2$MnH(SiCl$_3$)]</td>
<td>9.70</td>
<td>–</td>
<td>–</td>
<td>Graham (1971)$^{206}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(SiPh$_3$)]</td>
<td>–11.5</td>
<td>18.5$^{209}$</td>
<td>64.7$^{209}$</td>
<td>Graham (1971)$^{206}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(SiH(α-Naph))]</td>
<td>–11.23,</td>
<td>7.5$^{209}$</td>
<td>69$^{209}$</td>
<td>Corriu (1979)$^{283}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(SiCl(α-Naph))]</td>
<td>–10.68$^{209}$</td>
<td>58.3$^{209}$</td>
<td>–</td>
<td>Corriu (1979)$^{283}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(SiF(α-Naph))]</td>
<td>–11.70$^{209}$</td>
<td>57.3$^{209}$</td>
<td>–</td>
<td>Corriu (1979)$^{283}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(Si(OMe)(α-Naph))]</td>
<td>–12.03$^{209}$</td>
<td>–</td>
<td>–</td>
<td>Corriu (1979)$^{283}$</td>
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<tr>
<td>[MeCp(OC)$_2$MnH(SiHPh$_2$)]</td>
<td>–a</td>
<td>13.5$^{284}$</td>
<td>64$^{284} {–63, –68}$</td>
<td>Schubert (1981)$^{280}$</td>
</tr>
<tr>
<td>[MeCp(OC)$_2$MnH(SiFPh$_2$)]</td>
<td>–12.03$^{241}$</td>
<td>60.7$^{241}$</td>
<td>57$^{241} {–52}$</td>
<td>Schubert (1981)$^{280}$</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>[MeCp(OC)(Ph$_3$P)MnH(SiClPh$_2$)]</td>
<td>–11.1$^{286}$</td>
<td>23.8</td>
<td>62</td>
<td>Schubert (1984)$^{284}$</td>
</tr>
<tr>
<td>[MeCp(OC)(Bu$_3$P)MnH(SiHet)]</td>
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<td>24.8</td>
<td>37</td>
<td>Schubert (1984)$^{284}$</td>
</tr>
<tr>
<td>[MeCp(OC)(Me$_2$P)MnH(SiHet)]</td>
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<td>26.0$^{287}$</td>
<td>38$\pm$2$^{287}$</td>
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<td>[MeCp(OC)((p-ClPh)$_2$P)MnH(SiHet)]</td>
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<td>22.0$^{287}$</td>
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<td>44.5$\pm$1.5$^{287}$</td>
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<td>24.9$^{287}$</td>
<td>39.7$\pm$0.6$^{287}$</td>
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<td>–</td>
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<tr>
<td>[MeCp(OC)(PrNC)MnH(SiHet)]</td>
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<td>–</td>
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<td>[MeCp(OC)$_2$MnH(SiCl$_3$)]</td>
<td>–</td>
<td>54.9</td>
<td>54.8$\pm$0.6, ${–38}$</td>
<td>Schubert (1986)$^{287}$</td>
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<tr>
<td>[MeCp(OC)(BuNC)MnH(SiHet)]</td>
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<td>22.6</td>
<td>57.5$\pm$0.6</td>
<td>Schubert (1986)$^{287}$</td>
</tr>
<tr>
<td>[MeCp(OC)(PrNC)MnH(SiHet)]</td>
<td>–</td>
<td>22.8</td>
<td>58$\pm$2</td>
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</tr>
<tr>
<td>Compound</td>
<td>∆H (kcal/mol)</td>
<td>T (K)</td>
<td>Ref.</td>
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<tr>
<td>--------------------------------------------------</td>
<td>---------------</td>
<td>-------</td>
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<td></td>
</tr>
<tr>
<td>$^{18}$Cp(OC)(Me$_3$P)MnH(SiCl$_3$)</td>
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<td>59.5</td>
<td>Schubert (1986)</td>
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<tr>
<td>[Cp$^*$5OC$_2$]MnH(SiHPh$_2$)</td>
<td>–</td>
<td>18.2</td>
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<td>[Cp(OC)$_2$]MnH(SiMe$_2$Et)</td>
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<td>–</td>
<td>Wrighton (1987)</td>
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<tr>
<td>$^{18}$Cp(OC)MnH($^{13}$C$_2$-P(Ph)$_2$CH$_2$CH$_2$SiMe$_2$)</td>
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<td>47.2</td>
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<td>$^{18}$Cp(OC)MnH$_2$($^{13}$C$_2$-P(Ph)$_2$CH$_2$CH$_2$SiPh$_2$)</td>
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<td>[Cp(dmpe)MnH(SiH$_2$Ph)]</td>
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<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>[Cp(dmpe)MnH(SiHPh$_2$)]</td>
<td>–14.42</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>[Cp(dmpe)MnH(SiPh$_3$)]</td>
<td>–14.13</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>[Cp(dmpp)MnH(SiH$_2$Ph)]</td>
<td>–14.58</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>[Cp(dmpp)MnH(SiHPh$_2$)]</td>
<td>–14.47</td>
<td>–</td>
<td>Sun (1994)</td>
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<tr>
<td>[Cp(dmpp)MnH(SiPh$_3$)]</td>
<td>–14.41</td>
<td>–</td>
<td>Sun (1994)</td>
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<tr>
<td>[Cp(dmpm)MnH(SiH$_2$Ph)]</td>
<td>–9.59</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
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<tr>
<td>[Cp(Me$_3$P)$_2$]MnH(SiH$_2$Ph$_3$)</td>
<td>–14.23</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>[Cp(Me$_3$P)$_2$]MnH(SiHPh$_2$)</td>
<td>–14.54</td>
<td>–</td>
<td>Sun (1994)</td>
<td></td>
</tr>
<tr>
<td>$^{18}$Cp(OC)$_2$MnH(SiEt$_3$)</td>
<td>–13.50</td>
<td>–</td>
<td>Hill (1996)</td>
<td></td>
</tr>
<tr>
<td>$^{18}$Cp(OC)$_2$MnH(SiMeEt$_3$)</td>
<td>–13.27</td>
<td>–</td>
<td>Hill (1996)</td>
<td></td>
</tr>
<tr>
<td>$^{18}$Cp(OC)$_2$MnH(SiMe$_2$Et)</td>
<td>–13.09</td>
<td>–</td>
<td>Hill (1996)</td>
<td></td>
</tr>
<tr>
<td>$^{18}$Cp(OC)$_2$MnH(SiH$_2$Et$_2$)</td>
<td>–12.63</td>
<td>–</td>
<td>Hill (1996)</td>
<td></td>
</tr>
<tr>
<td>[Cp(OC)$_2$]MnH(SiMe$_2$Et$_2$)</td>
<td>–13.50</td>
<td>–</td>
<td>Hill (1996)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)$_2$MnH(SiPh$_2$)(SiHPh$_2$)</td>
<td>–10.71</td>
<td>–2.62</td>
<td>Schubert (1997)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)$_2$MnH(SiMe$_2$)(SiMe$_2$H)H)</td>
<td>–12.3</td>
<td>–</td>
<td>Schubert (1998)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)(Me$_3$P)MnH(SiMe$_2$)(CH$_2$SiMe$_2$H)</td>
<td>–12.9</td>
<td>33.7</td>
<td>Schubert (1998)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)(Me$_3$P)MnH(SiMe$_2$(O)SiMe$_2$H)</td>
<td>–12.7</td>
<td>52.4</td>
<td>Schubert (1998)</td>
<td></td>
</tr>
<tr>
<td>[(OC)$_3$]MnH(κ$^3$-Si$_2$-xanthene)</td>
<td>–5.21</td>
<td>23.1</td>
<td>Tobita (2012)</td>
<td></td>
</tr>
<tr>
<td><a href="OC">(η$^5$-C$_5$H$_4$CH$_2$NH$_2$)</a>MnH(SiHPh$_2$)</td>
<td>–10.48</td>
<td>18.0</td>
<td>Valyev (2016)</td>
<td></td>
</tr>
<tr>
<td>[(η$^5$-C$_5$H$_4$CH$_2$CH$_2$NHC)(OC)MnH(SiHPh$_2$)]</td>
<td>–10.49</td>
<td>16.8</td>
<td>Valyev (2016)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)$_2$MnH(SiMe$_2$)$^b$</td>
<td>–</td>
<td>–</td>
<td>Scherer (2017)</td>
<td></td>
</tr>
<tr>
<td>$^{16}$Cp(OC)$_2$MnH(SiMe$_2$Cl)$^b$</td>
<td>–</td>
<td>–</td>
<td>Scherer (2017)</td>
<td></td>
</tr>
</tbody>
</table>
Solid state structures have only been obtained for a relatively small subset of silyl hydride/hydrosilane complexes (Figure 1.20). Nearly every example contains a Cp donor; the only exceptions are a pair of complexes reported by the Tobita group (j and k in Figure 1.20), which contain chelating silicon-based donors.

Discussions of the solid state structures of manganese silyl hydride complexes normally involve four parameters; the Mn–Si, Mn–H, and Si–H distances, as well as the Si–Mn–H angle (Table 1.6). However, three of these parameters involve hydrogen atoms, which are not accurately located from the difference map by X-ray crystallography. To obtain accurate values, authors often turn to DFT calculations or neutron crystallography.
Of particular interest are Si–H distances (1.60(2)-2.60(4) Å)\(^i\) and Si–Mn–H angles (35.1(9)-74(1)°)\(^j\), in that higher values are directly associated with a silyl hydride/hydrosilane complex lying further along the oxidative addition continuum. Si–H\(_{\text{Mn}}\) distances observed in the two silyl hydride/hydrosilane complexes for which neutron structures were obtained (1.802(5)-1.806(14) Å) are within the range associated with nonclassical hydrosilane complexes (\textit{vide supra}). The range of Mn–Si distances observed in manganese silyl hydride/hydrosilane complexes (2.254(1)-2.6174(5) Å)\(^k\) encompasses the range observed for hydride-free Mn(I) and Mn(III) silyl complexes (2.320(2)-2.564(6) Å; \textit{vide supra}), while the Mn–H distances in these complexes (1.45(3)-1.61(2) Å; if only values from neutron structures are included this range is 1.569(4)-1.575(14) Å) are similar to those in silyl-free Mn(I) hydride complexes (see section 1.4.4).

\(^i\) If the Si–H distance of 2.60(4) Å in the disilyl hydride complex [(OC)\(_3\)MnH(κ\(_3\)-Si\(_2\)-xanthene)] (j in Figure 1.20) is excluded as an outlier, the upper limit of this range becomes 1.97(3) Å.

\(^j\) If the Si–Mn–H angle of 74(1)° in the disilyl hydride complex [(OC)\(_3\)MnH(κ\(_3\)-Si\(_2\)-xanthene)] (j in Figure 1.20) is excluded as an outlier, the upper limit of this range becomes 55(1)°.

\(^k\) If the Mn–Si distance of 2.6174(5) Å in the disilyl hydride complex [(OC)\(_3\)MnH(κ\(_3\)-Si\(_2\)-xanthene)] (j in Figure 1.20) is excluded as an outlier, the upper limit of this range becomes 2.461(7) Å.
Table 1.6: Selected structural parameters determined by X-ray (or, if indicated, neutron) crystallography for silyl hydride/hydrosilane complexes of Mn. For clarity, all chemical formulae are given as the classical silyl hydride isomer. Letters correspond to Figure 1.20, and the references refer to the report of the structure (not the synthesis).

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(Mn–Si) (Å)</th>
<th>d(Mn–H) (Å)</th>
<th>d(Si–H) (Å)</th>
<th>∠(Si–Mn–H)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp(OC)₂MnH(SiPh₃)] (a)</td>
<td>2.424(2)</td>
<td>1.55(4)</td>
<td>1.76(4)</td>
<td>–</td>
<td>Corriu (1982)²⁰⁹</td>
</tr>
<tr>
<td>[MoCp(OC)₂MnH(SiPh₂F)] (b)</td>
<td>2.352(4)</td>
<td>1.569(4)</td>
<td>1.802(5)</td>
<td>50.0(2)</td>
<td>Schubert (1982)²⁰⁸</td>
</tr>
<tr>
<td>[MoCp(OC)₂MnH(SiPh₂F)] (b)</td>
<td>2.3509(2)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Scherer (2006)²¹⁹</td>
</tr>
<tr>
<td>[MoCp(OC)₂MnH(SiCl₃)] (c)</td>
<td>2.254(1)</td>
<td>1.47(3)</td>
<td>1.79(4)</td>
<td>52.26</td>
<td>Schubert (1983)²²³</td>
</tr>
<tr>
<td>[MoCp(OC)₂MnH{SiMePh(α-Naph)}] (d)</td>
<td>2.461(7)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Corriu (1984)²⁹⁷</td>
</tr>
<tr>
<td>[Cp*(OC)₂MnH(SiHPh₂)] (e)</td>
<td>2.395(1)</td>
<td>1.52(3)</td>
<td>1.77(3)</td>
<td>48(1)</td>
<td>Schubert (1986)²³⁷</td>
</tr>
<tr>
<td>[MoCp(OC)(Me₅P)MnH(SiHPh₂)] (f)</td>
<td>2.327(1)</td>
<td>1.49(4)</td>
<td>1.78(4)</td>
<td>50(2)</td>
<td>Schubert (1986)²³⁷</td>
</tr>
<tr>
<td>[MoCp(OC)MnH(κ²-P(Ph₂)CH₂CH₂SiMe₂)] (g)</td>
<td>2.457(2)</td>
<td>1.53(4)</td>
<td>1.75(4)</td>
<td>44.8(15)</td>
<td>Schubert (1987)²⁴⁹</td>
</tr>
<tr>
<td>[Cp(dmpe)MnH(SiHPh₂)] (h)</td>
<td>2.319(4)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Sun (1994)²⁹¹</td>
</tr>
<tr>
<td>[MoCp(OC)₂MnH(SiH₂)₂] (i)</td>
<td>2.391(12)</td>
<td>1.575(14)</td>
<td>1.806(14)</td>
<td>49.1(5)</td>
<td>Scherer (2009)²⁶⁹</td>
</tr>
<tr>
<td>[(OC)₃MnH(κ₁⁺-Si₂-xanthene)] (j)</td>
<td>2.3942(5),e</td>
<td>1.61(2)</td>
<td>2.60(4),e</td>
<td>74(1),e</td>
<td>Tobita (2012)²⁸⁵</td>
</tr>
<tr>
<td>[(η⁵-Toluene)(OC)MnH(κ₁⁺-Si₂-xanthene)] (k)</td>
<td>2.4062(7),</td>
<td>1.45(3)</td>
<td>1.88(3),</td>
<td>51(1), 55(1)</td>
<td>Tobita (2012)²⁸⁵</td>
</tr>
<tr>
<td>[(η⁵-C₅H₅C₅H₂MesNHC)OC]MnH(SiHPh₂)²⁻ (l)</td>
<td>2.3456(6)</td>
<td>1.47(3)</td>
<td>1.74(3)</td>
<td>48(1)</td>
<td>Valyaev (2016)²⁹⁶</td>
</tr>
</tbody>
</table>

---

a. Selected bond metrics were provided with citation of a PhD thesis (ref. 7 in ref. 209). No structure has been submitted to the CSD, and ∠(Si–Mn–H) was not included in the text, so is not included here.
b. Hydride ligand was fixed based on neutron diffraction data, so this data is not included.
c. Hydride ligand was not located from the difference map.
d. Another unpublished crystal structure of this complexes was also reported in a dissertation (ref. 22 in ref. 297).
e. Involving the Si atom not adjacent to a hydride moiety.
f. Involving the Si atom interacting with an adjacent hydride moiety.
The original, and by far most common, synthetic route for accessing silyl hydride/hydrosilane complex is substitution of CO by a free hydrosilane under photochemical conditions (a in Scheme 1.11), followed by (for nonclassical hydrosilane complexes) partial or (for classical silyl hydride complexes) complete oxidative addition. In rare situations, such complexes have been formed by photochemically-induced substitution of a σ-hydroborane ligand (b in Scheme 1.11) or thermal substitution of a very weak ligand (c in Scheme 1.11). As well, different silyl hydride/hydrosilane complexes have been prepared by modification of the silyl group on an already existing silyl hydride/hydrosilane complex.

Scheme 1.11: Synthetic routes to silyl hydride/hydrosilane complexes. For clarity, all these complexes are drawn as nonclassical hydrosilane complexes.
1.6 – Silylene Complexes of Transition Metals

1.6.1 – Scope of Subsection

The aim of this section is to provide an overview of known silylene transition metal complexes, with a focus on crystallographic and spectroscopic characterization. Comprehensive overviews are provided only for certain subsets of silylene complexes of particular relevance to this thesis; (a) base-free, non-electronically stabilized silylene complexes with hydride co-ligands, (b) base-free, non-electronically stabilized silylene complexes with terminal hydrogen substituents on Si, (c) NHC-stabilized silylene complexes, (d) silylene complexes of groups 3-5 and 7, and (e) reactions of silylene complexes with alkenes or alkynes. With the exception of Mn examples, only species with terminal (i.e. non-bridging) silylene ligands are discussed. In addition, a brief discussion of related species (with similar M–Si bond distances to silylene complexes) is included; $\eta^3$-$\eta^2$SiR$_2$ complexes and base-stabilized silylyne complexes. For the most part, synthetic methods and reactivity are beyond the scope of this review.

1.6.2 – Introduction to Silylene Complexes

Silylenes (:SiR$_2$), as heavy analogues of carbenes, are of great interest as extremely reactive moieties. While accessing non-transient free silylenes normally requires substantial electronic or steric stabilization, highly unstable simple silylenes can be observed by transition metal coordination.

The accessibility of transition metal silylene complexes has been postulated since the early 1970s, when Kumada et al. proposed a transient Pt dimethyl silylene complex as an intermediate in the catalytic disproportionation of RMe$_2$SiMe$_2$H (R = Me, H). A few years later, in 1977, Schmid and Welz isolated the first example of a silylene complex, [(OC)$_4$Fe{═SiMe$_2$(NHEt)$_2$}] (a in Figure 1.21). However, it took another decade before the Tilley and Zybill groups independently reported the first solid-state structural characterization of such complexes (b and c, respectively, in Figure 1.21). All these early isolated silylene complexes feature base-stabilization of the silicon centre.
Development of base-free silylene complexes started in the early 1990s when the Tilley group reported the first isolated (1990)\textsuperscript{309} and crystallographically characterized (1993)\textsuperscript{310} silylene complexes (d and e, respectively, in Figure 1.21). Over the past three decades, a wide range of terminal silylene complexes have been reported, mainly with late transition metals. In addition to interesting catalytic and stoichiometric reactivity, base-free terminal silylene complexes have been observed to feature short M–Si distances and highly electrophilic Si centres relative to ubiquitous silyl (–SiR\textsubscript{3}) complexes.\textsuperscript{302-304,311}

Figure 1.21: Early examples of isolated silylene complexes.

### 1.6.3 – Electronic Structure of Silylene Complexes

Bonding between a silylene ligand and a transition metal centre parallels that of carbene complexes, with a formal double bond between the Si and M atoms. The vast majority of reported examples are electrophilic at silicon, and are therefore analogous to Fischer-type carbene complexes. The electronic structure of these complexes has been discussed in a number of reports,\textsuperscript{312} and can be described most simply as involving σ-donation from a filled sp\textsuperscript{2} orbital of the silylene fragment to a vacant metal d-orbital (the singlet form of simple free silylenes is more stable than the triplet form),\textsuperscript{313} with concurrent π-backdonation from a metal d-orbital to the empty p-orbital of the silylene (which is orthogonal to the plane formed by Si and the two substituents); Figure 1.22.\textsuperscript{302} Compared to Fischer carbene complexes with equivalent substituents, the degree of π-backdonation is typically less, resulting in the M–Si bond being polarized towards the
metal, making the Si centre highly electrophilic and reducing the extent of M=Si double bond character.\(^{302}\)

**Figure 1.22:** Electronic structure of Fischer-type silylene complexes. For clarity, in the diagram for \(\sigma\)-donation, only one lobe is shown for each orbital (from a variety of potential orbitals on the transition metal, and an \(\text{sp}^2\) orbital on the Si centre).

A significant subset of Fischer-type silylene complexes involves \(N\)-heterocyclic silylene (NHSi) ligands. One class of NHSi (Figure 1.23; left) involves two N substituents on the Si centre forming part of a Si-containing ring (analogous to \(N\)-heterocyclic carbenes). These NHSi ligands are electronically stabilized because filled p orbitals on N donate some electron density to the empty p-orbital on silicon, and their complexes feature less electropositive Si centres than complexes with non-electronically stabilized silylene ligands.\(^{314}\) Silylene groups where one of the substituents on Si is a bidentate amidinate ligand are also commonly referred to as NHSi ligands, though could alternatively be considered a type of base-stabilized silylene (Figure 1.23; right).\(^{315,316}\) Free NHSi moieties are often stable in the absence of a transition metal centre.\(^{315,316}\)

**Figure 1.23:** \(N\)-heterocyclic silylene complexes (NHSi ligands).
1.6.4 – Characterization of Base-free non-Electronically Stabilized Silylene Complexes

X-ray crystallography is an important technique in the characterization of silylene complexes. Relative to other silicon-based ligands, silylene complexes display two diagnostic structural features. First, they feature a planar environment about the sp$^2$ Si centre (in which lies both substituents of Si, the Si centre, and the metal); the sum of angles about the Si centre is normally statistically equivalent to 360°. Second, these complexes usually feature shorter M–Si distance than in silyl complexes of the same metal, but longer than in silylyne complexes (a summary of M–Si distances in structurally characterized silylene complexes is provided in Table 1.7). In general, the only complexes with shorter M–Si bonds are silylyne complexes. However, it should be noted that exceptions to this have been reported, including the first structurally characterized silylene complex where the Os–Si distance matches that of a single bond (in this complex, alternative resonance structures could be envisaged where the silylene-character is removed). As well, chromium and nickel complexes with N-heterocyclic silylene complexes have been reported with shorter M–Si distances than non-electronically stabilized examples. In addition, the shortest Fe–Si bond is found in a complex with an η$^3$-H$_2$SiR$_2$ ligand (vide infra), and the shortest Pd–Si bonds are found in complexes with pincer ligands containing central silyl donors. Therefore, it is clear that bond lengths can be influenced by factors other than intrinsic bond strength, especially when Si is part of a multidentate or η$^n$-coordinated (n > 1) ligand.
Table 1.7: M–Si distances for base-free, non-electronically stabilized silylene complexes (Å), as determined by X-ray or neutron crystal structures. Only metals for which solid state structures of such complexes have been obtained are included. Values are accurate as of 2016, and given to two decimal places.

<table>
<thead>
<tr>
<th>M</th>
<th>d(M–Si) {# of complexes} (^{211})</th>
<th>M</th>
<th>d(M–Si) {# of complexes} (^{211})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>2.65 ({1})</td>
<td>Os</td>
<td>2.22-2.42 ({4})^(2)</td>
</tr>
<tr>
<td>Cr</td>
<td>2.36-2.48 ({4})</td>
<td>Co</td>
<td>2.12 ({1})^(2)</td>
</tr>
<tr>
<td>Mo</td>
<td>2.29-2.39 ({8}^a)</td>
<td>Ir</td>
<td>2.21-2.26 ({3})</td>
</tr>
<tr>
<td>W</td>
<td>2.33-2.64 ({14}^b)</td>
<td>Ni</td>
<td>2.09-2.13 ({2})</td>
</tr>
<tr>
<td>Fe</td>
<td>2.15 ({1})</td>
<td>Pd</td>
<td>2.24 ({1})</td>
</tr>
<tr>
<td>Ru</td>
<td>2.18-2.28 ({9}^c)</td>
<td>Pt</td>
<td>2.21-2.27 ({5})</td>
</tr>
</tbody>
</table>

a. This range includes two structures of [Cp*(dmpe)MoH(=SiEt\(_2\))], obtained by neutron and X-ray diffraction.

b. If [(OC)\(_5\)W(=SiPh(C\(_6\)H\(_4\)-2,6-{PO(O)Pr\(_2\)}\(_2\)-4-Bu)], with an extremely bulky substituent on Si, is excluded as an outlier, this range becomes 2.33-2.44 Å. Also, this range includes two structures of \([\text{EtMe}_4\text{Cp}(OC)\text{WH}(=\text{SiH}(C(SiMe}_3)_3))\], obtained by neutron and X-ray diffraction.

c. This does not include [(OC)\(_4\)Os(=Si(S\(_p\)tol)\(\{RuCp^*(PMe}_3\}_2\))], for which there is a contribution from a zwitterionic resonance structure with a Ru=Si bond (2.286(2) Å).\(^{310}\)

d. If [(OC)\(_4\)Os(=Si(S\(_p\)tol)\(\{RuCp^*(PMe}_3\}_2\))], for which are various resonance structures which dilute the silylene character of the Os–Si bond, is treated as an outlier then this range becomes 2.22-2.26 Å.

e. No Co examples of base-free, non-electronically stabilized silylene complexes had been reported prior to 2016, so the single reported example (from 2018) is included here.\(^{320}\)

NMR spectroscopy is also commonly used to definitively identify silylene complexes of transition metals. In particular, the high frequency \(^{29}\)Si NMR chemical shift (>200 ppm) of the sp\(^2\) Si centre in base-free, non-electronically stabilized silylene complexes is very diagnostic.\(^{304}\) This mirrors \(^{13}\)C NMR chemical shifts for carbene donors in transition metal complexes, which generally lie between 240 and 370 ppm.\(^{321}\) By contrast, the vast majority of \(^{29}\)Si NMR chemical shifts for N-heterocyclic silylene complexes lie in the 40-190 ppm range.\(^{316}\) In certain classes of base-free, non-electronically stabilized silylene complexes, complementary NMR information can also be diagnostic. For example, hydrogen substituents on silylene ligands give rise to unusually high frequency \(^1\)H NMR chemical shifts (6.34-12.1 ppm,\(^1\) in contrast to H-substituted silyl ligands which normally give rise to \(^1\)H NMR chemical shifts from 4 to 5.5 ppm).\(^{227}\) As well, for transition metals which are NMR active, the M–Si coupling

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\(^1\) See section 1.6.6 for references used to obtain \(^1\)H NMR chemical shifts of silylene complexes with terminal hydride substituents.
constants involving silylene ligands are significantly higher than those involving silyl ligands (for example, in \([\text{Cp}*{(OC)}_2\text{W(SiMe}_3\rangle(=\text{SiMes}_2)]\), which contains a silyl and a silylene ligand, the coupling constant between \(^{183}\text{W}\) and \(^{29}\text{Si}\) is 30.5 Hz for the former and 154.9 Hz for the latter).\(^{322}\)

1.6.5 – Silylene Hydride Complexes

In 1993, shortly after they reported the first X-ray crystal structure of a silylene complex (\textit{vide supra}), the Tilley group reported the synthesis and X-ray crystal structure of trans-\([\text{Cy}_3\text{P})_2\text{PtH}\{=\text{Si(SEt)}_2\}\]^+, the first silylene complex with a hydride co-ligand (a in Figure 1.24).\(^{323}\) One of the reasons that silylene hydride complexes are of great interest is that they can potentially be observed as a variety of isomers.\(^{324}\) Also, they often exist in equilibrium with silyl complexes (the product of 1,1-insertion of the hydride across the M=Si double bond; Scheme 1.12). This equilibrium is often implicated both in the synthesis of silylene hydride complexes (by initial generation of an \(\alpha\)-hydride containing silyl ligand)\(^{227-229}\) and reactions of silylene hydride complexes (the vacant coordination site generated in the isomerization of a silylene hydride to a silyl complex permits various reagents to coordinate to the metal centre prior to intramolecular reactivity involving the silyl ligand). As well, the presence of a hydride ligand offers an additional NMR handle for monitoring reactions involving silylene hydride complexes.

\[ \text{Figure 1.24: Early examples of silylene hydride complexes.} \]
Scheme 1.12: Equilibrium between silylene hydride and silyl complexes.

In many silylene-hydride complexes, significant Si–H interligand interactions have been observed. Silylene hydride complexes with interligand Si–H interactions were first reported in 2004 independently by the Tobita (b in Figure 1.24; $^{[\text{EtMe}_4\text{Cp}(\text{OC})_2\text{WH}(=\text{SiH}\{\text{C(SiMe}_3\}_3)\}))$ and Tilley (c in Figure 1.24; $^{[\text{Cp}^*(\text{dmpe})\text{MoH}(=\text{SiEt}_2)\})^m$) groups, and since that time solid-state structures of a variety of such complexes have been reported for W, Fe, Ru, and Ni. Structurally, the interacting metal hydride ligands are generally oriented so that they could interact with the vacant p orbital on Si (i.e. out of the plane formed by Si and its terminal substituents). These interligand interactions are apparent from short Si–H distances. While the range of Si–H distances from all crystallographically characterized examples of these complexes is 1.17(5)-1.94(6) Å (Table 1.8), this is misleading both because of the difficulty in accurately locating hydrogen atoms by X-ray diffraction, and the presence of outliers at both ends of this range. For a pair of these complexes (the first two reported; b and c in Figure 1.24), neutron structures were also obtained to allow for accurate determination of the Si$_{\text{sp}2}$–H$_{\text{M}}$ distances (1.68(1)-1.720(10) Å; Table 1.8), which are longer than a single bond (in base-free silylene complexes with a terminal hydride substituent, the Si$_{\text{sp}2}$–H$_{\text{Si}}$ distances range from 1.33-1.56 Å), though are close enough to suggest some degree of interligand interaction. Spectroscopically, interligand Si–H interactions are apparent in the magnitudes of $^{29}$Si–$^1$H coupling constants (28-62 Hz; Table 1.8), which are intermediate between those expected for 1-bond (~200 Hz) and 2-

---

$m$ A variety of other Mo silylene hydride complexes have been reported to feature Si–H interligand interactions, but for these complexes an X-ray crystal structure was not obtained, or the bridging hydride was not located from the difference map.
bond (< 10 Hz) coupling\textsuperscript{261} (as discussed in section 1.5.5, determining the sign of $J_{\text{Si,H}}$ is necessary for accurate interpretation of this data, especially at low magnitudes; however this has not been normally done in the literature for silylene hydride complexes).

Table 1.8: Structural and spectroscopic data for silylene hydride complexes for which solid state structures have been reported and the metal hydride was located from the difference map. Unless otherwise noted, values were obtained by X-ray diffraction.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Structural Data</th>
<th>Spectroscopic Data</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo $\text{[Cp^*(dmpe)MoH(=SiEt\textsubscript{2})]}$</td>
<td>$d(\text{M}–\text{Si}) = 2.34(1)^a$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 358.9(5)^a$</td>
<td>Tilley (2004)\textsuperscript{266}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.68(1)^a$</td>
<td>$J_{\text{H,Si}} = 44$</td>
<td></td>
</tr>
<tr>
<td>W $\text{[\text{MeCp}Cp\text{OC}_\text{2}WH(=\text{SiH}{\text{C(SiMe}_3})}}}^f$</td>
<td>$d(\text{M}–\text{Si}) = 2.359(8)^a$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 359.4(5)^a$</td>
<td>Tobita (2004, 2012)\textsuperscript{277}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.72(1)^a$</td>
<td>$J_{\text{H,Si}} = 28.3$</td>
<td></td>
</tr>
<tr>
<td>W $\text{[ArOC}_\text{2}WH(=\text{Si}{\text{O}^{\text{Pr}}} {\text{C(SiMe}_3})}^d\text{Ar} = \text{MeCp}$</td>
<td>$d(\text{M}–\text{Si}) = 2.3760(9)$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 360.0(2)$</td>
<td>Tilley (2012)\textsuperscript{277}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.94(6)$</td>
<td>$J_{\text{H,Si}} = 34.3$</td>
<td></td>
</tr>
<tr>
<td>Fe $\text{[Cp^*(\text{Pr}_3\text{MeP})FeH(=\text{SiH(Trip)})]}$</td>
<td>$d(\text{M}–\text{Si}) = 2.129(1)$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 357(2)$</td>
<td>Tilley (2018)\textsuperscript{279}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.67(5)$</td>
<td>$J_{\text{H,Si}} = –$</td>
<td></td>
</tr>
<tr>
<td>Ru $\text{[(RNC)\text{PhB(CH}_2\text{PP}_3\text{)}_3\text{RuH}(=\text{SiMes}_2)]}$</td>
<td>$d(\text{M}–\text{Si}) = 2.246(1)$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 360.0(5)$</td>
<td>Tilley (2013)\textsuperscript{300}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.74(6)^d$</td>
<td>$J_{\text{H,Si}} = 62.3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R = \text{o-xylyl}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru $\text{[Cp^*(\text{IXy})RuH(=\text{SiH(Trip)})\cdot\text{AgOTf}]}^g$</td>
<td>$d(\text{M}–\text{Si}) = 2.264(1)$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 355(2)$</td>
<td>Tilley (2014)\textsuperscript{314}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.77(5)$</td>
<td>$J_{\text{H,Si}} = 36.6$</td>
<td></td>
</tr>
<tr>
<td>Ni $\text{[(dtbpe)NiH(=\text{SiMes}_2)]}$</td>
<td>$d(\text{M}–\text{Si}) = 2.147(2)$</td>
<td>$\Sigma(\text{X}–\text{Si}–\text{Y}) = 360.0(2)$</td>
<td>Hillhouse (2010)\textsuperscript{333}</td>
</tr>
<tr>
<td></td>
<td>$d(\text{H}–\text{Si}) = 1.64(7)$</td>
<td>$J_{\text{H,Si}} = 43.4$</td>
<td></td>
</tr>
</tbody>
</table>

a. From neutron structure data.
b. From X-ray structure data.
c. The neutron structure was obtained from an analogue where the hydride substituents on W and Si were replaced with $^7$H.
d. It is possible that the solid state structure does not accurately reflect the solution state structure; the large $J_{\text{Si,H}}$ is indicative of a strong interligand Si–H interaction in solution while the long Si–H crystallographically determined distance (and the position of the interacting hydride close to the plane formed by Si and its terminal substituents) is indicative of a negligible interligand interaction.
e. The position of one of the hydride ligands (not included in Table 1.8) was unstable under refinement.
f. The author noted that this value is unrealistically short.
g. This structure involves the Ag ion also interacting with the Ru=Si bond.
Surprisingly, no apparent weakening of the M–Si bond is observed relative to complexes without these interligand interactions (in stark contrast to Lewis base coordination to Si in silylene complexes, which result in significant weakening of this bond; vide infra); the M–Si distances (Table 1.8) are well within the range of base-free silylene complexes (Table 1.7). As well, this interaction does not appear to impart significant pyramidalization to the Si centre (sum of angles around Si, not including H, is $\geq 355^\circ$; Table 1.8), suggesting that the character of the Si atom remains sp$^2$ (again in contrast to Lewis base coordination to Si in silylene complexes; vide infra). Finally, the $^{183}\text{W}–^{29}\text{Si}$ coupling constants for the two W complexes in Table 1.8 (109.9 and 132 Hz) are comparable to those in related hydride-free silylene complexes.

1.6.6 – Silylene Complexes with Terminal SiH Substituents

Silylene complexes with a terminal SiH substituent are relatively rare; such a complex, \([(\text{Et}_3\text{P})_3\text{IrH}_2(\text{=SiH}(\text{C}_6\text{H}_3-\text{Mes}_2-2,6))]\text{[B(C}_6\text{F}_5)_4}\), was first reported by Tessier and Youngs in 2002 (a in Figure 1.25). The same year, Tilley et al. suggested \([\{\text{PhB(CH}_2\text{PPh}_2)_3\}\text{IrH}_2(\text{=SiH(Trip)})]\) (b in Figure 1.25) as an intermediate in the synthesis of a disubstituted silylene hydride complex, and two years later, the Tobita and Tilley groups independently reported the first structurally characterized examples, \([\text{EtMe}_4\text{Cp}(\text{OC})_2\text{WH}(\text{=SiH}(\text{C}(\text{SiMe}_3)_3))]\) (c in Figure 1.25; the same complex as b in Figure 1.24) and \([\text{Cp}^*(\text{dmpe})\text{MoH}(\text{=SiHPh})]\) (d in Figure 1.25), respectively. Aside from Ir examples, these types of complexes have only been reported for groups 6 and 8, and group 7 examples are notably absent. Extensive studies by the Tilley and Tobita groups have demonstrated that hydride substituents on the sp$^2$ Si centres permit these silylene complexes to demonstrate unusual reactivity, including alkene insertion into that Si–H bond (vide infra) and accessing silylyne (M≡SiR) complexes.

As well, the iron complex \([\text{Cp}^*(\text{Pr}_2\text{MeP})\text{FeH}(\text{=SiH(Trip)})]\), which was reported in 2018, features a shorter Fe–Si distance than the single iron silylene complex in Table 1.7, which only includes species reported prior to 2017.
The first reported examples of transition metal silylene complexes were stabilized by Lewis base coordination to the silicon centre (*vide supra*). Of the various base-stabilized silylene complexes that have since been reported, one of the common classes involves *N*-heterocyclic carbenes (NHCs; various examples are outlined in Figure 1.26) as the Lewis base. One of the reasons for this is the accessibility of stable NHC-silylene adducts which can act as precursors in the synthesis of such complexes. While the first reported NHC-silylene adduct involved an otherwise stable parent free silylene, in 2009, the Roesky and Filippau groups simultaneously reported the synthesis of stable NHC-silylene adducts $X_2Si\cdot IPr$ ($X = Cl$ or $Br$; a and b, respectively, in Figure 1.27) which involve stabilization of unstable parent free dihalosilylenes. These adducts contain a lone pair and were proposed to be able to act as Lewis bases. The following year, both groups investigated the reactions of these adducts with transition metal precursors to prepare NHC-stabilized silylene transition metal complexes (Roesky group; c and d in Figure 1.27) or an NHC-stabilized silylyne transition metal complex (Filippau group). In the past decade, many NHC-stabilized silylene transition metal complexes have been reported for V, Cr, W, Fe, Co, Rh, and Ni (Table 1.9; *vide infra*), and the most common method for their synthesis is substitution of neutral ligands by an intact silylene-NHC adduct. However, there are a handful of examples which were formed by addition of a free carbene to a base-free silylene complex or a pyridine-stabilized silylene complex (via substitution of pyridine). As well, carbene association to a transient (unobserved) base-free silylene complex is presumably the final step in the syntheses of a pair of NHC-stabilized iron silylene complexes.
Figure 1.26: Glossary of NHCs.

Figure 1.27: The first reported NHC-silylene adducts and NHC-stabilized silylene complexes. The M–Si bond is shown as a double bond for clarity, and does not reflect the bond strength.

Coordination of a Lewis base such as an NHC to the sp\(^2\) Si centre of a silylene complex significantly affects the M–Si bond (Figure 1.28). First, the degree of \(\pi\)-backdonation is significantly reduced because of much poorer overlap of the pertinent orbitals and build up of electron density in the accepting Si-based orbital (a Si–C\(_{\text{NHC}}\) \(\sigma\) antibonding orbital). Second, the formerly vacant p orbital on Si has been hybridized, leading to pyramidalization. Because of these effects, the M–Si bond is significantly weaker than in base-free silylene complexes, though usually stronger than in silyl complexes.\(^{302}\)
Weaker bonding in base-stabilized silylene complexes is reflected in significantly longer M–Si bond lengths than in base-free silylenes (Table 1.9), though they remain on the shorter end of the range normally observed in silyl complexes. This reflects that the bond strength is intermediate between that in base-free silylene (sp²-hybridized Si) and silyl (sp³-hybridized Si) complexes. For most NHC-stabilized silylene complexes, this is also reflected by NMR spectroscopy; their $^{29}$Si NMR chemical shifts typically fall within the 25-100 ppm range (Table 1.9; shifted to higher frequency of silyl complexes, but not nearly to the extent observed for silylene complexes). However, in a number of NHC-stabilized silylene complexes, very low frequency $^{29}$Si chemical shifts have been observed (Table 1.9). This has been rationalized by adoption of a zwitterionic bonding motif which results in limited π-backdonation to the Si centre from the metal. As well, terminal H substituents on NHC-stabilized silylene ligands give rise to $^1$H NMR environments in the range associated with silyl complexes or free hydrosilanes (4.16-7.27 ppm).

Figure 1.28: Electronic structure of NHC-stabilized silylene complexes. Dashed line in the Chemdraw figure indicates a single or double bond. For clarity, in the diagram for σ-donation, only one lobe is shown for each orbital.
### Table 1.9: Structurally characterized NHC-stabilized silylene complexes. NHC names relate to those in Figure 1.26.

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(M–Si) (Å)</th>
<th>δ^{29}Si (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>2.4043(7)</td>
<td>88.7</td>
<td>Roesky (2011)(^\text{350})</td>
</tr>
<tr>
<td>[Cp(OC)(_3)V{=SiCl(_2)(IPr)}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>2.4128(7)</td>
<td>39.6</td>
<td>Filippau (2014)(^\text{351})</td>
</tr>
<tr>
<td>[Cp*(OC)(_3)Cr{=Si(OH)(_2)(SIdipp)}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(OC)(_2)Cr{=SiCl(_2)(IPr)}] (_2)</td>
<td>2.3111(12), 2.3118(12)</td>
<td>64.57</td>
<td>Ghadwal and Frenking (2017)(^\text{352})</td>
</tr>
<tr>
<td>[(OC)(_2)W{=SiH(_2)(IPr)}]</td>
<td>2.573(4)</td>
<td>–71.6</td>
<td>Rivard (2012)(^\text{352})</td>
</tr>
<tr>
<td>W</td>
<td>2.6342(7)</td>
<td>31.12</td>
<td>Scheschkewitz (2015)(^\text{353})</td>
</tr>
<tr>
<td>[Cp*(OC)(_2)WH{=SiH{C(SiMe(_3))}_3} (MENHC)}]</td>
<td>2.5206(8)</td>
<td>–16.7</td>
<td>Tobita (2015)(^\text{356})</td>
</tr>
<tr>
<td>[(OC)(_4)W{=SiCl(_2)(IPr)}] (_2)</td>
<td>2.464(2), 2.4707(19)</td>
<td>24.84</td>
<td>Ghadwal and Frenking (2017)(^\text{352})</td>
</tr>
<tr>
<td>[(OC)(_2)W{=SiH(Si(_t)Bu(_3))(MeNHC)}]</td>
<td>2.668(2)</td>
<td>–94.2</td>
<td>Inoue (2017)(^\text{355})</td>
</tr>
<tr>
<td>Fe</td>
<td>2.229(11)</td>
<td>59.2</td>
<td>Roesky (2011)(^\text{356})</td>
</tr>
<tr>
<td>[(OC)(_3)Fe{=SiCl(_2)(IPr)}] (_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[L(_2)FeH(_2)(\eta(_3)-HSiPh(_2))){=SiHPh(L)}] (L = IEt(_2)Me(_2))</td>
<td>2.170(1)</td>
<td>27.55</td>
<td>Deng (2014)(^\text{359})</td>
</tr>
<tr>
<td>[(OC)(_4)Fe{=SiHAr(MENHC)}] (Ar = 2,6-bis(2,4,6-trisopropylphenyl)phenyl)</td>
<td>2.3268(6)</td>
<td>–11.1</td>
<td>Müller (2016)(^\text{357})</td>
</tr>
<tr>
<td>[(OC)(_3)Fe{=SiHCl(IPr)}] (_2)</td>
<td>2.189(3), 2.213(3)</td>
<td>44.02, 44.32</td>
<td>Robinson (2016)(^\text{358})</td>
</tr>
<tr>
<td>Ni</td>
<td>2.3323(4)</td>
<td>26.3</td>
<td>Scheschkewitz and Jana (2019)(^\text{361})</td>
</tr>
<tr>
<td>[(OC)(_2)Ni{=SiCl(_2)(IPr)}] (_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(IPr)(_2)Fe(\eta(_2)-H(_2)SiHPh(_2))){=SiH(_2)(IPr)}]</td>
<td>2.2227(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(OC)(_2)Fe{=SiMe(_2)(IPr(_2)Me(_2)})]</td>
<td>2.3323(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>2.2276(12), 2.2278(13)</td>
<td>44.11</td>
<td>Roesky (2010)(^\text{347})</td>
</tr>
<tr>
<td>[(OC)(_2)Co{=SiCl(_2)(IPr)}] (_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(Cp(OC)Co{=SiCl(_2)(IPr)}]</td>
<td>2.1349(4)</td>
<td>31.86</td>
<td>Roesky (2011)(^\text{350})</td>
</tr>
<tr>
<td>Rh</td>
<td>2.3605(8)</td>
<td>27.9</td>
<td>Rivard (2012)(^\text{352})</td>
</tr>
<tr>
<td>[(OC)(_2)Rh{=SiCl(_2)(IPr)}] (_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>2.1854(7), 2.1955(9)</td>
<td>43.19</td>
<td>Roesky (2010)(^\text{348})</td>
</tr>
<tr>
<td>[(Me(_3)Si)(_2)Ni{=SiMe(_2)(IPr)}]</td>
<td>2.223(5)</td>
<td></td>
<td>Tilley (2019)(^\text{362})</td>
</tr>
</tbody>
</table>
Two NHC-stabilized silylene complexes with hydride co-ligands have been reported (not considering complexes where all hydride co-ligands are involved in interligand interactions with other co-ligands); the iron complex $[(\text{IEt}_2\text{Me}_2)_2\text{FeH}_2(\eta^2-\text{HSiPh}_2)\{=\text{SiHPh}(\text{IEt}_2\text{Me}_2)\}]$ (a in Figure 1.29) and the tungsten complex $\left[\text{Cp}^*(\text{OC})_2\text{WH}(=\text{SiH}\{\text{C(SiMe}_3)_3}\{^{\text{Me}}\text{NHC})\}\right]$ (b in Figure 1.29). While significant Si–H interactions were observed in the iron system, the tungsten complex only features a weak interligand Si–H interaction ($J_{\text{Si,H}} = 27.0$ Hz). A base-free silylene analogue of this complex, $\left[\text{Cp}^*(\text{OC})_2\text{WH}(=\text{SiH}\{\text{C(SiMe}_3)_3}\}\right]$, was not included in Table 1.8 because no X-ray crystal structure was obtained. However, this complex features a much higher $J_{\text{Si,H}}$ coupling of $109.9$ Hz, suggesting that NHC coordination to a silylene hydride complex significantly weakens any interligand Si–H interactions.

Figure 1.29: NHC-stabilized silylene hydride complexes. The M–Si bond is shown as a double bond for clarity, and does not reflect bond strength.

1.6.8 – Silylene Complexes of Early/Mid Transition Metal Centres

The majority of reported silylene complexes involve late transition metal centres, and of silylene complexes involving gr. 3-7, the vast majority are group 6 complexes. Only a handful of base-free silylene complexes have been reported for gr. 3-5 metals (Figure 1.30). To date, the only group 3 example involves an N-heterocyclic silylene ligand (a in Figure 1.30). Meanwhile, the only group 4 examples are a series of related N-heterocyclic silylene titanium(II) complexes (b-d in Figure 1.30), a series of titanium silylene complexes with a chelating $\kappa^2$-disilyl substituent on the sp$^2$ Si centre ($[\text{Cp}_2\text{LTi}(=\text{Si}\{\kappa^2-\text{Si(SiMe}^\prime\text{Bu}_2)\}\text{C(SiMe}^\prime\text{Bu}_2)_2\text{Si(SiMe}^\prime\text{Bu}_2)\})$; L = THF, PMe$_3$, o-xylylNC:
e-g in Figure 1.30), and the hafnium complexes \( [{^1}E^1\text{Cp}(\text{Me}_3\text{P})_n\text{Hf}\{\text{=Si}(\text{SiMe'}\text{Bu}_2)_2}\} \) (n = 0 or 1; h and i in Figure 1.30) and \([\text{Cp}_2\text{Hf}\{\text{=Si}\{\kappa^2\text{-C}(\text{SiMe}_2)\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{SiMe}_3)\}\} \) (j in Figure 1.30; decomposes above -70 °C). The only vanadium example to have been structurally characterized involves an N-heterocyclic silylene (k in Figure 1.30). In addition, a pair of base-free vanadium silylene complexes with non-electronically stabilized silylene ligands have also been reported with limited characterization; in 2005 Egorov et al. reported \([\text{Cp}^*_2\text{V}\{\text{=SiMe}_2\}\] based on EPR spectroscopic observation (l in Figure 1.30), and in 2008 the Tilley group reported \([\text{Cp}(\text{dmpe})\text{V}\{\text{=SiPh}_2\}\] on the basis of elemental analysis (m in Figure 1.30). These early transition metal silylene complexes have generally been proposed to be nucleophilic at Si (akin to Schrock-type carbene complexes), on the basis of reactions with various nucleophiles which result in reactivity which does not involve nucleophile coordination to the Si centre, in contrast to the bulk of reported silylene complexes which are electrophilic at silicon (\textit{vide supra}).

Figure 1.30: Base-free silylene complexes of gr. 3-5.

In addition, a pair of donor-stabilized silylene complexes of gr. 5 transition metals have been reported. In 2005, the Tobita group reported the tantalum complex \([\text{Cp}_2\text{Ta}\{\kappa_2\text{-Me}_2\text{Si}(\text{OMe})\text{SiMe}_2\}\], which features a bidentate alkoxy-bridged bis(silylene) ligand (a in Figure 1.31). Six years later, the NHC-stabilized vanadium silylene complex \([\text{Cp}(\text{OC})_3\text{V}\{\text{=SiCl}_2(\text{IPr})\}\] was reported by Dittrich and Roesky et al. (b in Figure 1.31).
Figure 1.31: Donor-stabilized silylene complexes of gr. 4-5.

Despite the numerous examples of gr. 6 and 8 silylene complexes, no base-free, monometallic, non-electronically stabilized group 7 silylene complexes have been isolated. No Tc silylene complexes of any nature have been reported (as expected due to its radioactivity), and the only structurally characterized Re examples involve N-heterocyclic silylene ligands which would be stable even in the absence of transition metal coordination (a and b in Figure 1.32).\(^ {372}\) Additionally, in 1991 the Gladysz group reported the base-stabilized silylene complex \([\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}(=\text{SiMe}_2(\text{NC}_5\text{H}_5))]^+\) (c in Figure 1.32), and suggested the involvement of a base-free rhenium silylene intermediate ([\text{Cp}(\text{ON})(\text{Ph}_3\text{P})\text{Re}(=\text{SiMe}_2)]^+) in a number of chemical transformations.\(^ {373}\) As well, a pair of radical silylene complexes have been observed by EPR spectroscopy (d and e in Figure 1.32).\(^ {374}\)

Figure 1.32: Reported silylene complexes of rhenium.

A handful of manganese complexes involving bridging or electronically stabilized silylene ligands have been reported. As early as 1973, Simon and Dahl reported the
dinuclear complex \[\{(OC)_4Mn\}_2(\mu_2-SiPh_2)_2\], for which an X-ray crystal structure was obtained that showed two silylene ligands, each bridging between the two Mn atoms (a in Figure 1.33). A decade later, Herrmann et al. reported the dimetallic complex \[\{\text{Cp}^*(OC)_2\text{MnH}\}_2(\mu-SiH_2)\] and trimetallic complex \[\{\text{Cp}(OC)_2\text{Mn}\}_3(\mu_2-SiH_2)\] (b and c, respectively, in Figure 1.33), and an X-ray crystal structure was later obtained for the former. Herrmann’s complexes (like the earlier 1973 example) each contain a silylene ligand bridging between two Mn atoms. The Mn–Si distances in these bridging complexes (2.402(2)-2.434(3) Å) are nearly equivalent to the average over all structurally characterized manganese silyl complexes (2.45 Å), suggestive of negligible double bond character.

In 1991, the Corriu and Ogino groups independently reported the first monometallic manganese silylene complexes, which in both cases featured base-stabilization. The Corriu example (for which a crystal structure was not obtained) featured coordination to the sp\(^2\) Si centre by a pendant amine (\[\text{MeCp}(OC)_2\text{Mn}\{\kappa^2-SiPh(C_{12}H_{14}N)\}\]; d in Figure 1.33), and the electronically-stabilized nature of the silylene ligand is apparent by the stability of the free silylene in the absence of a transition metal centre. Ogino’s report (\[\{(OC)_4\text{Mn}\{\kappa^2-\text{Me}_2\text{Si(OMe)SiMe}_2\}\}\]) involved a delocalized bis(silylene)ligand where the Si centres were bridged by an oxymethyl group (e in Figure 1.33), and a base-free manganese silylene complex (\[\{(OC)_4\text{Mn(OMe)}\text{SiMe}_2\{\mu_2-\text{SiMe}_2\}\}\]) was proposed as an intermediate in its synthesis. Twenty years later, the Roesky group reported a pair of complexes featuring N-heterocyclic silylene ligands, where the free ligand is stable in the absence of a transition metal centre (f and g in Figure 1.33). The Mn–Si distances of 2.2789(8)-2.3571(7) Å in these reports are at the very low end of known metal silyl complexes (the shortest Mn–Si bond in a silyl complex is 2.254(1) Å in \[\{\text{MeCp}(OC)_2\text{MnH(SiCl}_3)\}\]), and the \(^{29}\text{Si}\) NMR chemical shifts of 61.11-124.0 ppm are consistent with a limited degree of silylene character (as expected for base-stabilized or N-heterocyclic silylene complexes; \textit{vide supra}). Very recently (following publication of the base-free silylene hydride complexes discussed in Chapter 4), the Driess group reported X-ray crystal structures for a series of
$N$-heterocyclic silylene manganese(II) complexes (h-j in Figure 1.33).\textsuperscript{380} However, the Mn–Si distances in these divalent manganese complexes of 2.5923(5)-2.6347(7) Å are significantly longer than those in Roesky’s monovalent examples (\textit{vide supra}).

![Image of silylene complexes of manganese]

**Figure 1.33:** Silylene complexes of manganese.

1.6.9 – Reactions of silylene complexes with alkenes and alkynes

Given that reactions of transition metal silylene complexes with various reagents have been reviewed elsewhere,\textsuperscript{303} we herein provide a comprehensive review only of reactions with alkene and alkyne reagents, as this pertains directly to a significant portion of the work presented in this thesis.

Alkene hydrosilylation, the addition of a H–Si bond across an unsaturated C=C bond, is an industrially important chemical transformation.\textsuperscript{381,382-385} In 2003, the Tilley group reported a new mechanism for hydrosilylation mediated by transition metal silylene complexes with a terminal hydrogen substituent, which has subsequently become known as the Glaser-Tilley mechanism (Figure 1.34 bottom).\textsuperscript{340} This mechanism is unusual in that it selectively converts primary hydrosilanes ($\text{H}_3\text{SiR}$, R = Ph, Hex, Mes, Cy) to secondary hydrosilanes.\textsuperscript{385,386} A key step in this mechanism is the direct insertion
of an alkene into the Si–H bond of a terminal silylene ligand with a terminal SiH substituent. This stoichiometric reaction was first observed in the reaction of \([\{\text{PhB}(\text{CH}_2\text{PPh}_2)_3\}\text{IrH}_2\{=\text{SiH(Trip)}\}]\) (b in Figure 1.25; *vide supra*) with cyclooctene, and subsequently demonstrated in the stoichiometric reactions of \([\text{Cp*}(\text{iPr}_3\text{P})\text{RuH}_2\{=\text{SiHPh(ET}_2\text{O)}\}]^+\) (the catalyst in the initial report on the Glaser-Tilley mechanism) with 1-hexene and the base-free analogue \([\text{Cp*}(\text{iPr}_3\text{P})\text{RuH}_2(=\text{SiHMes})]^+\) with various alkenes in the absence of free hydrosilanes. Calculations have shown that this mechanism is lower in energy than the conventional Chalk-Harrod or modified Chalk-Harrod mechanisms (Figure 1.34 top left and top right, respectively) for model cationic Ru systems. Cationic Ru and Ir catalysts have been shown to be active towards hydrosilylation of a variety of terminal linear (ethylene, 1-hexene, 1-octene, vinyltrimethylsilane, tert-butylethylene, styrene, and \(p\)-chlorostyrene) and internal cyclic (1-methylcyclohexene, cyclopentene, cyclohexene, and \(cis\)-cyclooctene) olefins. Unlike other hydrosilylation mechanisms, no vinylsilane byproducts were observed in these reactions.
Figure 1.34: Common mechanisms for olefin hydrosilylation.\textsuperscript{340} Key alkene insertion steps are highlighted in grey.

It appears that a very electropositive Si centre is required for the Glaser-Tilley mechanism to proceed. Aside from the initial (stoichiometric) report of alkene insertion into the terminal Si–H bond of $\{\text{PhB(} \text{CH}_2\text{PPh}_2\}_3\text{IrH}_2\{=\text{SiH(Trip)}\}$ (which can be considered to be zwitterionic with a positive charge on Ir), all such reactions have involved cationic systems. Furthermore, in the reaction of neutral $\{\text{PhB(} \text{CH}_2\text{PPh}_2\}_3\text{IrH}_2\{=\text{SiH(Trip)}\}$ with cyclooctene, various alternative mechanisms for alkene insertion (i.e. not direct insertion into the Si–H bond, as in the Glaser-Tilley mechanism) were proposed.\textsuperscript{335}
While the cationic osmium complex $[\text{Cp}^*(\text{Pr}_3\text{P})\text{OsH}_2\{=\text{SiH(Trip)}\}]^+$ was observed to react rapidly with alkenes even at low temperatures (though it proved to be inactive towards catalytic hydrosilylation),\(^{340}\) the neutral complex $[\text{Cp}^*(\text{Pr}_3\text{P})\text{OsH}\{=\text{SiH(Trip)}\}]$ was unreactive towards either alkenes or alkynes. As well, calculations have shown that the $\Delta G$ barrier for ethylene insertion into the terminal Si–H bond (including ethylene coordination to the Si centre) for models of these Os complexes indicated that the activation barrier is 77 kJ mol\(^{-1}\) lower for the cationic system.\(^{342}\)

Reactions of silylene complexes with alkynes are uncommon. In 2002, Tilley et al. reported the reaction of the cationic iridium complex $[\text{Cp}^*(\text{Me}_3\text{P})\text{IrH}\{=\text{SiPh}_2\}]^+$ with 4-ethynyltoluene (the reactions of the same complex with 2-butyne or 1,2-propadiene yielded a mixture of products) to form the $\eta^3$-silaallyl complex $[\text{Cp}^*(\text{Me}_3\text{P})\text{Ir}\{\eta^3\text{-Ph}_2\text{SiCHCH(\text{p-tol})}\}]^+$ (f in Figure 1.43; see section 1.7.8). This reaction was proposed to proceed either by initial 2+2 cycloaddition of the C≡C and Ir=Si bonds, or 1,2-insertion of the triple bond into the Ir–Si bond of a silyl isomer.\(^{389}\) The former of these two proposed mechanisms (2+2 cycloaddition) was observed directly in the reactions of the titanium silylene complexes $[\text{Cp}_2\text{Li}(=\text{Si}\{\mu-\text{SiSi(SiMe}_2\text{Bu}_2)\}_2\{\text{Si}(\text{SiMe}_2\text{Bu}_2)_2\}])$ (L = THF, PMe$_3$, o-xylylNC: e-g in Figure 1.30) with terminal alkynes $\text{R}C≡\text{CH}$ ($\text{R} = \text{SiMe}_3$, o-Bu, or Ph) to generate silatitanacyclobutane complexes.\(^{365,390}\) In addition, the latter of these two proposed mechanisms (1,2-insertion of the alkyne into a metal-silyl bond) was also proposed for the reaction of $[\text{Cp}^*(\text{dmpe})\text{MoH}(=\text{SiMe}_2)]$ with $\text{Me}_3\text{SiC≡CH}$ to form the vinylidene complex $[\text{Cp}^*(\text{dmpe})\text{MoH}\{=\text{C}(\text{SiHMe}_2)(\text{SiMe}_3)\}]$ (the product of silylene isomerization to a silyl complex followed by 1,2-insertion of the alkyne into the Mo–Si bond to form a vinyl complex, and subsequent α-hydride elimination).\(^{326}\) Very recently, Driess et al. reported that (NHSi)$_2\text{MnCl}_2$ complexes (and $\text{MnCl}_2$ or [(OC)$_3\text{MnBr}$] in the presence of free $N$-heterocyclic silylenes) catalyze hydrogenation of alkynes to alkenes.\(^{380}\) A Glaser-Tilley mechanism for catalytic alkyne hydrosilylation has not been reported, but various alkynes have been observed to insert into the terminal Si–H bond of
cationic \([\text{Cp\#(Pr}_3\text{P})\text{RuH(SiHMes)}][\text{B(C}_6\text{F}_5)_4]\)\(^{387}\) and a neutral \(N\)-heterocyclic silylene complex of \(\text{Ni}\),\(^{391}\) forming silylene complexes with a vinyl substituent on \(\text{Si}\).

Reactions of silylene complexes with alkenes and alkynes can also result in simple substitution of the silylene ligand. For example, in the reactions of \([(\text{Cy}_3\text{P})_2\text{Pt(SiMes}_2\text{)}\)] with ethylene, propyne, and 2-butyne all resulted in substitution of the silylene ligand, affording a variety of \(\text{Si}\)-containing byproducts, which likely arise from decomposition of the extruded silylene.\(^{392}\)

1.6.10 – Complexes related to silylene complexes

Any discussion of silylene complexes would be incomplete without discussion of species which feature a similar M–Si environment. For example, \(\eta^3\)-\(\text{H}_2\text{SiR}_2\) complexes are isomers of silylene dihydride complexes and bear significant similarities. The first structurally characterized complexes which can be described in this manner were a pair of dimetallic species, each with a bridging \(\text{SiH}_4\) ligand reported by Sabo-Etienne et al. in 2000 (a-b in Figure 1.35).\(^{393}\) Six years later, the Peters group reported a pair of monometallic iron examples, which they described as adducts of \(\text{H}_2\text{SiR}_2\) (c-d in Figure 1.35).\(^{318}\) Over the past decade, the Tilley group has reported a series of \(\text{Ru } \eta^3\)-\(\text{H}_2\text{SiR}_2\) complexes (e-n in Figure 1.35).\(^{394}\) These complexes can often be described with a bonding scheme along the continuum from a silylene dihydride complex to an \(\text{H}_2\text{SiR}_2\) adduct. A detailed description of the nature of bonding in these complexes is beyond the scope of this chapter, though various bonding descriptions used in the literature are shown in Figure 1.36 (some of these were reported as a resonance structure).
Figure 1.35: $\eta^3$-$\text{H}_2\text{SiR}_2$ complexes of transition metals. For clarity, all structures have been drawn with single bonds between Si and the metal, and between each of those and the bridging hydride ligands.

Figure 1.36: Structures used to describe $\eta^3$-$\text{H}_2\text{SiR}_2$ complexes of transition metals.

Many similarities exist between $\eta^3$-$\text{H}_2\text{SiR}_2$ complexes and silylene complexes. Of structurally characterized examples, with one exception, the M–Si distances in $\eta^3$-$\text{H}_2\text{SiR}_2$ complexes (Table 1.10) are either within or below the range of silylene complexes involving their respective metal (Table 1.7). Also similar to base-free silylene complexes, the environment about the Si atom (excluding the ‘bridging’ hydride moieties) is planar; $\Sigma(\text{X–Si–Y})$ $(\text{X,Y}\neq \text{H}_{\text{br}}) \geq 359.5^\circ$ (Table 1.10). The two ‘bridging’ hydride moieties are located in a plane (with Si) significantly angled from the plane of Si and its terminal substituents, in most cases close to $90^\circ$ (Table 1.10), and like some silylene hydride complexes (vide supra), short Si–H$_{\text{bridging}}$ distances were observed (Table 1.10). Further
illustrating the silylene-like character of $\eta^3$-H$_2$SiR$_2$ complexes, some examples have displayed similar hydrosilylation activity.\textsuperscript{385}

**Table 1.10:** Structural and spectroscopic parameters for $\eta^3$-H$_2$SiR$_2$ complexes. Complexes are identified by the letter in Figure 1.35. H$_{br}$ is a hydride interacting with Si and the metal.

<table>
<thead>
<tr>
<th>Complex</th>
<th>d(M–Si) (Å)</th>
<th>$\Sigma$(X–Si–Y), X,Y≠H$_{br}$ (°)</th>
<th>d(H$_{br}$–Si) (Å)</th>
<th>$\angle$(X–Si–Y)–(H$<em>{br}$–Si–H$</em>{br}$), X,Y≠H$_{br}$ (°)</th>
<th>$\delta^{29}$Si in ppm (J$_{1H-29Si}$ in Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.1875(4)</td>
<td>359.5</td>
<td>1.69(3), 1.73(3)</td>
<td>69</td>
<td>–</td>
<td>Sabo-Etienne (2000)\textsuperscript{393}</td>
</tr>
<tr>
<td>b</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>290.2 (36)$^a$</td>
<td>Sabo-Etienne (2000)\textsuperscript{393}</td>
</tr>
<tr>
<td>c</td>
<td>2.1280(7)</td>
<td>360.0(1)</td>
<td>1.464(1)-1.552(2)</td>
<td>83</td>
<td>162 (68)$^a$</td>
<td>Peters (2006)\textsuperscript{318}</td>
</tr>
<tr>
<td>d</td>
<td>2.131(1)-2.141(1)</td>
<td>360.0(2)-360.1(2)</td>
<td>1.56(4)-1.74(4)</td>
<td>88-89</td>
<td>160 (70)$^a$</td>
<td>Peters (2006)\textsuperscript{318}</td>
</tr>
<tr>
<td>e</td>
<td>2.263(1)</td>
<td>359.9(2)</td>
<td>1.61(4)-1.66(7)</td>
<td>88</td>
<td>154 (65)$^a$</td>
<td>Tilley (2011)\textsuperscript{394}</td>
</tr>
<tr>
<td>f</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>141 (68)$^a$</td>
<td>Tilley (2011)\textsuperscript{394}</td>
</tr>
<tr>
<td>g</td>
<td>2.246(1)</td>
<td>360.0(5)</td>
<td>1.74(6)</td>
<td>–</td>
<td>228.7 (62.3)</td>
<td>Tilley (2013)\textsuperscript{330}</td>
</tr>
<tr>
<td>h</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>131 (65)$^a$</td>
<td>Tilley (2014)\textsuperscript{331}</td>
</tr>
<tr>
<td>i</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>175 (64)$^a$</td>
<td>Tilley (2014)\textsuperscript{331}</td>
</tr>
<tr>
<td>J</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>145 (69)$^a$</td>
<td>Tilley (2014)\textsuperscript{331}</td>
</tr>
<tr>
<td>k</td>
<td>2.3046(8)</td>
<td>360.0(1)</td>
<td>1.72(3)-1.73(2)</td>
<td>85</td>
<td>138 (105)</td>
<td>Tilley (2014)\textsuperscript{331}</td>
</tr>
<tr>
<td>l</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>123 (68)$^a$</td>
<td>Tilley (2018)\textsuperscript{395}</td>
</tr>
<tr>
<td>m and n</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Tilley (2018)\textsuperscript{395}</td>
</tr>
</tbody>
</table>

\textsuperscript{a.} The bridging hydride ligands are in rapid exchange with the terminal hydride ligand(s), so this is an average over both environments.

\textsuperscript{b.} One of the H atoms on Ru was not accurately located crystallographically (it was unstable under refinement).

NMR spectroscopy, however, highlights a significant electronic difference between $\eta^3$-H$_2$SiR$_2$ and base-free silylene complexes (including silylene hydride complexes with Si–H interactions; \textit{vide supra}). With two exceptions, the $^{29}$Si NMR chemicals shifts of $\eta^3$-H$_2$SiR$_2$ complexes (Table 1.10; 123-175 ppm) lie intermediate between silyl and silylene complexes. $\eta^3$-H$_2$SiR$_2$ complexes with higher frequency
chemical shifts can be considered to have greater silylene dihydride-like character. The magnitudes of the \( ^{29}\text{Si} - ^{1}\text{H} \) coupling constant involving the ‘bridging’ hydride ligands also could potentially provide insight into the nature of the bonding. If the two complexes with silylene-like \( ^{29}\text{Si} \) chemical shifts are excluded, it appears at first glance that the majority of \( J_{\text{Si,H}} \) (Table 1.10) are only slightly higher than those observed in silylene hydride complexes with Si–H interligand interactions (28-62 Hz; \textit{vide supra}). However, this is misleading because (with one exception) the ‘bridging’ hydride ligands are in rapid chemical exchange with terminal metal hydride ligands, so the \( ^{29}\text{Si} - ^{1}\text{H}_{\text{Br}} \) and \( ^{29}\text{Si} - ^{1}\text{H}_{\text{M}} \) coupling constants are averaged. Given that the 2-bond coupling constants involving the non-interacting metal hydrides would be around 10 Hz, the \( ^{29}\text{Si} - ^{1}\text{H} \) coupling constants involving the ‘bridging’ hydrides could be estimated to be around 90-100 Hz. This range is close to the single example where there are no additional metal hydride ligands present to exchange with the ‘bridging’ hydride (105 Hz), and suggests that in general, higher (non-averaged) \( J_{\text{Si,H}} \) couplings are indicative of less silylene character in \( \eta^3\text{-H}_2\text{SiR}_2 \) complexes.

Another class of complexes related to silylene complexes are silylyne complexes (Si analogues of carbyne complexes, with a formal M=Si triple bond). The first base-free silylyne complex was reported by the Tilley group in 2003 ([Cp*(dmpe)MoH(≡SiMes)]\(^+\); a in Figure 1.37).\(^{396}\) Since that time, base-free silylyne complexes have been reported for Nb, Cr, Os, and W, in addition to Mo, and the triple-bond character is apparent from M–Si distances shorter than in silylene complexes involving the same metal (where a comparable is available).\(^{397}\) As base coordination to the sp\(^2\) Si environment in silylene complexes results in significant weakening of the M–Si bond (\textit{vide supra}), base coordination to the sp Si centre in silylyne complexes likewise weakens the M–Si bond. Thus, base-coordinated silylyne complexes have a bonding situation very similar to base-free silylene complexes.
Figure 1.37: Selected silylyne complexes of transition metals. Base-stabilized structures are drawn with a triple bond between Si and the metal for clarity, and this does not reflect the bond strength.

The first base-stabilized silylyne complex was actually reported over a decade prior to the first base-free example; in 1992 the Tilley group reported a Ru dicaticonic silylyne structure with 2,2’-bipyridine coordination to the Si centre (b in Figure 1.37). The Ru–Si distance of 2.269(5) Å in this species is within the range associated with ruthenium silylene complexes (2.18-2.28 Å; Table 1.7). Two decades later, the Fillipou group reported NHC-stabilized silylyne complexes of Mo (c in Figure 1.37) and Cr (d and e in Figure 1.37), which feature M–Si bonds {d(Mo–Si) of 2.3474(6) Å and d(Cr–Si) of 2.160-2.162(1) Å} only slightly shorter than those in structurally characterized silylene complexes of Mo or Cr, respectively (Table 1.7). As well, the environment about Si (including the NHC substituent) in these complexes is nearly planar (ΣX–Si–Y ≥357°). Emphasizing the silylene-like nature of these complexes, Fillipou describes NHC-stabilized silylyne complexes as having a zwitterionic silylene structure (Figure 1.38). Though not directly related to silylene complexes, a pair of doubly NHC-coordinated silylyne complexes (with two NHCs bound to the Si centre) have been reported for Cr and W, and feature M–Si bonding consistent with a single bond.

Figure 1.38: Alternative bonding descriptions of NHC-stabilized silylyne complexes.
1.7 – Silene Complexes of Transition Metals

1.7.1 – Scope of Section

The aim of this section is to provide an overview of the synthesis and characterization of transition metal silene complexes, with a focus on those which have been directly observed. Special emphasis is given to silene hydride complexes with an Si–H interligand interaction. Also included are complexes with non-aromatic ligands in which a silene moiety is incorporated into a larger π-system (i.e. where a resonance structure can be drawn with a Si=C double bond). Not included in this review are reactions of silene complexes or reports of silene complexes as un-observed intermediates in chemical transformations.

1.7.2 – Introduction to Silene Complexes

Silenes (R₂Si=CR₂) are compounds with a double bond between sp² Si and C atoms; i.e. heavier analogues of alkenes where one of the carbon atoms has been replaced with a silicon. Evidence for the existence of a transient silene (Me₂Si=CH₂) was first provided in 1967 by Gusel’nikov and Flowers. The transient nature of many silenes is due to their propensity to spontaneously decompose by dimerization. By employing bulky substituents, Brook et al. were able to prepare, in 1979, the first spectroscopically observed silene (in equilibrium with the dimer cyclization product; a in Figure 1.39) and two years later reported the first isolable, stable (in the solid state) silene (b in Figure 1.39). When in solution, these silenes decomposed over weeks or days, respectively, to form acylsilanes. Over the past forty years, a variety of stable silenes have been prepared by similarly employing steric bulk to impart kinetic stabilization (i.e. prevent dimerization). Silenes are far more reactive than alkenes due to a significantly weaker π-bond. Silicon forms weaker π bonds than C in general, and this is reflected in the low π bond strengths of silenes (estimated from bond rotation barriers to be 119-192 kJ mol⁻¹ for a variety of free silenes, which is about half as strong as in olefins). This weakness is due in part to the poor size match between C and Si orbitals, leading to poor orbital...
Furthermore, the greater Si–C bond length in silenes (relative to the C–C bond lengths in olefins) caused by the greater atomic radius of Si ensures that silenes are sterically more susceptible to nucleophilic attack.\textsuperscript{300} As a result, free silenes are generally air-sensitive. The synthesis, reactivity, and structures of free silenes have been reviewed elsewhere.\textsuperscript{300,407,408}

Figure 1.39: Early examples of observed free silenes and silene transition metal complexes.

Otherwise unstable silene moieties (those lacking bulky substituents) have been stabilized by being brought within the coordination sphere of a transition metal.\textsuperscript{407} Pannell first proposed a transition metal silene complex as an intermediate in the isomerization of \([\text{Cp(OC)}_2\text{Fe(CH}_2\text{SiHMe}_2)]\) to \([\text{Cp(OC)}_2\text{Fe(SiMe}_3)]\) in 1970.\textsuperscript{409} Just over a decade later, Wrighton et al. reported the first spectroscopically observed silene complexes \{[(\text{η}^5-\text{C}_5\text{R}_5)(\text{OC})_n\text{MH(Me}_2\text{Si=CH}_2)]; \text{n = 2} (\text{M = W, R = H or Me, c-d in Figure 1.39})^420 \text{or } 1 \text{ (M = Fe, R = Me, e in Figure 1.39})^421\}, which were described as metallasilacyclopropane species (assignment of these species as metallasilacyclopropane complexes by the authors, as opposed to silene complexes, was somewhat arbitrary; \textit{vide infra}). Wrighton’s complexes were observed only at low temperature, and formed by β-hydride elimination from a –CH\textsubscript{2}SiHMe\textsubscript{2} ligand. The Fe complex (which differs from Pannell’s proposed intermediate by replacement of a Cp with a Cp* group) decomposed above 225 K in the presence of CO to form the silyl complex \([\text{Cp*}(\text{OC})_2\text{Fe(SiMe}_3)]\), thus supporting Pannell’s initial mechanistic proposal.
In 1988, the Tilley group reported the first isolable, thermally stable, and (for one analogue) crystallographically characterized silene complexes; \([\text{Cp}^* (R_3P) \text{RuH}(R'\_2\text{Si}=\text{CH}_2)]\) (f in Figure 1.39). Since that time, less than two dozen silene complexes of transition metals have been observed. The relatively small size of this field makes this a particularly exciting area of chemical exploration. Reviews of transition metal silene complexes can be found as sub-headings in more general silene reviews.\[^{300,407,410}\]

### 1.7.3 – Electronic Structure of Silene Complexes

Bonding between silene ligands and transition metals can be described in a similar manner to alkene complexes, based on the Dewar-Chatt-Duncanson model. This model describes bonding as involving both \(\sigma\) donation and \(\pi\) backdonation (Figure 1.40). Backdonation into the \(\pi^*\) antibonding orbital centred around the Si=C bond leads to elongation (weakening) of the Si=C bond upon silene coordination to the metal, as does \(\sigma\) donation (which involves removal of electron density from the Si–C \(\pi\) bonding orbital). Unlike alkene complexes (and disilene \(R_2\text{Si}=\text{Si}R_2\) complexes), the bonding environment is necessarily unsymmetrical in silene complexes. The \(\pi\)-bond of a free silene is polarized towards carbon, leading to a HOMO with a higher contribution from the carbon 2p atomic orbital relative to the silicon 3p atomic orbital, and the opposite is the case for the LUMO. Because of this, the \(\sigma\)-donor interaction is dominated by the C atom in the silene fragment (in contrast, \(\pi\)-backdonation involves both the Si and C silene atoms). Therefore, when the silene ligand is oriented \textit{trans} to a co-ligand, the carbon atom (as opposed to the C–Si centroid) occupies the position directly \textit{trans} to the co-ligand. Detailed descriptions of the electronic structure of silene-transition metal bonding are scarce, though a couple of reports have been published involving Pt silene complexes.\[^{411,412}\]
Figure 1.40: Dewar-Chatt-Duncanson model of σ donation and π backdonation from/to a silene ligand.

In situations where π backdonation is significant, silene complexes can be alternatively described as metallasilacyclopropane complexes (just as alkene complexes in similar situations can be described as metallacyclopropane complexes), which are the products of oxidative addition of the π bond across the metal centre. For both silene and alkene complexes, an accurate bonding picture involves resonance structures of the two extremes (Figure 1.41). Both terms are sometimes used interchangeably in the literature, though often one term is used to indicate the dominant resonance structure.
1.7.4 – Synthesis of Silene Complexes

Only a handful of silene complexes of transition metals have been isolated (Table 1.11), and examples are currently limited to complexes of Ir, Ru, W, Ni, and Pt. In solution, Tilley’s \([\text{Cp}^*\text{(PMe}_3\text{)}\text{IrH}\text{(Me}_2\text{Si=CH}_2)]\text{[B(C}_6\text{F}_5\text{]}_4]\) was observed to exist in equilibrium with another species (an Et\(_2\)O-coordinated silylene complex, presumably formed via a silyl intermediate; *vide infra*). However it was isolated in the solid state, so it is included in Table 1.11. The plurality of these complexes were prepared by initial installation of a β-hydride containing ligand (–CH\(_2\)SiR\(_2\)H or –SiR\(_2\)Me) followed by β-hydride elimination (a in Scheme 1.13). Installation of β-hydride containing ligand has been achieved via a variety of methods, including addition of Grignard reagents to metal halides and isomerization of a silylene complex. Other pathways to silene complexes have involved initial installation of a β-chloride containing ligand, followed by 1,2-deinsertion (for \([\text{Me}_3\text{P}_3\text{RuHCl}\text{(Me}_2\text{Si=CH}_2)]\); b in Scheme 1.13), reduction of an alkyl halide complex by Mg\(_0\) (for \([\text{Cp}_2\text{W(Me}_2\text{Si=CH}_2)]\); c in Scheme 1.13 (this may proceed via initial formation of a Grignard reagent followed by intramolecular reaction involving...
a chloride ligand), and phosphine or alkene substitution by an isolated or *in-situ* generated free silene {for group 10 complexes; d in Scheme 1.13 (this mechanism requires large substituents on the silene, and the limited number of silene complexes prepared by this method is presumably due to the dearth of isolable free silenes)}.

**Scheme 1.13:** Synthetic routes used to prepare isolated silene complexes. In some cases where the silene was generated by a mechanism that resulted in a hydride ligand, the silene complex underwent subsequent H–H or C–H bond-forming reductive elimination involving the hydride and another co-ligand to generate a hydride-free silene complex, and this subsequent reactivity is not shown in the scheme. For generality, charge is not included (both neutral and cationic species have been observed).
Table 1.11: Isolated silene complexes. n.o. = not observed, X = any non-metal.

<table>
<thead>
<tr>
<th>M</th>
<th>Complex</th>
<th>NMR: $\delta$ (ppm) $^{1}J_{CH}$ (Hz)</th>
<th>XRD (Å, °) Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir</td>
<td>![Ir complex diagram]</td>
<td>Si=C: 1.84(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ir complex diagram]</td>
<td>$^{13}$C: −16.8 {147.5}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ir complex diagram]</td>
<td>$^{29}$Si: 2.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ir complex diagram]</td>
<td>$^{13}$C: −33.37 {142}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ir complex diagram]</td>
<td>$^{29}$Si: −20.77</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>![Ru complex diagram]</td>
<td>Si=C: 1.78(2)-1.79(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ru complex diagram]</td>
<td>$^{29}$Si: 6.14 (a), n.o. (b), n.o. (c), n.o. (d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ru complex diagram]</td>
<td>$^{13}$C: −29.04 {143} (a), −29.68 (b), n.o. (c), −22.42 (d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ru complex diagram]</td>
<td>$^{13}$C: −11.2, −29.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>![Ru complex diagram]</td>
<td>$^{29}$Si: −19.4, −19.8</td>
<td></td>
</tr>
</tbody>
</table>

Tilley (1990)\(^{413}\)

Tilley\(^{a}\) (2001)\(^{414}\)

Tilley (1988, 1993)\(^{415}\)

Berry (2003)\(^{416}\)
Tilley’s silene complex \([\text{Cp}^*(\text{Me}_3\text{P})\text{IrH}(\text{Me}_2\text{Si}≡\text{CH}_2)]^+\) is of particular interest because, although it was isolated in the solid state, it was observed to exist in equilibrium with the base-stabilized silylene complex \([\text{Cp}^*(\text{Me}_3\text{P})\text{IrMe}\{≡\text{SiMe}_2(\text{OEt}_2)\}]^+\), formed via an unobserved silyl intermediate \([\text{Cp}^*(\text{Me}_3\text{P})\text{Ir}(%)\text{SiMe}_3]_+\) (Scheme 1.14). The silylene and silyl intermediate species in this equilibrium were trapped by reaction with nucleophiles (pyridine coordination to the Si centre of the silylene, or CO or ethylene coordination to the Ir centre in the silyl isomer; Scheme 1.14), and the ‘trapped’ species
were isolated.\textsuperscript{389,414} This equilibrium highlights the reversibility of the final step in the synthesis of many silene complexes (β-hydride elimination from a silyl complex; \textit{vide supra}).

\textbf{Scheme 1.14:} Equilibrium between \([\text{Cp}^\ast(\text{Me}_3\text{P})\text{IrH(Me}_2\text{Si=CH}_2)]^+\) and \([\text{Cp}^\ast(\text{Me}_3\text{P})\text{IrMe\{=SiMe}_2(\text{OEt}_2)\}]^+\), and trapping experiments.\textsuperscript{389,414}

Wrighton’s seminal synthesis of the first silene complexes (\textit{vide supra}) involved spectroscopic observation of W and Fe species (c-e in Figure 1.39), which could not be isolated due to instability at room temperature. Since that time, a handful of silene complexes of transition metals have been spectroscopically observed but not isolated (Table 1.12). For example, in 1999 Berry observed the ruthenium silene complex \([(\text{Me}_3\text{P})_3\text{RuH}_2(\text{Me}_2\text{Si=CH}_2)]\), which was thermally stable but existed in a solution equilibrium with the silyl complex \([(\text{Me}_3\text{P})_3\text{RuHSiMe}_3]\).\textsuperscript{419}
**Table 1.12:** Spectroscopically observed non-isolated silene complexes. n.o. indicates not observed. Complexes reported as metallasilacyclopropane complexes are shown as silene complexes for consistency.

<table>
<thead>
<tr>
<th>M</th>
<th>Complex</th>
<th>NMR: δ (ppm)</th>
<th>Reason not Isolated</th>
<th>Author</th>
</tr>
</thead>
</table>
| W  | ![W complex](image1) | $^{13}$C: $-27.6$  
(R = Me)  
$^{29}$Si: n.o. | Unstable at room temperature | Wrighton (1983) \(^{420}\) |
| Fe | ![Fe complex](image2) | $^{13}$C: $-20.39$  
$^{29}$Si: n.o. | Decomposition above 225 K | Wrighton (1987) \(^{421}\) |
| Ir | ![Ir complex](image3) | n.o. | Unable to purify from byproducts | Tilley (1990) \(^{413}\) |
| Rh | ![Rh complex](image4) | $^{13}$C: $66.07$ \{145.6\}  
$^{29}$Si: $-17.63$ | Unable to purify from byproducts | Tilley (1990) \(^{413}\) |
| Ru | ![Ru complex](image5) | $^{13}$C: $-20.75$  
$^{29}$Si: $-12.93$ | Exists in equilibrium with silyl complex. | Berry (1999) \(^{419}\) |
1.7.5 – Solid State Structural Characterization of Silene Complexes

X-ray crystal structures of silene complexes are relatively rare. To our knowledge, only 8 such complexes have been reported. The four key structural parameters generally analyzed are the Si–C, M–Si, and M–C distances, as well as the sum of non-M bond angles centred on the Si centre.

The bonding metric most directly descriptive of the nature of silene complexes is the Si–C distance. Reported values range from 1.78(2)-1.84(2) Å (Table 1.11) which, though shorter than the characteristic Si–C single bond length (1.87 Å),\(^{422}\) is significantly longer than in structurally characterized examples of electronically un-stabilized free silenes, despite the presence of very bulky substituents in the latter (for example, the Si–C distances in \(\text{Me}_2\text{Si}=\text{C}((\text{SiMe}_3)\text{SiMe}^\prime\text{Bu}_2),\) \((\text{Me}_3\text{Si})_2\text{Si}=\text{C}(1\text{-Ad})(\text{OSiMe}_3)\) and \((\text{Me}_3\text{Si})(\text{Me}_2\text{BuSi})\text{Si}=\text{Ad} (\text{Ad} = 2\text{-adamantyl})\) range from 1.702(5) to 1.764(3) Å\(^{403,423}\). The Si–C distance is a good measure of the nature of silene-metal bonding, as both ligand donation and metal backdonation result in elongation of the Si–C bond. Greater elongation of the Si–C bond is associated with greater contribution from a metallasilacyclopropane resonance structure.

Free silenes, like alkenes, feature \(\text{sp}^2\) hybridization of the silene C and Si atoms, and are therefore planar at both positions. Upon coordination to a transition metal, pyramidalization can be expected at both positions (again, analogous to alkene complexes). However, because one or both substituents on C are normally hydrogen atoms, which are not accurately located by X-ray diffraction, only the sum of the angles around Si is normally discussed. As expected, X-ray crystal structures show significant pyramidalization; the sum of bond angles centred on the Si atom (not including bonds to the metal) have been shown to range from 340-354° (360° would correspond to a planar \(\text{sp}^2\) environment, while 328.5° would correspond to an \(\text{sp}^3\) environment). Greater degrees of pyramidalization are associated with greater contribution of a metallasilacyclopropane resonance structure.
The final sets of bond metrics commonly analyzed in silene complexes are the M–Si and M–C distances. In all cases, the bond between the metal and silicon is 0.11-0.27 Å (5-12 %) longer than bond between the metal and carbon, reflecting both the greater atomic radius of silicon (the covalent radius of Si is 0.39 Å larger than C) and asymmetric orbital overlap (Figure 1.40). For nearly all silene complexes, the distances from the metal to Si are on the shorter side relative to those in silyl complexes, and distances to C are on the longer side relative to those in alkyl complexes (in both cases, of the same metal).

1.7.6 – Spectroscopic Characterization of Silene Complexes

NMR spectroscopy is commonly used for the characterization of silene complexes. Unfortunately, there is no single diagnostic environment indicative of a silene complex. Reported ²⁹Si NMR (Si=C) chemical shifts range from –20.77 to 23.7 ppm, falling within the range for transition metal silyl complexes. Similarly, ¹³C NMR (Si=C) chemical shifts normally range from –11.2 to –41.09 ppm, similar to that observed for M–CH₂SiR₃ environments in β-Si-containing alkyl ligands (the reported values of 66.07 and 137.8 ppm for [(Me₃P)Cp*Rh(Ph₂Si=CH₂)] and [(Cy₃P)Pt(Ad=Si(SiMe₃)₂], respectively, are clearly outliers). In complexes with an H substituent on the Si=C environment, the C–H coupling constant can also be used to probe the degree to which the sp² environment in a hypothetical free silene has been pyramidalized (for example, ethylene has a ¹J_C,H of 156.2 Hz and methane has a ¹J_C,H of 125.0 Hz). Silene complexes with Si=CH substituents feature ¹J_C,H values of 137-143 Hz, indicative of a structure intermediate between the canonical silene and metallasilacyclopropane complexes (Figure 1.41); lower ¹J_C,H values are associated with a greater contribution form a metallasilacyclopropane resonance structure. This parameter offers a relatively diagnostic signal to differentiate from a –CH₂SiR₃ alkyl group, which could potentially have similar ¹³C and ²⁹Si chemical shifts, but where the ¹J_C,H for the methylene bridge would be expected to range from 120-130 Hz (lower in the presence of an agostic interaction), which is lower than that expected for a silene complex.
For \([\text{Cp}_2\text{WH}(&\text{Me}_2\text{Si=CH}_2)]\), where the transition metal contains an NMR-active (spin \(\frac{1}{2}\)) \(^{183}\text{W}\) nucleus (\(\text{NA} = 14.28\%\)), coupling to \(^{183}\text{W}\) from the \(^{13}\text{C}\) or \(^{29}\text{Si}\) environments in the silene core was found to be 28.5 and 57.1 Hz, respectively.\(^{417}\) These values are much smaller than is normal for alkyl (43-89 Hz)\(^{427}\) or silyl (e.g. 83.0-117.6 Hz for a series of tungsten silyl complexes reported by the Berry group)\(^{417}\) complexes, respectively, and the latter is similar to the tungsten disilene complexes \([\text{Cp}_2\text{WH}(&\text{Me}_2\text{Si=SiMe}_2)]\) (50.7 Hz).\(^{428}\) As well, comparable \(^{183}\text{W}–^{29}\text{Si}\) coupling constants (54-55 Hz) were reported for Wrighton’s \(\left[(\eta^5\text{-C}_5\text{R}_5)(\text{OC})_2\text{WH}(&\text{Me}_2\text{Si=CH}_2)\right]\).\(^{420}\) This offers an additional diagnostic NMR handle for differentiating silene and \(\beta\)-Si-containing alkyl ligands for species with suitable NMR-active metal nuclei.

For some silene complexes where extensive NMR data could not be obtained (usually due to instability) identification has been based on mass spectrometry.\(^{413}\) Diagnostic MS peaks include the molecular ion, and the molecular ion minus the free silene moiety. In addition, iron and cobalt silene complexes have been generated in the gas phase and observed exclusively by MS.\(^{429}\) As well, Mori et al. reported observing the Zr silene complex \([\text{Cp}_2\text{Zr}(\text{PhMeSi=CH}_2)]\) in solution based on the observation of a transient Cp environment in the \(^1\text{H}\) NMR spectrum, without any other diagnostic data (though this complex was the expected intermediate in a variety of reported transformations).\(^{430}\)

### 1.7.7 – Silene Hydride Complexes; Interligand Si–H Interactions

Given that the most common method for preparing isolated silene complexes involves \(\beta\)-hydride elimination (\textit{vide supra}), hydrides are common co-ligands in silene complexes. While in most instances, no apparent interaction was observed between the silene and hydride ligands, \([\text{(Me}_3\text{P})_3\text{RuH}_2(&\text{Me}_2\text{Si=CH}_2)]\) featured a significant interligand interaction between the hydride and the Si centre of the silene ligand.\(^{416}\) This was apparent from short Si–\(\text{H}_{\text{Ru}}\) distances of 1.557-1.664 Å, and a large scalar \(^{29}\text{Si}–^1\text{H}\) coupling constant of 75 Hz (these parameters are similar to those observed for \(\sigma\)-hydrosilane complexes; see section 1.5.5).\(^{224,233,241}\) Furthermore, unlike other structurally
characterized silene complexes, [(Me$_3$P)$_3$RuH$_2$(Me$_2$Si=CH$_2$)] displayed a M–Si distance (2.468(2)-2.526(2) Å) which is on the longer edge of the range of Ru–Si bond lengths found in silyl complexes. Given these observations, a proper description of the bonding environment of these complexes requires employment of an additional resonance structure involving an alkyl ligand with a β-Si–H metal interaction (Figure 1.42). In fact, Sabo-Etienne et al. has described a pair of Ru complexes with similar bonding metrics to this as alkyl complexes with β-Si–H metal interactions, though they could alternatively have been described as silene hydride complexes with interligand interactions.$^{431}$

Figure 1.42: Resonance structures used to describe silene hydride complexes with an interligand Si–H interaction

1.7.8 – Complexes of Ligands Containing a π-system for which a Resonance Structure can be Drawn which Includes a Si=C Bond

A variety of complexes have been structurally characterized where a silene moiety is incorporated into a ligand where the π system is delocalized over additional (usually carbon, sometimes also germanium) atoms. In these situations, a resonance structure can be envisaged involving a silene ‘Si=C’ donor. While many such complexes have been reported for aromatic systems where one or more Si atoms have been incorporated into an η$^4$-cyclobutadiene, η$^5$-cyclopentadienyl$^{433}$ or η$^6$-benzene$^{434}$ ligand, the number of non-aromatic systems is relatively scarce. The simplest of these, and first to be reported, are heavy analogues of allene complexes where one of the terminal carbon atoms is replaced by a silicon; 1-silaallenes. In 1995, Jones et al. reported the Ru silaallene complexes [Cp*(R$_3$P)RuH(η$^2$-Me$_2$Si=C=CPh$_2$)] {R$_3$ = Cy$_3$ (for which an X-ray
crystal structure was obtained) or Me₂Ph; a and b, respectively, in Figure 1.43), in which the ‘Si=C’ portion of the silaallene is the bonding site (the ‘C=C’ portion does not interact with the metal) and which contains a significant interligand Si–H interaction {d(Si–H) = 1.70(3) Å, J_{Si,H} = 57-66 Hz). Thus, the bonding scheme involved is very similar to that in the silene hydride complex [(Me₃P)₃RuH₂(Me₂Si=CH₂)] reported by Berry (vide supra), and the Si–C bond length of 1.805(6) Å is within the range observed for transition metal silene complexes.

Figure 1.43: Transition metal η²-silaallene, η³-silaallyl, or η³-silapropargyl complexes.

Related to this, Sakaba et al. has reported crystal structures for η³-silaallyl complexes, which feature ligands that are heavy analogues of η³-allyl ligands where one terminal carbon atom was supplanted by Si; [Cp*(OC)₂W(η³-Me₂SiCHMe₂)] and [Cp*(OC)₂Mo(η³-Ph₂SiCHMe₂)] (c and e, respectively, in Figure 1.43). Despite the fact that these complexes involve η³ coordination of all three atoms in the π system, the Si–C distances of 1.800(4)-1.817(3) are very similar to that in the η²-silaallene complex reported by Jones, indicative of some double bond character. Additional examples of η³-
silaallyl complexes have been reported by the Sakaba \{[(OC)\textsubscript{2}Cp*W(\eta^3-\text{Me}_2\text{SiCHCH})]; d in Figure 1.43\}\textsuperscript{436} and the Tilley \{[(Cp*(Me\textsubscript{3}P)Ir(\eta^3-\text{Ph}_2\text{SiCHCH}(p-tol))]\}\textsuperscript{+} and \{[(dtbpm)Rh(\eta^3-Mes\textsubscript{2}SiCR'CHR)]; f-i in Figure 1.43\}\textsuperscript{273,389} groups without solid-state characterization. Calculations by Sakaki et al. have suggested that the bonding in these systems can best be described with resonance contributions from canonical \eta^3-silaallene and \kappa^2-alkene-silyl structures (Figure 1.44; left).

\textbf{Figure 1.44:} Resonance structures of \eta^3-silaallyl and \eta^3-silapropargyl complexes.

In 1995 and 1998, Rosenthal et al. reported a series of Ti and Zr \kappa^2-alkyne-silyl complexes \{[Cp\textsubscript{2}MH(\eta^3-\text{SiMe}_2CCR)]; j and k, respectively, in Figure 1.43\} feature very short Si–C distances of 1.766(7) and 1.787(3) Å, which are statistically equivalent to the shortest values reported for a silene transition metal complex (\textit{vide supra}), suggestive of appreciable double-bond character. Subsequent reports by the Sakaki group (which proposed such complexes based on DFT calculations)\textsuperscript{437} and Sakaba (who reported similar complexes in 2009)\textsuperscript{439} have described these complexes utilizing contributions of \kappa^2-alkyne-silyl and \eta^3-silapropargyl resonance structures, analogous to the bonding description of \eta^3-silaallyl complexes (Figure 1.44; right). Sakaba’s \{Cp*(OC)\textsubscript{2}Mo(\eta^3-\text{Ph}_2\text{SiCCR})\} \{l and m in Figure 1.43\} displayed Si–C lengths of 1.795(3)-1.806(3) Å, which though marginally longer than in Rosenthal’s group 4 complexes, are also within the range expected for silene complexes (\textit{vide supra}).
A number of other non-aromatic complexes featuring ‘delocalized’ silene moieties have been reported. First, in 1998, a Co complex with a 1,3-dibora-5-silapenta-1,4-diene ligand was serendipitously prepared by Berndt and Siebert et al. (a in Figure 1.45), which is structurally similar to an η⁵-pentadienyl ligand with some carbon atoms substituted by B and Si. The internal Si–C distance of 1.809(3) Å is within the range associated with silene complexes. Second, in 2010 the Tokitoh group reported a silacyclohexadienyl chromium complex with the Si atom in the π-system (b in Figure 1.45). The π-system Si–C distance of 1.822(4) Å, though slightly longer than expected for silene complexes, is shorter than the Si–C distance of 1.853(5) Å involving the sp³ carbon atom in the same ligand, suggesting some degree of double bond character in the former. Lastly, in 2013, Tobita et al. reported η³-α-silabenzyl complexes of W and Mo ([(OC)₂Cp*M(η³-R₂SiAr)]; c-e in Figure 1.45), which each contain an analogue of an η³ benzyl ligand where the exo-cyclic donor carbon atom has been replaced with a silicon atom. While the Si–C distances of the bonding moiety are significantly elongated relative to known silene complexes (1.834(5)-1.850(3) Å), some double-bond character is apparent because they are slightly shorter than the Si–C distances for the terminal Si substituents in the same complexes (1.867(5)-1.873(3) Å).

**Figure 1.45:** Complexes containing non-aromatic ligands featuring extended π-systems that include a “Si=C” moiety (not including η²-silaallene, η³-silaallyl, or η³-silaproparyl complexes; see Figure 1.43).

In addition, DFT calculations have been used to discard silene-containing resonance structures as contributors to the description for the bridging moieties in a pair
of dinuclear complexes reported by Sakaki and Sakaba et al. in 2011 ([Cp*(CO)₂M(Ph₂SiCCSiPh₂)M(CO)₂Cp*]; M = W, Mo) and a disilacyclopent-3-ynyl zirconium complex reported by Rosenthal et al. in 2010. Also, in 2014 the Tokitoh group reported the X-ray crystal structure of a chromium complex with a 9-silaphenanthrene ligand where the bonding mode appears to be an η²-silene donor, with very short Si–C distances of 1.782(9)-1.790(9) Å. However, while the X-ray crystal structure was submitted to the Cambridge Structural Database and appears in the electronic supporting information of the publication, the text of the report does not discuss the structure at all, and surprisingly indicates that they were unable to prepare this complex.
Chapter 2

Dialkylmanganese(II) Complexes; Synthesis, Characterization, and Solution-state Reactivity for Deposition of Elemental Manganese

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2.1 – Introduction to Chapter 2

The Emslie group has previously investigated the use of metal alkyl complexes (e.g. ZnEt\textsubscript{2}) as co-reactants for copper metal ALD,\textsuperscript{447} and in this work we set out to determine whether highly reactive electropositive transition metal alkyl complexes could exhibit the reactivity, volatility, and thermal stability suitable to effect electropositive metal deposition in combination with reagents such as H\textsubscript{2} or ZnEt\textsubscript{2} (hydrogen gas has previously been used as a co-reactant for ALD of Fe,\textsuperscript{448} Ru,\textsuperscript{449} Co,\textsuperscript{448} Ir,\textsuperscript{450} Ni,\textsuperscript{448,451} Pd,\textsuperscript{452} and Cu;\textsuperscript{23,448,453} ZnEt\textsubscript{2} has been used as a co-reactant for ALD of Cu\textsuperscript{28}).

Reactivity envisaged between a dialkylmanganese precursor and H\textsubscript{2} or ZnEt\textsubscript{2} is shown in Scheme 2.1. With H\textsubscript{2}, a mixed alkyl hydride complex (MnHR) should be accessible by σ-bond metathesis, or oxidative addition of H\textsubscript{2} followed by reductive elimination of HR. This mixed alkyl hydride complex can be expected to be particularly susceptible to HR reductive elimination for both thermodynamic and kinetic reasons,\textsuperscript{93} leading to manganese metal deposition. With ZnEt\textsubscript{2}, stepwise alkyl exchange with MnR\textsubscript{2} would provide Mn(Et)R and then MnEt\textsubscript{2}, which can be expected to undergo rapid β-hydride elimination to form either MnHR or MnHEt respectively. MnHR is the same intermediate targeted in reactions with H\textsubscript{2}, and MnHEt will decompose via either HEt reductive elimination to form manganese metal, or β-hydride elimination to form MnH\textsubscript{2}; an unstable species observed only in low temperature matrices.\textsuperscript{454} While HR (R =
CH$_2$EMe$_3$, E = C, Si) is the only byproduct expected in reactions with H$_2$, byproducts in the reactions with ZnEt$_2$ can include ZnEtR (or ZnR$_2$; not shown in Scheme 1), ethylene, HR, HEt, and H$_2$.

**Scheme 2.1:** Possible pathways for Mn$_{(s)}$ deposition using dialkylmanganese(II) complexes in combination with H$_2$ or ZnEt$_2$ co-reactants.

The aforementioned reactivity can only be utilized for manganese ALD if a dialkylmanganese(II) precursor with an appropriate balance of thermal stability, volatility, and reactivity can be identified. A review of known dialkylmanganese(II) complexes, and their Lewis base adducts, is provided in section 1.3. Herein we describe the synthesis of both new and previously reported dialkylmanganese(II) complexes (8 in total), detailed solution and solid state characterization, including single crystal X-ray diffraction, PXRD, NMR, and UV-Visible spectroscopy, and variable temperature solution state (Evans) and solid state (SQUID) magnetic measurements, evaluation of thermal stability and volatility, and solution reactivity studies with H$_2$ and ZnEt$_2$ leading to manganese metal and manganese-zinc alloy electroless deposition. This work targets base-free as well as dmpe- {bis(dimethylphosphino)ethane-} and dmpm- {bis(dimethylphosphino)methane-} coordinated bis(trimethylsilylmethyl-) and dineopentyl- manganese(II) complexes, since (a) they have fairly low molecular weights and do not contain aromatic groups, maximizing the potential for appreciable volatility, (b) they do not contain β-hydrogen atoms, imparting thermal stability, (c) they are free
from oxygen or nitrogen donors, precluding manganese oxide or nitride deposition, and
d) the chelate effect will help to prevent phosphine ligand dissociation during
sublimation. The base-free compounds\textsuperscript{95,96} and the 1:1 \( \text{MnR}_2: \text{dmpe} \) adducts\textsuperscript{111} have
previously been reported, but a high quality X-ray crystal structure has only been
reported for \( \{ \text{Mn}(\mu-\text{CH}_2\text{SiMe}_3)_2 \}_x \).

2.2 – Synthesis and X-ray Crystal Structures

Base-free \( \text{bis}(\text{trimethylsilylmethyl})\text{manganese(II)} \) (1) and
dineopentylmanganese(II) (2) were prepared via the reactions of \( \text{MnCl}_2 \) with
\( \text{MgR}_2(\text{dioxane})_x \) (\( R = \text{CH}_2\text{SiMe}_3 \) or \( \text{CH}_2\text{CMe}_3; x = 0.25-0.8 \)), following modifications of
the literature procedures (Scheme 2.2).\textsuperscript{96} The 1:1 \( \text{Mn:dmpe} \) (dmpe = 1,2-
\text{bis(dimethylphosphino)ethane}) complexes, \( [(\text{dmpe})\text{Mn}(\text{CH}_2\text{SiMe}_3)_2] \) (3) and
\( \{ (\mu-\text{dmpe})\text{Mn}(\text{CH}_2\text{CMe}_3)_2 \}_2 \) (4), were also prepared as previously reported (Scheme
2.2),\textsuperscript{111} while the 2:1 \( \text{Mn:dmpe} \) complexes, \( \{ (\mu-\text{dmpe})\{\text{Mn}(\text{CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2 \} \) (5) and
\( \{ (\mu-\text{dmpe})\{\text{Mn}(\text{CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)\}_2 \}_2 \) (6), were synthesized by addition of 1
equivalent of the corresponding base-free dialkylmanganese(II) precursor to 3 and 4,
respectively (Scheme 2.2). Compounds 1 and 2 reacted with
\( \text{bis(dimethylphosphino)methane} \) (dmpm) to form exclusively
\( \{ (\mu-\text{dmpm})\{\text{Mn}(\text{CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2 \} \) (7) and
\( \{ (\mu-\text{dmpm})\{\text{Mn}(\text{CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)\}_2 \}_2 \) (8), even when an excess of dmpm was
added (Scheme 2.2).
Scheme 2.2: Synthesis of complexes 1-8.

Compound 4 is colourless, 3 is yellow, and 2 is dark brown, whereas 1 and 5-8 are red or black when crystalline, and pale pink when powdered. All eight compounds display high oxygen sensitivity, and were characterized by combustion elemental analysis, single crystal X-ray diffraction (except 1), PXRd on the bulk sample, $^1$H NMR spectroscopy (except nearly insoluble 1), UV/Vis spectroscopy (except nearly insoluble 1 and colourless 4), and both SQUID and Evans solution magnetic measurements (except 1); vide infra. Additionally, melting points and sublimation temperatures were determined, and thermal stability was assessed.

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$^o$ Complex 1 has previously been characterized by X-ray diffraction and SQUID; ref. 96 and 99.
A good quality X-ray structure has not previously been reported for base-free dineopentylmanganese(II) (2). However, Wilkinson et al. noted in 1976 that 2 is a tetramer in the solid state, citing a personal communication from M. B. Hursthouse and P. Raithby (and a poor quality crystal structure was later submitted to the CSD). Additionally, an electron diffraction study was reported for 2, revealing a monometallic structure in the vapor phase. In this work, dark brown X-ray quality crystals of 2 were obtained from hexanes at –30 °C, confirming a tetrametallic structure (Figure 2.1), with the two outer manganese atoms in a distorted trigonal planar geometry (Σ(C–Mn(1)–C) = 359.82(6)°; C–Mn(1)–C = 105.16(3), 122.62(3) and 132.04(4)°) and the inner manganese atoms in a distorted tetrahedral geometry (C–Mn(2)–C = 100.06(3)-122.50(3)°). The only other neutral dialkylmanganese(II) complex known to contain a trigonal planar manganese centre is [{Mn(CH2CMe2Ph)(μ-CH2CMe2Ph)}2], though it deviates more from planarity (Σ(C–Mn–C) = 354.7(1)°) than complex 2, likely due to an η2 interaction between each manganese atom and the phenyl ring of a bridging CH2CMe2Ph group. The tetrametallic structure of 2 presumably differs from the polymeric structure of 1 due to the increased steric demands of neopentyl versus trimethylsilylmethyl ligands.
Figure 2.1: X-ray crystal structure for $\left[\{\text{Mn(CH}_2\text{CMe}_3}\}(\mu-\text{CH}_2\text{CMe}_3)\}_2\{\text{Mn}(\mu-\text{CH}_2\text{CMe}_3)_2\text{Mn}\}\right]$ (2). Hydrogen atoms are omitted for clarity, and ellipsoids are set to 50% probability. Bond distances (Å) and angles (°): Mn(1)···Mn(2) 2.7022(4), Mn(2)···Mn(2') 2.7165(4), Mn(1)–C(1) 2.1211(9), Mn(1)–C(6) 2.2322(9), Mn(2)–C(16) 2.232(1), Mn(2)–C(11) 2.213(1), Mn(1)–C(16) 2.3265(7), Mn(2)–C(6) 2.3939(7), Mn(2)–C(11') 2.4092(9), Mn(1)–C(6)–Mn(2) 71.38(3), Mn(1)–C(16)–Mn(2) 72.67(3), Mn(2)–C(11)–Mn(2') 71.85(3), C(1)–Mn(1)–C(6) 132.04(4), C(1)–Mn(1)–C(16) 122.62(3), C(6)–Mn(1)–C(16) 105.16(3).

Compound 2 has an inversion centre between the central manganese atoms, and the terminal Mn(1)–C(1) bond distance of 2.1211(9) Å is significantly shorter than the Mn–C bonds to the bridging neopentyl ligands. For each bridging neopentyl group, one Mn–C bond is approximately 0.1-0.2 Å shorter than the other, with the short Mn–C distances ranging from 2.213(1) to 2.232(1) Å, and long Mn–C distances of 2.3265(7) to 3-coordinate Mn(1), and 2.3939(7) and 2.4092(9) Å to 4-coordinate Mn(2). Bridging alkyl groups in multimetallic manganese alkyl complexes in the literature also exhibit one short and one long Mn–C bond (see Section 1.3), as do all μ-alkyl manganese complexes in this work (vide infra). The Mn(1)–Mn(2) and Mn(2)–Mn(2') distances in 2 are 2.7022(4) and 2.7165(4) Å, which are almost 0.2 Å shorter than the Mn–Mn distances previously reported for $\left[\{\text{Mn(CH}_2\text{SiMe}_3)_2\}_2\right]_\infty$ (1). Furthermore, the Mn–C–Mn angles in
2 (71.38(3)-72.67(3)°) are approximately 5° more acute than those in 1, while the Mn–C distances are comparable. The Mn–Mn distances in 2 lie between the sum of ionic (2.58 Å) and Van der Waals radii (4.10 Å), and are within the range previously reported (2.5-3.2 Å) for single Mn–Mn bonds in the vast majority of coordination and organometallic complexes. However, they are longer than the shortest Mn–Mn distances in elemental manganese (2.26, 2.37 and 2.47 Å for α-, β- and γ-Mn, respectively). 

X-ray quality crystals of the 1:1 Mn:dmpe complexes, [(dmpe)Mn(CH₂SiMe₃)₂] (3) and {[(μ-dmpe)Mn(CH₂CMe₃)₂]₂} (4), were obtained from hexanes at –30 °C. Compound 3 (Figure 2.2; left) is monometallic with a tetrahedral geometry that is distorted due to the small bite angle of dmpe (78.76(2)° in 3). By contrast, 4 (Figure 2.3; right) is dimetallic with bridging dmpe ligands and a Mn–Mn distance of 6.756(2) Å, which is far greater than the sum of the van der Waals radii. Compound 4 features tetrahedral manganese centres (X–Mn–X = 94.79(2)-122.20(9)°; X = C or P) and a central 10-membered ring with a boat-chair-boat conformation, which is the dominant conformation of cyclodecane. An organometallic complex featuring a similar M₂(μ-dppe)₂ core (dppe = bis(diphenylphosphino)ethane) has been structurally characterized for Mo. The Mn–P and Mn–C distances in 3 and 4 are unremarkable, ranging from 2.6241(9) to 2.6541(5) Å (Mn–P) and 2.1320(14) to 2.160(2) Å (Mn–C), similar to the Mn–P and Mn–C₈ terminal bond lengths in 1, 2, [(PMe₃)₂Mn(CH₂Ph)₂], and [(TMEDA)Mn(CH₂SiMe₃)₂] (TMEDA = N,N,N′,N′-tetramethyl-ethylenediamine). By contrast, significantly longer Mn–P and Mn–C distances were reported for [(dmpe)Mn{CH(SiMe₃)₂}]₂ presumably due to greatly increased steric hindrance at the metal centre.
Figure 2.2: X-ray crystal structures for (left) [(dmpe)Mn(CH$_2$SiMe$_3$)$_2$] (3) and (right) [{(μ-dmpe)Mn(CH$_2$CMe$_3$)$_2$}]$_2$ (4). Hydrogen atoms are omitted for clarity, and ellipsoids are set to 50%. For 3, all carbon atoms in the dmpe ligand are disordered over two positions, and only the dominant conformation (69%) is shown above. Bond distances (Å) and angles (°): Mn–C 2.1320(14), Mn–P 2.6541(5), P–Mn–P 78.76(2), C–Mn–C 144.34(9), P(1)–Mn–C(1) 108.59(5), P(1)–Mn–C(1') 98.89(4). For 4, bond distances (Å) and angles (°): Mn···Mn 6.756(2), Mn(1)–P(1) 2.6241(9), Mn(1)–P(2') 2.643(1), Mn(1)–C(1) 2.160(2), Mn(1)–C(6) 2.160(2), P(1)–Mn(1)–P(2) 94.79(2), C(1)–Mn(1)–C(6) 122.20(9), C(1)–Mn(1)–P(1) 104.25(7), C(6)–Mn(1)–P(1) 106.94(7), C(1)–Mn(1)–P(2) 119.20(7), C(6)–Mn–P(2) 105.25(7).

Bright red X-ray quality crystals of [{(μ-dmpe){Mn(CH$_2$SiMe$_3$)(μ-CH$_2$SiMe$_3$)}$_2$}] (5) were obtained at –30 °C from both toluene and hexanes. The unit cell for the structure obtained from toluene (Figure 2.3; left) contains three independent molecules, while the structure obtained from hexanes (Figure 2.3; middle) has only one independent molecule in the unit cell. Black X-ray quality crystals of the neopentyl analogue, [{(μ-dmpe){Mn(CH$_2$CMe$_3$)(μ-CH$_2$CMe$_3$)}$_2$}] (6) (Figure 2.3; right) were obtained from toluene at –30 °C. Both 5 and 6 are dimetallic with tetrahedral manganese centres (C–
Mn–X = 94.4(1)-131.4(4)°; X = C or P) coordinated to one terminal alkyl group, two bridging alkyl groups, and one phosphorus atom of a bridging dmpe ligand. The terminal Mn–C distances in 5 and 6 (2.123(2)-2.141(5) Å in 5; 2.160(6) and 2.18(1) Å in 6) are shorter than the bridging Mn–C distances, and as in base-free 1 and 2, each of the bridging alkyl groups is closer to one manganese atom than the other; the short Mn–C_{bridging} distances range from 2.183(2) to 2.211(4) Å in 5 and 2.252(5) to 2.27(1) Å in 6, whereas the long Mn–C_{bridging} distances range from 2.362(2) to 2.379(4) Å in 5 and 2.300(9) to 2.342(6) Å in 6.
Figure 2.3: X-ray crystal structures for $[(\mu\mbox{-}\text{dmpe})\{\text{Mn(CH}_2\text{SiMe}_3})(\mu\mbox{-}\text{CH}_2\text{SiMe}_3)\}]_2$ (5) obtained by crystallization from toluene (left) or hexanes (middle), and (right) the X-ray crystal structure for $[(\mu\mbox{-}\text{dmpe})\{\text{Mn(CH}_2\text{CMe}_3)(\mu\mbox{-}\text{CH}_2\text{CMe}_3)\}]_2$ (6). Hydrogen atoms are omitted for clarity, and ellipsoids are set to 50%. For 5 (obtained from toluene), the unit cell contains three independent and essentially isostructural molecules, and only one is shown. Atoms below with a ‘B’ or ‘C’ suffix are the atoms related to those with the same identifying number and the suffix ‘A’, but in the structures not shown in the figure. Bond distances (Å) and angles (°): Mn(1A)···Mn(1A') 2.7202(6), Mn(1B)···Mn(1B') 2.7177(6), Mn(1C)···Mn(1C') 2.7322(6), Mn(1A)–P(1A) 2.6007(9), Mn(1B)–P(1B) 2.5909(9), Mn(1C)–P(1C) 2.6020(9), Mn(1A)–C(1A) 2.123(2), Mn(1B)–C(1B) 2.137(2), Mn(1C)–C(1C) 2.136(2), Mn(1A)–C(6A) 2.183(2), Mn(1B)–C(6B) 2.200(2), Mn(1C)–C(6C) 2.208(2), Mn(1A)–C(6A') 2.366(2), Mn(1B)–C(6B') 2.370(2), Mn(1C)–C(6C') 2.362(2), Mn(1A)–C(6A)–Mn(1A') 73.34(7), Mn(1B)–C(6B)–Mn(1B') 72.88(7), Mn(1C)–C(6C)–Mn(1C') 73.35(8). For 5 (obtained from hexanes), bond distances (Å) and angles (deg): Mn(1)···Mn(2) 2.7255(9), Mn(1)–P(1) 2.581(1), Mn(2)–P(2) 2.603(2), Mn(1)–C(1) 2.133(4), Mn(2)–C(11) 2.141(5), Mn(1)–C(6) 2.211(4), Mn(2)–C(16) 2.210(4), Mn(1)–C(16) 2.379(4), Mn(2)–C(6) 2.372(4), Mn(1)–C(6)–Mn(2) 72.9(1), Mn(1)–C(16)–Mn(2) 72.8(1). For 6, positions of all carbon atoms in three of the four...
neopentyl groups (C(1)-C(15)) are disordered over two positions. The figure shows only one position for each of the disordered groups (occupancy: 50 % for C1-C5, 82 % for C6-C10, and 87 % for C11-C15). Bond distances (Å) and angles (°): Mn(1)···Mn(2) 2.685(1), Mn(1)–P(1) 2.605(1), Mn(2)–P(2) 2.641(1), Mn(1)–C(1) 2.160(6), Mn(2)–C(11) 2.18(1), Mn(1)–C(16) 2.252(5), Mn(2)–C(6) 2.27(1), Mn(1)–C(6) 2.300(9), Mn(2)–C(16) 2.342(6), Mn(1)–C(6)–Mn(2) 72.0(3), Mn(1)–C(16)–Mn(2) 71.5(2).

The Mn–P distances in 5 and 6 are similar and unexceptional. However, the Mn–Mn distances of 2.7177(6)-2.7322(6) Å in 5 are shorter than those in base-free 1 by over 0.15 Å, likely due to the tethering influence of the bridging bis(phosphine) ligand. The Mn–C–Mn angles in 5 (72.88(7)-73.35(8)°) are also more acute than those in base-free 1 (76.82(4) and 77.19(5)°), consistent with the shorter Mn–Mn distance in the former compound. The Mn–Mn distance of 2.685(1) Å in 6 is less than 0.05 Å shorter than the corresponding distance in base-free 2, but it is significantly shorter than the Mn–Mn distance in 5. The Mn–Cterminal and average Mn–Cbridging distances (vide supra) are slightly longer in 6 than in 5, and the Mn–C–Mn angles in 6 (71.5(2)-72.0(3)°) are slightly more acute than those in 5 (vide supra). These geometric trends mirror those observed for base-free 1 and 2. An even shorter Mn–Mn distance of 2.616(5) Å, and a particularly acute Mn–C–Mn angle of 69.6(4)°, were previously reported for isostructural [(μ-dmpe){MnCy(μ-Cy)}₂] (Cy = cyclohexyl), which features more sterically demanding and electron donating secondary alkyl groups.

Bright red X-ray quality crystals of [(μ-dmpm){Mn(CH₂SiMe₃)(μ-CH₂SiMe₃)}₂] (7) were obtained from hexanes at –30 °C (Figure 2.4 left), revealing a dimetallic structure analogous to the structures of the 2:1 MnR₂:dmpe complexes, 5 and 6. The Mn–Mn, Mn–C and Mn–P distances and Mn–C–Mn angles in 7 are very similar to those in 5, although the dmpm ligand in 7 is bound less symmetrically than the dmpe ligand in 5 (the Mn–P distances in 7 differ by approx. 0.06 Å in 7, compared with approx. 0.02 Å in 5). The solid state structure of [(μ-dmpm){Mn(CH₂CMe₃)(μ-CH₂CMe₃)}₂] (8) was also determined using crystals obtained (a) from hexanes at –30 °C (not shown), and (b) by
slow evaporation of a hexanes solution at 20 °C (Figure 2.4 right). However, the quality of the both data sets was only suitable to establish connectivity, which is analogous to that of 7.

Figure 2.4: X-ray crystal structures for (left) $\left[\left(\mu\text{-dmpm}\right)\{\text{Mn(CH}_2\text{SiMe}_3\}(\mu\text{-CH}_2\text{SiMe}_3)\}\right]_2$ (7) and (right) $\left[\left(\mu\text{-dmpm}\right)\{\text{Mn(CH}_2\text{CMe}_3\}(\mu\text{-CH}_2\text{CMe}_3)\}\right]_2$ (8). Hydrogen atoms are omitted for clarity, and ellipsoids are set to 50 %. For 7, bond distances (Å) and angles (°): Mn(1)···Mn(2) 2.7243(5), Mn(1)–P(1) 2.6584(5), Mn(2)–P(2) 2.6016(6), Mn(1)–C(1) 2.134(1), Mn(2)–C(11) 2.121(1), Mn(1)–C(6) 2.220(2), Mn(2)–C(16) 2.233(1), Mn(1)–C(16) 2.340(1), Mn(2)–C(6) 2.337(1), Mn(1)–C(6)–Mn(2) 73.38(5), Mn(1)–C(16)–Mn(2) 73.08(4). For 8, poor quality of data means that the structure is only suitable to establish connectivity. The unit cell contains five independent and essentially isostructural molecules, and only one is shown.

The structures of 5 and 7 can also be compared with $\left[\left(\text{PMe}_3\right)\{\text{Mn(CH}_2\text{SiMe}_3\}(\mu\text{-CH}_2\text{SiMe}_3)\}\right]_2$ (for which an X-ray crystal structure has...
previously been reported),\textsuperscript{110} and an isostructural PEt\textsubscript{3} complex, 
\[ \{(\text{PEt}_3)\text{Mn}(\text{CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2 \] \textsuperscript{(9)},\textsuperscript{112} for which we have obtained an X-ray crystal structure (Figure 2.5). Key differences are that the phosphine ligands in the PR\textsubscript{3} (R = Me or Et) complexes are trans to one another across the Mn–Mn axis, and the Mn–Mn distances (2.772(1) Å (R = Me) and 2.7937(3) Å (R = Et)) are 0.05 to 0.07 Å longer than those in 5 and 7. Furthermore, the Mn–C–Mn angles in the monophosphine complexes (74.5(1)° for R=Me and 75.21(3)° for R=Et) are marginally less acute than those in 5 and 7 (\textasciitilde 73°), while Mn–P and Mn–C distances are comparable. These data highlight the substantial influence of the bidentate dmpe ligand on the relative orientation of the phosphorus donors, the Mn–Mn distance, and the Mn–C–Mn angle. The neopentyl complex, 
\[ \{(\text{PMe}_3)\text{Mn}(\text{CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)\}_2 \],\textsuperscript{112} has also been reported, featuring an elongated Mn–Mn distance (2.718(3) Å) and statistically equivalent Mn–C–Mn angles (69.6(6)° and 71.0(6)°) relative to 6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{X-ray crystal structure for \[ \{(\text{Et}_3\text{P})\text{Mn}(\text{CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2 \] \textsuperscript{(9)}. Hydrogen atoms are omitted for clarity, and ellipsoids are set to 50 %. Bond distances (Å) and angles (°): Mn–Mn 2.7937(3), Mn–P 2.6473(4), Mn–C(1) 2.136(1), Mn–C(6) 2.215(1), Mn–C(6’) 2.3588(9), Mn–C(6)–Mn 75.21(3).
\end{figure}
2.3 – NMR Spectroscopy and Magnetic Measurements

The $^1$H NMR spectra of complexes 2-8 (Figure 2.6 left; C$_6$D$_6$, 500 MHz) show paramagnetically broadened and shifted peaks, between 5 and 60 ppm, with full width at half maximum values from 1150 to 8200 Hz. Further spectra were collected in $d_8$-toluene between 186 K and room temperature {Figure 2.6 (middle) for 6}. A spectrum was not collected for 1 due to insolubility in non-coordinating solvents.

Figure 2.6: Left: Room temperature $^1$H NMR spectra for 2-8 (500 MHz, C$_6$D$_6$). Black tick marks indicate broad peaks associated with organomanganese(II) complexes, while the sharp signals are due to residual C$_6$D$_5$H in the NMR solvent and trace hexanes. Middle: low frequency portion of the $^1$H NMR spectra for [(μ dmpe){Mn(CH$_2$CMe$_3$)(μ CH$_2$CMe$_3$)}$_2$] (6) from 186 to 298 K (500 MHz, $d_8$-toluene). Broad signals (|) are due to 6, while sharp signals are due to residual $d_7$-toluene solvent impurity (≠) and hexanes (*). Right: Region of the $^1$H NMR spectra used for Evans measurements for 6 between 186 and 298 K (500 MHz, 40:1 $d_8$-toluene:toluene); the methyl group from external toluene (†) is calibrated to 2.11 ppm, and the methyl group of internal toluene (‡) is observed to shift with temperature. Shoulders to the right of the two toluene (C$_7$H$_8$) signals are the residual solvent signals due to $d_7$-toluene, C$_6$D$_5$(CHD$_2$).
Based on the solid-state structure of phosphine-free 2, six $^1$H NMR signals are predicted with integrations of 36H, 18H, 18H, 8H, 4H and 4H. However, it is not unreasonable to expect that the MnCH$_2$ signals would be broadened to the point at which they cannot be located, due to their proximity to the high spin d$^5$ metal centres; in this case, a total of three $^1$H NMR signals would be observed. At room temperature, the $^1$H NMR spectrum of 2 shows only a single broad $^1$H NMR resonance, but at –32 °C this peak splits into the expected three signals.

The $^1$H NMR spectra for dmpe complexes 3 and 4, which do not contain bridging alkyl groups, would be expected to give rise to three signals (18H, 12H and 4H, not including MnCH$_2$ signals), whereas the $^1$H NMR spectra for 5-8 should give rise to four signals (18H, 18H, 12H, and either 4H or 2H, not including MnCH$_2$ signals). The expected number of signals was observed for 3, 4 and 7 at 25 °C, below 10 °C for 5, and below –28 °C for 8. For compound 6, just two $^1$H NMR signals were observed at room temperature, and at –15 °C the largest of these signals split into two, yielding three broad peaks; the observation of just three signals (–15 to –80 °C) in the spectrum for 6 is likely due to coincidental overlap of two signals (Figure 2.6; middle). The increased number of signals in the low temperature $^1$H NMR spectra of 2, 5, 6 and 8 may be attributed to (a) different temperature dependencies for overlapping paramagnetically shifted signals, or (b) decoalescence of signals that are averaged at room temperature due to exchange processes. For compound 8, explanation ‘a’ is most likely on the basis of solution magnetic measurements (vide infra). By contrast, for compounds 2, 5 and 6, explanation ‘b’ seems likely, given that solution magnetic measurements indicate that these tetrametallic or dimetallic complexes exist in equilibrium with other manganese-containing species in solution (vide infra).

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$^p$ Attempts to determine whether the dimeric structure of complex 4 (Figure 2.2 right) remained intact in solution or dissociated into monometallic species using DOSY NMR spectroscopy failed due to very short $T_1$ relaxation times (the average for the three signals in complex 4 is 0.282 ms at 0.03 gmL$^{-1}$).
Solid state and solution magnetic measurements were carried out on complexes 2-8 (Table 2.1). SQUID magnetic measurements have previously been reported for 1, and show antiferromagnetic coupling/exchange between the manganese atoms. SQUID magnetic measurements on 3, which is monometallic, and 4, which is a dimer with spatially separated manganese centres, show that both complexes obey the Curie-Weiss law (Figure 2.7; 300 to 5 K), leading to effective magnetic moments ($\mu_B$) of 5.8 ± 0.2 and 5.83 ± 0.03 BM, respectively, and magnetic susceptibilities ($\chi_{M\text{(corr)}}$) of $1.40 \times 10^{-3}$ ± 1.2×10^{-3} and 14.08×10^{-3} ± 0.13×10^{-3} cm$^3$/mol of Mn at room temperature (for a high spin d$^5$ metal centre, the ideal values for $\mu_B$ and $\chi_{M\text{(corr)}}$ are 5.92 BM and 14.6 × 10^{-3} cm$^3$/mol, respectively). Compounds 3 and 4 are therefore paramagnetic with no antiferromagnetic exchange.

Table 2.1: Room temperature solution and solid state magnetic data for 2-8. $\chi_{M\text{(corr)}}$ = corrected molar magnetic susceptibility; $\mu_B$ = effective magnetic moment; $\theta$ = Weiss temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\chi_{M\text{(corr)}}$ per Mn centre ($10^{-3} \text{ cm}^3/\text{mol}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in C$_6$D$_6$ at 298 K</td>
</tr>
<tr>
<td>2</td>
<td>4.2 ± 0.1$^c$</td>
</tr>
<tr>
<td>3</td>
<td>13.6 ± 0.5 ($\mu_B = 5.71$ BM ± 0.11)$^d$</td>
</tr>
<tr>
<td>4</td>
<td>14.4 ± 0.5 (5.87 BM ± 0.10)</td>
</tr>
<tr>
<td>5</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>6</td>
<td>6.5 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>8</td>
<td>3.4 ± 0.1</td>
</tr>
</tbody>
</table>

a. $\theta = -0.6$ ± 0.1 K for 3.
b. $\theta = 0.04$ ± 0.06 K for 4.
c. Lit: 3.9 BM.$^{96}$
d. Lit: 5.6 BM.$^{111}$

By contrast, the SQUID magnetic data (Figure 2.7) for complexes 2 and 5-8, which feature Mn–Mn distances between 2.685(1) and 2.7322(6) Å, do not obey the Curie law, and are indicative of significant antiferromagnetic exchange/coupling between neighboring manganese centres (with paramagnetic impurity tails at low temperature). At room temperature, the magnetic susceptibility per manganese centre is $2.82 \times 10^{-3}$ cm$^3$/mol.
for tetrametallic 2, and ranges from $3.24 \times 10^{-3}$ to $3.48 \times 10^{-3}$ cm$^3$/mol for bimetallic 5-8; these values are far lower than that expected for a paramagnetic metal centre with five unpaired d-electrons ($14.6 \times 10^{-3}$ cm$^3$/mol). The variable temperature magnetic behaviour of 2 and 5-8 is qualitatively similar to that reported for polymeric 1$^{99}$ and dimetallic [{(THF)Mn(CH$_2$SiMe$_3$)$_2$}$_2$]$^{117}$ and for the latter compound, Gambarotta and Thompson et al. concluded that the significant magnetism observed at low temperatures indicates an absence of Mn–Mn bonding, despite the short Mn–Mn distance of 2.7878(9) Å.$^{117}$

![Figure 2.7: SQUID magnetic susceptibility data from 5 to 300 K. Left: $\chi_{\text{M(corr)}}$ vs. $T$ (solid lines) and $(1/\chi_{\text{M(corr)}})$ vs. $T$ (dashed lines) for paramagnetic 3 (red) and 4 (blue). Right: $\chi_{\text{M(corr)}}$ vs. $T$ (solid lines) and $\chi_{\text{M(corr)}}*T$ vs. $T$ (dashed lines) for 2 (red), 5 (blue), 6 (purple), 7 (orange), and 8 (green), which feature antiferromagnetic interactions.](image)

The SQUID magnetic susceptibility data for dinuclear 5-8 and tetranuclear 2 was fitted to an exchange expression for simple high spin Mn(II) systems using MAGMUN-4.1,$^{460}$ and the resulting fits (Table 2.2) are in good agreement with the experimental data. The resulting calculated g factors are close to 2.0, as expected for high spin organomanganese(II) complexes which lack an orbital contribution to the magnetic moment, and the exchange coupling constants ($J$) for 2 and 5-8 range from $-107$ to $-117$ cm$^{-1}$, indicative of strong antiferromagnetic coupling ($J$ is an averaged value for compound 2).

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Table 2.2: Magnetic parameters determined by fitting an exchange expression to the SQUID magnetic susceptibility data for compounds 2 and 5-8. $J$ = exchange coupling constant; $\rho$ = fraction paramagnetic impurity; $\theta$ = Weiss-like temperature correction; $R = [(\Sigma \chi_{obs} - \chi_{calc})^2 / (\Sigma \chi_{obs})^2]^{1/2}$.

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<thead>
<tr>
<th>Compound</th>
<th>Mean g-value</th>
<th>Intradimer $J$ (cm$^{-1}$)</th>
<th>$\rho$</th>
<th>$\theta$ (K)</th>
<th>100R</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.07 ± 0.01</td>
<td>−117 ± 1</td>
<td>0.005</td>
<td>2.4</td>
<td>0.71</td>
</tr>
<tr>
<td>5</td>
<td>2.12 ± 0.02</td>
<td>−112 ± 2</td>
<td>0.02</td>
<td>4.9</td>
<td>1.47</td>
</tr>
<tr>
<td>6</td>
<td>2.10 ± 0.02</td>
<td>−112 ± 2</td>
<td>0.01</td>
<td>1.1</td>
<td>1.03</td>
</tr>
<tr>
<td>7</td>
<td>2.07 ± 0.01</td>
<td>−109 ± 1</td>
<td>0.007</td>
<td>3.4</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>2.04 ± 0.03</td>
<td>−107 ± 2</td>
<td>0.011</td>
<td>5.1</td>
<td>1.06</td>
</tr>
</tbody>
</table>

a. The calculated temperature independent paramagnetism (TIP) is 0 cm$^3$/mol for 2, 6 and 7, $4 \times 10^{-5}$ cm$^3$/mol for 5, and $3 \times 10^{-5}$ cm$^3$/mol for 8.

b. For 2, $J$ is average over the three Mn–Mn interactions present.

Solution state magnetic measurements were conducted using the Evans NMR method. Measurements were taken at room temperature for all complexes (in a 40:1 mixture of C$_6$D$_6$:C$_6$H$_6$; Table 2.1), and between 298 and 186 K for 2 and 5-7 (in a 40:1 mixture of $d_8$-toluene:toluene; for 6 see Figure 2.6 (right)). Complexes 3 and 4, which are monometallic or feature well-separated manganese centres, have room temperature solution effective magnetic moments of 5.71 BM and 5.87 BM, respectively, which are very close to the theoretical value of 5.92 BM, and are statistically equivalent to the solid state effective magnetic moments. Dmpm complexes 7 and 8 gave rise to statistically identical solution and solid state magnetic susceptibilities at room temperature, indicating that the solid state structures of 7 and 8 remain intact in solution. Additionally, variable temperature Evans magnetic measurements on compound 7 (Figure 2.8; 298 to 186 K) yielded magnetic susceptibility values that are statistically equivalent to those from SQUID measurements over the same temperature range.
Figure 2.8: Solution magnetic susceptibilities per mole of Mn calculated from Evans measurements at various temperatures for

\[ \{\text{Mn(CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)\}_2\{\text{Mn(\mu-CH}_2\text{CMe}_3)\}_2\text{Mn}\} \quad (2) \quad \text{(blue diamonds)}, \\
[(\mu-\text{dmpe})\{\text{Mn(CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2] \quad (5) \quad \text{(green triangles)}, \\
[(\mu-\text{dmpe})\{\text{Mn(CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)\}_2] \quad (6) \quad \text{(red squares), and} \\
[(\mu-\text{dmpm})\{\text{Mn(CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)\}_2] \quad (7) \quad \text{(purple ‘×’ symbols).}

By contrast, the solution magnetic susceptibilities for base-free 2 and dimetallic 6 are significantly higher than the solid state values (although they are still much lower than those expected in the absence of antiferromagnetic exchange). For dimetallic 6, the solution magnetic susceptibility values decreased as the temperature was lowered, until an asymptote was reached at a value corresponding to that from solid state SQUID measurements; compound 5 showed analogous behavior, but with a much less pronounced change in magnetic susceptibility (Figures 2.7 and 2.8). This behavior is consistent with a solution equilibrium (significant above 245 K for 5, and above 210 K for 6) between the dimetallic solid state structures and entropically favored paramagnetic species; most likely mononuclear \(((\text{dmpe})\text{Mn(CH}_2\text{EMe}_3)_2) [E = \text{Si (3)} \text{ or C (4)}] \text{ and base-free ‘Mn(CH}_2\text{EMe}_3)_2]”. Our inability to directly observe the proposed minor solution species by variable temperature $^1$H NMR spectroscopy is consistent with both the low concentrations of these species in solution, the broadness of the observed $^1$H NMR
signals, and the likelihood of rapid exchange between these species and 5 and 6, especially at the upper end of the temperature range.

Unlike the solution magnetic susceptibility data for complexes 5 and 6, the solution magnetic susceptibility of base-free 2 increased as the temperature was reduced and did not reach a plateau (Figure 2.8), moving increasingly further from the solid state magnetic susceptibility value of $2.82 \times 10^{-3}$ cm$^3$/mol of Mn. This increase in magnetic susceptibility is indicative of an equilibrium that shifts at lower temperature towards species with weaker antiferromagnetic coupling than is observed in tetrametallic 2. Above room temperature, the magnetic susceptibility of the solution (per manganese atom) continued to decrease towards the solid state value, but magnetic measurements were not accessible above 60 °C ($\chi_{M(\text{corr})} = 3.8 \times 10^{-3}$ cm$^3$/mol) due to slow decomposition of solutions of 2 above this temperature.

2.4 – Physical Properties of 1-8

Melting points ranging from 62 to 176 °C were measured for 1-8 in a flame sealed glass capillary under an atmosphere of argon (Table 2.3). All complexes were found to melt without noticeable decomposition (determined visually and by $^1$H NMR spectroscopy and/or PXRD after cooling to room temperature) if the temperature was reached quickly (5 °C/min.), with the exception of 6 which showed minor decomposition. Importantly, the melting points of 3 and 4 match those reported by Wilkinson et al., confirming that the originally reported complexes were 1:1 Mn:dmpe complexes as proposed, rather than 2:1 complexes.
Table 2.3: Physical properties of complexes 1-8.

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Sublimation Temp. at 5 mTorr (°C)</th>
<th>Thermal Decomp. Data (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>151-153 (lit. 98)°⁰</td>
<td>150-160 (lit. 150)°⁰</td>
<td>195 (rapid decomp.)</td>
</tr>
<tr>
<td>2</td>
<td>99-102</td>
<td>90 (lit. 100)°⁰</td>
<td>110 (&gt; 50 % after 24 h)</td>
</tr>
<tr>
<td>3</td>
<td>62-63 (lit. 62-64)°¹¹</td>
<td>60</td>
<td>120 (v. little over 24 h)</td>
</tr>
<tr>
<td>4</td>
<td>132 (lit. 132-133)°¹¹</td>
<td>80</td>
<td>120 (complete after 5-6 hours)</td>
</tr>
<tr>
<td>5</td>
<td>145-146</td>
<td>115-135 (decomp. products sublime)</td>
<td>120 (complete after 5-6 hours)</td>
</tr>
<tr>
<td>6</td>
<td>149-151.5 (part. decomp.)</td>
<td>110</td>
<td>110 (visible after 2-3 hours)</td>
</tr>
<tr>
<td>7</td>
<td>176</td>
<td>100</td>
<td>120 (v. little over 24 h)</td>
</tr>
<tr>
<td>8</td>
<td>161.5-165</td>
<td>100-120</td>
<td>110 (v. little over 24 h)</td>
</tr>
</tbody>
</table>

a. Amount of decomposition assessed visually and by ¹H NMR spectroscopy and/or PXRD after cooling to room temperature.

Base-free \[{\text{Mn(}{\mu}\text{-CH}_2\text{SiMe}_3\text{)}_2}_\infty\] (1), though very thermally stable (rapid decomp. 195 °C), is not especially volatile (sublim. at 150-160 °C; 5 mTorr). This low volatility can be explained by the polymeric nature of 1 in the solid state. By contrast, \[{\text{Mn(CH}_2\text{CMe}_3)(}{\mu}\text{-CH}_2\text{CMe}_3\text{)}_2}\{\text{Mn(}{\mu}\text{-CH}_2\text{CMe}_3\text{)}\_2\text{Mn}\} \) (2), which exists as a monomer in the vapor phase,sublimed at 90 °C (5 mTorr), but was more than 50 % decomposed after 24 h at 110 °C. The remaining complexes, 3-8, sublimed between 60 and 135 °C at 5 mTorr, although 5 underwent extensive decomposition during sublimation, and 6 and 8 decomposed slowly at the sublimation temperature (Table 2.3). The 1:1 MnR₂:dmpe complexes, monometallic 3 and dimetallic 4, exhibited the most promising volatility/thermal stability characteristics for possible applications in ALD or CVD, subliming at 60 and 80 °C, respectively, with negligible decomposition after 24 h at 120 and 110 °C, respectively. Furthermore, 3 has a melting point of 62-63 °C, so would be a liquid at the delivery temperature in a typical ALD or CVD experiment.

2.5 – Reactions with Hydrogen and Diethyl Zinc

Solutions of complexes 2-8, or a slurry of 1, were placed under 2 atm. of H₂ in an aromatic solvent, the reactions were monitored by ¹H NMR spectroscopy, and insoluble products were characterized using PXRD. Reactions took place between 25 and 120 °C (Table 2.4), and in each case, a clear colourless or very pale beige solution was formed with a metallic-looking silver-grey mirror on the walls of the NMR tube (Scheme 2.3), or
in one case (complex 1) a precipitate of black powder. The diamagnetic reaction byproducts were tetramethylsilane or neopentane, accompanied by dmpe or dmpm in the case of compounds 3-8 (Scheme 2.3). The deposited solid was identified as manganese metal by PXRD. Additionally, conducting the reactions of 3 and 5 with H₂ in the presence of hexaethylbenzene as an internal NMR standard yielded exactly two and four equivalents of SiMe₄, respectively,⁹ illustrating complete removal of the alkyl groups from manganese. The appearance of the deposited films is also consistent with metallic manganese.

**Table 2.4:** Reaction conditions and by-products for: (i) the solution reactions of 1-8 with H₂ yielding Mn metal (determined by PXRD), and (ii) solution reactions of 1-8 with ZnEt₂ to deposit a 1:1 Mn/Zn alloy (determined by PXRD, and in some cases XPS; accompanied by Zn metal deposition in the reaction of 2 with ZnEt₂). Complex 10 is trans-[(dmpe)₂MnH(C₂H₄)].

<table>
<thead>
<tr>
<th>Complex</th>
<th>T&lt;sub&gt;reaction&lt;/sub&gt; with H₂ (°C) / time (h)</th>
<th>H₂ reaction by-products&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T&lt;sub&gt;reaction&lt;/sub&gt; with ZnEt₂ (°C) / time (h)</th>
<th>ZnEt₂ reaction by-products&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 / 48</td>
<td>SiMe₄</td>
<td>25 / 12</td>
<td>C₂H₆, C₂H₄, SiMe₂, ZnRX</td>
</tr>
<tr>
<td>2</td>
<td>25 / 72</td>
<td>CMe₄</td>
<td>25 / 12</td>
<td>C₂H₆, C₂H₄, CMe₂, ZnRX</td>
</tr>
<tr>
<td>3</td>
<td>120 / 24</td>
<td>SiMe₄, dmpe</td>
<td>60 / 1</td>
<td>C₂H₆, C₂H₄, 10, SiMe₂, u.p.</td>
</tr>
<tr>
<td>4</td>
<td>70 / 216 (or 100 / 24)</td>
<td>CMe₄, dmpe</td>
<td>25 / 72</td>
<td>C₂H₆, C₂H₄, 10, ZnRX</td>
</tr>
<tr>
<td>5</td>
<td>120 / 4</td>
<td>SiMe₄, 3</td>
<td>25 / 48</td>
<td>C₂H₆, C₂H₄, 10, SiMe₂, ZnRX,</td>
</tr>
<tr>
<td>6</td>
<td>25 / 168 (or 60 / 1)</td>
<td>CMe₄, 4</td>
<td>25 / 12</td>
<td>C₂H₆, C₂H₄, 10, ZnRX, u.p.</td>
</tr>
<tr>
<td>7</td>
<td>120 / 4</td>
<td>SiMe₄, dmpm, u.p.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>90 / 0.5</td>
<td>C₂H₆, C₂H₄, ZnRX, dmpm</td>
</tr>
<tr>
<td>8</td>
<td>100 / 4</td>
<td>CMe₄, dmpm</td>
<td>95 / 1</td>
<td>C₂H₆, C₂H₄, ZnRX, dmpm</td>
</tr>
</tbody>
</table>

<sup>a</sup> By-products identified by ¹H NMR spectroscopy.

<sup>b</sup> R = CH₂EMe₃; X = Et or R; E = C or Si.

<sup>c</sup> u.p. = unidentified phosphorus-containing product.

⁹ For 5, 4 equivalents of SiMe₄ was observed after the intermediate (3) had reacted with excess H₂ at 120 °C for 12 h.
Scheme 2.3: Reactions of 1-8 with H₂ in benzene or toluene.

Polymeric complex 1 was the least reactive towards hydrogen, requiring several days at 120 °C to react completely, most likely due to very low solubility. By contrast, highly soluble tetrametallic 2 reacted to completion within three days at room temperature; 2 is far more reactive than 1 and 3-8, likely due to the presence of 3-coordinate manganese centres. Complexes 3 and 4, which contain one equivalent of dmpe per manganese centre, showed low reactivity towards H₂; the reaction with 3 was only complete after 12 hours at 120 °C, and the reaction with 4 was complete after 24 hours at 100 °C. Dimetallic 5 and 6, which contain half an equivalent of dmpe per manganese
centre, reacted with H\(_2\) to form 3 or 4, accompanied by tetramethylsilane or neopentane and manganese metal. Complete consumption of 5 required 4.5 hours at 120 °C,\(^1\) and the analogous reaction with 6 proceeded over a week at room temperature. The similarity in the reaction conditions required for consumption of 6 and 2 supports the proposal (vide supra) that in solution, 6 exists in equilibrium with 2 and 4 (i.e. H\(_2\) likely reacts with 2 that is in equilibrium with 6 in solution, leaving unreacted 4). Compounds 7 and 8 reacted with H\(_2\) over the course of 4 hours at 120 °C and 100 °C, respectively. However, unlike the dmpe analogues (5 and 6), compounds 7 and 8 reacted with H\(_2\) to provide manganese metal without formation of an observable monometallic intermediate. A general trend for 1-8 is the greater reactivity of the neopentyl complexes towards H\(_2\).

Overall, the reactions of the dialkylmanganese(II) complexes and their bis(phosphine) adducts with H\(_2\) highlight the utility of metal alkyl complexes for electropositive metal deposition, demonstrating the thermodynamic feasibility of key reaction steps en route to manganese deposition. In solution, base-free 2 and dmpe complex 6 displayed the highest reactivity. However, solution reaction temperatures may not be of direct relevance to thermal ALD, given that adsorption to the surface of the growing thin film during ALD is likely to result in phosphine dissociation and/or formation of surface-bound species with coordination geometries and steric environments which differ significantly from those in the intact precursor complex.

Complexes 1-8 were also reacted with 1-3 equivalents of ZnEt\(_2\) (per Mn) in C\(_6\)D\(_6\) (2-8) or d\(_8\)-toluene (1) in a sealed NMR tube, the reactions were monitored by \(^1\)H and/or \(^{31}\)P NMR spectroscopy, and precipitated solids were characterized by PXRD and in some cases XPS. Complexes 1-2 and 4-6 reacted completely over 12-72 hours at room temperature, whereas 3 required heating for 1 hour at 60 °C, and dmpm complexes 7 and 8 required heating at 90-95 °C for 30-60 minutes. In each of these reactions, a silver-coloured mirror was deposited onto the walls of the NMR tube, and ethane, ethylene and

\(^1\) Complex 5 slowly decomposed to 3 at 120 °C in solution. However, this decomposition proceeded much more slowly than the reaction to form 3 in the presence of H\(_2\).
ZnX(CH₂EMe₃) (X = Et or CH₂EMe₃; E = Si or C) were released, accompanied in some cases by a small amount of EMₑ₄ (E = Si or C); H₂ formation was not observed. Compounds 7 and 8 released free dmmp, whereas dmpe compounds 3-6 formed trans-[(dmpe)₂MnH(C₂H₄)] (10) (0.5 equiv. per Mn in 3-4 and 0.25 equiv. per Mn in 5-6; Scheme 2.4), and free dmpe was not liberated.¹

Scheme 2.4: Reactions of dmpe complexes 3-6 with ZnEt₂ (R = CH₂EMe₃; X = Et or R; E = C or Si) in benzene.

The reactivity of 5 and 6 with ZnEt₂ is greater than that of 3 and 4, respectively, implying that 3 and 4 are not formed as intermediates in the reactions of 5 and 6 with ZnEt₂, in contrast to the analogous reactions with H₂ (vide supra). The aforementioned manganese(I) hydride compound, diamagnetic trans-[(dmpe)₂MnH(C₂H₄)] (10), was first prepared by Wilkinson et al. via the reactions of manganese dihalides with MgEt₂,¹²⁰,¹⁷² and may be formed in this work by i) initial generation of a Mn(II) ethyl intermediate followed by β-hydride elimination and bi-molecular HR reductive elimination, ii) bi-molecular HR reductive elimination from manganese dihydride and manganese hydrido/alkyl centres, or iii) comproportionation between a manganese dihydride species and elemental manganese (or an unobserved zero-valent manganese species formed en route to manganese metal).

¹ NMR signals for free dmmp were shifted by 0.05-0.1 ppm (¹H NMR) and 1-3 ppm (³¹P NMR) relative to a reference sample.

¹ A small amount of an unidentified phosphorus-containing product was observed in the reaction of 3 with ZnEt₂ at 60 °C. This product was not observed in the reaction of 5 with ZnEt₂, most likely due to milder reaction conditions.
By PXRD, the insoluble product from the reactions of 1-8 with ZnEt₂ was an approximate 1:1 manganese-zinc alloy, accompanied by zinc metal in the case of 2. The presence of both zinc and manganese was further confirmed by XPS on representative samples (Zn:Mn = 0.68 : 1 for 2 and 1.32 : 1 for 7). Elemental zinc deposition could potentially occur via hydride transfer from a manganese hydride intermediate to a dialkyl zinc compound, leading to a zinc hydrido/alkyl species with very limited thermal stability; the only isolated zinc hydrido hydrocarbyl compounds (not counting heterobimetallic species or those with pendent amine coordination to the metal) contain extremely large aryl groups {e.g. R = (C₆H₃-2,6-(C₆H₃-2,6-Pr₂)₂, C₆H₃-2,6-(C₆H₂-2,4,6-Pr₃)₂, and C₆H₂-2,6-(C₆H₂-2,4,6-Pr₃)₂-4-SiMe₃}, although ZnHMe has been observed in an argon matrix and spectroscopically in the gas phase. In addition, ZnH₂ is reported to decompose to Zn and H₂ at 90 °C.

2.6 – Summary and Conclusions for Chapter 2

In the solid state, dineopentylmanganese(II) (2) is tetrametallic with two terminal alkyl groups and six bridging alkyl groups. The outer manganese centres are trigonal planar, whereas the inner manganese centres are tetrahedral. Dmpe complexes of bis(trimethylsilylmethyl)manganese(II) and dineopentylmanganese(II) adopt three distinct structural types: monometallic [LMnR₂] (3), dimetallic [R₂Mn(μ-L)₂MnR₂] (4), and dimetallic [(μ-L){RMn(μ-R)}₂] (5-6). By contrast, dmpm only yielded [(μ-L){RMn(μ-R)}₂] complexes (7-8). All polymetallic complexes feature doubly bridging alkyl groups with one long and one short Mn–C bond, and the neopentyl complexes exhibit more acute Mn–C–Mn angles and shorter Mn–Mn distances than trimethylsilylmethyl analogues.

All complexes have non-zero magnetic susceptibilities between 300 and 5 K. Both [(dmpe)Mn(CH₂SiMe₃)₂] (3) and [(μ-dmpe)Mn-(CH₂CMe₃)₂] (4) obey the Curie-Weiss law, whereas tetrametallic dineopentylmanganese(II) (2) and [(μ-L){RMn(μ-R)}₂] (L = dmpe (5-6) or dmpm (7-8)) engage in strong antiferromagnetic
coupling with $J$ values from $\text{--107}$ to $\text{--117}$ cm$^{-1}$. Comparison of solution and solid state magnetic data indicates that the structures of the dmpm complexes (7 and 8) are maintained in solution, whereas the $[\langle\mu\text{-dmpe}\rangle\{R\text{Mn(}\mu\text{-R})\}_2]$ complexes (5 and 6) exist in equilibrium at 25 °C with species with a higher average magnetic susceptibility; most likely $[(\text{dmpe})\text{MnR}_2]$ and “$\text{MnR}_2$”. However, the solution magnetic susceptibilities of 5 and 6 decreased with decreasing temperature until an asymptote was reached, consistent with the presence of only 5 or 6 in solution at low temperature. In contrast, the solution state magnetic susceptibility (per Mn) of dineopentylmanganese(II) (2) almost doubled as the temperature was reduced from 335 to 185 K, implying that the tetrametallic solid state structure is in equilibrium with species which exhibit less effective antiferromagnetic coupling and are favored at lower temperatures.

The two compounds without bridging alkyl groups (3 and 4) exhibited the most desirable thermal stability and volatility for ALD or CVD applications, and all CH$_2$SiMe$_3$ derivatives exhibited slightly increased thermal stability relative to CH$_2$CMe$_3$ analogues; monomeric 3 was the most promising, melting at 62-63 °C, subliming at 60 °C (5 mTorr), and undergoing negligible decomposition after 24 h at 120 °C.

Solution reactions of 1-8 with H$_2$ yielded manganese metal with elimination of 2 equiv. of HR (R = CH$_2$EMe$_3$; in all cases, neopentyl complexes displayed higher reactivity towards H$_2$ than trimethylsilylmethyl analogues), demonstrating the thermodynamic feasibility of the key reaction steps required for manganese(II) dialkyl complexes to serve, in combination with H$_2$, as precursors for metal ALD or pulsed-CVD. By contrast, the solution reactions of 1-8 with ZnEt$_2$ yielded a zinc-manganese alloy with an approximate 1:1 Zn:Mn ratio, eliminating ethane and ethylene, accompanied by dmpm, $\text{trans-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ (10), EMe$_4$ and/or ZnXR (R = CH$_2$EMe$_3$; X = Et or R).
Chapter 3

Analysis of Wilkinson and Girolami’s trans-[(dmpe)_2MnH(C_2H_4)]

Portions of this chapter have been adapted with permission from Price, J. S.; Emslie, D. J. H.; Vargas-Baca, I.; Britten, J. F. [(dmpe)_2MnH(C_2H_4)] as a Source of a Low-Coordinate Ethyl Manganese(I) Species: Reactions with Primary Silanes, H_2, and Isonitriles, Organometallics 2018, 37, 3010-3023.

3.1 – Introduction to Chapter 3

trans-[(dmpe)_2MnH(C_2H_4)] (trans-10) was first reported by Girolami and Wilkinson et al. in 1983. This complex was originally prepared by the reaction of MnBr_2(dmpe)_2 and MgEt_2, and two years later, they reported an analogous synthesis using MnCl_2 and free dmpe (Scheme 3.1).\(^{120,172}\) The authors proposed a potential reaction mechanism involving initial formation of MnEtX(dmpe)_2, followed by bi-molecular C–C bond-forming reductive elimination to generate MnX(dmpe)_2 (X = Cl, Br) from which alkylation and β-hydride elimination would generate the observed product. Based on NMR spectroscopy, an octahedral environment with trans-disposed hydride and rapidly rotating ethylene ligands was proposed. A decade later, Jones et al. reported the synthesis of 10 from an alternative route; substitution by ethylene of a H_2 ligand in [(dmpe)_2MnH(H_2)] (11); Scheme 3.1.\(^{173}\) However, neither Wilkinson nor Jones reported an X-ray crystal structure of 10.

\[
\begin{array}{c}
\text{Wilkinson/Girolami} \\
\text{i. dmpe} \\
\text{ii. MgEt}_2 \\
\text{Et}_2\text{O} \\
\rightarrow \begin{array}{c}
\text{MnX}_2 \\
\text{(10)} \\
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{Jones et al.} \\
\text{C}_2\text{H}_4 \\
\text{C}_6\text{D}_6 \\
\rightarrow \begin{array}{c}
\text{Mn} \\
\text{H} \\
\text{H} \\
\text{(11)} \\
\end{array}
\end{array}
\]

Scheme 3.1: Reported synthetic routes to [(dmpe)_2MnH(C_2H_4)] (10). X = Cl, Br.\(^{120,172,173}\)
In 1985, Girolami and Wilkinson reported the lithiation of 10 to form \[\{(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMeCH}_2)_2\text{MnH}(\text{C}_2\text{H}_5)\}_2\text{Li}_4(\text{OEt}_2)_2\]. To our knowledge, this is the only report regarding the potential reactivity of complex 10. Complex 10 is a rare example of a first row transition metal ethylene hydride complex. As well, it is stable indefinitely under an inert atmosphere at room temperature and is diamagnetic.

3.2 – X-ray Crystal Structure of trans-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\)

X-ray quality crystal of trans-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (trans-10) were grown from a dilute solution in hexanes at –30 °C (Figure 3.1 left), and confirmed that the trans octahedral structure proposed by Wilkinson in solution by analysis of the NMR spectra\(^{120}\) is maintained in the solid state, with the equatorial girdle of phosphine donors displaced toward the smaller hydride ligand. Complex trans-10 shows significant metallacyclopropane character, which is apparent from the elongated C–C distance of 1.420(2) Å (compared to 1.329 Å in ethylene and 1.535 Å in ethane).\(^{468}\) The C–C distance is similar to those in previously characterized \[\{(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMeCH}_2)_2\text{MnH}(\text{C}_2\text{H}_4)\}_2\text{Li}_4(\text{OEt}_2)_2\] (bottom right in Figure 3.3) and [Na(pmdeta)]_2-[\((\kappa^2\text{C}_4\text{H}_8)\text{Mn}(\text{C}_2\text{H}_4)_2\)] (pmdeta = pentamethyldiethylenetriamine) of 1.41(1)-1.444(4) Å.\(^{120,469}\)

Substantial metallacyclopropane character in trans-10 is also supported by DFT calculations (ADF, gas phase, all-electron, PBE, D3-BJ, TZ2P, ZORA); Figure 3.1 right. In particular, the C–C Mayer bond order is 1.03 (compared to 1.85 for free ethylene and 0.91 for free ethane) and in a fragment \{(\text{dmpe})_2\text{MnH} and \text{C}_2\text{H}_4\} interaction calculation, a substantially negative Hirschfield charge of –0.273 was observed for the ethylene fragment. Furthermore, ETS-NOCV (extended transition state method for energy decomposition analysis with natural orbitals for chemical valence; Figure 3.2) calculations on trans-10 partitioned the ethylene-manganese interaction into σ donation and π-backdonation contributions of 103.9 and 300.1 kJ mol\(^{-1}\) respectively.
Figure 3.1: Left: X-ray crystal structure of $\textit{trans}$-[(dmpe)$_2$MnH(C$_2$H$_4$)] ($\textit{trans}$-10) with ellipsoids drawn at 50% probability. Hydrogen atoms on the metal centre and ethylene ligand were located from the difference map and refined isotropically. Most hydrogen atoms have been omitted for clarity. Bond distances (Å) and angles (deg): Mn–H(1) 1.56(4), Mn–C(1) 2.123(2), Mn–C(2) 2.121(2), C(1)–C(2) 1.420(2), $\Sigma$(H–C(1)–X) (X = C, H) 349(3), $\Sigma$(H–C(2)–X) (X = C, H) 349(3), $\Sigma$(P–Mn–P) ($\textit{cis}$) 356.44(4). Right: geometry optimized (DFT calcd.) structure of $\textit{trans}$-[(dmpe)$_2$MnH(C$_2$H$_4$)] ($\textit{trans}$-10). Most hydrogen atoms have been omitted for clarity.
Figure 3.2: ETS-NOCV analysis of bonding between [(dmpe)$_2$MnH] (equatorial dmpe geometry) and ethylene in trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (trans-10). Inset: SCF deformation density isosurface from a fragment interaction calculation using neutral [(dmpe)$_2$MnH] (equatorial dmpe geometry) and ethylene fragments for trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (trans-10).
3.3 – Potential Pathways for Reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] with Hydrides

$\text{trans-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ ($\text{trans-10}$) could potentially react with reagents such as hydrosilanes, hydrostannanes, hydroboranes, and H$_2$ though two different pathways (A and B; Scheme 3.2). The simplest of these pathways would be ethylene substitution, labelled pathway A in Scheme 3.2. The combined bonding energies of ethylene and a [(dmpe)$_2$MnH] (12) fragment with an equatorial dmpe arrangement (i.e. the products of ethylene dissociation from $\text{trans-10}$) are 182 kJ mol$^{-1}$ higher in energy than $\text{trans-10}$. This, in combination with an entropic driving force, suggests that dissociation of ethylene (the rate determining step in dissociative substitution, assuming the simplest possible mechanism not involving partial dmpe dissociation) may be possible at elevated temperature.$^a$ Pathway A would yield ethylene and [(dmpe)$_2$MnH$_2$R] (where R is an anionic ligand). An analogous mechanism could also be envisaged for the reactions of 10 with non-hydride Lewis bases (e.g. PR$_3$; see Chapter 9), which would yield [(dmpe)$_2$MnHL] (where L is a neutral ligand), again with ethylene elimination.

Scheme 3.2: Potential pathways (A and B) for the reaction of $\text{trans-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ (10) with various reagents. Only one isomer of all complexes except 10 is shown. E = SiR$_3$, SnR$_3$, BR$_2$, H.

An alternative reaction pathway could involve initial isomerization of the alkene hydride complex $\text{trans-10}$ to a 5-coordinate ethyl complex [(dmpe)$_2$MnEt] (13); pathway B in Scheme 3.2. This putative intermediate would be formed by initial isomerization of $\text{trans-10}$ to $\text{cis-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ ($\text{cis-10}$), which could generate 13 by 1,2 insertion

---

$^a$ Complex 10 displays significant thermal stability, decomposing slowly at 140 °C.
of the ethylene into the Mn–H bond. Intermediate 13 could then react with an E–H reagent (e.g. hydrosilanes, hydroboranes, H2) via either σ-bond metathesis or oxidative addition followed by reductive elimination to install a new anionic ligand in place of the ethyl group (with ethane as the byproduct); Scheme 3.2. Thus, trans-10 could act as a masked form of a highly reactive low-coordinate Mn(I) alkyl species.

Equilibria between alkene hydride and coordinatively unsaturated alkyl complexes (as envisaged in pathway B) have been observed for a range of 2nd and 3rd row transition metal complexes. For example, the NMR spectra of isolable ethylene hydride complexes typically indicate exchange between the protons of the alkene and the hydride ligands, and in some cases (e.g. in complexes of Nb, Ta, W, Re, Os, Ru, Rh, Ir, Pd, and Pt), reaction with a neutral donor has been shown to trap the alkyl isomer. However, in several cases, there is experimental evidence to suggest that exchange between the hydride and alkene protons occurs via a β-agostic alkyl complex, with "in-place" exchange of the bridging hydrogen atom rather than via a true low-coordinate (i.e. non-agostic) species. This is indicated by dynamic NMR studies, including pairwise coalescence of the four 31P NMR resonances observed for [(cis-Ph2PCH=CHPh2)2MoH(C2H4)2]+ at low temperature, exchange of the hydride and C2H4 environments in [κ1,η6-Cy2P(o-C6H4)(o-C6H4NMe2)]RuH(C2H4)]+ without epimerization, and exchange of the hydride and C2H4 environments in [(κ3-POCOP)MH(C2H4)]+ {M = Rh or Ir; POCOP = o-C6H3(OPtBu2)2} while maintaining top-bottom asymmetry.

In contrast to ethylene hydride complexes of 2nd and 3rd row transition metals, 1st row transition metal examples are scarce (Figure 3.3), and their isomerization to afford alkyl complexes has rarely been investigated. In fact, for the complexes in Figure 3.3, an equilibrium with an ethyl isomer has only been reported for the cobalt complex [(Me3P)3CoH(C2H4)] (though in this case calculations suggested very similar energies for the non-agostic and β-agostic cobalt ethyl structures) and the iron cyclopentadienyl complex [Cp*FeH(C2H4)(PMe3)]. However, from the reverse perspective, the 1st row
transition metal (Sc, Ti, Ni, and Co) ethyl complexes in Figure 3.4 all feature a β-agostic C–H–M interaction, and the cobalt, nickel α-diimine, and nickel β-diketiniminate complexes undergo NMR-observable exchange of the ethyl group CH$_2$ and CH$_3$ protons and/or carbon atoms, presumably via an undetected ethylene hydride complex.

Figure 3.3: First-row transition metal (Fe, Ni, Co, or Mn) alkene hydride complexes (not including complex 10).

Figure 3.4: First row transition metal ethyl complexes reported to feature a β-agostic interaction.
In contrast to pathway A (which generates ethylene and \([(\text{dmpe})_2\text{MnH}_2\text{R}]\); *vide supra*), reactions proceeding by pathway B would initially yield ethane and \([(\text{dmpe})_2\text{MnR}]\) (where R is an anionic ligand). As the initially generated complex \([(\text{dmpe})_2\text{MnR}]\) is coordinately unsaturated, it is susceptible to further inter- or intra-molecular reactivity to generate a coordinately saturated complex. Furthermore, unlike the substitution mechanism A (which involves generation of a potentially highly-reactive byproduct in ethylene), the putative ethane byproduct in pathway B would not react further with the generated complex. Furthermore, pathway B features a significant driving force in effectively irreversible C–H bond formation when eliminating ethane, in contrast to pathway A where the product and reactant may be in equilibrium if ethylene is not removed.

3.4 – DFT calculations for isomerization of *trans*-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) to \([(\text{dmpe})_2\text{MnEt}]\)

Reactions of *trans*-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (*trans-10*) with a variety of hydridic reagents are, in many cases (i.e. those which proceed via pathway B in Scheme 3.2), predicated on the thermodynamic accessibility of the Mn(I) ethyl complex \([(\text{dmpe})_2\text{MnEt}]\) (13). However, in all the reactions for which this mechanism is proposed (Chapters 4, 5, and 9), neither \([(\text{dmpe})_2\text{MnEt}]\) (13) nor putative intermediate *cis*-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (*cis-10*) were detected spectroscopically. Therefore, to investigate the accessibility of these complexes we turned to DFT calculations (ADF, gas phase, all-electron, PBE, D3-BJ, TZ2P, ZORA; Figure 3.5 and Table 3.1).
Figure 3.5: Potential energies ($E; \text{kJ mol}^{-1}$) relative to $\text{trans-10}$, calculated for structures (left to right) i. $\text{trans-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ ($\text{trans-10}$), ii. an isomer of $\text{cis-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ in which the ethylene ligand is oriented perpendicular to the plane formed by manganese, the hydride, and the ethylene centroid ($\text{cis-10}^\perp$), iii. the transition state for isomerization of $\text{cis-10}^\perp$ to $\text{cis-10}^\parallel$ {($\text{cis-10}^{\perp\parallel}$)}$^\dagger$, iv. an isomer of $\text{cis-}[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ in which the ethylene carbon atoms lie within the plane formed by manganese, the hydride, and the ethylene centroid ($\text{cis-10}^\parallel$), v. the transition state for isomerization of $\text{cis-10}^\parallel$ to $13^\beta$-agostic {($10/13$)}$^\dagger$, vi. $[(\text{dmpe})_2\text{MnEt}]$ with a $\beta$-agostic interaction ($13^\beta$-agostic), vii. $[(\text{dmpe})_2\text{MnEt}]$ without an agostic interaction where the Mn–C$_\alpha$–C$_\beta$ angle was restrained to 109.5° ($13^{109.5}$), viii. the transition state for isomerization of $13^\beta$-agostic to $13^\alpha$-agostic {($13^{\beta/\alpha}$)}$^\dagger$, and ix. $[(\text{dmpe})_2\text{MnEt}]$ with an $\alpha$-agostic interaction ($13^\alpha$-agostic). All structures except $13^{109.5}$ correspond to an energy minimum. The geometry optimized cores are depicted above each Chemdraw structure, showing Mn in blue, C in dark grey, and H in light grey, accompanied by stick bonds to the phosphorus donor atoms. Relative energies are those before zero-point energy (ZPE) correction.
Table 3.1: Selected angles (deg), distances (Å) (and Mayer bond orders) for DFT calculated structures in Figure 3.5.\(^a\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(\text{cis}-10)(^1)</th>
<th>(\text{cis}-10)(^{14})(^b)</th>
<th>(\text{cis}-10)(^1)</th>
<th>(\text{trans}-10)(^{13})(^b)</th>
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<th>13(^\beta)agostic</th>
<th>13(^\alpha)agostic</th>
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<td>(&lt;0.05)</td>
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<td>(0.82)</td>
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<td>(0.34)</td>
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<td>(&lt;0.05)</td>
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<td>2.76</td>
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<td>(&lt;0.05)</td>
<td>(&lt;0.05)</td>
<td>(&lt;0.05)</td>
<td>(&lt;0.05)</td>
<td>(&lt;0.20)</td>
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<td>1.10</td>
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<td>(0.32)</td>
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<td>(0.96)</td>
<td>(0.96)</td>
<td>(0.97)</td>
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<td>–</td>
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<td>1.09</td>
<td>1.11</td>
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<td>1.11</td>
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<tr>
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<td>(1.02)</td>
<td>(0.99)</td>
<td>(0.87)</td>
<td>(1.01)</td>
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<td>75.2</td>
<td>121.6</td>
<td>132.4</td>
<td>109.5</td>
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<td>–</td>
<td>–</td>
<td>–</td>
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<td>96.8</td>
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<td>–</td>
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<td>–</td>
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<td>–</td>
<td>–</td>
<td>–</td>
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<td>97.1</td>
<td>133.1</td>
<td>151.0</td>
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<td>136.4</td>
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<td>171.1</td>
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<tr>
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<td>–2.8</td>
<td>–2.2</td>
<td>–54.7</td>
<td>–34.9</td>
<td>–58.4</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Atom labels correspond to those in Figure 3.5. For alkyl isomers ([10/13]\(^\alpha\)agostic, [13\(^\alpha\)]agostic, and 13\(^\alpha\)agostic), C(1) is C\(_\alpha\), C(2) is C\(_\beta\), H(1) is the closest H on C\(_\beta\) to the Mn centre, and H(2) is the closest H on C\(_\beta\) to the Mn centre. For alkene hydride isomers (\(\text{cis}-10\)\(^1\), (\(\text{cis}-10\)\(^{14}\)\(^b\)), and \(\text{cis}-10\)\(^1\)), H(2) is the metal hydride, while C(1) and C(2) are ethylene carbon atoms.

\(^b\) For \(\text{cis}-10\)\(^1\), (\(\text{cis}-10\)\(^{14}\)\(^b\)), and \(\text{cis}-10\)\(^1\), all carbon–H\(_{\text{ethylene}}\) distances were calculated to be 1.09 Å with Mayer bond orders ranging from 1.01 to 1.04.

\(^c\) Mn–C(2)–(C1) angles for \(\text{cis}-10\)\(^1\), (\(\text{cis}-10\)\(^{14}\)\(^b\)), and \(\text{cis}-10\)\(^1\) are similar to the Mn–C(1)–(C2) angles: 70.3°, 71.8°, and 71.2° respectively.

Geometry optimization of \(\text{cis}–[(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (\(\text{cis}-10\)) yielded two local minima; an isomer of lower energy, \(\text{cis}-10\)\(^1\), where the ethylene carbon atoms lie within the plane formed by manganese, the hydride, and the ethylene centroid, and an isomer of higher energy, \(\text{cis}-10\)\(^{13}\), in which the ethylene ligand is perpendicular to the aforementioned plane. Isomers \(\text{cis}-10\)\(^1\) and \(\text{cis}-10\)\(^{13}\) are interconverted by an approximate 90° rotation of the ethylene ligand {via transition state (\(\text{cis}-10\)\(^{14}\)\(^b\))} with activation barriers of 19 or 38 kJ mol\(^{-1}\);Table 3.2}, and are 39 and 58 kJ mol\(^{-1}\) higher in energy than the \(\text{trans}\) isomer (\(\text{trans}-10\)) respectively (Figure 3.5).
Table 3.2: Activation Parameters for Transformations a-f in Figure 3.5; ΔE‡ (calculated before ZPE correction), ΔH‡, and ΔG‡ (kJ mol⁻¹ at 298.15 K), ΔZPE¶ (kJ mol⁻¹ at 0 K), and ΔS‡ (J mol⁻¹ K⁻¹ at 298.15 K).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE‡</th>
<th>ΔZPE¶</th>
<th>ΔH‡</th>
<th>ΔS‡</th>
<th>ΔG‡</th>
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</thead>
<tbody>
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<td>cis-10⁻ → cis-10⁻ (a)</td>
<td>19</td>
<td>-0.7</td>
<td>17</td>
<td>-18</td>
<td>22</td>
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<tr>
<td>cis-10⁻ → cis-10⁻ (b)</td>
<td>38</td>
<td>0.8</td>
<td>37</td>
<td>-21</td>
<td>44</td>
</tr>
<tr>
<td>cis-10⁻ → 1α-agostic (c)</td>
<td>5</td>
<td>-3.1</td>
<td>2</td>
<td>-9</td>
<td>4</td>
</tr>
<tr>
<td>1α-agostic → cis-10⁻ (d)</td>
<td>15</td>
<td>-6.0</td>
<td>8</td>
<td>-9</td>
<td>11</td>
</tr>
<tr>
<td>13α-agostic → 13β-agostic (e)</td>
<td>58</td>
<td>-4.4</td>
<td>56</td>
<td>29</td>
<td>47</td>
</tr>
<tr>
<td>13β-agostic → 13β-agostic (f)</td>
<td>16</td>
<td>-1.9</td>
<td>14</td>
<td>12</td>
<td>11</td>
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</tbody>
</table>

To probe the origin of the greater stability of trans-10 versus cis-10⁻ and cis-10⁻ظروف, geometry optimizations were carried out on cis- and trans-[(PH₃)₄MnH(C₂H₄)] (10PH₃), in which steric hindrance between phosphine groups is minimized (Figure 3.6, Table 3.3). In this case, cis-10⁰PH₃ (the cis isomer isostructural to cis-10⁻) is lower in energy than the trans isomer, trans-10⁰PH₃, by 5 kJ mol⁻¹, whereas cis-10⁻⁰PH₃ (the cis isomer isostructural to cis-10⁻ظروف) is higher in energy than trans-10⁰PH₃ by 22 kJ mol⁻¹. These data imply that unfavorable steric interactions between the dmpe ligands in cis-10⁻ and cis-10⁻ظروف are responsible for their diminished stability relative to trans-10. This steric penalty for adoption of a disphenoidal arrangement of the dmpe ligands also explains why trans-10 is isolated as a trans alkene hydride rather than as an ethyl isomer (despite the fact that the latter are usually lower in energy for 1st row transition metal complexes; vide supra), since the latter would require a disphenoidal arrangement of the dmpe ligands if an agostic interaction is to be accommodated to saturate the metal's coordination sphere (vide infra).
Figure 3.6: Potential energies (E; kJ mol\(^{-1}\)) relative to \textit{trans-10PH}_3, calculated for structures (left to right) i. \textit{trans-}[(PH\(_3\)_4MnH(C\(_2\)H\(_4\))] (\textit{trans-10PH}_3), ii. an isomer of \textit{cis-}[(PH\(_3\)_4MnH(C\(_2\)H\(_4\))] in which the ethylene ligand is oriented perpendicular to the plane formed by manganese, the hydride, and the ethylene centroid (\textit{cis-10PH}_3\(^{\perp}\)), and iii. an isomer of \textit{cis-}[(PH\(_3\)_4MnH(C\(_2\)H\(_4\))] in which the ethylene carbon atoms lie within the plane formed by manganese, the hydride, and the ethylene centroid (\textit{cis-10PH}_3\(^{\parallel}\)). Geometry optimized cores are depicted above each Chemdraw structure, showing Mn in blue, C in dark grey, and H in light grey, accompanied by stick bonds to the phosphorus donor atoms. Relative energies are those before zero-point energy (ZPE) correction.

Table 3.3: Selected angles (deg), distances (Å) (and Mayer bond orders) for DFT calculated PH\(_3\) analogues of ethylene hydride complexes.

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<tr>
<th>Parameter</th>
<th>\textit{trans-10PH}_3</th>
<th>\textit{cis-10PH}_3(^{\perp})</th>
<th>\textit{cis-10PH}_3(^{\parallel})</th>
</tr>
</thead>
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<td>Mn–C</td>
<td>2.11 (0.59)</td>
<td>2.15 (0.48-0.49)</td>
<td>2.10-2.14 (0.57-0.58)</td>
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<td>Mn–H</td>
<td>1.56 (0.90)</td>
<td>1.57 (0.83)</td>
<td>1.57 (0.80)</td>
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<td>Mn–P</td>
<td>2.18 (0.98-1.02)</td>
<td>2.17-2.19 (0.98-1.10)</td>
<td>2.16-2.18 (1.00-1.11)</td>
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<td>C–C (ethylene)</td>
<td>1.42 (1.03)</td>
<td>1.41 (1.08)</td>
<td>1.42 (1.04)</td>
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<td>C–H (ethylene)</td>
<td>1.09 (1.03)</td>
<td>1.09 (1.03-1.04)</td>
<td>1.09 (1.03)</td>
</tr>
<tr>
<td>C–Hydride</td>
<td>–</td>
<td>–</td>
<td>2.27 (0.09)</td>
</tr>
<tr>
<td>Σ(H–Mn–Y) (X,Y = C,H)</td>
<td>350.4</td>
<td>351.1-351.2</td>
<td>351.5</td>
</tr>
<tr>
<td>Σ(P–Mn–P) (\textit{cis})</td>
<td>359.2</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Geometry optimization of [(dmpe)$_2$MnEt] (13) led to an energy minimum (13$^{\beta$-agostic}) featuring a $\beta$-agostic interaction to the otherwise vacant coordination site. This structure exhibits an acute Mn–C$\alpha$–C$\beta$ angle of 75.2°, a short Mn–H$\beta$ distance of 1.71 Å, an elongated C$\beta$–H distance of 1.22 Å, and an acute (relative to a complex with an anagostic interaction) Mn–H–C$\beta$ angle of 96.8°, collectively indicative of a $\beta$-agostic interaction.$^{497}$ 13$^{\beta$-agostic} is 29 kJ mol$^{-1}$ higher in energy than the trans ethylene hydride isomer (trans-10), but lies 10 kJ mol$^{-1}$ below the most stable cis ethylene hydride isomer (cis-10$^1$). Structure 13$^{\beta$-agostic} is accessed via 1,2-insertion with a transition state $\{(10/13)^{\ddagger}\}$ only 5 kJ mol$^{-1}$ higher in energy than starting complex cis-10$^1$ (Table 3.2). This energy barrier is quite low, but lies within the range reported for related first row transition metal complexes. For example, $\Delta E^{\ddagger}$ was calculated to be 82 kJ mol$^{-1}$ for [(PMe$_3$)$_3$CoH(C$_2$H$_4$)] and less than 2 kJ mol$^{-1}$ for [CpCoH(C$_2$H$_4$)(PMe$_3$)]$^+$.$^{488,498}$

With respect to the reactivity of an ethyl isomer of trans-10 with various hydridic reagents, a cis vacant coordination site is presumably required on the metal centre, necessitating dissociation of the $\beta$-agostic interaction in 13$^{\beta$-agostic}. However, no such energy minimum could be located; the energy of such a species was estimated by restraining the Mn–C$\alpha$–C$\beta$ angle to 109.5°, yielding a structure (13$^{109.5}$) 49 kJ mol$^{-1}$ higher in energy than 13$^{\beta$-agostic}. This energy difference is consistent with the typical strength of a first row transition metal $\beta$-agostic interaction.$^{491,498}$ However, it differs significantly from that calculated for the ethyl isomer of [(PMe$_3$)$_3$CoH(C$_2$H$_4$)],$^{488}$ where the non-agostic structure was reported to be 4 kJ mol$^{-1}$ lower in energy than the $\beta$-agostic isomer.

A second energy minimum (13$^{\alpha$-agostic}) was located for [(dmpe)$_2$MnEt] (13) with an obtuse Mn–C$\alpha$–C$\beta$ angle of 132.4°, featuring an agostic interaction between one of the $\alpha$ C–H bonds and the metal centre. This structure features a very acute Mn–C$\alpha$–H angle of 72.3°, as well as a short Mn–H$\alpha$ distance of 1.95 Å, and a slightly elongated C$\alpha$–H$\alpha$ distance of 1.16 Å. Conversion of 13$^{\beta$-agostic} to 13$^{\alpha$-agostic} not only involves cleavage of the $\beta$-agostic interaction and establishment of an $\alpha$-agostic interaction, but also migration of
the Mn–C bond into the position previously occupied by the β-agostic interaction, with concomitant Mn–Cα–Cβ angle expansion and rotation about the Mn–Cα and Cα–Cβ bonds (Table 3.1). 13α-agostic is 42 kJ mol⁻¹ higher in energy than 13β-agostic, and is accessed via a transition state {13β/a‡} located 58 kJ mol⁻¹ higher in energy than 13β-agostic (Table 3.2), so could conceivably play a role in the reactivity of *trans*-10 with hydridic reagents such as hydrosilanes (Chapters 4-5), H₂, or hydroboranes (Chapter 9). This energy barrier lies within the 44–85 kJ mol⁻¹ range calculated for this type of isomerization in a series of Co(III) ethyl cations derived from \{[(C₅R'₅)CoH(C₂H₄)(PR₃)]⁺; R = Me, P(OMe)₃, R' = H, Me\}.⁴⁹⁹

An energy minimum was also located for an ethyl isomer with the vacant coordination site *trans* to the ethyl ligand and no agostic interaction (13trans). However, this minimum featured 2 unpaired electrons and is 85 kJ mol⁻¹ higher in energy than 13β-agostic. The restricted calculation (modelling a diamagnetic structure) afforded a minimum 5 kJ mol⁻¹ higher in energy than the paramagnetic minimum, with a HOMO-LUMO gap of just 69 kJ mol⁻¹ (cf. 250, 160, 115, and 116 kJ mol⁻¹ for 13β-agostic, 13α-agostic, 13109.5, and (13β/a)‡ respectively; none of these species geometry optimized to a lower energy paramagnetic isomer). Therefore, 13trans presumably does not play an important role in the reactivity of *trans*-10.

The largest activation energy associated with conversion of *trans*-10 to 13β-agostic or 13α-agostic is presumably associated with *trans* to *cis* isomerization of 10 (likely via a 5-coordinate intermediate formed by phosphine or ethylene dissociation), rather than 1,2-insertion to convert *cis*-10¹ to 13β-agostic or isomerization of 13β-agostic to 13α-agostic, since the activation barriers for the latter two transformations are only 5 and 58 kJ mol⁻¹ respectively (Figure 3.5, Table 3.2).

### 3.5 – Trapping of the Putative [(dmpe)₂MnEt] Intermediate

In pursuit of experimental corroboration for the accessibility of [(dmpe)₂MnEt] (13) from *trans*-[((dmpe)₂MnH(C₂H₄))] (*trans*-10), a trapping experiment was conducted
with tert-butyl isonitrile (CN\textsuperscript{t}Bu) at 50 °C, affording [(dmpe)\textsubscript{2}MnEt(CN\textsuperscript{t}Bu)] (14a) (Scheme 3.3). This reaction initially formed a low-symmetry species identified by NMR spectroscopy as the cis isomer of 14a, featuring \textsuperscript{1}H NMR resonances for two diastereotopic MnCH\textsubscript{2} protons (−0.12 and 0.22 ppm; Figure 3.7) and three broad \textsuperscript{31}P NMR signals (61.6, 74.4, and 81 ppm; broadening is presumably due to reversible isonitrile or phosphine donor dissociation in solution). Upon cooling to 207 K, the \textsuperscript{31}P signals sharpened and one signal split into two, giving the expected four \textsuperscript{31}P environments. At the temperature of synthesis (50 °C), cis-14a slowly converted into trans-14a (Scheme 3.3), which gave rise to a single sharp \textsuperscript{31}P NMR signal at 74.7 ppm and an apparent octet in the \textsuperscript{1}H NMR spectrum due to the MnCH\textsubscript{2} protons (0.47 ppm; apparent octet due to very similar \textsuperscript{3}J\textsubscript{H,H} and \textsuperscript{3}J\textsubscript{H,P} coupling to the adjacent CH\textsubscript{3} group and 4 equivalent phosphines; Figure 3.7). This cis-trans isomerization did not proceed to completion, but an equilibrium was established (over many days at 50 °C, or a few hours at 80 °C), dominated by trans-14a. The reaction to form complex 14a is, to the best of our knowledge, only the second example where an ethyl complex could be trapped by Lewis base addition to an isolable 1\textsuperscript{st} row transition metal ethylene hydride complex.\textsuperscript{484} Complex 14a shows surprising thermal stability for a β-hydrogen containing alkyl complex; in solution, negligible decomposition was observed after 12 hours at 80 °C.
Scheme 3.3: Reactions of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with isonitriles to afford ethyl complexes [(dmpe)$_2$MnEt(CNR)] (14a: R = t-Bu, 14b: R = o-xylyl) and further insertion products, including [(dmpe)Mn(CNXyl)$_3$\{C(=NXyl)CEt(=NXyl)\}] (15).

Assignment of the two species produced in the reaction of 10 with CN$_t$Bu as isomers of 14a, as opposed to iminoacyl complexes, was corroborated by the observation of NMR coupling between the α ethyl protons and the $^{31}$P nuclei, indicating the close (in this case, 3 bond) proximity of these nuclei. Upon $^{31}$P decoupling of the $^1$H NMR spectrum, the multiplets associated with the MnCH$_2$ environments collapsed to signals with the expected $^1$H–$^1$H coupling; doublets ($^2$J$_{H,H}$ = 11 Hz) of quartets ($^3$J$_{H,H}$ = 7 Hz) for the diastereotopic MnCH$_2$ protons of cis-14a, and a quartet ($^3$J$_{H,H}$ = 8 Hz) for the MnCH$_2$ protons of trans-14a (Figure 3.7).
Figure 3.7: Regions of the $^1$H{${}^{31}$P} (above) and $^1$H (below) NMR spectra for the MnCH$_2$ environments in a) cis-$[\text{dmpe}]_2\text{MnEt}(\text{CN}^t\text{Bu})$ (cis-14a) and b) trans-$[\text{dmpe}]_2\text{MnEt}(\text{CN}^t\text{Bu})$ (trans-14a).

In contrast to the clean reactivity of 10 with CN$^t$Bu, the reaction of 10 with o-xylyl isonitrile (CNXyl, Xyl = o-xylyl) produced a mixture of products (Scheme 3.3), including a minor product identified by X-ray crystallography and NMR spectroscopy as trans-$[\text{dmpe}]_2\text{MnEt}(\text{CNXyl})$ (trans-14b; b in Figure 3.8). A low concentration of a short lived, low symmetry, species was also observed, and is presumed to be the cis isomer of $[(\text{dmpe})_2\text{MnEt}(\text{CNXyl})]$ (cis-14b), with two $^1$H signals for the diastereotopic MnCH$_2$ environments at 0.03 and 0.27 ppm, and an apparent triplet for the MnCH$_2$CH$_3$ environment (1.92 ppm, $^3J_{H,H} = 8$ Hz). DFT calculations support the thermodynamic accessibility of both cis- and trans- isomers of ethyl complexes 14a,b in solution, given that the former are only 12-18 kJ mol$^{-1}$ higher in energy than the latter.

Both trans-14a,b were characterized by X-ray diffraction (Figure 3.8), and are the first crystallographically characterized examples of terminal manganese ethyl complexes, although $[\text{Mn(μ-Et)}_4\{\text{Li(TEMEDA)}\}_2]$, which features ethyl ligands bridging between Mn and Li centres, has been reported.$^{500}$ In the solid state, these manganese(I) ethyl complexes feature an octahedral environment around the manganese centre, with the ethyl ligand trans to the isonitrile ligand. X-ray crystal structures of trans-14a,b also
feature notably acute C–N–C angles \( \{14\text{a}: 146.0(5)^\circ\text{–}148.3(5)^\circ; \quad 14\text{b}: 159(1)^\circ\}\), long N–C\text{terminal} \( \{14\text{a}: 1.207(5)\text{–}1.214(4) \text{\AA; } 14\text{b}: 1.22(1) \text{\AA}\}\), and short Mn–C\text{CNR} \( \{14\text{a}: 1.803(4)\text{–}1.813(3) \text{\AA; } 14\text{b}: 1.793(3) \text{\AA}\}\), consistent with strong π-backdonation from the electron rich “(dmpe)\textsubscript{2}MnEt” fragment to the isonitrile ligand.

\(501\)

**Figure 3.8:** X-ray crystal structures of a) \textit{trans}-[(dmpe)\textsubscript{2}MnEt(CN\textsubscript{t}Bu)] (\textit{trans}-14\text{a}) and b) \textit{trans}-[(dmpe)\textsubscript{2}MnEt(CN\textsubscript{xyl})] (\textit{trans}-14\text{b}) with ellipsoids drawn at 50\% probability. Hydrogen atoms have been omitted for clarity. In the case of \textit{trans}-14\text{a}, all atoms except P and Mn are disordered over two positions, and only one conformation \(\{50.1(2)\%\text{ and } 52.8(2)\%\} \text{ for the two dmpe ligands, } 50.5(2)\% \text{ for the isonitrile ligand, and } 56.0(3)\% \text{ for the ethyl ligand}\} \text{ is shown. In the case of } \textit{trans}-14\text{b}, \text{ one dmpe ligand and the N atom are both disordered over two positions, and only one conformation } \{51.4(3)\% \text{ for the dmpe ligand and } 55(2)\% \text{ for N}\} \text{ is shown. Atoms below with an ‘A’ suffix are the atoms related to those with the same identifying number without a suffix, but in the conformation not}
shown in the figure. For trans-14a,\(^v\) bond distances (Å) and angles (deg): Mn–C(1) 2.222(2), Mn–C(1A) 2.226(3), Mn–C(3) 1.803(4), Mn–C(3A) 1.813(3), C(1)–C(2) 1.528(4), C(1A)–C(2A) 1.526(6), C(3)–N(1) 1.207(5), C(3A)–N(1A) 1.214(4), N(1)–C(4) 1.456(5), N(1A)–C(4A) 1.458(5), Mn–C(3)–N(1) 168.2(6), Mn–C(3A)–N(1A) 171.0(6), C(3)–N(1)–C(4) 148.3(5), C(3A)–N(1A)–C(4A) 146.0(5), Mn–C(1)–C(2) 120.4(2), Mn–C(1A)–C(2A) 120.6(3), \(\Sigma(P–Mn(1)–P)\) (cis) 360.04(4). For trans-14b, bond distances (Å) and angles (deg): Mn–C(1) 2.212(2), Mn–C(3) 1.794(2), C(1)–C(2) 1.520(4), C(3)–N(1) 1.223(7), C(3)–N(1A) 1.219(9), N(1)–C(4) 1.391(7), N(1A)–C(4) 1.394(9), C(1)–Mn–C(3) 174.1(1), Mn–C(3)–N(1) 173.1(7), Mn–C(3)–N(1A) 165.4(6), C(3)–N(1)–C(4) 159(1), C(3)–N(1A)–C(4) 159(1), Mn–C(1)–C(2) 122.8(2), \(\Sigma(P–Mn(1)–P)\) (cis) 360.34(6).

Attempts to purify either of the two isomers of 14b from the reaction mixture failed, and the additional products formed in the reaction of 14b with CNXyl are presumed to result from phosphine substitution by excess o-xylyl isonitrile and/or multiple isonitrile insertion reactions. Support for these reaction pathways was provided by crystallization of [(dmpe)Mn(CNXyl)\(_3\)]\(\{C(=NXyl)CEt(=NXyl)\}\) (15) from the reaction mixture, which features an octahedral coordination environment composed of a single dmpe ligand, three isonitrile ligands, and a \(\kappa^1\)-C(=NXyl)CEt(=NXyl) ligand trans to one of the isonitriles (Figure 3.9 and Scheme 3.3).\(^w\) NMR spectra of complex 15, which could be isolated in approximately 90% purity, show two \(^{31}\)P NMR signals (53.9 and 66.2 ppm) and three xylyl-Me \(^1\)H NMR signals (correlating to four \(^{13}\)C NMR signals

\(\uparrow\) Due to approximately 50:50 positional disorder in the isonitrile ligand, two possible sets of N–C\(_{\text{terminal}}\), C–N–C, and Mn–C–N values exist. The first set of values is tabulated in this caption, while the second set of values is C(3)–N(1A) and C(3A)–N(1) = 1.307(5) and 1.362(5) Å; C(3A)–N(1)–C(4) and C(3)–N(1A)–C(4A) =137.4(4)° and 131.4(4)°; Mn–C(3)–N(1A) and Mn–C(3A)–N(1): 146.9(5)° and 144.7(6)°. Only the first set of values is consistent with literature values, and DFT calculations also afforded bond lengths and angles in much closer agreement to the first set of values: N–C\(_{\text{terminal}}\) = 1.22 Å, C–N–C = 147.2°, and Mn–C–N = 169.2°. Therefore, only the first set of values is discussed further.

\(\uparrow\) Examples of manganese complexes with iminoacyl ligands (all of which are \(\kappa^2\)-coordinated) can be found in ref. 502.
in the $^1$H–$^{13}$C HSQC spectrum) integrating to a total of five isonitrile ligands per dmpe ligand and ethyl substituent. Unlike ethyl complexes $14a,b$, the Mn$\text{CH}_2$ environment in the $^1$H NMR spectrum of $15$ displays no coupling to $^{31}$P, due to a separation of 5 bonds between the Mn$\text{CH}_2$ protons and phosphorus.

**Figure 3.9:** X-ray crystal structure of [(dmpe)Mn(CNXyl)$_3$\{C(=NXyl)CEt(=NXyl)\}] (15), with ellipsoids drawn at 50% probability. Methyl groups on the o-xylyl ligands and all hydrogen atoms have been omitted for clarity. The phenyl group of one isonitrile ligand is disordered over two positions and only the dominant conformation {51.4(6)%} is shown. C(40A) is the counterpart to C(40) in the conformation not shown. Bond distances (Å) and angles (deg): Mn–C(1) 2.110(5), Mn–C(21) 1.837(5), Mn–C(30) 1.848(6), Mn–C(39) 1.832(6), C(1)–C(2) 1.522(8), C(2)–C(3) 1.540(7), C(3)–C(4) 1.522(7), C(1)–N(1) 1.307(6), C(2)–N(2) 1.291(6), N(1)–C(5) 1.425(7), N(2)–C(13) 1.419(7), C(21)–N(3) 1.198(7), C(30)–N(4) 1.198(6), C(39)–N(5) 1.133(6), N(3)–C(22) 1.408(6), N(4)–C(31) 1.401(6), N(5)–C(40) 1.486(5), N(5)–C(40A) 1.49(1), Mn–C(1)–C(2) 120.2(3), Mn–C(1)–N(1) 121.2(4), C(1)–N(1)–C(5) 125.3(5), C(2)–C(3)–C(4) 113.4(5), C(2)–N(2)–C(13) 123.6(4), C(1)–C(2)–C(3) 118.6(4), C(1)–C(2)–N(2) 117.8(4), Mn–C(21)–N(3) 175.8(5), Mn–C(30)–N(4) 171.9(4), Mn–C(39)–N(5) 177.3(5), C(21)–N(3)–C(22) 160.3(5), C(30)–N(4)–C(31) 166.5(5), C(39)–N(5)–C(40) 155.1(5), C(39)–N(5)–C(40A) 169.7(6).
3.6 – Summary and Conclusions for Chapter 3

Girolami and Wilkinson reported the synthesis and NMR spectra of trans-[(dmpe)\(_2\)MnH(C\(_2\)H\(_4\))] (trans-10) decades ago, but until now the reactivity of this complex has remained largely unexplored. We have now obtained an X-ray crystal structure which confirmed that the trans hydride-ethylene structure reported in solution based on NMR spectroscopy is maintained in the solid state. Analysis of the solid state structure, in combination with DFT calculations, suggests significant metallacyclopentane character.

Two potential pathways for reactions of 10 with hydridic reagents were discussed, involving either ethylene substitution or initial isomerization to a 5-coordinate ethyl intermediate [(dmpe)\(_2\)MnEt] (13). DFT calculations and trapping experiments with isonitriles demonstrated the accessibility of 13 from trans-10. Isolated ethyl complex [(dmpe)\(_2\)MnEt(CN\(_t\)Bu)] (14a) is a rare example of a thermally stable \(\beta\)-hydride-containing alkyl complex, showing negligible decomposition over 12 hours at 80 °C.

This work contributes to fundamental understanding of the equilibrium between transition metal ethylene hydride and ethyl complexes. As described in the Section 3.3, examples of 1\(^{st}\) row transition metal ethylene hydrides are extremely scarce (the equilibrium typically lies to the side of the ethyl isomer), and the equilibrium between ethylene hydride and alkyl complexes has rarely been investigated. Compound trans-10 provided a unique opportunity to study this process, and key computational findings are (a) two isomers of a cis ethylene hydride are energetically accessible from trans-10 (cis-10\(^L\) and cis-10\(^l\)), differing in the orientation of the alkene relative to the plane formed by manganese, the hydride, and the ethylene centroid, (b) the trans ethylene hydride isomer is 39 kJ mol\(^{-1}\) lower in energy than the most energetically favorable cis isomer (cis-10\(^l\)), primarily due to increased steric hindrance between the dmpe ligands in either isomer of cis-10, (c) the most energetically favorable cis ethylene hydride complex (cis-10\(^l\)) is 10 kJ mol\(^{-1}\) higher in energy than the \(\beta\)-agostic ethyl isomer (13\(^\beta\)-agostic), (d) the barrier to 1,2-insertion, converting cis-10\(^l\) to 13\(^\beta\)-agostic, is only 5 kJ mol\(^{-1}\), (e) an \(\alpha\)-agostic ethyl isomer (13\(^\alpha\)-agostic) is energetically accessible, 42 kJ mol\(^{-1}\) higher in energy than 13\(^\beta\)-agostic,
(f) the barrier to conversion of $\text{13}^{\beta}$-agostic to $\text{13}^{\alpha}$-agostic is 58 kJ mol$^{-1}$, and (g) an energy minimum for a non-agostic ethyl complex with a cis vacant coordination site was not located, but a structure optimized with the Mn–C$_{\alpha}$–C$_{\beta}$ angle restrained to 109.5° ($\text{13}^{109.5}$) was 49 kJ mol$^{-1}$ higher in energy than $\text{13}^{\beta}$-agostic.
Chapter 4

Synthesis of Silylene Hydride Complexes and Reactivity with Ethylene to Afford Silene Hydride Complexes

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4.1 – Introduction to Chapter 4

Manganese hydride complexes with silicon-based co-ligands could be potential precursors for use in CVD of Mn-containing thin films. Complexes bearing electronically unstabilized silylene or silene ligands are extremely reactive, and no group 7 examples have yet been reported. Overviews of transition metal silylene and silene complexes are provided in sections 1.6 and 1.7. Herein, we show that [(dmpe)$_2$MnH(C$_2$H$_4$)] (10), which we discussed as a potential precursor for new manganese chemistry in Chapter 3, can be used to access silylene hydride complexes. These are the first examples of isolable group 7 complexes bearing an unstabilized terminal silylene ligand. Furthermore, we also show the unprecedented transformation of a silylene hydride complex to a silene hydride complex. One of the the two silene hydride complexes prepared in this work is the first isolated example of a 1st row transition metal complex bearing a sterically and electronically unstabilized silene ligand, and the other is the first such complex to be crystallographically characterized.

4.2 – Synthesis and Characterization of Manganese Silylene Hydride Complexes

Girolami and Wilkinson's trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (trans-10) complex$^{172}$ reacted with H$_2$SiEt$_2$ (4.5 equiv.) at room temperature to form [(dmpe)$_2$MnH(=SiEt$_2$)] (16$^{Et_2}$) with release of ethane (scheme 4.1). Compound 16$^{Et_2}$ gave rise to one $^{31}$P
resonance, a hydride $^1$H NMR signal at –10.46 ppm, and a $^{29}$Si resonance at 365.3 ppm, characteristic of a $C_{2v}$ symmetric trans silylene hydride complex (note: 1-2% of an unidentified product was always observed in $^1$H NMR spectra of $^{16}$Et$_2$, and may be the cis isomer). An X-ray crystal structure of $^{16}$Et$_2$ (Figure 4.1) confirmed this assignment, revealing an octahedral geometry at manganese, trigonal planar geometry at silicon (Σ(C–Si–X) = 360.0(1)°; X = C or Mn), and a Mn–H distance of 1.60(3)-1.62(3) Å. The Mn–Si distance in $^{16}$Et$_2$ is 2.1880(12)-2.1948(12) Å, which compares well with the Fe–Si distance of 2.154(1) Å in [CpFe(SiMe$_3$)(CO)(=SiMes$_2$)]$_2$, taking into consideration the larger ionic radius of Mn(I) vs Fe(II), and is much shorter than the Mn–Si distances of 2.2789(9)-2.3571(7) Å in the $N$-heterocyclic silylene complexes [(CO)$_4$Mn(=SiR{PhC(N'tBu)$_2$})$_2$]+ (R = Cl, NPh$_2$) and 2.402(2)-2.434(3) Å in the bridging silylene complexes [{CpMnH(CO)$_2$}$_2$(µ-SiH$_2$)]$_2$ and [{Mn(CO)$_4$}$_2${µ-SiPh$_2$}$_2$]$_2$.

**Scheme 4.1:** Reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with H$_2$SiR$_2$ to form (when R = Et) trans-[(dmpe)$_2$MnH(=SiEt$_2$)] (trans-$^{16}$Et$_2$), or (when R = Ph) a mixture of cis- and trans-[(dmpe)$_2$MnH(=SiPh$_2$)] (cis-$^{16}$Ph$_2$ and trans-$^{16}$Ph$_2$) along with [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (18Ph$_2$). Subsequent reactions of the silylene hydride complexes (trans-$^{16}$Et$_2$ or cis- and trans- $^{16}$Ph$_2$) with H$_2$ to form [(dmpe)$_2$MnH$_2$(SiHR$_2$)] (18$_{^{16}R_2}$: R = Et, 18$_{^{18}R_2}$: R = Ph) are also included. Only one isomer of 18$_{^{18}R_2}$ is shown.
**Figure 4.1:** X-ray crystal structure of $\text{trans-}[\text{(dmpe)}_2\text{MnH(=SiEt}_2\text{)}]$ ($\text{trans-16}^{\text{Et}_2}$) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity and the hydrogen atom on Mn was located from the difference map and refined isotropically. The unit cell contained four independent and essentially isostructural molecules, and only one is shown. Atom labels with suffixes A-C are complementary to those without the suffix in the molecule shown. Distances (Å) and angles (deg): Mn(1)–Si(1) 2.195(1), Mn(1A)–Si(1A) 2.188(1), Mn(1B)–Si(1B) 2.192(1), Mn(1C)–Si(1C) 2.191(1), Mn(1)–H(1) 1.61(3), Mn(1A)–H(1A) 1.61(3), Mn(1B)–H(1B) 1.61(3), Mn(1C)–H(1C) 1.60(3), Si(1)–C(1) 1.933(2), Si(1A)–C(1A) 1.929(2), Si(1B)–C(1B) 1.929(2), Si(1C)–C(1C) 1.933(3), H(1)–Mn(1)–Si(1) 180.0, H(1A)–Mn(1A)–Si(1A) 180.0, H(1B)–Mn(1B)–Si(1B) 180.0, H(1C)–Mn(1C)–Si(1C) 180.0, Mn(1)–Si(1)–C(1) 130.45(7), Mn(1A)–Si(1A)–C(1A) 130.6(8), Mn(1B)–Si(1B)–C(1B) 130.50(7), Mn(1C)–Si(1C)–C(1C) 130.59(8), C(1)–Si(1)–C(1’) 99.1(2), C(1A)–Si(1A)–C(1A’) 98.8(2), C(1B)–Si(1B)–C(1B’) 99.0(2), C(1C)–Si(1C)–C(1C’) 98.8(2).

The reaction to form $\text{16}^{\text{Et}_2}$ and ethane likely occurs via an undetected 5-coordinate manganese ethyl complex, [(dmpe)MnEt] (13), formed by isomerization of 10 to place the hydride and alkene $\text{cis}$ to one another, followed by 1,2-insertion (see sections 3.4-3.5). This ethyl complex can undergo $\sigma$-bond metathesis with H$_2$SiEt$_2$ {or Si–H bond oxidative addition (OA) followed by C–H bond reductive elimination (RE)} to form a
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low-coordinate hydrosilyl intermediate, \( [(\text{dmpe})_2\text{Mn(SiHEt}_2)] \) (17\textsubscript{Et2}), which isomerizes to 16\textsubscript{Et2} by α-hydride elimination.

Compound 10 also reacted with H\textsubscript{2}SiPh\textsubscript{2} at 60 °C to afford \( [(\text{dmpe})_2\text{MnH(=SiPh}_2)] \) (16\textsubscript{Ph2}) as an approximate 50:50 mixture with \( [(\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)] \) (18\textsubscript{Ph2}), releasing ethane and HSiEtPh\textsubscript{2} (scheme 4.1). Compound 18\textsubscript{Ph2} may form by initial σ-bond metathesis (or OA/RE) between \( [(\text{dmpe})_2\text{MnEt}] \) (13) and H\textsubscript{2}SiPh\textsubscript{2} to afford “(dmpe)_2MnH” (12) and HSiEtPh\textsubscript{2}, followed by oxidative addition of a second equivalent of H\textsubscript{2}SiPh\textsubscript{2}. Compounds 16\textsubscript{Ph2} and 18\textsubscript{Ph2} could not be separated, but the mixture could be converted entirely to 18\textsubscript{Ph2} by reaction with H\textsubscript{2}. Similarly, compound 16\textsubscript{Et2} reacted cleanly with H\textsubscript{2} to generate \( [(\text{dmpe})_2\text{MnH}_2(\text{SiHEt}_2)] \) (18\textsubscript{Et2}) (Scheme 4.1). A detailed discussion of silyl dihydride complexes 18\textsubscript{R2}, along with solution and solid state characterization, can be found in Chapter 6. Compound 16\textsubscript{Ph2} was characterized in solution, and shown to exist as an 88:12 mixture of interconverting silylene hydride isomers: a major \( C_1 \)-symmetric cis-isomer with a hydride \( ^1\text{H} \) NMR signal at –16.22 ppm, a \( ^{29}\text{Si} \) NMR shift of 210.2 ppm, and four broad \( ^{31}\text{P} \) environments at –20 °C; and a minor \( C_{2v} \) trans-isomer with one \( ^{31}\text{P} \) environment, a hydride \( ^1\text{H} \) NMR signal at –9.78 ppm, and a \( ^{29}\text{Si} \) NMR shift of 285.1 ppm.

Maintaining a toluene solution of 16\textsubscript{Ph2}/18\textsubscript{Ph2} at –30 °C afforded crystals containing a 50:50 mixture of cis-16\textsubscript{Ph2} and central-18\textsubscript{Ph2} (confirmed by NMR spectroscopy) with superimposed (dmpe)_2Mn fragments and phenyl rings. Distinct silicon

\[ ^5 \text{Formation of HSiEtPh}_2 \text{in the reaction to form 16}^{\text{Ph2}} \text{and 18}^{\text{Ph2}} \text{could alternatively occur via the following sequence: 1) dissociation of ethylene from [(dmpe)_2MnH(C}_2H_4)] (10), and oxidative addition of H}_2\text{SiPh}_2 \text{to form 18}^{\text{Ph2}, 2) concurrent formation of 16}^{\text{Ph2}} \text{(cis- and trans-isomers) via the mechanism proposed in the text, 3) reaction of 16}^{\text{Ph2}} \text{with ethylene (formed in step 1) to generate silylene complex 19}^{\text{Ph2}, and 4) an equilibrium between 19}^{\text{Ph2}} \text{and [(dmpe)_2Mn(CH(Me)(SiPh}_2H)] (24}^{\text{Ph2}) or [(dmpe)_2Mn(SiPh}_2Et)], either of which could undergo σ-bond metathesis with additional H}_2\text{SiPh}_2 \text{to form HSiEtPh}_2 \text{and [(dmpe)_2Mn(SiHPh}_2)] (17}^{\text{Ph2}), which would isomerize to 16}^{\text{Ph2}} \text{by α-hydride elimination. Indeed, 19}^{\text{Ph2}} \text{does react rapidly and cleanly with H}_2\text{SiPh}_2 \text{at 60 °C to form 16}^{\text{Ph2}} \text{and HSiEtPh}_2.} \]
atom positions are observed for cis-16\textsuperscript{Ph2} and central-18\textsuperscript{Ph2}, but the resulting structures are only suitable to establish connectivity. In the structure of cis-16\textsuperscript{Ph2} (Figure 4.2 left), the four phosphorus atoms and silicon form an approximate trigonal bipyramid, with the Si-phenyl groups perpendicular to the equatorial plane. Silicon is trigonal planar, and electron density consistent with the hydride ligands in cis-16\textsuperscript{Ph2} and co-crystallized central-18\textsuperscript{Ph2} was located on either side of the Mn–Si bond (resulting from crystallographic disorder in the case of cis-16\textsuperscript{Ph2}), above and below the C(1)/Si/C(1’) plane. DFT calculations (gas phase, all-electron, PBE, TZ2P, ZORA, D3-BJ) support a close interaction between the hydride ligand and the silicon atom in cis-16\textsuperscript{Ph2}, yielding distances of 2.168 and 1.665 Å for the Mn–Si and Mn–H bonds, a Si–H distance of 1.726 Å, and angles of 51.5 and 49.0° for the H–Mn–Si and H–Si–Mn linkages (Figure 4.2 right). These values compare well with those of other silylene hydride featuring strong Si–H interactions, including the X-ray structures of [(C\textsubscript{5}Me\textsubscript{4}Et)(OC)\textsubscript{2}WH{:=SiHC(SiMe\textsubscript{3})\textsubscript{3}}] and [{1,2-C\textsubscript{2}H\textsubscript{4}(P\textsuperscript{t}Bu\textsubscript{2})\textsubscript{2}}NiH(=SiMes\textsubscript{2})]\textsuperscript{+},\textsuperscript{325,333} and the neutron structure of [Cp*(dmpe)MoH(=SiEt\textsubscript{2})]\textsuperscript{326} (Si–H [Å] = 1.71(6), 1.64(7), 1.68(1). H-M-Si [°]: 46(2), 49(2), and 45.5(4). H-Si-M [°]: 50(2), 51(2), and 51.5(4)).
Compound 16\textsuperscript{Ph2} is the first silylene hydride complex observed to exist as distinct isomers with and without an M-H-Si interaction, providing a unique opportunity to probe the nature of the Mn–Si and Si–H interactions. Surprisingly, DFT calculations show slightly shorter Mn–Si distances in cis-16\textsuperscript{R2} versus trans-16\textsuperscript{R2} (Mn–Si [Å]: 2.168-2.175 (cis), 2.184-2.187 (trans)). However, the Mn–Si Mayer bond orders for cis-16\textsuperscript{R2} (1.25
and 1.19) are notably less than those for trans-$16^{R2}$ (1.54 and 1.52), and the same trend is observed in Nalewajski-Mrozek and Gopinathan-Jug bond orders.

4.3 – DFT Fragment Interaction Analysis of Silylene Hydride Complexes

Fragment interaction analysis of cis- and trans-$16^{Et2}$ using the combined Extended Transition State and Natural Orbitals for Chemical Valence (ETS-NOCV) method revealed similarities in the bonding between the (dmpe)$_2$MnH and SiEt$_2$ fragments in both isomers of $16^{Et2}$ (Figures 4.3 and 4.4). In particular, bonding in both complexes involves $\sigma$-donation from the silylene highest occupied molecular orbital (HOMO) to the (dmpe)$_2$MnH lowest unoccupied molecular orbital (LUMO), accompanied by $\pi_{\parallel}$-backdonation into a silylene orbital that is $\sigma$-antibonding with respect to the Si–C bonds. However, $\pi_{\perp}$-backdonation primarily involves the silylene LUMO and a filled Mn-H $\sigma$-bonding orbital (HOMO–3) in cis-$16^{Et2}$, versus a filled manganese d-orbital in trans-$16^{Et2}$. The Hirshfeld charge on the SiEt$_2$ fragment is more negative in trans-$16^{Et2}$ than cis-$16^{Et2}$ (–0.29 vs –0.18), indicative of less effective $\sigma$-donation and/or more effective $\pi$-backdonation in the former. Nevertheless, the silicon atoms in both isomers of $16^{Et2}$ and $16^{Ph2}$ are electrophilic, based on positive Hirshfeld charges on the silicon atoms (0.20 to 0.22), negative Hirshfeld charges on manganese (–0.25 to –0.27), and positive electrostatic potentials at silicon.
Figure 4.3: Deformation density contributions $\Delta \rho_1$, $\Delta \rho_2$, and $\Delta \rho_3$ to bonding between the SiEt$_2$ and (dmpe)$_2$MnH fragments in a) $trans$-[(dmpe)$_2$MnH(=SiEt$_2$)] ($trans$-16$^{Et_2}$), b) $cis$-[(dmpe)$_2$MnH(=SiEt$_2$)] ($cis$-16$^{Et_2}$), and c) [(dmpe)$_2$MnH(Et$_2$Si=CHMe)] (19$^{Et_2}$). Increased (green) and decreased (yellow) electron density is presented relative to the fragments; isosurfaces are set to 0.003.
Figur 4.4: Key fragment orbitals contributing to $\Delta \rho_1$ and $\Delta \rho_2$ in a) cis-$[\text{dmpe}]_2\text{MnH}($=SiEt$_2$) ($\text{cis-16}_\text{Et2}$) and b) $[\text{dmpe}]_2\text{MnH}($Et$_2$Si=CHMe$)$ ($\text{19}_\text{Et2}$); isosurfaces are set to 0.04.

4.4 – Synthesis and Characterization of Silene Hydride Complexes

Both $\text{16}_\text{Et2}$ and $\text{16}_\text{Ph2}$ reacted with ethylene (1.7 atm, 25 °C) to form silene hydride products, cis-$[\text{dmpe}]_2\text{MnH}(R_2\text{Si=CHMe})$ ($\text{19}_\text{Et2}$: R = Et, $\text{19}_\text{Ph2}$: R = Ph) (Scheme 4.2), conceptually achieving addition of the carbene isomer of ethylene (CHMe) to the silylene (SiEt$_2$ or SiPh$_2$); compound $\text{19}_\text{Et2}$ was isolated in pure form, whereas $\text{19}_\text{Ph2}$ was isolated as an approximately 50:50 mixture with $\text{18}_\text{Ph2}$, which was present in the starting material. Compounds $\text{19}_R$ gave rise to hydride $^1\text{H}$ NMR signals at $-15.30$ and $-14.56$ ppm, $^{29}\text{Si}$ resonances at $-2.95$ and $1.47$ ppm, low frequency $^{13}\text{C}$ NMR signals at $-19.37$ and $-22.93$ ppm, and a characteristic silene $^1J_{\text{C,H}}$ coupling constant of 137 and 136 Hz, for $R = \text{Et, Ph}$ respectively.
Scheme 4.2: Reaction of silylene hydride complexes [(dmpe)$_2$MnH(=SiR$_2$)] {R = Et (16$^{Et2}$) or Ph (16$^{Ph2}$)} with ethylene to form [(dmpe)$_2$MnH(R$_2$Si=CHMe)] {R = Et (19$^{Et2}$) or Ph (19$^{Ph2}$)}.

An X-ray crystal structure of 19$^{Ph2}$ (Figure 4.5) revealed a distorted octahedral geometry in which the hydride interacts with the silicon atom of the silene. The silene Si–C(1) distance in 19$^{Ph2}$ is 1.781(5) Å, which is at the short end of the range previously reported for silene complexes (1.773(4)-1.838(11) Å),$^{413-417,419,431}$ and the Mn–C(1) distance is over 0.10 Å shorter than the M–Si distance (2.270(4) vs 2.409(2) Å), as observed for all other silene complexes. The sum of the X–C(1)–X (X = Si, H or C) and C–Si–C angles (346(2) and 343.5(2)$^\circ$) are also consistent with considerable silene character. However, the Mn–H and H–Si distances of 1.56(5) and 1.55(4) Å (calcd. 1.653 and 1.648 Å), as well as a large $^1J_{Si,H}$ coupling with a magnitude of 90 Hz in 19$^{Ph2}$, clearly indicate a significant interaction between the hydride ligand and silicon.

$^y$ Pt and Ni silene complexes featuring coordination to a stabilized silene; see ref. 411 and 418.
Figure 4.5: X-ray crystal structure of [(dmpe)$_2$MnH(Ph$_2$Si=CHMe)] (19$^{Ph2}$) with ellipsoids drawn at 50 % probability. Most hydrogen atoms have been eliminated for clarity, and hydrogen atoms on Mn(1) and C(1) (H(1) and H(2)) were located from the difference map and refined isotropically. Inset shows the metal, silene, and hydride core, with most H atoms, the dmpe ligands, and the most of the phenyl substituents on Si (aside from the ipso carbons) removed for clarity. Distances (Å) and angles (deg): Mn(1)–Si(1) 2.409(2), Mn(1)–C(1) 2.270(4), Mn(1)–H(1) 1.56(5), Si(1)–C(1) 1.781(4), Si(1)–C(3) 1.898(4), Si(1)–C(9) 1.906(5), Si(1)–H(1) 1.55(4), C(1)–C(2) 1.532(6), C(2)–H(2) 1.11(4), Mn(1)–C(1)–Si(1) 71.8(1), Mn(1)–Si(1)–C(1) 63.5(1), Si(1)–Mn(1)–C(1) 44.6(1), C(1)–Si(1)–H(1) 103(2), Mn(1)–H(1)–Si(1) 103(2), H(1)–Mn(1)–Si(1) 39(2), C(1)–Si(1)–C(3) 120.7(2), C(1)–Si(1)–C(9) 119.5(2), C(3)–Si(1)–C(9) 103.3(2).

4.5 – Fragment Interaction Analysis of Silene Hydride Complex [(dmpe)$_2$MnH(Et$_2$Si=CHMe)]

Fragment interaction and ETS-NOCV calculations on [(dmpe)$_2$MnH(Et$_2$Si=CHMe)] (19$^{Et2}$) (Figures 4.3 and 4.4) revealed three major interactions between the silene and (dmpe)$_2$MnH fragments. The first two contributions involve σ-donation from the silene π-bond (HOMO) to the LUMO of the (dmpe)$_2$MnH
fragment, combined with $\pi||$-backdonation from a filled Mn–H $\sigma$-bonding orbital (HOMO–3) into the silene $\pi^*$ orbital (LUMO), whereas the third contribution appears to involve $\pi\perp$-backdonation to silicon. Parallels in the bonding descriptions for $\textit{cis-16}^{\text{Et2}}$ and $\textit{19}^{\text{Et2}}$ arise from the very similar geometries of the (dmpe)$_2$MnH fragments in these complexes, and the analogous symmetries and orientations of the HOMO and LUMO of the silylene and silene fragments relative to the Mn–H bond.

4.6 – Potential Mechanisms for Silene Hydride Synthesis

Several mechanisms could be proposed for the formation $\textit{19}^{R_2}$, but the reactions of $\textit{17}^{R_2}$ with $d_4$-ethylene to form cis-[(dmpe)$_2$MnH(R$_2$Si=CDCD$_3$)] ($d_4$$\textit{19}^{R_2}$: $R = \text{Et}$, $d_4$$\textit{19}^{\text{Ph2}}$: $R = \text{Ph}$) rule out a mechanism involving initial insertion of ethylene into a Mn–H bond. Alternative possibilities are shown in Scheme 4.3. In pathway I, a low-coordinate silyl complex, [(dmpe)$_2$Mn(SiHR$_2$)] ($R = \text{Et}$ ($\textit{17}^{\text{Et2}}$) or Ph ($\textit{17}^{\text{Ph2}}$)), is accessed from the $\textit{cis}$-silylene hydride complex. From this point, two cycles of 1,2-insertion and $\beta$-hydride elimination would afford the silene hydride product. In pathway II, the Si=C double bond of the silene initially engages in 2+2 cycloaddition with ethylene to form a metallasilacyclobutane, which then undergoes Si–H bond-forming reductive elimination. These pathways involve primary alkyl ([(dmpe)$_2$Mn(CH$_2$CH$_2$SiHR$_2$)]; $R = \text{Et}$ (23$^{\text{Et2}}$) or Ph (23$^{\text{Ph2}}$)) and secondary alkyl ([(dmpe)$_2$Mn{CH(Me)(SiHR$_2$)}]; $R = \text{Et}$ (24$^{\text{Et2}}$) or Ph (24$^{\text{Ph2}}$)) intermediates, which we have implicated as catalytically competent species in ethylene hydrosilylation (see Chapter 8).
Scheme 4.3: Two potential pathways for the formation of \([(\text{dmpe})_2\text{MnH}(\text{R}_2\text{Si} = \text{CHMe})]\) (19\text{Et}^2: R = Et, 19\text{Ph}^2: R = Ph) via reaction of \([(\text{dmpe})_2\text{MnH}(=\text{SiR}_2)]\) (16\text{Et}^2: R = Et, 16\text{Ph}^2: R = Ph) with ethylene. Key: \([\text{Mn}] = (\text{dmpe})_2\text{Mn}, [\text{MnH}] = (\text{dmpe})_2\text{MnH}.

Mechanism II lacks precedent in silicon chemistry, although silylene 2+2 cycloaddition chemistry has been observed for isocyanates,\textsuperscript{504} proposed as a possibility for nitriles,\textsuperscript{343} isothiocyanates,\textsuperscript{505} and ketones,\textsuperscript{506} and observed for alkynes in combination with Schrock-type titanium silylene complexes.\textsuperscript{365} By contrast, mechanism I is supported by: 1) the likely intermediacy of \([(\text{dmpe})_2\text{Mn(SiHR}_2)]\) (17\text{Et}^2: R = Et, 17\text{Ph}^2: R = Ph) in the reaction of \(10\) to form 16\text{Et}^2 (\textit{vide supra}); 2) DFT calculations, which show that 17\text{R}^2, which are the low-coordinate hydrosilyl isomers of 16\text{R}^2, exist as minima located 25 and 42 kJ mol\(^{-1}\) higher in energy than \textit{cis}-16\text{Et}^2 and \textit{cis}-16\text{Ph}^2 respectively; and 3) the reactions of 16\text{Ph}^2 and 16\text{Ph}^2 with D\(_2\) which exclusively form \([(\text{dmpe})_2\text{MnD}_2(\text{SiHR}_2)]\).
(d$_2$18$^{\text{Ph}}$2: R = Ph, d$_2$18$^{\text{Et}}$2: R = Et), indicative of reactivity stemming from intermediate 17$^{\text{R}}$2 rather than directly from a silylene hydride.

4.7 – Summary and Conclusions for Chapter 4

Silylene hydride complexes [(dmpe)$_2$MnH(=SiR$_2$)] (16$^{\text{Et}}$2: R = Et, 16$^{\text{Ph}}$2: R = Ph) were prepared from the reaction of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with secondary hydrosilanes, and are the first group seven examples to be observed bearing an unstabilized silylene ligand. Complex 16$^{\text{Et}}$2 crystallized as the trans isomer, while the diphenyl analogue 16$^{\text{Ph}}$2 crystallized as the cis isomer. Uniquely, 16$^{\text{Ph}}$2 existed in solution as interconverting cis and trans isomers with and without an interligand Si–H interaction.

Silene hydride complexes [(dmpe)$_2$MnH(R$_2$Si=CHMe)] (19$^{\text{Et}}$2: R = Et, 19$^{\text{Ph}}$2: R = Ph) were prepared by exposing silylene hydride complexes 16$^{\text{R}}$2 to ethylene. Complex 19$^{\text{Ph}}$2 and complex 19$^{\text{Et}}$2 are the first crystallographically characterized or isolated, respectively, examples of a 1st row transition metal complex with a sterically and electronically unstabilized silene ligand. Furthermore, the silylene-hydride to silene-hydride transformation is, to our knowledge, also unique.

Fragment interaction calculations were conducted on both isomers of silylene hydride 16$^{\text{Et}}$2, and the silene hydride complex 19$^{\text{Et}}$2. In each case, the interaction between the metal and Si-based ligand (silylene or silene) was observed to have three contributions; σ-donation, π∥-backdonation, and π⊥-backdonation. Of note are the similarities between the Mn–Si interaction in cis-silylene and silene complexes, and that two orthogonal π-backdonation interactions were calculated.
Chapter 5

Synthesis of Manganese Disilyl Hydride Complexes and Reactivity with Ethylene to Afford Silene Hydride Complexes

Portions of this chapter have been reprinted (adapted) with permission from Price, J. S.; Emslie, D. J. H.; Vargas-Baca, I. [(dmpe)\(_2\)MnH(C\(_2\)H\(_4\))] as a Source of Low-Coordinate Ethyl Manganese(I) Species: Reactions with Primary Silanes, H\(_2\), and Isonitriles, Organometallics 2018, 37, 3010-3023 (Copyright 2018 American Chemical Society), and Price, J. S.; Emslie, D. J. H. Interconversion and reactivity of manganese silyl, silylene, and silene complexes, Chem. Sci. 2019, Advance Articles, DOI: 10.1039/C9SC04513A (Published by The Royal Society of Chemistry).

5.1 – Introduction to Chapter 5

In Chapter 4, we discussed reactions of the ethylene hydride complex, [(dmpe)\(_2\)MnH(C\(_2\)H\(_4\))] (10),\(^{120,172}\) with secondary silanes (H\(_2\)SiR\(_2\)); Scheme 5.1. The reaction of 10 with H\(_2\)SiEt\(_2\) afforded the trans silylene hydride complex trans-[(dmpe)\(_2\)MnH(=SiEt\(_2\))] (trans-16\(^{\text{Et2}}\)) via ethane elimination. By contrast, the reaction of 10 with H\(_2\)SiPh\(_2\) afforded ethane and [(dmpe)\(_2\)MnH(=SiPh\(_2\))] (16\(^{\text{Ph2}}\)), as a mixture of a trans isomer (minor) and a cis isomer (major; featuring a Mn–H–Si bridging interaction), as well as [(dmpe)\(_2\)MnH\(_2\)(SiHPh\(_2\))] (18\(^{\text{Ph2}}\)) and HSiEtPh\(_2\).\(^{507}\) Compounds 16\(^{\text{Et2}}\) is the only isolated example of a group 7 complex bearing an unstabilized terminal silylene ligand, and the phenyl derivative (16\(^{\text{Ph2}}\)) is the first silylene hydride complex observed to exist as distinct isomers with and without a M–H–Si interaction. Silylene hydride complexes 16\(^{\text{R2}}\) were found to react with ethylene to form silene hydride complexes [(dmpe)\(_2\)MnH(R\(_2\)Si=CHMe)] (19\(^{\text{R2}}\): R = Et, 19\(^{\text{Ph2}}\): R = Ph); an unprecedented transformation.
Scheme 5.1: Reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with R$_2$SiH$_2$ (R = Et, Ph) to afford silylene hydride compounds $^{16}$R$^2$ and silyl dihydride complex $^{18}$Ph$^2$, and subsequent reactivity with ethylene to afford silene hydride complexes $^{19}$R$^2$. cis-10, 13, $^{17}$R$^2$, and 12 are hypothesized intermediates, for which DFT calculations have located energy minima. Only one isomer is shown for all complexes, except 10 and $^{16}$R$^2$.

The reactions to form $^{16}$R$^2$ proceed (Scheme 5.1) via isomerization of trans-10 to yield cis isomer cis-10, followed by 1,2-insertion to generate a coordinatively unsaturated ethyl complex (13), reaction with H$_2$SiR$_2$ to afford a low-coordinate manganese silyl
complex ($^{17}R_2^2$, formed via σ-bond metathesis or Si–H bond oxidative addition followed by C–H bond-forming reductive elimination), and finally α-hydride elimination. In the reaction of 10 with H$_2$SiPh$_2$, the formation of complex $^{18}$Ph$_2^2$ also likely proceeds via ethyl intermediate 13. However, in this case the reaction of 13 with H$_2$SiPh$_2$ also generates HSiEtPh$_2$ and a low-coordinate manganese hydride complex (12), which oxidatively adds a second equivalent of H$_2$SiPh$_2$ (Scheme 5.1). The reaction pathway in Scheme 5.1 relies upon conversion of alkene hydride complex 10 to a coordinatively unsaturated alkyl isomer, and this isomerization is discussed in Chapter 3.

Herein, we report that complex 10 reacts with primary hydrosilanes to generate disilyl hydride complexes, which can act as ‘masked’ sources of either a 5-coordinate silyl complex or a silylene hydride complex with an H substituent on the silicon centre. Upon exposure to ethylene, these manganese disilyl hydride complexes react in a similar manner to silylene hydride complexes to form silene hydride complexes with a H substituent on Si. These are, to our knowledge, the first example of transition metal silene complexes with an H substituent on silicon, and themselves react with an additional equivalent of ethylene to form new silene hydride complexes with two alkyl substituents on silicon, the product of apparent insertion of ethylene into the Si–H bond (a reaction which, to our knowledge, is unprecedented). Manganese silyl complexes, transition metal silylene complexes, and transition metal silene complexes are reviewed in sections 1.5, 1.6, and 1.7, respectively.

5.2 – Synthesis and Characterization of Manganese Disilyl Hydride Complexes

In contrast to reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with the secondary silanes H$_2$SiEt$_2$ and H$_2$SiPh$_2$ (vide supra), exposure of 10 to an excess of the primary silanes H$_3$SiPh or H$_3$Si’’Bu at 60 °C formed the disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] ($^{20}$Ph: R = Ph, $^{20}$Bu: R = ’’Bu) with elimination of ethane
Both complexes gave rise to two $^{31}$P NMR resonances (60.2 and 67.4 ppm for $^{20}$Ph, 58.6 and 72.6 ppm for $^{20}$Bu), a single $^{29}$Si NMR resonance (–4.2 and 1.6 ppm respectively), two diastereotopic Si–H $^1$H NMR resonances (5.28 and 5.31 ppm for $^{20}$Ph, 4.36 and 4.53 ppm for $^{20}$Bu), and a single metal hydride $^1$H NMR signal (–14.55 and –13.27 ppm respectively).

Scheme 5.2: Reactions of $[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ (10) with primary hydrosilanes to afford disilyl hydride complexes $[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]$ ($^{20}$Ph: R = Ph, $^{20}$Bu: R = $^n$Bu). Only one isomer of all complexes is shown.

These reactions, like those involving secondary hydrosilanes ($vide$ supra), presumably proceed via initial isomerization of 10 to the 5-coordinate ethyl species $[(\text{dmpe})_2\text{MnEt}]$ (13), which reacts with a single equivalent of hydrosilane to generate a 5-coordinate silyl complex $[(\text{dmpe})_2\text{Mn(SiH}_2\text{R})]$ ($^{17}$Ph: R = Ph, $^{17}$Bu: R = $^n$Bu); Scheme 5.2. However, unlike in the reactions involving H$_2$SiR$_2$, a second equivalent of primary

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$^z$ The reaction of 10 with 10 equivalents of H$_3$SiPh proceeded more quickly than the analogous reaction to 5 equivalents, implying that isomerization of $[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ (10) to an ethyl isomer is not the rate-determining step.
hydrosilane oxidatively adds to the metal centre to generate the observed disilyl hydride products. Presumably, such reactivity is not observed for secondary hydrosilanes due to their increased steric bulk.

Crystals of 7-coordinate [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] ($20^{\text{Ph}}$) were obtained by cooling a saturated solution in hexanes to $-30$ °C, and an X-ray structure (Figure 5.1) revealed an octahedral arrangement of the four phosphorus and two silicon atoms about manganese, with a disphenoidal arrangement of the phosphorus donors, and the hydride ligand (located from the difference map) situated equidistant between the two silicon atoms. Complex $20^{\text{Ph}}$ is the first structurally characterized disilyl hydride complex of manganese with non-chelating silyl ligands, although Tobita et al. previously reported a series of disilyl hydride and silyl hydrosilane complexes in which both silicon-based donors are tethered by a xanthene backbone (Figure 5.2). The Mn–Si distance of 2.3851(2) Å in $20^{\text{Ph}}$ is within the range previously observed for manganese silyl hydride complexes \{2.254(1)-2.4702(9) Å\}, and is shorter than those in Tobita’s most closely related disilyl hydride complex \{T3 in Figure 5.2: d(Mn–Si) = 2.4026(7)-2.4069(7) Å\}.  

Figure 5.1: X-ray crystal structure of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] ($20^\text{Ph}$) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity. Hydrogen atoms on Mn and Si were located from the difference map and refined isotropically. Dmpe ligands are disordered over two positions and only the dominant conformation {94.7(8)\%} is shown. Bond distances (Å) and angles (deg): Mn–H(1A) 1.49(2), Mn–Si 2.3851(2), Si–H(1A) 1.9163(8), Si–H(1B) 1.44(2), Si–H(1C) 1.44(1), Si–Si 3.8319(4), Si–C 1.9091(7), H(1A)–Mn–Si 53.418(7), Si–Mn–Si 106.83(1).

Figure 5.2: Disilyl hydride and silyl hydrosilane complexes reported by Tobita et al.$^{295}$

The central position of the hydride ligand between the two silyl ligands in $20^\text{Ph}$ and $20^\text{Bu}$ appears to be maintained on the NMR time scale in solution, given that the $^1\text{H}$
NMR spectra indicate $C_2$ symmetry between 25 and $-87 \, ^{\circ}C$. In the solid state (for $20^{\text{Ph}}$), the Si(1)–H(1A) distance is 1.9163(8) Å (caled: 1.92 Å), which is significantly longer than a typical Si–H single bond (1.48 Å), but much shorter than the sum of the Van der Waals radii (3.1 Å). The related calculated distance in a model of $20^{\text{Bu}}$ where $^\text{a}\text{Bu}$ groups were replaced by methyl groups ($20^{\text{Me}}$), 1.88 Å, also falls into this range. These geometries are suggestive of a nonclassical silyl hydride ligand resulting from incomplete oxidative addition to the metal centre, leaving some degree of Si–H bonding intact.

Computationally, this bonding picture in both $20^{\text{Ph}}$ and $20^{\text{Me}}$ is supported by fractional Mayer bond orders for the Mn–Si ($20^{\text{Ph}}$: 0.83, $20^{\text{Me}}$: 0.82-0.83), Mn–H ($20^{\text{Ph}}$: 0.53, $20^{\text{Me}}$: 0.53), and Si–H$_{\text{MnH}}$ ($20^{\text{Ph}}$: 0.25-0.26, $20^{\text{Me}}$: 0.25) linkages. Coupling constants between $^{29}\text{Si}$ and the metal hydride were measured as $-31 \, \text{Hz}$ ($20^{\text{Ph}}$) and $-30 \, \text{Hz}$ ($20^{\text{Bu}}$), and DFT calculations afforded similar $^{29}\text{Si}$–$^1\text{H}$ coupling constants of $-24 \, \text{Hz}$ ($20^{\text{Ph}}$) and $-27 \, \text{Hz}$ ($20^{\text{Me}}$), indicative of a nonclassical silyl hydride bonding environment.

5.3 – Reactions of Manganese Disilyl Hydride Complexes with Ethylene

The disilyl hydride complexes $[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]$ ($20^{\text{Ph}}$: R = Ph, $20^{\text{Bu}}$: R = $^\text{a}\text{Bu}$) reacted with ethylene at room temperature to afford the silene hydride complexes $[(\text{dmpe})_2\text{MnH(RHSi=CHMe)}]$ ($19^{\text{Ph,H}}$: R = Ph, $19^{\text{Bu,H}}$: R = $^\text{a}\text{Bu}$). This reaction mirrors the reactions of silylene hydride complexes $16^{\text{R2}}$ with ethylene ($\text{vide supra}$: Scheme 1). Moreover, complexes $19^{\text{R,H}}$ reacted with a second equivalent of ethylene to form silene hydride complexes with two hydrocarbyl groups on Si, $[(\text{dmpe})_2\text{MnH(RET}_{\text{Si=CHMe})}]$ ($19^{\text{Ph,Et}}$: R = Ph, $19^{\text{Bu,Et}}$: R = $^\text{a}\text{Bu}$); the products of apparent ethylene insertion into the Si–H bond (Scheme 5.3, Figure 5.3). This silene SiH to SiR conversion reaction is unprecedented. Complexes $19^{\text{R,Et}}$ also reacted further with ethylene to generate $[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)]$ (10), potentially by substitution of the silene ligand which undergoes subsequent decomposition to unidentified products.

$\text{aa}$ These coupling constants were measured using $^{29}\text{Si}$_{\text{edited}} $^1\text{H}–^1\text{H}$ COSY, as described in Chapter 6. These data were published in ref. 510.
Scheme 5.3: Reactions of disilyl hydride complexes \([(\text{dmpe})_2\text{MnH}(\text{SiH}_2\text{R})_2]\) (\(20^{\text{Ph}}\): \(R = \text{Ph}\), \(20^{\text{Bu}}\): \(R = \text{Bu}\)) with one, two, or three equivalents of ethylene to afford SiH-containing silene hydride complexes \([(\text{dmpe})_2\text{MnH}((\text{RHSi=CHMe})_2]\) (\(19^{\text{Ph,H}}\): \(R = \text{Ph}\), \(19^{\text{Bu,H}}\): \(R = \text{Bu}\)), silene hydride complexes with two hydrocarbyl groups on Si \([(\text{dmpe})_2\text{MnH}((\text{REtSi=CHMe})_2]\) (\(19^{\text{Ph,Et}}\): \(R = \text{Ph}\), \(19^{\text{Bu,Et}}\): \(R = \text{Bu}\)), and ethylene hydride complex \([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (10), respectively. Only one isomer is shown for each silene hydride complex.
Figure 5.3: $^1$H NMR spectra (298 K, $^6$CD$_6$, 600 MHz) for the reaction of \([\text{dmpe}]_2\text{MnH(SiH}_2\text{Ph})_2\) (20$^{\text{Ph}}$) with ethylene over time (initial, $n_{\text{C}_2\text{H}_4} \approx n_{\text{silane}}$). The x-axis corresponds to the bottom spectrum, and for clarity, each spectrum above that is shifted by 0.15 ppm to lower frequency. The inset shows the relative concentration of hydride-containing species versus time; reactant \([\text{dmpe}]_2\text{MnH(SiH}_2\text{Ph})_2\) (20$^{\text{Ph}}$; light blue ✴), silene hydride \([\text{dmpe}]_2\text{MnH(PhHSi=CHMe)}\) (19$^{\text{Ph,H}}$; purple ×), silene hydride \([\text{dmpe}]_2\text{MnH(PhEtSi=CHMe)}\) (19$^{\text{Ph,Et}}$; red ■), and \([\text{dmpe}]_2\text{MnH(C}_2\text{H}_4)\) (10; dark blue ♦).

$^{\text{bb}}$ Over the 4 days that this reaction was monitored by $^1$H NMR spectroscopy, the ethylene concentration in solution decreased by 40 %. Relative concentrations in Fig. 5.3 were calculated by integrating $^1$H NMR data; integration relative to the residual solvent signal from $^6$CD$_6$ indicated that the total moles of manganese-containing species in the inset in Figure 5.3 remained constant.
A range of byproducts was observed in the syntheses of silene hydride complexes, including primary, secondary, and tertiary hydrosilanes \( \{H_{(3-n)SiEt_n}R \ (n = 0, 1, 2; \ R = \text{Ph, }^\text{"Bu})\}\);\(^{cc}\) the latter two are formed by stepwise manganese-catalysed hydrosilylation reactions between the primary hydrosilane byproduct and excess ethylene (see Chapter 8). For \( R = ^\text{"Bu} \), silene \( SiH \) to \( SiEt \) conversion did not proceed until all of the primary hydrosilane byproduct had been consumed, so conversion of \( 20^{\text{Bu}} \) to \( 19^{\text{Bu,H}} \), and then to \( 19^{\text{Bu,Et}} \), proceeded in a stepwise fashion. By contrast, for \( R = \text{Ph} \), silene \( SiH \) to \( SiEt \) conversion commenced as soon as \( 19^{\text{Ph,H}} \) was available (Figure 5.3).

Compounds \( 19^{\text{Bu,H}} \) and \( 19^{\text{Ph,Et}} \) were isolated as a red oil and a brown solid, respectively, in > 95% purity. By contrast, \( 19^{\text{Ph,H}} \) and \( 19^{\text{Bu,Et}} \) were characterized \textit{in situ} by NMR spectroscopy (Table 5.1). Compounds \( 19^{\text{Ph,H}} \) and \( 19^{\text{Bu,Et}} \) were not isolated due to the formation of mixtures of products (e.g. \( 19^{\text{Ph,H}} \) accompanied by \( 19^{\text{Ph,Et}} \) and \( 10 \)), combined with instability in solution over a period of days at room temperature.

\(^{cc}\) In the reaction of \( 20^{\text{Ph}} \) with ethylene, no tertiary hydrosilane was observed. However, small amounts of vinyl hydrosilane were.
Table 5.1: Selected $^1$H, $^{13}$C, $^{29}$Si and $^{31}$P NMR chemical shifts (ppm) and coupling constants (Hz) for silene hydride complexes [(dmpe)$_2$MnH(RR'Si=CHMe)] ($^{19}$Ph$_2$: R = R' = Ph; $^{19}$Et$_2$: R = R' = Et; $^{19}$Ph$_{H}$: R = Ph, R' = H; $^{19}$Bu$_{H}$: R = 'Bu, R' = H; $^{19}$Ph$_{Et}$: R = Ph, R' = Et; $^{19}$Bu$_{Et}$: R = 'Bu, R' = Et); in C$_6$D$_6$ ($^{19}$R$_2$ and $^{19}$Ph$_{H}$; and $^{19}$Bu$_{H}$) or d$_8$-toluene ($^{19}$R$_{H}$ and $^{19}$Bu$_{Et}$). Unless otherwise noted, values are from NMR spectra at 298 K. For $^{19}$R$_{H}$, NMR environments are reported for both observed isomers.

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a. Due to the minor isomer of $^{19}$Bu$_{H}$.
b. Due to the major isomer of $^{19}$Bu$_{H}$.
c. Both isomers have identical chemical shifts.
d. Measured at 213 K (because this environment was not located by $^{29}$Si{${^1}$H} or 2D $^1$H–$^{29}$Si (HSQC or HMBC) NMR spectroscopy at 298 K).
e. Coupling between the Si=C and Si=CHCH$_3$ environments.
f. $^1$J$_{C,H}$ could only be resolved for one isomer.

In solution (in the absence of ethylene or free hydrosilanes), SiH-containing silene hydride complex $^{19}$Bu$_{H}$ underwent isomerization to the silylene hydride complex trans-[(dmpe)$_2$MnH(=SiEt'nBu)] (trans-16$^{Bu}_{Et}$; Scheme 5.4), with 20% conversion after 2 days.
at room temperature in C$_6$D$_6$. NMR spectra of \textit{trans}-16$^{16}$Bu,Et feature an MnH $^1$H NMR peak at $-10.48$ ppm (a pentet with $^2J_{H,P}$ of 51 Hz), two sharp singlets in the $^{31}$P$^1$H NMR spectrum at 80.35 and 80.50 ppm, and a high-frequency peak in the $^{29}$Si$^1$H NMR spectrum at 364 ppm. These data are consistent with a high-symmetry base-free silylene complex, and are nearly identical to the NMR data for \textit{trans}-[(dmpe)$_2$MnH($=$SiEt$_2$)] (\textit{trans}-16$^{16}$Et$_2$).\textsuperscript{ee} Isomerization was accompanied by formation of small amounts ($\sim$ 10% combined relative to 16$^{16}$Bu,Et) of an unidentified manganese hydride complex (with a pentet $^1$H NMR peak at $-9.06$ ppm; $^2J_{H,P}$ = 47 Hz) and the silene hydride complex [(dmpe)$_2$MnH("BuEtSi=CHMe)] (19$^{16}$Bu,Et).

![Scheme 5.4: Solution decomposition of [(dmpe)$_2$MnH("BuHSi=CHMe)] (19$^{16}$Bu,H) to form silylene complex \textit{trans}-[(dmpe)$_2$MnH(="SiEt"Bu)] (\textit{trans}-16$^{16}$Bu,Et) as the major product.](image)

Isomerization of a silene hydride complex to a silylene hydride complex is, to our knowledge, unprecedented. However, this isomerization is related to Tilley and Bergman’s report of an equilibrium between the silylene alkyl complex [Cp*(Me$_3$P)Ir(Me)(="SiMe$_2$)]$^+$ and the silene hydride isomer, [Cp*(Me$_3$P)Ir(Me)(="SiMe$_2$)]$^-$.

\textsuperscript{dd} DFT calculations indicated that isomerization of SiH-containing silene hydride complexes 19$^{16,R,H}$ to silylene hydride complexes \textit{trans}-[(dmpe)$_2$MnH(="SiEtR)] (\textit{trans}-16$^{16,E,R}$) is thermodynamically favourable for R = Ph and "Bu; minima for the latter were located 20-34 kJ mol$^{-1}$ lower in energy than the lowest energy silene hydride isomer. In addition, cis silylene hydride isomers were determined to be 1 (16$^{16,Phe}$) and 9 (16$^{16,Bu,Et}$) kJ mol$^{-1}$ higher in energy than the respective \textit{trans} isomers.

\textsuperscript{ee} NMR data for \textit{trans}-[(dmpe)$_2$MnH("SiEt$_2$)] (\textit{trans}-16$^{16}$Et$_2$) includes an MnH $^1$H NMR peak at $-10.46$ ppm (pentet with $^2J_{H,P}$ of 51 Hz), a single sharp singlet in the $^{31}$P$^1$H NMR spectrum at 80.95, and a $^{29}$Si NMR chemical shift of 365 ppm.
[Cp*(Me$_3$P)IrH(Me$_2$Si=CH$_2$)]$^+$, which relies upon reversible α-Me and β-H elimination from a trimethylsilyl intermediate (see Scheme 1.14).

For silene hydride complexes 19$^{R,H}$ (those with a hydride substituent on Si), two sets of NMR signals were observed due to a pair of isomers present in solution with a 1:1 (19$^{Ph,H}$; Figure 5.3) or 1.9:1 (19$^{Bu,H}$) ratio, whereas only a single set of NMR signals (indicative of a single isomer) were observed for 19$^{R,Et}$ (silene hydride complexes with two hydrocarbyl substituents on Si). NMR spectra of the silene hydride complexes feature (for each isomer) four $^{31}$P NMR signals, a single $^{29}$Si NMR environment (at –17.4 to 0.7 ppm), a low frequency $^{13}$C NMR signal for the Si=CH$_2$ environment (at –19.3 to –21.7 ppm), and a silene $^{1}J_{C,H}$ coupling constant (137-139 Hz) intermediate between those typical for sp$^2$ and sp$^3$ hybridized carbon atoms; Table 5.1. Additionally, the Mn$^H$ signal was located at –14.5 to –15.3 ppm in the $^1$H NMR spectra of 19$^{R,H}$ and 19$^{R,Et}$, and the Si$^H$, Si=CH(CH$_3$) and Si=CH(CH$_3$)$_2$ signals were observed at 3.7 to 4.5 ppm, –0.2 to 0.2 ppm, and 1.7 to 1.9 ppm, respectively. These data are very similar to those for [(dmpe)$_2$MnH(R$_2$Si=CHMe)] (19$^{Ph_2}$: R = Ph, 19$^{Et_2}$: R = Et; pertinent NMR data are included in Table 5.1), which have been spectroscopically, and (for 19$^{Ph_2}$) crystallographically, characterized (Chapter 4). To the best of our knowledge, 19$^{R,H}$ are the first spectroscopically observed\footnote{Iron or cobalt silene complexes with hydrogen substituents on Si have been detected in the gas phase by mass spectrometry and postulated as an intermediate in the gas-phase activation of H$_3$SiEt by Co cations; see ref. 429.} examples of transition metal silene complexes with a hydrogen substituent on silicon.

Despite numerous attempts, we were unable to obtain X-ray quality crystals of 19$^{R,H}$ or 19$^{R,Et}$. Therefore, we turned to DFT calculations in order to gain further insight into the structures of these complexes {ADF, gas-phase, all-electron, PBE, D3-BJ, TZ2P, ZORA}. For all four complexes, energy minima were located for four $cis$ silene hydride isomers\footnote{Not including enantiomers where the stereochemistry at manganese is switched from Λ to Δ.} with E or Z silene stereochemistry, and differing in the orientation of the silene...
methyl substituent (RR'Si=CHMe) relative to the two dmpe ligands, as shown in Figure 5.4 (see Figure 5.5 for the lowest energy isomer of $19^{Bu,H}$). In all cases, isomers i and ii are within a few kJ mol$^{-1}$ of one another, and are 13-22 kJ mol$^{-1}$ lower in energy than isomers iii and iv, consistent with observation of just 2 isomers in the solution NMR spectra of $19^{R,H}$. By contrast, the apparent formation of a single isomer of compounds $19^{R,Et}$ suggests that these reactions proceed under kinetic control.

Figure 5.4: Calculated isomers (i-iv) of silene hydride complexes [(dmpe)$_2$MnH(RR'Si=CHMe)] ($19^{Ph,H}$: $R = Ph$, $R' = H$; $19^{Bu,H}$: $R = ^nBu$, $R' = H$; $19^{Ph,Et}$: $R = Ph$, $R' = Et$; $19^{Bu,Et}$: $R = ^nBu$, $R' = Et$) featuring Si–H interligand interactions.

$^{hh}$ The dominant isomer for $19^{Bu,H}$ was assigned as isomer I given that the SiH $^1$H NMR signal for this isomer exhibits a large (18 Hz) $^3$J$_{H,31P}$ coupling to one of the phosphorus donor atoms, and in the calculated structures of isomers (i) and (ii) (for a model of $19^{Bu,H}$ where the $^nBu$ group was replaced with an Et group), only isomer (i) exhibited a $^1$H–$^{31P}$ coupling of comparable magnitude (23 Hz). As well, isomer I of $19^{Bu,H}$ is slightly (4 kJ mol$^{-1}$) lower in energy than isomer (ii).
Figure 5.5: Calculated structure (ball and stick diagram) for the lowest energy isomer of silene hydride complex [(dmpe)$_2$Mn("BuHSi=CHMe]) ($19_{\text{Bu,H}}$). All hydrogen atoms have been omitted for clarity except those on Mn or the Si=C unit. The inset shows a top-down view of the Mn silene hydride core, with selected bond distances.

In the calculated structures of silene hydride isomers i and ii, the Si=C bond distances of 1.80-1.81 Å fall within the range for previously reported transition metal silene complexes (1.78(2)-1.838(11) Å), and correspond to Mayer bond orders ranging from 0.96 to 1.10 (cf. 0.70-0.91 for Si–C single bonds in the same complexes). Also, as in $19_{\text{R}_2}$ (Chapter 4), significant interligand interactions exist between silicon and the hydride. Computationally, this is illustrated by short Si–H$_{\text{Mn}}$ distances (1.64-1.66 Å), with substantial Mayer bond orders (0.45-0.49), and is also reflected by a large negative $^{29}\text{Si–}^1\text{H}_{\text{Mn}}$ coupling constant of –80 Hz (measured using $^{29}\text{Si}$ edited 2D $^1\text{H}–^1\text{H}$ COSY NMR spectroscopy; see Chapter 6) for the major isomer of $19_{\text{Bu,H}}$ (cf. –30 to –31 Hz for $20_{\text{R}}$ and > 0 in classical silyl hydride complexes). Short Mn–Si distances (2.35-2.42 Å) with Mayer bond orders of 0.49-0.53, and Mn–H distances of 1.64-1.66 Å with Mayer bond orders of 0.52-0.56, combined with the short Si=C distance (vide supra),

\[\text{ii By comparison, terminal Si–H distances and Mayer bond orders in } 19_{\text{R,H}} \text{ are } 1.50-1.51 \text{ Å and } 0.82-0.86, \text{ respectively.}\]
support the identification $19^{R,H}$ and $19^{R,Et}$ as cis silene hydride complexes, as opposed to 5-coordinate alkyl complexes with a strong $\beta$-Si–H–Mn interaction.

5.3 – DFT Calculations on Low-Coordinate Silyl and Silylene Hydride Intermediates Derived from $20^R$

The reactions of the disilyl hydride complexes $[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]$ ($20^{Ph}$: $R = \text{Ph}$, $20^{nBu}$: $R = ^n\text{Bu}$) with $\text{C}_2\text{H}_4$ (vide supra) likely proceed via either (a) 5-coordinate mono-silyl intermediates, $[(\text{dmpe})_2\text{Mn(SiH}_2\text{R})]$ ($17^{Ph}$: $R = \text{Ph}$, $17^{nBu}$: $R = ^n\text{Bu}$), or (b) silylene-hydride intermediates, $[(\text{dmpe})_2\text{MnH(=SiHR})]$ ($16^{Ph, H}$: $R = \text{Ph}$, $16^{nBu, H}$: $R = ^n\text{Bu}$), formed by sequential hydrosilane reductive elimination and $\alpha$-hydride elimination from disilyl hydride complexes $20^R$ (Scheme 5.6; vide infra). Therefore, DFT calculations (ADF, gas-phase, all-electron, PBE, D3-BJ, TZ2P, ZORA) were carried out to assess the thermodynamic accessibility of such intermediates (Table 5.2, Figure 5.6).

Table 5.2: Thermodynamic parameters calculated by DFT for the formation of intermediates in Figure 5.6 from disilyl hydride complexes $[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]$ ($20^{Ph}$ ($R = \text{Ph}$) / $20^{nBu}$ ($R = ^n\text{Bu}$)); $\Delta E$ (calculated before ZPE correction), $\Delta H$, $\Delta G^{298.15K}$, $\Delta G^{335K}$ (kJ mol$^{-1}$ at 298.15 K or, for $\Delta G^{335K}$, 335 K), and $\Delta S$ (J mol$^{-1}$K$^{-1}$ at 298.15 K).$^a$

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$^a$ n.o. = not observed (i.e. energy minimum not located).
Figure 5.6: DFT calculated Gibbs free energies at 298.15 K ($\Delta G^{298.15K}$; kJ mol$^{-1}$) to access reactive intermediates (and the H$_3$SiR byproduct) from disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] ($20^\text{Ph}$: $R = \text{Ph}$, blue dotted lines; $20^\text{Bu}$: $R = \text{''Bu}$, red dashed lines). Calculated intermediates (left to right) are: (i) an isomer of [(dmpe)$_2$Mn(SiH$_2$R)] with an equatorial dmpe arrangement ($\text{trans}$-$17^\text{Ph}$: $R = \text{Ph}$, $\text{trans}$-$17^\text{Bu}$: $R = \text{''Bu}$), (ii) an isomer of [(dmpe)$_2$Mn(SiH$_2$R)] with a disphenoidal dmpe arrangement and a hydrocarbyl substituent on silicon oriented towards the vacant coordination site {rotamer 1 of $\text{cis}$-$17^\text{R}$: $R = \text{Ph}$ ($\text{cis}$-$17^\text{Ph}$), ''Bu ($\text{cis}$-$17^\text{Bu}$)}, (iii) an isomer of [(dmpe)$_2$Mn(SiH$_2$R)] with a disphenoidal dmpe arrangement and an SiH substituent oriented towards the vacant coordination site {rotamer 2 of $\text{cis}$-$17^\text{R}$: $R = \text{Ph}$ ($\text{cis}$-$17^\text{Ph}$); a minimum was not located for $R = \text{''Bu}$}, (iv) an isomer of [(dmpe)$_2$MnH(=SiHR)] with interacting $\text{cis}$-disposed silylene and hydride ligands ($\text{cis}$-$16^\text{Ph,H}$: $R = \text{Ph}$, $\text{cis}$-$16^\text{Bu,H}$: $R = \text{''Bu}$), and (v) $\text{trans}$-[(dmpe)$_2$MnH(=SiHR)] ($\text{trans}$-$16^\text{Ph,H}$: $R = \text{Ph}$, $\text{trans}$-$16^\text{Bu,H}$: $R = \text{''Bu}$). Geometry optimized cores of the phenyl analogues of reactive intermediates are depicted below each energy level, showing Mn in red, Si in pink, C in dark grey, and H in light grey, accompanied by stick bonds to the phosphorus donor atoms.
In the case of low-coordinate silyl species, energy minima were located for structures in which the silyl group is either cis (cis-17R) or trans (trans-17R) to the vacant coordination site generated by hydrosilane reductive elimination. At 298 K, ΔG for the formation of these monosilyl compounds and free hydrosilane from 20R is very similar (63-71 kJ mol⁻¹).

In the global minima for the cis isomers (rotamer 1 of cis-17R), the hydrocarbyl substituent on silicon engages in a γ-agostic interaction with manganese (via an ortho-CH bond in cis-17Ph or a CH₂CH₂CH₃ bond in cis-17Bu), with Mn–Hᵦ distances of 1.91-1.93 Å. The Mn–Hᵦ–Cᵦ angles in this rotamer of cis-17R are 115.9° and 131.4°, respectively, and the presence of a γ-agostic interaction is further supported by Mayer bond orders of 0.22-0.24 between Mn and Hᵦ, and 0.13-0.15 between Mn and Cᵦ.

For the phenyl analogue 17Ph, a higher-energy cis isomer was located, corresponding to a rotamer where one of the two hydrogen substituents on silicon is now oriented in the direction of the vacant coordination site (rotamer 2 of cis-17Ph; Figure 5.6, Table 5.2). Relative to rotamer 1, this structure features an acute Mn–Si–HᵦSi angle of 101° (cf. 119°), an Mn–Hₛᵦ Mayer bond order of 0.06 (cf. < 0.05), a marginally elongated Si–Hₛᵦ distance of 1.53 Å (cf. 1.51 Å), and a marginally lower Si–Hₛᵦ Mayer bond order of 0.80 (cf. 0.85), together suggestive of a weak α-Si–H–Mn interaction. Rotamer 2 of 17R is presumably involved in silylene hydride formation via α-hydride elimination, and indeed, all attempts to locate an analogous energy minimum for the "Bu analogue structure led instead to a silylene hydride structure (cis-16Bu,H; vide infra).

As with the 5-coordinate silyl species (vide supra), multiple energy minima (Table 5.2, Figure 5.6) were located for silylene hydride structures [(dmpe)₂MnH(=SiHR)] (16Ph,H: R = Ph, 16Bu,H: R = "Bu). The two lowest energy structures are (a) a cis silylene hydride isomer with a significant interaction between silicon and the neighbouring hydride ligand (the Si···HᵦMn distances are 1.68 Å, with Mayer bond orders of 0.52; cf. 0.84-0.85 for the terminal Si–H bonds), and (b) a trans silylene hydride isomer. These isomers are isostructural to the X-ray crystal structures of
cis-[(dmpe)$_2$MnH(=SiPh$_2$)] (16$^{Ph2}$) and trans-[(dmpe)$_2$MnH(=SiEt$_2$)] (16$^{Et2}$), respectively (Chapter 4). Calculated $\Delta$G values to access 16$^{R,H}$ from 20$^R$ range from 41 kJ mol$^{-1}$ (trans isomers) to 47-60 kJ mol$^{-1}$ (cis isomers) at 298.15 K, decreasing to 33-34 kJ mol$^{-1}$ (trans isomers) and 39-52 kJ mol$^{-1}$ (cis isomers) at 335 K, highlighting their thermodynamic accessibly.

In silylene hydride complexes 16$^{R,H}$, Mn–Si double bond character is apparent from relatively short Mn–Si distances (2.16-2.20 Å), Mn–Si Mayer bond orders ranging from 1.17 (cis-16$^{R,H}$) to 1.54-1.57 (trans-16$^{R,H}$), and a planar or near-planar environment about Si ($\Sigma$(R–Si–R) > 356°). These parameters are comparable to those for the two isomers of [(dmpe)$_2$MnH(=SiR$_2$)] (16$^{R2}$; R = Et or Ph) discussed in Chapter 4.

5.4 – High Temperature NMR Spectra of 20$^R$: in situ Generation of trans-Silylene Hydride (trans-16$^{R,H}$) Species

At 335 K, $^1$H NMR spectra of the disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] ($^{20}_{Ph}$: R = Ph, $^{20}_{Bu}$: R = $^n$Bu) revealed the formation of a small amount of a new manganese complex and free hydrosilane (H$_3$SiR; R = Ph or $^n$Bu). This process is reversible, and clean spectra of 20$^R$ were observed upon cooling back to room temperature. The new manganese complex exhibits a high frequency (9.83 or 9.53 ppm) and a low frequency (~9.01 or ~9.60 ppm) $^1$H NMR signal. The former is in the range observed for the terminal =SiRR (R = hydrocarbyl substituent) environment in diamagnetic silylene complexes of Mo, W, Fe, Ru, Os, and Ir, (6.34-12.1 ppm; see Section 1.6.6), while the latter is consistent with a metal hydride environment. The low frequency hydride signal is a pentet ($^2J_{^1H,^{31}P}$ = 54 or 51 Hz) consistent with a hydride ligand apical to a plane of four equivalent phosphine donors. Taken together, these data indicate that the new complex observed at elevated temperature is trans-[(dmpe)$_2$MnH(=SiHR)] (trans-16$^{Ph,H}$: R = Ph, trans-16$^{Bu,H}$: R = $^n$Bu); the most thermodynamically accessible silyl or silylene species in Figure 5.6.
Characterization of $\text{trans-16}^{\text{R,H}}$ by $^{29}\text{Si}$ NMR spectroscopy was not possible since the new species were formed at very low concentrations (~4% and ~2% relative to $20^{\text{Ph}}$ or $20^{\text{Bu}}$, respectively). However, EXSY NMR spectroscopy at 335 K indicates exchange between the two diastereotopic Si$H$ protons in $20^{\text{Ph}}$ or $20^{\text{Bu}}$, the free hydrosilane Si$H$ peak, the high frequency $\text{trans-16}^{\text{R,H}}$ silylene Si$H$ environment, and the Mn$H$ signals from both $20^{\text{R}}$ and $\text{trans-16}^{\text{R,H}}$ (shown in Figure 5.7 for $R = n^{\text{Bu}}$). This is consistent with an equilibrium in which $20^{\text{R}}$ eliminates free $H_3\text{SiR}$ to form $\text{trans-16}^{\text{R,H}}$ (vide infra).

\[\text{In the case of } 20^{\text{Ph}}, \text{ an additional low frequency } ^1\text{H NMR signal (a broad singlet with } < 2\% \text{ intensity relative to the Mn}$H$ \text{ peak of } 20^{\text{Ph}} \text{ was observed at } -12.1 \text{ ppm (335 K), which could potentially be from the Mn}$H$ \text{ environment of cis-[(dmpe)$_2$MnH(=SiPh)] (cis-16}^{\text{Ph,H}}\text{). However, EXSY NMR spectroscopy did not show chemical exchange between this peak and those from } 20^{\text{Ph}} \text{ or } \text{trans-16}^{\text{Ph,H}} \text{ (potentially due to broadness and low intensity of the signal). A further low frequency } ^1\text{H NMR signal (also a broad singlet, but present in the room temperature and high temperature NMR spectra in similar intensities; } \sim 1.5\% \text{ relative to the Mn}$H$ \text{ region of } 20^{\text{Ph}} \text{ was observed at } -13.8 \text{ ppm, which could potentially be from another isomer of } 20^{\text{Ph}}, \text{ this environment was observed by EXSY NMR spectroscopy to be in chemical exchange with the Si}$H$ \text{ and Mn}$H$ \text{ environments of both } 20^{\text{Ph}} \text{ and } \text{trans-16}^{\text{Ph,H}}.\]
Figure 5.7: 1D NOESY/EXSY NMR spectrum of a solution of [(dmpe)$_2$MnH(SiH$_2$Bu)$_2$] (20$_{Bu}$) at 335 K with excitation at the SiH signal of 20$_{Bu}$, showing chemical exchange between the SiH and MnH environments of [(dmpe)$_2$MnH(SiH$_2$Bu)$_2$)] (20$_{Bu}$) and trans-[(dmpe)$_2$MnH(=SiH$_n$Bu)] (trans-16$_{Bu,H}$), and the SiH environment of free H$_3$Si$^n$Bu. Positive (EXSY) peaks are indicative of chemical exchange and negative (NOESY) peaks are indicative of through-space coupling (500 MHz, C$_6$D$_6$).

5.5 – Trapping Experiments with Isonitriles and $N$-Heterocyclic Carbenes

To provide experimental corroboration for the accessibility of 5-coordinate silyl [(dmpe)$_2$Mn(SiH$_2$R)] (17$_{Ph}$: R = Ph, 17$_{Bu}$: R = $^n$Bu) and silylene hydride [(dmpe)$_2$MnH(=SiH$_n$R)] (16$_{Ph,H}$: R = Ph, 16$_{Bu,H}$: R = $^n$Bu) species from 20$_R$, reactions with neutral donor ligands were carried out, with a view towards coordination to manganese in 17$_R$ or silicon in 16$_R,H$ (Scheme 5.5).
Scheme 5.5: Trapping of putative silyl (17R) and silylene hydride (16R,H) intermediates: synthesis of silyl isonitrile complexes [(dmpe)₂Mn(SiH₂R)(CNR')] (21a: R = Ph, R' = o-xylyl; 21b: R = 'Bu, R' = o-xylyl; 21c: R = Ph, R' = 'Bu; 21d: R = 'Bu, R' = 'Bu) and NHC-stabilized silylene hydride complexes [(dmpe)₂MnH{=SiHR(NHC)}] (22a: NHC = iPrNHC, R = Ph; 22b: NHC = iPrNHC, R = 'Bu; 22c: NHC = MeNHC, R = Ph; 22d: NHC = MeNHC, R = 'Bu.
Addition of $o$-xylylN≡C or $^t$BuN≡C to solutions of $20^R$ resulted in hydrosilane elimination, and isolation of yellow or orange silyl isonitrile complexes $[(\text{dmpe})_2\text{Mn(SiH}_2\text{R})(\text{CNR}')]$ {R' = $o$-xylyl, R = Ph (21a) or $^t$Bu (21b); R' = $^t$Bu, R = Ph (21c) or $^t$Bu (21d)}, effectively trapping silyl complexes $17^R$ (Scheme 5.5). In solution, all four reactions initially led to mixtures of two complexes identified by NMR spectroscopy as cis (85-97%) and trans (3-15%) isomers of 21a-d. Slow isomerization was observed between the cis and trans isomers of 21a-d in solution, and unexpectedly, these isomerization reactions proceeded in the direction of the trans isomers at elevated temperature (resulting in an increase in the proportion of trans isomer to 44-74% after heating solutions containing exclusively the cis isomer at 65-80° for 4-21 days), and in the opposite direction upon leaving the same solutions at room temperature for 3 weeks (e.g. leaving cis/trans mixtures of 21a,b containing 44-48% trans isomer at room temperature resulted in solutions containing 99% cis isomer after 3 weeks).

X-ray quality crystals were obtained for the four silyl isonitrile complexes 21a-d, in each case as the cis isomer (Figure 5.8). All four structures are octahedral with Mn–Si distances of 2.3552(5)-2.3618(5) Å and Mn–C distances of 1.805(4)-1.847(3) Å. The isonitrile ligands show elongated C–Mn–N distances of 1.176(4)-1.225(9) Å and non-linear C–N–C angles of 159.2(8)-167.5(1)°, indicative of appreciable π-backbonding.

In contrast to reactions with isonitriles, reactions of disilyl hydride complexes $20^R$ with 1,3-diisopropylimidazolin-2-ylidene ($^{i}r$NHC) or 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene ($^{Me}$NHC) afforded the base-stabilized silylene hydride complexes $[(\text{dmpe})_2\text{MnH}=$SiHR(NHC)] {NHC = $^{i}r$NHC, R = Ph (22a) or $^t$Bu (22b); NHC = $^{Me}$NHC, R = Ph (22c) or $^t$Bu (22d)}, trapping the proposed silylene hydride species $16^R$H (Scheme 5.5). Compounds 22b-d were isolated as analytically pure red powders, whereas 22a evaded purification.
Figure 5.8: X-ray crystal structures of (top left) cis-[(dmpe)$_2$Mn(SiH$_2$Ph)(CNxylyl)] (cis-21a), (top right) cis-[(dmpe)$_2$Mn(SiH$_2$"Bu)(CNxylyl)] (cis-21b), (bottom left) cis-[(dmpe)$_2$Mn(SiH$_2$Ph)(CNtBu)] (cis-21c), and (bottom right) cis-[(dmpe)$_2$Mn(SiH$_2$"Bu)(CNtBu)] (cis-21d), with ellipsoids drawn at 50% probability. Hydrogen atoms on Si were located from the difference map and refined isotropically, and all other hydrogen atoms have been omitted for clarity. In the case of cis-21a, the dmpe ligands are disordered over two positions, and only the dominant (95%) are shown. In the case of cis-21b, the dmpe ligands and N atom are disordered (one dmpe and the N atom over two positions and the other dmpe over three), and only the dominant conformation (66% for the dmpe ligands, and 72% for N) is shown. In the case of cis-21c, the unit cell contains two independent and essentially isostructural molecules (one of
which his shown) both of which have one dmpe ligand disordered over two positions and the other over three, and only the dominant conformation (96% and 81%) is shown. In the case of *cis-21d*, the unit cell contains two independent and essentially isostructural molecules both of which have one dmpe ligand disordered over two positions and the other over three, and one has both butyl groups disordered and only the structure without butyl disorder is shown with the dominant (62%) dmpe configuration. Atom labels with suffixes correspond to those without suffixes in conformations or molecules not shown.

For *cis-21a*, bond distances (Å) and angles (deg): Mn–Si 2.3618(5), Mn–C(1) 1.820(1), C(1)–N(1) 1.200(1), N(1)–C(2) 1.386(1), Si–H(1A) 1.45(1), Si–H(1B) 1.47(2), Si–C(10) 1.920(1), Mn–C(1)–N(1) 176.3(1), C(1)–N(1)–C(2) 167.5(1), Mn–Si–C(10) 123.66(4), Mn–Si–H(1A) 115.9(7), Mn–Si–H(1B) 115.5(7). For *cis-21b*, bond distances (Å) and angles (deg): Mn–Si 2.360(1), Mn–C(1) 1.805(4), C(1)–N(1) 1.225(9), C(1)–N(1A) 1.22(2), N(1)–C(2) 1.394(9), N(1A)–C(2) 1.39(2), Si–C(10) 1.910(4), Si–H(1A) 1.40(6), Si–H(1B) 1.48(5), Mn–C(1)–N(1) 173.1(5), Mn–C(1)–N(1A) 166(1), C(1)–N(1)–C(2) 159.2(8), C(1)–N(1A)–C(2) 161(2), Mn–Si–C(10) 118.7(2), Mn–Si–H(1A) 118(2), Mn–Si–H(1B) 115(2). For *cis-21c*, bond distances (Å) and angles (deg): Mn(1)–Si(1) 2.3562(7), Mn(1C)–Si(1C) 2.3568(7), Mn(1)–C(1) 1.841(2), Mn(1C)–C(1C) 1.847(3), C(1)–N(1) 1.181(4), C(1C)–N(1C) 1.176(4), N(1)–C(2) 1.442(4), N(1C)–C(2C) 1.441(4), Si(1)–C(6) 1.920(3), Si(1C)–C(6C) 1.925(3), Si(1)–H(1A) 1.46(3), Si(1)–H(1B) 1.45(4), Si(1C)–H(1CA) 1.39(4), Si(1C)–H(1CB) 1.44(3), Mn(1)–C(1)–N(1) 177.7(2), Mn(1C)–C(1C)–N(1C) 177.4(2), C(1)–N(1)–C(2) 167.4(3), C(1C)–N(1C)–C(2C) 172.6(3), Mn(1)–Si(1)–C(6) 124.08(8), Mn(1C)–Si(1C)–C(6C) 123.54(8), Mn(1)–Si(1)–H(1A) 117(1), Mn(1C)–Si(1C)–H(1B) 116(2), Mn(1C)–Si(1C)–H(1CA) 114(2), Mn(1C)–Si(1C)–H(1CB) 117(1). For *cis-21d*, bond distances (Å) and angles (deg): Mn(1)–Si(1) 2.3551(5), Mn(1C)–Si(1C) 2.3559(7), Mn(1)–C(1) 1.838(2), Mn(1C)–C(1C) 1.828(2), Si(1)–C(6) 1.914(2), Si(1C)–C(6C) 1.930(3), Si(1C)–C(6D) 1.88(1), Si(1)–H(1A) 1.48(2), Si(1)–H(1B) 1.42(3), Si(1C)–H(1CA) 1.44(2), Si(1C)–H(1CB) 1.46(2).

A variety of NHC-stabilized silylene complexes have been reported for V, Cr, W, Fe, Co, Rh, and Ni (see Section 1.6.7), and relative to base-free silylene complexes, they
feature longer metal–silicon bond distances, pyramidalization at silicon, and lower frequency $^{29}\text{Si}$ NMR chemical shifts (typically 25-100 ppm, kk compared with > 200 ppm for base-stabilized silylene complexes). 304

Room temperature NMR spectra of $^{iPr}$NHC adducts 22a,b revealed two sets of broad NMR signals in the process of coalescence/decalscence, due to a pair of rapidly interconverting isomers. Cooling the solutions afforded two sets of well resolved NMR signals corresponding to compounds with a disphenoidal arrangement of the phosphorus donor atoms, each with a single SiH signal (5.1 to 6.4 ppm), a single MnH resonance (–12.3 to –12.6 ppm), a single $^{29}\text{Si}$ NMR environment (22.2 to 29.6 ppm), and four unique $^{31}\text{P}$ NMR environments (65.6-81.9 ppm). These data are indicative of NHC-coordinated cis silylene hydride complexes existing as a pair of interconverting diastereomers (due to chirality at Si and Mn).

In contrast, NMR spectra of the MeNHC silylene hydride complexes (22c,d) revealed the same two rapidly interconverting cis diastereomers plus a third isomer which afforded a sharp set of $^1\text{H}$ and $^{31}\text{P}$ NMR signals at room temperature. This third isomer corresponds to an NHC-coordinated trans silylene hydride complex, as evidenced by a single MnH ($–14.9$ or $–15.0$ ppm) signal with a pentet coupling pattern ($^2J_{\text{H,P}} = 48-49$ Hz) and two sharp signals in the $^{31}\text{P}$$^1\text{H}$ NMR spectra (78.7-80.6 ppm) due to diastereotopic phosphorus atoms. The $^1\text{H}$ NMR SiH and $^{29}\text{Si}$ NMR chemical shifts in these trans isomers (4.9-5.8 ppm and 22.4 ppm, respectively) are similar to those in the cis isomers.

At 335 K, the two cis diastereomers of 22a-d gave rise to a single set of averaged signals, with the MnH peak at $–12.5$ to $–12.7$ ppm (pentets for cis-22a,c,d with $^2J_{\text{H,P}} = 32-34$ Hz, while the NMR spectrum of 22b remained a broad singlet in the process of

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kk A handful of NHC-stabilized silylene complexes have also been reported with $^{29}\text{Si}$ chemical shifts lower than 25 ppm (see ref. 354-357), and this has been rationalized by adoption of a zwitterionic bonding motif which results in limited π-backdonation to the Si centre from the metal (see ref. 357).

ll We could not determine the $^{29}\text{Si}$ NMR chemical shift of trans-22c due to the low proportion of trans isomer in solution (cis : trans ratio of 14 : 1).
coalescence), accompanied by (in solutions of 22c,d only) a set of sharp signals for the trans isomer. For 22c,d, EXSY NMR spectroscopy at 335 K showed cross peaks between the MnH and SiH 1H NMR signals due to both the cis and trans isomers (i.e. chemical exchange between all four environments). This equilibrium between cis- and trans- 22c,d mirrors that discussed in Chapter 4 between the cis and trans isomers of base-free [(dmpe)2MnH(=SiPh2)] (16Ph2).

Possible mechanisms for ambient temperature exchange between the cis diastereomers of 22a-d are (a) phosphine donor dissociation, isomerization of the 5-coordinate product, and phosphine re-coordination, or (b) NHC dissociation to generate cis-[(dmpe)2MnH(=SiHR)] (cis-16Ph,H: R = Ph, cis-16Bu,H: R = "Bu), followed by re-coordination to the opposite face of the silylene ligand. The latter mechanism would imply that 22a-d, like disilyl hydride complexes 20R, could react as sources of either base-free silylene hydride complexes 16R,H, or 5-coordinate silyl complexes 17R. The accessibility of this pathway is implied by the reactions of 22d with tBuNC, and 22b with ethylene, which afforded [(dmpe)2Mn(SiH2"Bu)(CN"Bu)] (21d) and [(dmpe)2MnH("BuHSi=CHMe)] (19Bu,H), respectively; these are the same complexes formed in reactions of these reagents with 20Bu. Furthermore, the accessibility of 17R provides a mechanism for the observed exchange between the SiH and MnH environments in the EXSY NMR spectra of 22c,d at 335 K (vide supra).

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**nm** The lability of NHCs in 22a-d was also illustrated by initial generation of mixtures of reagents and products upon addition of free NHCs to 20R; complete conversion to 22a-d required removal of the free hydrosilane byproducts. For 22b-d, this was achieved by periodically removing all solvent and hydrosilane byproducts in vacuo. By contrast, for 22a this was achieved by the reaction of the H3SiPh byproduct with excess tPrNHC to form 1-phenyl-2,5-diisopropyl-3,4-dehydro-2,5-diazasilinane; this reaction has previously been reported at 100 °C (see ref. 511), and in our hands 98% conversion was observed after 24 h at 55 °C (consistent with the reaction conditions involved in the synthesis of 22a).

**nn** Unlike the reaction of 20Bu with ethylene, the reaction of 22b with ethylene does not generate H3Si"Bu as a byproduct, and under these conditions, complex 19Bu,H reacted readily with a further equivalent of ethylene, so that both 19Bu,H and 19Bu,Et were formed concurrently.
X-ray quality crystals were obtained for complexes 22a-d by recrystallization from concentrated hexanes solutions (22a,b), toluene layered with pentane (22c), or a dilute hexanes solution (22d) at –30 °C. The solid state structures of 22a-c (Figure 5.9; top row and bottom left) feature a cis arrangement of the hydride and base-stabilized silylene ligands, corresponding to one of the two cis diastereomers observed in solution. By contrast, 22d crystallized as the trans isomer (Figure 5.9; bottom right). In all four structures {complementary DFT calculations modelled 22b,d with an sBu group in place of the Et group; [(dmpe)$_2$MnH{=SiHEt(NHC)}] where NHC = iPrNHC (22b*) or MeNHC (22d*)}, NHC coordination to silicon resulted in elongated Mn–Si distances (2.255(1)-2.299(1) Å; calcd. 2.26-2.30 Å for both isomers of 22a,b*,c,d*), and correspondingly weaker Mayer bond orders of 1.03-1.08, relative to base-free silylene complexes 16\textsubscript{RH} (2.16-2.20 Å and 1.17-1.57, respectively). Unlike base-free analogues (vide supra), cis-22a-d display only negligible interligand Si–H interactions (with Mayer bond orders ≤ 0.13). Additionally, substantial pyramidalization at silicon was observed for both isomers of 22a-d, where the sum of the angles around silicon (for non-NHC substituents) ranged from 322(3) to 342(2)° (calcd. 336.1-341.5°; cf. > 356° in 16\textsubscript{RH}). Nevertheless, the Mn–Si distances are significantly shorter than those in related silyl complexes 21a-d (the Mn–Si distances in 21a-d range from 2.3552(5)-2.3618(5) Å {calcd. 2.35-2.36 Å (cis) and 2.41-2.42 Å (trans), with Mayer bond orders of 0.89-0.93}), indicative of residual Mn–Si multiple bond character in 22a-d.

\footnote{In the structures of cis-22a,b, the dmpe ligands are disordered, and modelling this disorder allowed the structures of both diastereomers observed in solution to be elucidated.}

\footnote{21b,d were computationally modelled with Et groups in place of sBu groups; [(dmpe)$_2$Mn(SiH$_2$Et)(CNR)] (21b*: R = o-xylyl, 21d*: R = tBu).}
Figure 5.9: X-ray crystal structures of (top left) *cis*-[\(\text{dmpe}\)\(_2\)MnH\{\(\text{SiHPh}^{(i\text{Pr})\text{NHC}}\)\}] (*cis-\(22\text{a}\)*), (top right) *cis*-[\(\text{dmpe}\)\(_2\)MnH\{\(\text{SiH}^{\text{nBu}}\text{Bu}^{(i\text{Pr})\text{NHC}}\)\}] (*cis-\(22\text{b}\)*), (bottom left) *cis*-[\(\text{dmpe}\)\(_2\)MnH\{\(\text{SiHPh}^{\text{MeNHC}}\)\}] (*cis-\(22\text{c}\)*), and (bottom right) *trans*-[\(\text{dmpe}\)\(_2\)MnH\{\(\text{SiH}^{\text{nBu}}\text{Bu}^{(\text{MeNHC}}\)\}] (*trans-\(22\text{d}\)*) with ellipsoids drawn at 50% probability. Hydrogen atoms on Mn and Si were located from the difference map and refined isotropically, and all others have been omitted for clarity. In the case of *cis-\(22\text{a}\)*, the dmpe ligands are disordered over 3 positions, the dominant (51%) of which is shown. In the case of *cis-\(22\text{b}\)*, the dmpe ligands are disordered over 2 positions, the dominant (95%) of which is shown. For *cis-\(22\text{a}\)*, bond distances (Å) and angles (deg): Mn–Si 2.292(2), Mn–H(1) 1.58(6), Si–C(1) 2.004(6), Si–C(10) 1.954(5), Si–H(2) 1.49(5), H(1)–Mn–Si 86(2), Mn–Si–C(10) 133.0(2), Mn–Si–H(2) 118(2), Mn–Si–C(1) 122.9(2). For *cis-\(22\text{b}\)*, bond
distances (Å) and angles (deg): Mn–Si 2.299(1), Mn–H(1) 1.45(2), Si–C(1) 1.994(3), Si–C(10) 1.927(3), Si–H(2) 1.43(3), H(1)–Mn–Si 78(1), Mn–Si–C(10) 125.15(9), Mn–Si–H(2) 120(1), Mn–Si–C(1) 118.47(8). For cis-22c, bond distances (Å) and angles (deg): Mn–Si 2.255(1), Mn–H(1) 1.29(3), Si–C(1) 1.956(4), Si–C(8) 1.939(4), Si–H(2) 1.51(3), H(1)–Mn–Si 62(1), Mn–Si–C(8) 121.6(1), Mn–Si–H(2) 124(1), Mn–Si–C(1) 121.3(1). For trans-22d, bond distances (Å) and angles (deg): Mn–Si 2.2956(6), Mn–H(1) 1.52(3), Si–C(1) 1.985(1), Si–C(8) 1.948(2), Si–H(2) 1.46(1), H(1)–Mn–Si 173.0(9), Mn–Si–C(8) 125.96(5), Mn–Si–H(2) 119.4(7), Mn–Si–C(1) 125.70(4), ΣP–Mn–P (cis only) 356.93(4).

5.6 – Pathways for Reactions of $20^R$ with Ethylene

In Chapter 4, we showed that the silylene hydride complexes, $[(\text{dmpe})_2\text{MnH} (=\text{SiR}_2)]$ ($16^\text{Ph2}$: R = Ph, $16^\text{Et2}$: R = Et), react with ethylene to form the silene hydride complexes $[(\text{dmpe})_2\text{MnH} (\text{R}_2\text{Si} = \text{CHMe})]$ ($19^\text{Ph2}$: R = Ph, $19^\text{Et2}$: R = Et), potentially via a 5-coordinate silyl isomer. Given that disilyl hydride complexes $20^R$ exist in equilibrium with analogous low-coordinate silyl and silylene hydride complexes (vide supra), it is likely that the reactions of $20^R$ with ethylene proceed via a parallel mechanism, as illustrated in Scheme 5.6. The initial steps in this scheme involve either (a) ethylene coordination to a silylene hydride intermediate ($16^R^H$) followed by 2+2 cycloaddition (to form $A^R$) and subsequent Si–H bond-forming reductive elimination, or (b) coordination of ethylene to a low coordinate silyl intermediate ($17^R$), forming $B^R$, followed by 1,2-insertion. Both of these pathways generate primary alkyl complex $23^R$, which can provide access to $19^R^H$ by sequential β-hydride elimination (to form $C^R$), 1,2-insertion to generate secondary alkyl complex $24^R$, and a second β-hydride elimination involving the hydrogen substituent on silicon. Consistent with this mechanism, the reactions of $[(\text{dmpe})_2\text{MnH}(\text{SiH}_2^a\text{Bu})_2]$ ($20^\text{Bu}$) or $[(\text{dmpe})_2\text{Mn} ( = \text{SiH}^a\text{Bu} ([\text{Pr}^\text{NHC}])]$ ($22b$) with $d_4$-ethylene yielded $[(\text{dmpe})_2\text{MnH}(^a\text{BuHSi}=\text{CDCD})]$ as the only observed isotopomer of $19^\text{Bu,H}$. 
Scheme 5.6: Proposed pathways for reactions of disilyl hydride complexes $[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]$ ($20^\text{Ph}$: $R = \text{Ph}$, $20^\text{Bu}$: $R = \text{^nBu}$) with ethylene to form silene hydride complexes $[(\text{dmpe})_2\text{MnH(RHSi=CHMe)}] (19^\text{Ph,H}; R = \text{Ph}$, $19^\text{Bu,H}; R = \text{^nBu})$. [Mn] = Mn(dmpe)$_2$. Only one isomer of $16^\text{R,H}$ is shown. Boxes indicate complexes which have been isolated or spectroscopically observed.

After conversion of $20^R$ to $19^R,H$, reaction with a second equivalent of ethylene resulted in conversion of a silene SiH group in $19^R,H$ to an SiEt group, yielding $19^R,\text{Et}$ (vide supra). This reactivity likely involves the experimentally observed isomerization of $19^R,H$ to silylenes $16^R,\text{Et}$ (vide supra), presumably via a low-coordinate silyl intermediate ($17^R,\text{Et}$ in Scheme 5.7) formed from $19^R,H$ by C–H bond-forming 1,2-insertion. Conversion to $19^R,\text{Et}$ can then take place via previously discussed pathways (Scheme 5.6) involving reactions of the silylene or low-coordinate silyl species with ethylene to afford
intermediates $A^{R,Et}$ and $B^{R,Et}$, respectively ($A^{R,Et}$ and $B^{R,Et}$ are analogues of $A^R$ and $B^R$ in Scheme 5.6, but with an ethyl group in place of one hydrogen atom on silicon).

Deuterium labelling studies were employed to provide experimental support for these mechanistic proposals. Specifically, $\left[\left(\text{dmpe}\right)_2\text{MnH}(^{19}\text{BuHSi=CD}_{3})\right]$ ($d_4^{19}_{19}\text{Bu,H}$) isomerized to exclusively form $\text{trans-}\left[\left(\text{dmpe}\right)_2\text{MnH}(^{14}\text{Si}^{14}\text{Bu(CHCD}_3)\right]$ ($\text{trans-}d_4^{16}_{14}\text{Bu,Et}$), and the reaction of $\left[\left(\text{dmpe}\right)_2\text{MnH}(^{14}\text{BuHSi=CHMe})\right]$ ($19^{Bu,H}$) with $d_4$-ethylene yielded $\left[\left(\text{dmpe}\right)_2\text{MnH}(^{14}\text{BuEtSi=CD}_{3})\right]$ ($d_4^{19}_{16}\text{Bu,Et}$). Additionally, $\left[\left(\text{dmpe}\right)_2\text{MnH}(=\text{SiEt}_2)\right]$ ($16^{Et2}$) exclusively forms $\left[\left(\text{dmpe}\right)_2\text{MnH}(\text{Et}_2\text{Si=CD}_{3})\right]$ ($d_4^{19}_{16}\text{Et}$) upon exposure to $d_4$-ethylene (see Chapter 4).

**Scheme 5.7:** Initial steps in the pathway proposed for reactions of silene hydride complexes $\left[\left(\text{dmpe}\right)_2\text{MnH}(\text{RHSi=CHMe})\right]$ ($19^{Ph,H}_{19}\text{Bu,Et}$; $R = \text{Ph}$, $19^{Bu,H}_{19}\text{Bu,Et}$; $R = ^{14}\text{Bu}$) with ethylene to afford $\left[\left(\text{dmpe}\right)_2\text{MnH}(\text{ReSi=CHMe})\right]$ ($19^{Ph,Et}_{19}\text{Bu,Et}$; $R = \text{Ph}$, $19^{Bu,Et}_{19}\text{Bu,Et}$; $R = ^{14}\text{Bu}$). $[\text{Mn}] = \text{Mn(dmpe)}_2$. Intermediates $A^{R,Et}$ and $B^{R,Et}$ are analogous to intermediates $A^R$ and $B^R$ in Scheme 5.6, but with an ethyl group in place of one hydrogen atom on silicon. Only one isomer of $16^{R,Et}$ is shown. Boxes indicate complexes which have been isolated or spectroscopically observed.

$^{99}$ Alternative pathways requiring initial dissociation of a phosphine donor in $19^{R,H}$ followed by ethylene coordination (with subsequent oxidative coupling or 1,2-insertion reactivity) cannot be ruled out.
5.7 – Summary and Conclusions for Chapter 5

\[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)\] (10) reacted with two equivalents of primary hydrosilanes to generated disilyl hydride complexes \[(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2\] (20\text{Ph}: \text{R} = \text{Ph}, 20\text{Bu}: \text{R} = \text{nBu}), presumably via a 5-coordinate ethyl intermediate \[(\text{dmpe})_2\text{MnEt}\] (13). Crystallographic and NMR characterization of 20\text{R} suggests the presence of nonclassical Si–H interligand interactions. These are the first reported manganese disilyl hydride complexes where the Si donors are not chelating.

The disilyl hydride manganese complexes 20\text{R} reversibly dissociate H\text{3SiR} to access low-coordinate silyl ([(\text{dmpe})_2\text{Mn(SiH}_2\text{R})]; 17\text{R}) and silylene hydride ([(\text{dmpe})_2\text{MnH(=SiHR)}]; 16\text{R,H}) complexes. The trans isomers of the silylene hydride complexes were observed in small amounts (<5% relative to the disilyl hydride) by NMR spectroscopy at 335 K, and are the first spectroscopically observed examples of group 7 L\text{M=SiHR} compounds. DFT calculations support the thermodynamic accessibility of cis- and trans- isomers of these low coordinate silyl and silylene species, and both sets of intermediates were trapped by coordination of isonitriles (to manganese) or N-heterocyclic carbenes (to silicon).

The reactivity of 20\text{R} with ethylene was investigated, affording silene hydride complexes \[(\text{dmpe})_2\text{MnH(RHSi=CHMe)}\] (19\text{R,H}). This reaction represents a unique method to access silene complexes (analogous to reactions of ethylene with [(\text{dmpe})_2\text{MnH(=SiR})_2] compounds discussed in Chapter 4), and the resulting silene complexes are the first spectroscopically observed transition metal examples with an SiH substituent. As such, they displayed unusual reactivity: for example, 19\text{Bu,H} slowly converted to a more stable silylene hydride isomer, [(\text{dmpe})_2\text{MnH(=SiEt}n\text{Bu})] (16\text{Bu,Et}); the first example of isomerization of a silene hydride complex to a silylene hydride complex. Furthermore, 19\text{R,H} reacted with a second equivalent of ethylene to convert the SiH substituent to an SiEt substituent, which is an unprecedented transformation for a silene ligand.
Chapter 6

Manganese Silyl Dihydride Complexes: A Spectroscopic, Crystallographic and Computational Study of Nonclassical Silicate and Hydrosilane Hydride Isomers

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6.1 – Introduction to Chapter 6

Section 1.5.5 provided a brief introduction to ‘nonclassical’ hydrosilane complexes and silicate (H$_2$SiR$_3^-$) complexes, both of which involve substantial but incomplete Si–H bond oxidative addition. These complexes are notable for containing significant interactions between MnSi and MnH environments, which can be evaluated crystallographically (by the Si–H distance; albeit with low accuracy when measured by XRD) and spectroscopically (e.g. using the $^{29}$Si–$^1$H coupling constant, although proper interpretation of the NMR data requires knowledge of both the magnitude and sign of $J_{\text{Si},H}$).

Chapter 4 briefly noted that silyl dihydride complex ([(dmpe)$_2$MnH$_2$(SiHPh$_2$)]) ($^{18}$Ph$_2$) was formed as a byproduct in the synthesis of the silylene hydride complex [(dmpe)$_2$MnH(=SiPh$_2$)] ($^{16}$Ph$_2$), and that silyl dihydride complexes $^{18}$Ph$_2$ and [(dmpe)$_2$MnH$_2$(SiHEt$_2$)] ($^{18}$Et$_2$) could be prepared pure by exposure of silylene hydride complexes to H$_2$. Herein we discuss the synthesis and characterization of the silyl dihydride complexes $^{18}$R$_2$ and [(dmpe)$_2$MnH$_2$(SiH$_2$R)] {R = Ph ($^{18}$Ph), R = $^t$Bu ($^{18}$Bu$_2$)}, with an examination of the nature of Si–H interactions in different geometric isomers via NMR spectroscopy (including determination of the sign and magnitude of $J_{\text{Si},H}$) combined with X-ray diffraction and DFT calculations.
6.2 – Synthesis of Silyl Dihydride Complexes

Both silylene hydride complexes \([(\text{dmpe})_2\text{MnH(=SiR}_2\text{)}]\) (16\text{Ph}_2: R = Ph, 16\text{Et}_2: R = Et; see Chapter 4 for synthesis and characterization) and disilyl hydride complexes \([(\text{dmpe})_2\text{MnH(SiH}_2\text{R}_2\text{)}]\) (20\text{Ph}: R = Ph, 20\text{Bu}: R = "Bu; see Chapter 5 for synthesis and characterization) reacted with \(\text{H}_2\) to afford a family of silyl dihydride complexes \([(\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{R})]\) (18\text{Ph}: R = R’ = Ph; 18\text{Et}_2: R = R’ = Et; 18\text{Ph}: R = Ph, R’ = H; 18\text{Bu}: R = "Bu, R’ = H) differing in the number and nature of the hydrocarbyl substituents on silicon (Scheme 6.1). Both of these reactions presumably proceed via a low-coordinate silyl intermediate \([(\text{dmpe})_2\text{Mn}(\text{SiH}_{3-x}\text{R}_x)]\) (17), generated either by 1,1-insertion from silylene hydride complexes 16\text{R}_2, or hydrosilane reductive elimination from disilyl hydride complexes 20\text{R} (see Chapter 5 for a discussion of the accessibility of 17 from 20\text{R}). Thermal decomposition of 20\text{R} (12 h at 90 °C) also yielded 18\text{R} as the dominant manganese complexes in solution, accompanied by \(\text{H}_2\text{SiR}_2\) (R = Ph or "Bu) and other unidentified products, although the mechanism for this reaction is unknown.

\[\text{Scheme 6.1: Syntheses of } [(\text{dmpe})_2\text{MnH}_2(\text{SiHR}_2)] \{R = \text{Ph (18Ph}_2), R = \text{Et (18Et}_2)\} \text{ and } [(\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{R})] \{R = \text{Ph (18Ph)}, R = "Bu (18Bu)}\].

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6.3 – 1D NMR Characterization of Silyl Dihydride Complexes

Room temperature solution NMR spectra (\(^1\)H, \(^{13}\)C, and \(^{31}\)P) of 18 display very broad signals indicative of multiple isomers in rapid equilibrium. However, upon cooling, NMR spectra corresponding to both a low symmetry (apparent \(C_2\) symmetry) and a high symmetry (apparent \(C_{2v}\) symmetry) isomer were observed (shown for 18\(^R\) in Figure 6.1).

![Figure 6.1](image)

**Figure 6.1:** Selected regions of the room temperature and low temperature NMR spectra for (top) \([\text{dmpe}]_2\text{MnH}_2(\text{SiH}_2\text{Ph})\] (18\(^\text{Ph}\)) and (bottom) \([\text{dmpe}]_2\text{MnH}_2(\text{SiH}_2\text{nBu})\] (18\(^\text{Bu}\)) showing, from left to right, the silicon hydride and metal hydride regions of the \(^1\)H NMR spectra, the \(^{31}\)P\(^{\{1\}H}\) NMR spectra, and \(^{29}\)Si\(^{\{1\}H}\) NMR spectra. Signals in the low temperature spectra are assigned to low symmetry (†; central) and high symmetry (*; \(\text{transHSi}\)) isomers.

\(^{\text{rr}}\) Many \(^{13}\)C NMR signals and all \(^{29}\)Si NMR signals were not located due to broadness at room temperature.
NMR signals for the low symmetry isomer of 18 feature one low frequency MnH \(^1\)H NMR resonance at \(-12.5\) to \(-12.8\) ppm, integrating to two protons, one (\(18^{R2}\)) or two (\(18^R\)) terminal SiH resonance(s) (6.0-6.6 ppm for \(18^{Ph2}\) and \(18^{Ph}\); 5.0-5.4 ppm for \(18^{Et2}\) and \(18^{Bu}\)), two \(^{31}\)P NMR resonances (71.0-75.2 ppm), and a single \(^{29}\)Si resonance (10.0 ppm for \(18^{Ph2}\), 14.2 ppm for \(18^{Et2}\), \(-15.7\) ppm for \(18^{Ph}\), and \(-22.0\) ppm for \(18^{Bu}\)). The two relatively broad \(^{31}\)P NMR signals, and the complex \(^{31}\)P coupling pattern of the MnH signals, are indicative of a disphenoidal arrangement of the phosphorus donors. These data are consistent with a central isomer (Scheme 6.2) featuring a meridional H–Si–H bonding motif involving the silyl and metal hydride ligands (as opposed to a lateral isomer with an H–H–Si bonding motif; *vide infra*).

**Scheme 6.2:** Isomers of \([(\text{dmpe})_2\text{MnH}_2(\text{SiHR}_2)]\) \{R = Ph (18\(^{Ph2}\), R = Et (18\(^{Et2}\))\} and \([(\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{R})]\) \{R = Ph (18\(^{Ph}\)), R = \(^n\)Bu (18\(^{Bu}\))\} observed in solution.

In contrast, low temperature NMR spectra for the high symmetry isomer of 18 consist of two low frequency MnH \(^1\)H NMR resonances located between \(-10.9\) and \(-14.4\) ppm (1H each), a single terminal SiH \(^1\)H NMR resonance \{4.7-6.2 ppm; integrating to 1H (\(18^{R2}\)) or 2H (\(18^R\))\}, and single \(^{31}\)P NMR (77.5-78.5 ppm) and \(^{29}\)Si NMR (23.8 ppm for \(18^{Et2}\), \(-1.6\) ppm for \(18^{Ph}\), \(-6.9\) ppm for \(18^{Bu}\), not located for \(18^{Ph2}\) due to the low concentration of this isomer) resonances. The single sharp \(^{31}\)P NMR signal and pentet coupling pattern of the higher frequency MnH signal in this isomer of 18 (\(^2J_{\text{H,P}} = 52-56\) Hz) are indicative of two equivalent dmpe ligands lying in a plane with a hydride...
ligand in an apical site.\textsuperscript{ss} By contrast, the $^{2}J_{P,H}$ coupling constants for the lower frequency MnH signal in the same isomer of 18\textsuperscript{Et2} and 18\textsuperscript{R} are significantly smaller (22-23 Hz; the analogous signal in 18\textsuperscript{Ph2} is a multiplet from which $^{2}J_{P,H}$ could not be determined), consistent with literature examples of $^{2}J_{P,H}$ for the proton involved in $\eta^{2}$-(H–SiR\textsubscript{3}) coordination in nonclassical hydrosilane complexes.\textsuperscript{tt} These data are consistent with a transHSi isomer (Scheme 6.2) featuring trans-disposed hydride and nonclassical hydrosilane ligands (as opposed to a transH\textsubscript{2} isomer with trans disposed silyl and dihydrogen ligands; \textit{vide infra}), with rapid rotation of the hydrosilane ligand about the Mn–(hydrosilane centroid) axis.

The \textit{central:transHSi} ratios observed by NMR spectroscopy are 87:13 for 18\textsuperscript{Ph2} (271 K), 75:25 for 18\textsuperscript{Et2} (229 K), 62:38 for 18\textsuperscript{Ph} (186 K), and 27:73 for 18\textsuperscript{Bu} (205 K). To our knowledge, this is only the second report of an equilibrium between two silyl dihydride isomers which differ in whether the silyl group interacts with one or both hydride co-ligands; in 2006 Sakaba reported a pair of isostructural tungsten silyl dihydride complexes, [((CO)\textsubscript{2}Cp*WH\textsubscript{2}(SiHRPh)) (R = H, Ph), existing in solution as an equilibrium between two isomers; one complex crystallized as an isomer with two close Si–H interactions (1.91(3) and 2.00(4) Å), while the other crystallized as an isomer with a single close Si–H interaction (2.02(4) Å).\textsuperscript{513}

Interconversion between the \textit{central} and \textit{transHSi} isomers of 18 could hypothetically involve initial HSiR\textsubscript{3} or H\textsubscript{2} dissociation. However, the terminal SiH environment(s) and the metal hydride environments do not undergo facile exchange at room temperature; upon selective deuteration of the metal hydride environment in 18\textsuperscript{Et2}, 18\textsuperscript{Ph}, and 18\textsuperscript{Bu}, no deuterium incorporation into the terminal SiH environment was

\textsuperscript{ss} These coupling constants are very similar to the $^{2}J_{H,P}$ coupling of 56.5 Hz in Wilkinson and Girolami’s [(dmpe)\textsubscript{2}MnH(C\textsubscript{2}H\textsubscript{4})] (10), which also contains a hydride ligand apical to a plane formed by two $\kappa^{2}$-dmpe ligands; see ref.120.

\textsuperscript{tt} For selected examples, see refs. 244, 249, 272, 273, and 512.
observed after 12 hours in solution.\(^{uu}\) This indicates that isomerization (which is rapid at room temperature for all four members of the family), does not involve hydrosilane dissociation to form 5-coordinate "(dmpe)\(_2\)MnH" (12) as an intermediate. Likewise, addition of D\(_2\) to 18\(^{Ph}\) did not result in any observable deuteration of the complex after 72 h in solution at room temperature, suggesting that H\(_2\) dissociation to form a 5-coordinate "(dmpe)\(_2\)Mn(SiR\(_3\))" intermediate (17) does not play a significant role in isomerization. However, after heating a solution of [(dmpe)\(_2\)MnD\(_2\)(SiH\(_2\)"Bu\())\] (\(d_2\_18^{Bu}\)) for three days at 70-80 °C, the MnH and terminal SiH signals both achieved 50% deuterium incorporation, suggesting that hydrosilane elimination may be possible at elevated temperatures. Furthermore, hydrosilane exchange reactions were found to occur in the presence of excess free silane, including very slow reactions at room temperature. For example, [(dmpe)\(_2\)MnH\(_2\)(SiHPh\(_2\))] (18\(^{Ph2}\)) reacted with ~6 equiv. of PhSiH\(_3\) to generate [(dmpe)\(_2\)MnH\(_2\)(SiH\(_2\)Ph\(_2\))] (18\(^{Ph}\)); after three days at room temperature this reaction had proceeded to a 2 : 1 mixture of 18\(^{Ph2}\) : 18\(^{Ph}\), whereas heating overnight at 90 °C afforded complete conversion to 18\(^{Ph}\), with no remaining 18\(^{Ph2}\) observed by \(^1\)H NMR spectroscopy.

\[\textbf{6.4 – X-ray Crystal Structures of Silyl Dihydride Complexes}\]

X-ray quality crystals of 18\(^{Ph2}\) and 18\(^{Ph}\) (Figure 6.2; Table 6.1) were obtained from toluene (18\(^{Ph2}\)) or hexanes (18\(^{Ph}\)) at –30 °C, and in both cases the central isomer (the low symmetry isomer observed in solution) was obtained. The geometry at manganese can be described as capped octahedral, with the four phosphorus donors and two cis-hydride ligands at the points of a distorted octahedron, and the silyl ligand positioned close to the H–H edge; nearly equidistant from the two hydride ligands, but with a 30.4-37.6° angle between the H(1A)–Si–H(1B) and H(1A)–Mn–H(1B) planes. The Si–H(1A) and Si–H(1B) distances of 1.75(4)-1.79(2) Å in 18\(^{Ph2}\) and 1.77(4)-1.82(3) Å in 18\(^{Ph}\) are suggestive of significant H–Si interactions, consistent with an \(\eta^3-\)

\(^{uu}\) Selective deuteration of the metal hydride environment in 18\(^{Ph2}\) was not carried out because the starting complex, 16\(^{Ph2}\), could not be purified.
coordinated silicate \( (\text{H}_2\text{SiR}_3^-) \) ligand. Crystallographically well-characterized monometallic examples of \textit{central} \( \eta^3\text{H}_2\text{SiR}_3 \) ligand systems have been reported for Fe,\(^{247}\) Co,\(^{271}\) Mo,\(^{274}\) Rh,\(^{273}\) and Ru,\(^{244,248,251,270,272,275}\) and exhibit Si–H distances ranging from 1.69(3)-2.15 Å, encompassing the distances in \( \text{18}^{\text{Ph2}} \) and \( \text{18}^{\text{Ph}} \). As in these literature examples, the substituents on silicon in \( \text{18}^{\text{Ph2}} \) and \( \text{18}^{\text{Ph}} \) form a distorted square pyramid with both \( \mu \)-H atoms in the square plane.

**Figure 6.2:** X-ray crystal structures of (a) the \textit{central} isomer of [\((\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)\)] (\textit{central-18}^{\text{Ph2}}), and (b) the \textit{central} isomer of [\((\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{Ph})\)] (\textit{central-18}^{\text{Ph}}). Ellipsoids are drawn at 50% probability. Hydrogen atoms on Mn and Si were located from the difference map and refined isotropically. All other hydrogen atoms have been omitted for clarity. Bond distances (Å) and angles (deg) for \textit{central-18}^{\text{Ph2}}: Mn(1)–Si(1) 2.3176(3), Mn(1)–H(1A) 1.46(3), Mn(1)–H(1B) 1.62(3), Si(1)–H(1A) 1.79(2), Si(1)–H(1B) 1.75(4), Si(1)–H(1C) 1.37(4), Mn(1)–Si(1)–C(1) 117.65(3), Mn(1)–Si(1)–C(7) 119.69(3), H(1A)–Mn(1)–Si(1) 50(1), H(1B)–Mn(1)–Si(1) 49(1), H(1A)–Mn(1)–H(1B) 92(2). Bond distances (Å) and angles (deg) for \textit{central-18}^{\text{Ph}}: Mn(1)–Si(1) 2.3148(8), Mn(1)–H(1A) 1.49(3), Mn(1)–H(1B) 1.54(3), Si(1)–H(1A) 1.82(3), Si(1)–H(1B) 1.77(4), Si(1)–H(1C) 1.44(3), Si(1)–H(1D) 1.48(3), Mn(1)–Si(1)–C(1) 120.48(9), H(1A)–Mn(1)–Si(1) 52(1), H(1B)–Mn(1)–Si(1) 50(1), H(1A)–Mn(1)–H(1B) 97(2).

By contrast, crystallization of \( \text{18}^{\text{Ru}} \) from hexanes at –30 °C afforded a structure (a in Figure 6.3) consistent with the \textit{transHSi} isomer (the high symmetry isomer observed in
solution). The geometry at manganese can be described as octahedral, with a hydride ligand coordinated \textit{trans} to a hydrosilane ligand. Unfortunately, four-fold disorder of the silicon moiety prevented location of the three hydrogen atoms bound to Si (two terminal on Si and one bridging between Si and Mn) from the difference map. However, DFT calculations on a model of \textit{trans}HSi-18\textsuperscript{Bu} where the \textsuperscript{Bu} group has been replaced by an Et group (\textit{trans}HSi-18\textsuperscript{Et}) afforded a structure with very similar placement of the terminal manganese hydride ligand and the heavy atoms around Mn and Si (b in Figure 6.3): the calculated Mn–Si distance is 2.36 Å (cf. 2.388(3) Å in the X-ray structure), and the Mn–Si–C(1) and Si–Mn–H(1) angles are 121.8° and 162.3° (cf. 121.8(3)° and 163.0(6)°, respectively, in the X-ray structure).

The calculated structure of \textit{trans}HSi-18\textsuperscript{Et} also features two terminal Si–H bonds (Si–H = 1.52 Å) accompanied by one hydrogen atom (H\textsubscript{MnSi}) bridging between Mn and Si, with bond lengths and angles (Si–H\textsubscript{MnSi} = 1.79 Å; Mn–H\textsubscript{MnSi} = 1.56 Å; Mn–H\textsubscript{MnSi}–Si = 49.2°) suggestive of a nonclassical hydrosilane ligand; the result of incomplete hydrosilane oxidative addition. Other crystallographically characterized monometallic complexes featuring a nonclassical \(\eta^2\)-(Si–H)-coordinated hydrosilane ligand accompanied by at least one non-interacting metal hydride ligand have been reported for Fe,\textsuperscript{514} Nb,\textsuperscript{237} Mo,\textsuperscript{274} W,\textsuperscript{515} and Ru.\textsuperscript{243,244,249,252,253,512,516}

\textsuperscript{vv} Discussed values are those from the dominant disordered conformer.
Figure 6.3: a) X-ray crystal structure of the transHSi isomer of [[(dmpe)$_2$MnH$_2$(SiH$_2^n$Bu)] (transHSi-18$_{Bu}$) with ellipsoids drawn at 50% probability. The terminal metal hydride atom was located from the difference map and refined isotropically. All other hydrogen atoms have been omitted for clarity. The Si atom is disordered over 4 positions (2 sets of 2 related by symmetry), the butyl group is disordered over 2 positions (related by symmetry), and the dmpe ligands are disordered over 8 positions (4 sets of 2 related by symmetry). Only one conformation is shown for clarity, with occupancies of 36.8(3)% and 16.0(1)% for silicon and the dmpe ligands, respectively. Bond distances (Å) and angles (deg), where Si(1A) is the Si position that is not shown in the depicted conformation: Mn(1)–Si(1) 2.388(3), Mn(1)–Si(1A) 2.386(3), Mn(1)–H(1) 1.75(5), Mn(1)–Si(1)–C(1) 121.8(3), Mn(1)–Si(1A)–C(1) 127.8, H(1)–Mn(1)–Si(1) 163.0(7), H(1)–Mn(1)–Si(1A) 158(1). b) Overlay of the X-ray crystal structure (blue) of transHSi-[(dmpe)$_2$MnH$_2$(SiH$_2^n$Bu)] (transHSi-18$_{Bu}$) and DFT calculated structure (red) of transHSi-[(dmpe)$_2$MnH$_2$(SiH$_2^Et$)] (transHSi-18$_{Et}$), with selected H atoms in the calculated structure depicted as spheres. Methyl groups on the dmpe ligands, and most hydrogen atoms, have been omitted for clarity.
6.5 – DFT Calculations on Silyl Dihydride Complexes

To investigate the nature of Si–H ‘interligand’ interactions in the central and transHSi isomers of 18, and the thermodynamic stability of alternative isomers (transH₂, lateralH₂, and lateralHSi; Figure 6.4), we turned to DFT calculations {ADF, gas-phase, all-electron, PBE, D3-BJ, TZ2P, ZORA; 18Bu was modelled as [(dmpe)₂MnH₂(SiH₂Et)] (18Et), with an ethyl group in place of the “Bu group}. These calculations yielded energy minima (see Figure 6.5) corresponding to four sets of isomers; the two experimentally observed isomers shown in Scheme 6.2 (central and transHSi, with good agreement in the relevant bond lengths and angles; Table 6.1) and two higher energy isomers: transH₂ and lateralH₂ (Figure 6.4, Table 6.2, and for 18Et₂, Figure 6.6). However, in no case was an energy minimum located for a lateralHSi isomer (Figure 6.4).

Figure 6.4: Structures of experimentally unobserved transH₂, lateralH₂, and lateralHSi isomers of [(dmpe)₂MnH₂(SiHRR’)] (18Ph₂: R = R’ = Ph; 18Et₂: R = R’ = Et; 18Ph: R = Ph, R’ = H; 18Et: R = Et, R’ = H). Of these, energy minima were only located for the transH₂ and lateralH₂ isomers by DFT calculations. For structures of the experimentally observed central and transHSi isomers (for which energy minima were also located via DFT), see Scheme 6.2.
Figure 6.5: Relative total bonding energies (kJ mol\(^{-1}\)) of the central, transHSi, trans\(H_2\), and lateral\(H_2\) isomers of [(dmpe)\(_2\)MnH\(_2\)(SiHPh\(_2\))] (18\(^{Ph2}\); blue ♦), [(dmpe)\(_2\)MnH\(_2\)(SiHEt\(_2\))] (18\(^{Et2}\); red ■), [(dmpe)\(_2\)MnH\(_2\)(SiHPh)] (18\(^{Ph}\); green ▲), and [(dmpe)\(_2\)MnH\(_2\)(SiH\(_2\)Et)] (18\(^{Et}\); purple ●).

As in the X-ray structures of 18\(^{Ph2}\) and 18\(^{Ph}\), the central isomers have an octahedral arrangement of the phosphorous and H\(_{Mn}\) atoms, with silicon located approximately between the two bridging H\(_{MnSi}\) atoms (the angle between the H\(_{MnSi}/Mn/H_{MnSi2}\) and H\(_{MnSi}/Si/H_{MnSi2}\) planes ranges from 17 to 36°). The transHSi isomers feature an approximately octahedral arrangement of the phosphorous donors, H\(_{Mn}\), and an \(\eta^2\)-nonclassical hydrosilane ligand, with H\(_{Mn}\) approximately trans to the centroid of the Si–H\(_{MnSi}\) bond, and the four phosphorous donors distorted away from the nonclassical hydrosilane unit. Similarly, the trans\(H_2\) isomer is octahedral with trans-disposed dihydrogen and silyl ligands. By contrast, the lateral\(H_2\) isomer features cis-disposed H\(_2\) and silyl ligands, with Mn, Si, and both H atoms of the dihydrogen ligand located nearly in a plane. The geometry at manganese is approximately octahedral, although the dihydrogen ligand is displaced in the direction of the neighboring silyl.
ligand (centroid$_{H_2}$–Mn–Si = 79–82°). In all four calculated isomers of $^{18}_{\text{Ph}^2}$, $^{18}_{\text{Ph}}$, $^{18}_{\text{Et}^2}$, and $^{18}_{\text{Et}}$, the Mn–Si–C angles lie between 114 and 126°, while the Mn–Si–H$_{Si}$ angles range from 111 to 118°.

Table 6.1: Selected angles (deg) and distances (Å) (and Mayer bond orders) for experimentally observed central and transHSi isomers from calculated {or X-ray} structures of 18. Atom labels correspond to those for $^{18}_{\text{Et}^2}$ in Figure 6.6.

<table>
<thead>
<tr>
<th>[(dmpe)$_2$MnH$_2$(SiHR)]$'$</th>
<th>18$^{\text{Ph}^2}$</th>
<th>18$^{\text{Et}^2}$</th>
<th>18$^{\text{Ph}}$</th>
<th>18$^{\text{Bu}}$/18$^{\text{Et}^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiHR$'$</td>
<td>SiHPh$_2$</td>
<td>SiHEt$_2$</td>
<td>SiH$_2$Ph</td>
<td>SiH$_2$Bu/3</td>
</tr>
<tr>
<td>Mn–Si</td>
<td>2.31 (0.63)</td>
<td>2.35 (0.69)</td>
<td>2.31 (0.69)</td>
<td>2.32 (0.69)</td>
</tr>
<tr>
<td></td>
<td>{2.3176(3)}</td>
<td>{2.3148(8)}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–H$_{MeSi}$</td>
<td>1.57, 1.59</td>
<td>1.56, 1.57</td>
<td>1.57, 1.58</td>
<td>1.57 (0.68, 0.70)</td>
</tr>
<tr>
<td></td>
<td>(0.62, 0.67)</td>
<td>(0.70, 0.71)</td>
<td>(0.66, 0.70)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>{1.46(3), 1.62(3)}</td>
<td>{1.49(3), 1.54(3)}</td>
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<tr>
<td>Si–H$_{MeSi}$</td>
<td>1.82, 1.85</td>
<td>1.85, 1.88</td>
<td>1.84, 1.87</td>
<td>1.83, 1.88</td>
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<tr>
<td></td>
<td>(0.28, 0.33)</td>
<td>(0.25, 0.26)</td>
<td>(0.28, 0.29)</td>
<td>(0.27, 0.28)</td>
</tr>
<tr>
<td></td>
<td>{1.75(4), 1.79(2)}</td>
<td>{1.77(4), 1.82(3)}</td>
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</tr>
<tr>
<td>central isomer</td>
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<tr>
<td>Si–H$_{Si}$</td>
<td>1.52 (0.81)</td>
<td>1.51 (0.81)</td>
<td>1.50, 1.51</td>
<td>1.51, 1.52</td>
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<tr>
<td></td>
<td>{1.37(4)}</td>
<td>{1.37(4)}</td>
<td>(0.83, 0.88)</td>
<td>(0.84)</td>
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<td></td>
<td></td>
<td></td>
<td>{1.44(3), 1.48(3)}</td>
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<tr>
<td>H$_{MeSi}$–Mn–Si</td>
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<td>52.3, 53.4</td>
<td>51.8, 53.5</td>
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<tr>
<td></td>
<td>{49(1), 50(1)}</td>
<td>{50(1), 52(1)}</td>
<td>{50(1), 52(1)}</td>
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</tr>
<tr>
<td>H$<em>{MeSi}$–Mn–H$</em>{MeSi}$</td>
<td>98.3 (92(2))</td>
<td>103.8</td>
<td>101.1 {97(2)}</td>
<td>103.0</td>
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<tr>
<td></td>
<td>116.5, 118.4</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Mn–Si–C</td>
<td>{117.65(3), 119.69(3)}</td>
<td>117.5, 120.3</td>
<td>119.6 {120.48(9)}</td>
<td>119.9</td>
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<tr>
<td></td>
<td></td>
<td>119.6 {120.48(9)}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–Si–H$_{Si}$</td>
<td>116.3 {114(2)}</td>
<td>111.7</td>
<td>114.9, 117.7</td>
<td>113.8, 116.9</td>
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<td></td>
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<td>{115(1), 120(1)}</td>
<td></td>
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<tr>
<td>H$<em>{MeSi}$/$H</em>{MeSi}$plane</td>
<td>36.4 {37.6}</td>
<td>16.6</td>
<td>30.7 {30.4}</td>
<td>22.2</td>
</tr>
<tr>
<td>to $H_{MeSi}/Si$/$H_{MeSi}$</td>
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<td></td>
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</tr>
<tr>
<td>transHSi isomer</td>
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<td></td>
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<tr>
<td>Mn–Si</td>
<td>2.36 (0.77)</td>
<td>2.39 (0.71)</td>
<td>2.35 (0.81)</td>
<td>2.36 (0.78)</td>
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<td></td>
<td></td>
<td>{2.386(3), 2.388(3)}</td>
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</tr>
<tr>
<td>Mn–H$_{MeSi}$</td>
<td>1.57 (0.57)</td>
<td>1.57 (0.64)</td>
<td>1.57 (0.62)</td>
<td>1.56 (0.63)</td>
</tr>
<tr>
<td></td>
<td>1.57 (0.83)</td>
<td>1.57 (0.80)</td>
<td>1.57 (0.83)</td>
<td>1.57 (0.83)</td>
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<tr>
<td></td>
<td>{1.75(5)}</td>
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<tr>
<td>Si–H$_{MeSi}$</td>
<td>1.80 (0.34)</td>
<td>1.75 (0.33)</td>
<td>1.82 (0.31)</td>
<td>1.79 (0.30)</td>
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<td></td>
<td>1.51, 1.52</td>
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<tr>
<td></td>
<td>(0.79, 0.86)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.52 (0.81, 0.82)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_{MeSi}$–Mn–Si</td>
<td>49.6</td>
<td>47.1</td>
<td>50.8</td>
<td>49.2</td>
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<tr>
<td></td>
<td>{158(1), 163.0(7)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_{Me}$–Mn–Si</td>
<td>162.3</td>
<td>162.4</td>
<td>161.7</td>
<td>162.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>{162.3}</td>
<td></td>
</tr>
<tr>
<td>H$<em>{Me}$–Mn–Si–SiH$</em>{MeSi}$</td>
<td>178.1</td>
<td>178.7</td>
<td>177.2</td>
<td>178.4</td>
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<tr>
<td>(centroid)</td>
<td>{121.8(3)}, 127.8</td>
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<tr>
<td>Mn–Si–C</td>
<td>118.3, 119.0</td>
<td>116.2, 118.1</td>
<td>120.0</td>
<td>121.8</td>
</tr>
<tr>
<td></td>
<td>{121.8(3), 127.8}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–Si–H$_{Si}$</td>
<td>115.6</td>
<td>112.6</td>
<td>115.9, 116.1</td>
<td>114.2, 115.3</td>
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</table>
Figure 6.6: Geometry optimized structures of the isomers of [(dmpe)$_2$MnH$_2$(SiHEt$_2$)]($^{18}_{\text{Et}_2}$) determined by DFT calculations. Spheres represent Mn (red), Si (pink), P (orange), and H (white), whereas carbon atoms are represented by grey vertices. $P$-methyl groups and most H atoms have been omitted for clarity.
Table 6.2: Selected angles (deg) and distances (Å) (and Mayer bond orders) for experimentally unobserved trans\(H_2\) and lateral\(H_2\) isomers from calculated structures of 18. Atom labels correspond to those for 18\(\text{Et}^2\) in Figure 6.6.

<table>
<thead>
<tr>
<th>SiHRR’</th>
<th>(18^{\text{Ph}^2})</th>
<th>(18^{\text{Ph}^2})</th>
<th>(18^{\text{Ph}})</th>
<th>(18^{\text{Bu}}/18^{\text{Et}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–Hsi</td>
<td>1.51 (0.78)</td>
<td>1.52 (0.77)</td>
<td>1.51, 1.52 (0.81)</td>
<td>1.52, 1.53 (0.79, 0.80)</td>
</tr>
<tr>
<td>Mn–Si</td>
<td>2.41 (0.95)</td>
<td>2.41 (0.89)</td>
<td>2.37 (0.96)</td>
<td>2.36 (0.93)</td>
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<tr>
<td>Mn–Hsi</td>
<td>1.58, 1.59 (0.55)</td>
<td>1.58 (0.61)</td>
<td>1.59 (0.56)</td>
<td>1.59 (0.59, 0.60)</td>
</tr>
<tr>
<td>Si–Hsi</td>
<td>3.93, 3.96 (&lt;0.05)</td>
<td>3.94, 3.95 (&lt;0.05)</td>
<td>3.91, 3.92 (&lt;0.05)</td>
<td>3.90 (&lt;0.05)</td>
</tr>
<tr>
<td>H_{Mn–H}</td>
<td>0.96 (0.43)</td>
<td>0.99 (0.38)</td>
<td>0.96 (0.44)</td>
<td>0.98 (0.41)</td>
</tr>
<tr>
<td>H_{Mn–Mn–H}</td>
<td>35.3</td>
<td>36.7</td>
<td>35.3</td>
<td>36.1</td>
</tr>
<tr>
<td>H_{(centroid)–Mn–Si}</td>
<td>177.0</td>
<td>177.3</td>
<td>175.1</td>
<td>174.2</td>
</tr>
<tr>
<td>Mn–Si–C</td>
<td>122.9, 124.2</td>
<td>120.9, 121.6</td>
<td>123.6</td>
<td>124.8</td>
</tr>
<tr>
<td>Mn–Si–Hsi</td>
<td>111.4</td>
<td>113.9</td>
<td>115.0, 115.8</td>
<td>114.8, 115.7</td>
</tr>
<tr>
<td>Si–Hsi</td>
<td>1.52 (0.76)</td>
<td>1.53 (0.76)</td>
<td>1.52 (0.79, 0.82)</td>
<td>1.52, 1.53 (0.80, 0.81)</td>
</tr>
<tr>
<td>Mn–Hsi</td>
<td>2.39 (0.91)</td>
<td>2.40 (0.90)</td>
<td>2.35 (0.91)</td>
<td>2.36 (0.91)</td>
</tr>
<tr>
<td>Mn–Hsi</td>
<td>1.57 (0.48)</td>
<td>1.56 (0.53)</td>
<td>1.57 (0.51)</td>
<td>1.57 (0.53)</td>
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<tr>
<td>Mn–Hsi</td>
<td>1.59 (0.62)</td>
<td>1.59 (0.63)</td>
<td>1.59 (0.62)</td>
<td>1.59 (0.62)</td>
</tr>
<tr>
<td>Si–Hsi</td>
<td>2.17 (0.12)</td>
<td>2.12 (0.13)</td>
<td>2.16 (0.14)</td>
<td>2.13 (0.14)</td>
</tr>
<tr>
<td>Si–Hsi</td>
<td>3.05 (&lt;0.05)</td>
<td>3.03 (&lt;0.05)</td>
<td>3.07 (&lt;0.05)</td>
<td>3.04 (&lt;0.05)</td>
</tr>
<tr>
<td>H_{Mn–H}</td>
<td>0.99 (0.40)</td>
<td>1.00 (0.39)</td>
<td>1.01 (0.41)</td>
<td>1.00 (0.41)</td>
</tr>
<tr>
<td>H_{Mn–Si}</td>
<td>62.6</td>
<td>60.6</td>
<td>63.5</td>
<td>62.1</td>
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<td>H_{Mn–H}</td>
<td>36.6</td>
<td>36.8</td>
<td>37.2</td>
<td>37.0</td>
</tr>
<tr>
<td>H_{(centroid)–Mn–Si}</td>
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<td>79.0</td>
<td>82.2</td>
<td>80.7</td>
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<tr>
<td>Mn–Si–C_1</td>
<td>117.1</td>
<td>113.8</td>
<td>120.8</td>
<td>119.4</td>
</tr>
<tr>
<td>Mn–Si–C_2</td>
<td>125.9</td>
<td>123.6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mn–Si–Hsi</td>
<td>113.9</td>
<td>113.2</td>
<td>115.8, 116.7</td>
<td>116.2</td>
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<tr>
<td>H_{Mn–Si–C_1}</td>
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<td>5.5</td>
<td>–12.0</td>
<td>0.5</td>
</tr>
<tr>
<td>H_{Mn–Si–C_2}</td>
<td>–103.4</td>
<td>–118.6</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

For all complexes (\(18^{\text{Ph}^2}\), \(18^{\text{Ph}}\), \(18^{\text{Et}^2}\), and \(18^{\text{Et}}\)), the central and trans\(HSi\) isomers are within 4 kJ mol\(^{-1}\) of each other (Figure 6.5), consistent with their observation by solution NMR spectroscopy (\textit{vide supra}). In contrast, the two higher energy isomers (trans\(H_2\) and lateral\(H_2\)) are 8–44 kJ mol\(^{-1}\) higher in energy than the most stable experimentally observed isomer, with a larger energy difference in the case of more
sterically hindered $18^R_2$ complexes (Figure 6.5). These isomers likely exist in equilibrium with the experimentally observed isomers, but in concentrations too low for NMR spectroscopic observation. In fact, a trans$H_2$ or lateral$H_2$ isomer is presumably formed initially in the synthesis of 18 via the reactions of $H_2$ with silylene hydride complexes $16^R_2$ or disilyl hydride complexes $20^R$ (vide supra).

Both experimentally observed isomers (central and trans$HSi$) feature nonclassical bonding situations. This is apparent from Mayer bond orders of 0.25-0.34 between silicon and the bridging hydride ligands (Si–H$_{MnSi}$), as well as Mn–Si Mayer bond orders ranging from 0.63 to 0.81 (cf. 0.89 to 0.96 for the trans$H_2$ and lateral$H_2$ isomers, which feature silyl ligands without strong interactions to neighboring hydride ligands; vide infra). The trans$HSi$ isomers can simply be described as nonclassical hydrosilane complexes; structures intermediate between classical $\eta^2$-hydrosilane and classical silyl hydride extremes, as a consequence of substantial but incomplete Si–H bond oxidative addition. By contrast, the similar Si–H$_{MnSi}$ and Mn–H$_{MnSi}$ Mayer bond orders involving both H$_{MnSi}$ atoms in the central isomers are indicative of a nonclassical $\eta^3$-$H_2SiHRR'$ (silicate) anion.

In contrast to the nonclassical central and trans$HSi$ isomers, the trans$H_2$ and lateral$H_2$ isomers can be described as silyl $\eta^2$-$H_2$ complexes. These isomers feature significant H–H interactions, reflected by H–H distances of 0.96-1.01 Å (relative to 0.75 Å for free $H_2$), Mayer H–H bond orders of 0.38-0.44, and acute H–Mn–H angles of 35.3-37.2° (Table 6.2). Nevertheless, the lateral$H_2$ isomers feature small but non-negligible Si–H$_{Mn1}$ Mayer bond orders (0.12-0.14), a Mn–H$_{Mn1}$ Mayer bond order which is 0.09-0.14 lower than that of Mn–H$_{Mn2}$, as well as acute (79-82°) angles between the centroid of the $H_2$ ligand, Mn and Si (Table 6.2). These features suggest a minor degree of bonding between Si and H$_{Mn1}$, and the lower extent of Si–H$_{Mn1}$ bonding in the lateral$H_2$ versus the central or trans$HSi$ isomers is also reflected in Si–Mn–H$_{Mn1}$ angles

The calculated Si–H$_{MnSi}$ distances are different from one another by 0.03-0.05 Å, consistent with a limited degree of second order Jahn-Teller distortion, as described in reference 232.
of 60.6-63.5° in the former, which are much more obtuse than the corresponding Si–Mn–H angles in the latter (central; 51.8-53.5°, transHSi; 47.1-50.8°).

The lack of substantial interligand Si–H interactions in the lateralH₂ isomers lies in contrast to the literature on transition metal complexes with a meridional Si–H–H arrangement of SiR₃ and H moieties, which suggests that complexes featuring a hydrosilane and a hydride ligand (i.e. the proposed lateralHSi isomer in Figure 6.4) should typically be favored relative to a silyl dihydrogen complex (i.e. the lateralH₂ isomer). Such a preference has been rationalized based primarily on H–H and Si–H bond strengths. In this work, the expected trend is reflected in the experimental observation of the transHSi isomer of 5 but not the transH₂ isomer.

Our inability to locate an energy minimum for a lateralHSi isomer (vide supra) was surprising, and prompted us to investigate sterically less encumbered PH₃ analogues of 18; ([PH₃]₄MnH₂(SiHRR’)): 18⁴₈Ph₂:PH₃; R = R’ = Ph, 18⁴₈Et₂:PH₃; R = R’ = Et, 18⁴₈Ph:PH₃, R =H, R’ = Ph, and 18⁴₈Et:PH₃, R = H, R’ = Et). These calculations afforded energy minima corresponding to the four previously calculated isomers (central, transHSi, transH₂, and lateralHSi), as well as a lateralHSi isomer (relative energies are plotted in Figure 6.7). In all cases these lateralHSi isomers were lower in energy than the lateralH₂ isomers, and feature a significant Si–Hₐₓ interaction (Si–Hₐₓ dist. 1.88-1.93 Å, Mayer bond order 0.25-0.32, Si–Mn–Hₐₓ angle 51.3-54.0°) and minimal Hᵧ−Hₐₓ interactions (H–H dist. 1.57-1.63 Å, Mayer bond order 0.05-0.08, Hᵧ−Mn–Hₐₓ angle 60.7-63.4°), consistent with cis-disposed hydride and nonclassical hydrosilane ligands. Computational

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xx See refs. 234, 250, 267, and 517. Examples of dihydrogen silyl complexes have also been observed, and some computational results have suggested that these complexes should have similar energies to hydrosilane hydride complexes; see refs. 245 and 518.
observation of the lateralHSi isomers for the PH$_3$ analogues, but not the dmpe complexes, suggests that the lateralHSi isomers are sterically disfavored in the dmpe complexes.\textsuperscript{yy}

Figure 6.7: Relative total bonding energies (kJ mol$^{-1}$) of the central, transHSi, transH$_2$, lateralH$_2$, and lateralHSi isomers of silyl dihydride complexes where the two dmpe ligands have been replaced with four PH$_3$ ligands; [(PH$_3$)$_4$MnH$_2$(SiHPh$_2$)] (18$^{Ph2;PH3}$; blue ♦), [(PH$_3$)$_4$MnH$_2$(SiHEt$_2$)] (18$^{Et2;PH3}$; red ■), [(PH$_3$)$_4$MnH$_2$(SiH$_2$Ph)] (18$^{Ph;PH3}$; green ▲), and [(PH$_3$)$_4$MnH$_2$(SiH$_2$Et)] (18$^{Bu;PH3}$; purple ●).

6.6 – Determination of Sign and Magnitude of $J_{Si,H}$

As noted previously (section 1.5.5), the $^{29}$Si–$^1$H coupling constant ($J_{Si,H}$) can provide a sensitive experimental measure of where a structure lies along the continuum from a classical hydrosilane complex to a classical silyl hydride complex. However, this requires knowledge of both the magnitude and sign of $J_{Si,H}$.

Scherer has used standard 2D $^1$H–$^1$H COSY NMR spectroscopy to unambiguously determine the sign of $J_{Si,H}$ in transition metal silyl hydride/hydrosilane complexes; specifically, those where silicon bears at least one terminal hydrogen substituent.\textsuperscript{241,256} This method takes advantage of passive coupling; coupling which is not

\textsuperscript{yy} The experimentally and computationally unobserved lateralHSi isomer of dmpe-coordinated 18 would require H$_{Mn1–Mn–Si–X}$ dihedral angles of approximately 60° ($\times$2) and 180° ($\times$1), where X represents any one of the 3 substituents on silicon, bringing the hydrocarbyl substituent(s) on silicon into closer proximity to the dmpe ligands than in a lateralH$_2$ isomer.
directly responsible for the formation of a particular cross-peak. For example, in an AMX spin system (A and M are proton environments, and X is a spin ½ nucleus) where active A–M coupling gives rise to a $^1\text{H}--^1\text{H}$ COSY cross-peak, passive A–X and M–X coupling results in additional splitting of the cross-peak into a doublet where a diagonal line can be drawn between the two peaks which compose the doublet; the slope of which can be used to determine the relative sign of the two passive coupling constants ($J_{XA}$ and $J_{XM}$).

In Scherer's experiment, this involves measurement of the vector between $^{29}\text{Si}$ satellites of a $^1\text{H}--^1\text{H}$ COSY cross-peak between a terminal SiH signal (H$_{Si}$) and a metal-coordinated hydride signal (H$_{M}$). If the slope of this vector is positive, then the two passive $J_{Si,H}$ couplings ($J_{Si,H}$ to H$_{M}$, the sign of which is unknown, and $^1J_{Si,H}$ to H$_{Si}$, which is known to be negative) have the same sign, so $J_{Si,H}$ to H$_{M}$ is negative. By contrast, if the slope is negative, the two passive $J_{Si,H}$ couplings have opposite signs, and $J_{Si,H}$ to H$_{M}$ is positive; $^1J_{Si,H}$ coupling to the terminal SiH proton (H$_{Si}$) therefore serves as an internal reference. The magnitudes of the two passive $J_{Si,H}$ couplings can also be measured directly from the 2D $^1\text{H}--^1\text{H}$ dqf COSY NMR spectrum, since the horizontal and vertical distances between the $^{29}\text{Si}$ satellites provide the magnitudes of $J_{Si,H}$ to H$_{M}$ and H$_{Si}$.

However, for silyl dihydride complexes 18, we had difficulty obtaining standard $^1\text{H}--^1\text{H}$ dqf COSY NMR spectra with well-defined $^{29}\text{Si}$ satellites (Figure 6.8); in some cases the signal could not be detected from the noise, while in others the signals were too broad for accurate measurement, or could not be resolved from the parent cross-peak. In an effort to more clearly resolve the $^{29}\text{Si}$ satellites of the COSY NMR cross-peaks, two modifications of a standard 2D COSY experiment were investigated. One modification involved applying broadband $^{31}\text{P}$ decoupling during FID acquisition of a dqf COSY $^1\text{H}--^1\text{H}$ NMR experiment (a 2D $^1\text{H}--^1\text{H}\{^{31}\text{P}\}$ dqf COSY NMR experiment), as a means to increase the signal/noise and improve resolution of the cross-peaks by concentrating the signal (which is spread into a multiplet by coupling to four $^{31}\text{P}$ atoms) over a smaller area. The second modification was $^{29}\text{Si}$ editing to filter out all of the signal which is not
interacting with $^{29}\text{Si}$. This 2D $^{29}\text{Si}\_\text{edited}$ $^1\text{H}^-^1\text{H}$ COSY NMR experiment eliminates the parent cross-peak (which contains 95% of the intensity), allowing $^{29}\text{Si}$ satellites which overlap with the parent cross-peak to be resolved. Furthermore, it increases the signal-to-noise for the $^{29}\text{Si}$ satellites by removing unnecessary signal, allowing for a much higher receiver gain.

Figure 6.8 shows a comparison of the cross-peaks required to measure the sign of $J_{\text{Si},\text{H}}$ for various protons in $^1\text{H}^-^1\text{H}$ dqf COSY, $^1\text{H}^-^1\text{H}\{^{31}\text{P}\}$ dqf COSY, and $^{29}\text{Si}\_\text{edited}$ $^1\text{H}^-^1\text{H}$ COSY NMR spectra for the two experimentally observed isomers of $[(\text{dmpe})_2\text{MnH}_2(\text{SiHEt}_2)]$ (18$^{\text{Et}_2}$) at 229 K. These experiments used the same NMR sample, the same number of scans, and identical $\text{td}_{\text{eff}}$ values (leading to nearly identical experiment times), and it can be seen that the $^1\text{H}^-^1\text{H}\{^{31}\text{P}\}$ dqf COSY experiment provided only a marginal improvement in resolution relative to a standard $^1\text{H}^-^1\text{H}$ dqf COSY spectrum; likely because decoupling was only possible in the direct dimension, so the signal remained spread out in the indirect dimension (the y-axis). By contrast, the $^{29}\text{Si}\_\text{edited}$ $^1\text{H}^-^1\text{H}$ COSY experiment provided substantially more intense $^{29}\text{Si}$ satellites and allowed for more accurate identification of $^{29}\text{Si}$ satellite peak positions, as well as observation of satellites buried under the parent cross-peak in the standard $^1\text{H}^-^1\text{H}$ dqf COSY spectrum. Therefore, all further discussion focuses on the results of $^{29}\text{Si}\_\text{edited}$ $^1\text{H}^-^1\text{H}$ COSY experiments.

The top row of Figure 6.8 shows the cross-peak, in $\text{central-18}^{\text{Et}_2}$, between the terminal SiH proton (H$_\text{Si}$) and the hydride ligands bridging between Si and Mn (2 x H$_\text{MnSi}$; equivalent on the NMR timescale). The middle row of Figure 6.8 shows the cross-peak, in $\text{transHSi-18}^{\text{Et}_2}$, between the terminal SiH proton (H$_\text{Si}$) and the single hydride bridging between Si and Mn (H$_\text{MnSi}$). The positive slope of the line between the $^{29}\text{Si}$ satellites on both of these cross-peaks is indicative of negative $J_{\text{Si},\text{H}}$ values for the H$_\text{MnSi}$ protons in $\text{central-18}^{\text{Et}_2}$ and $\text{transHSi-18}^{\text{Et}_2}$ (−47 and −54 Hz, respectively). By contrast, the bottom row of Figure 6.8 shows the cross-peak between H$_\text{MnSi}$ and the terminal hydride ligand, H$_\text{Mn}$, in $\text{transHSi-18}^{\text{Et}_2}$. In this case, because $J_{\text{Si},\text{H}}$ has been determined to
be negative for H\textsubscript{MnSi} in \textit{transHSi-18\textsuperscript{Et2}} (\textit{vide supra}), the negative slope of the line between the \textsuperscript{29}Si satellites indicates that $J_{\text{Si,H}}$ for H\textsubscript{Mn} in \textit{transHSi-18\textsuperscript{Et2}} is positive (5 Hz), as expected for a 2-bond \textsuperscript{29}Si–\textsuperscript{1}H coupling.

\textbf{Figure 6.8:} Comparisons of \textsuperscript{1}H–\textsuperscript{1}H COSY spectra (500 MHz, $d_8$-toluene) of [(dmpe)$_2$MnH$_2$(SiHEt$_2$)] (18\textsuperscript{Et2}) at 229 K showing cross-peaks (with \textsuperscript{29}Si satellites) used to measure the sign and magnitude of $J_{\text{Si,H}}$ via coupling between (top row) central isomer H\textsubscript{Si} and H\textsubscript{MnSi} environments, (middle row) \textit{transHSi} isomer H\textsubscript{Si} and H\textsubscript{MnSi} environments, and (bottom row) \textit{transHSi} isomer H\textsubscript{MnSi} and H\textsubscript{Mn} environments. From left to right within a row, the same spectral regions are shown with equivalent acquisition parameters (e.g. ns, td1eff) in the standard \textsuperscript{1}H–\textsuperscript{1}H dqf COSY spectrum (black), the \textsuperscript{1}H–\textsuperscript{1}H\{\textsuperscript{31}P\} dqf COSY spectrum (red), and the \textsuperscript{29}Si\_edited \textsuperscript{1}H–\textsuperscript{1}H COSY spectrum (blue). Peak labels match those in Figure 6.6. In the structures to the left of each row, the blue arrow indicates the two \textsuperscript{1}H environments whose active coupling gives rise to the cross-peak shown, the red
The green arrow indicates the passive \(^1\text{H}\text{–}^{29}\text{Si}\) coupling used as an internal reference in the measurement, and the green arrow indicates the passive \(^1\text{H}\text{–}^{29}\text{Si}\) coupling being measured. The lines on the cross-peaks in the \(^{29}\text{Si}\) edited \(^1\text{H}\text{–}^1\text{H}\) COSY spectra represent the vector between the \(^{29}\text{Si}\) satellites (black line; used to determine relative sign), the magnitude of the coupling used as the internal reference (red line), and the magnitude of \(J_{\text{Si,H}}\) for which the sign is being determined (green line).

Analogous trends were observed for the central and transHSi isomers of \(18^{\text{Ph}}\) and \(18^\text{R}\) (Table 6.3). However, we were unable to observe coupling constants from particularly weak cross-peaks, precluding determination of the sign of \(J_{\text{Si,H}}\) for H\(_\text{MnSi}\) in the central isomers of \(18^{\text{Ph}}\) and \(18^{\text{Bu}}\) or for H\(_\text{Mn}\) in the transHSi isomer of \(18^{\text{Ph}}\) (present as a minor isomer; 13%). DFT-calculated coupling constants are also provided in Table 6.3, and are in good agreement with those determined experimentally.

Table 6.3: \(^{29}\text{Si}\text{–}^1\text{H}\) coupling constants \((J_{\text{Si,H}})\) measured by \(^{29}\text{Si}\) edited \(^1\text{H}\text{–}^1\text{H}\) COSY NMR spectroscopy (and calculated by DFT) for silyl dihydride complexes \(18\) (Hz).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(18^{\text{Ph}})</th>
<th>(18^{\text{Et}})</th>
<th>(18^{\text{Bu}})</th>
<th>(18^{\text{Bu}})/(18^{\text{Et}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silyl group</td>
<td>SiH(_{\text{Ph}})</td>
<td>SiH(_{\text{Et}})</td>
<td>SiH(_{\text{Ph}})</td>
<td>SiH(_{\text{Ph}})</td>
</tr>
<tr>
<td>(J_{\text{Si,H}}) for H(_{\text{MnSi}}) in the central isomer</td>
<td>n.o. (^b) (–45, –49)</td>
<td>–47 (–35, –45)</td>
<td>&lt;0 (–41, –44)</td>
<td>n.o. (^d) (&lt;38, –43)</td>
</tr>
<tr>
<td>(J_{\text{Si,H}}) for H(_{\text{MnSi}}) in the transHSi isomer</td>
<td>–41 (–38)</td>
<td>–54 (–47)</td>
<td>–38 (–26)</td>
<td>–43 (–33)</td>
</tr>
<tr>
<td>(J_{\text{Si,H}}) for H(_{\text{Mn}}) in the transHSi isomer</td>
<td>n.o. (^b) (13)</td>
<td>5 (12)</td>
<td>9 (13)</td>
<td>9 (14)</td>
</tr>
</tbody>
</table>

a. In the calculated complex, \(18^{\text{Et}}\), the silyl group is SiH\(_{\text{Et}}\).

b. n.o. = not observed.

c. This cross-peak was too broad to accurately measure.

For the central isomer of \(18^{\text{Et}}\), the \(J_{\text{Si,H}}\) coupling constant for H\(_{\text{MnSi}}\) is –47 Hz, and the average calculated values for \(18\) range from –40 to –47 Hz. Literature values of \(J_{\text{Si,H}}\) for H\(_{\text{MnSi}}\) in η\(^3\)-coordinated silicate (H\(_2\)SiR\(_3\)) complexes typically range in magnitude from 11 to 54 Hz.\(^{244,247,248,272,273,275}\) To the best of our knowledge, the sign of \(J_{\text{Si,H}}\) has not been experimentally determined for these literature complexes, but calculations have, in at least one case, been performed and indicate a negative sign.\(^{247}\)

Assuming that all of these \(J_{\text{Si,H}}\) values are negative, the \(J_{\text{Si,H}}\) coupling constants for H\(_{\text{MnSi}}\) in \(18\) lie towards the more negative end of the reported range, indicative of nonclassical silicate complexes with relatively strong Si–H\(_{\text{MnSi}}\) interactions.
For the \textit{transHSi} isomer of 18, the $J_{\text{Si,H}}$ coupling constants for $\text{H}_{\text{MnSi}}$ range from $-38$ to $-54$ Hz (calcd. $-26$ to $-47$ Hz), falling within the region typically associated with nonclassical hydrosilane complexes ($0$ to $-70$ Hz; \textit{vide infra}), indicative of partial oxidative addition of the Si–H$_{\text{MnSi}}$ bond. Using both experimental and calculated values, two clear trends can be observed in $J_{\text{Si,H}}$ for H$_{\text{MnSi}}$ in the \textit{transHSi} isomers; more negative $J_{\text{Si,H}}$ coupling constants were seen for aliphatic versus aromatic analogues, and for disubstituted versus monosubstituted analogues. This trend appears to reflect the trend in calculated bond metrics (\textit{vide supra}), for which stronger Si–H interactions were observed in aliphatic and disubstituted analogues (relative to aromatic and monosubstituted analogues respectively). The former can be rationalized based on a larger degree of $\pi$ backdonation to hydrosilanes with aryl substituents, whereas the latter is presumably steric in origin, with disubstituted hydrosilanes decreasing the extent of Si–H bond oxidative addition.

6.7 – Summary and Conclusions for Chapter 6

Silyl dihydride complexes of manganese, [(dmpe)$_2$MnH$_2$(SiHRR')] (18), were synthesized via the reactions of H$_2$ with silylene hydride ($\text{16}^{\text{R}2}$) and disilyl hydride ($\text{20}^{\text{R}}$) complexes. These reactions suggest that both $\text{16}^{\text{R}2}$ and $\text{20}^{\text{R}}$ exist in equilibrium with a shared low-coordinate silyl species, [(dmpe)$_2$Mn(SiH$_{3-x}$R$_x$)] (17), accessed via 1,1-insertion from $\text{16}^{\text{R}2}$, and hydrosilane reductive elimination from $\text{20}^{\text{R}}$.

Complexes 18 provide an uncommon opportunity to study silyl dihydride complexes differing in the number (1 vs 2) and nature (aromatic vs alkyl) of the hydrocarbyl substituents on silicon. In solution, these complexes exist as an equilibrium mixture of a \textit{central} isomer featuring a meridional H–Si–H arrangement of the silyl and hydride ligands, and a \textit{transHSi} isomer with \textit{trans}-disposed hydrosilane and hydride ligands. These isomers contain a single silicon centre involved in either one or two Si–H–Mn bridging interactions, and combined XRD, DFT, and NMR spectroscopic studies indicate that the \textit{central} and \textit{transHSi} isomers can be considered to contain a nonclassical
silicate ($\eta^3$-$H_2SiR_3$) anion, and a nonclassical hydrosilane ligand, respectively. Additionally, DFT calculations indicate the thermodynamic accessibility of lateral$H_2$ and trans$H_2$ isomers with cis- and trans-disposed silyl and dihydrogen ligands, respectively (these isomers may be present in solution at concentrations below that detectable by NMR spectroscopy). Furthermore, a lateral$HSi$ isomer featuring cis-disposed hydride and nonclassical hydrosilane ligands was observed in DFT calculations on sterically-minimized $PH_3$ analogues of 18.

Measurement of the sign and magnitude of $J_{Si,H}$ in the central and lateral$HSi$ isomers of 18 was made possible using a modification of Scherer’s method, employing 2D $^1$H–$^1$H COSY NMR spectroscopy with $^{29}$Si editing to remove all of the signal which is not interacting with $^{29}$Si. This $^{29}$Si_edited $^1$H–$^1$H COSY experiment allowed accurate location of $^{29}$Si satellites which were unobserved in ‘standard’ $^1$H–$^1$H dqf COSY experiments. Additionally, it allowed determination of small $J_{Si,H}$ couplings (e.g. 5 Hz) where the pertinent signals are broadened by $^{31}$P coupling; previous methods to determine the magnitude of similar couplings relied upon experiments requiring non-standard NMR probes which can simultaneously be tuned to $^{29}$Si and $^{31}$P (e.g. $^{29}$Si{$^{31}$P} INEPT$^{zz}$ and $^{29}$Si–$^1$H–{$^{31}$P} HMQC$^{aaa}$ experiments). By contrast, the $^{29}$Si_edited $^1$H–$^1$H COSY experiment used in this report can be run on a standard double resonance NMR probe with a single broadband channel.

The utility of the $^{29}$Si_edited $^1$H–$^1$H COSY NMR experiment was also highlighted by measurement of the sign and magnitude of $J_{Si,H}$ for $H_{MnSi}$ in the nonclassical disilyl hydride complexes [(dmpe)$_2$MnH(SiH$R_R$)$_2$] ($^{20}$Ph: $R$ = Ph, $^{20}$Bu: $R$ = $n$Bu). These experiments afforded coupling constants of –31 Hz ($^{20}$Ph) and –30 Hz ($^{20}$Bu), which are

$^{zz}$ For examples of these experiments used to determine $J_{Si,H}$, see refs. 249 and 512.

$^{aaa}$ For an example of such an experiment used to measure $J_{Si,H}$ in a nonclassical hydrosilane complex, see ref. 251.
in good agreement with the calculated values of –24 and –27 Hz, respectively (see Chapter 5).

Using 2D $^{29}\text{Si}^{-1}\text{H}$ HMBC NMR spectroscopy, we measured a magnitude for $J_{\text{Si,H}}$ of 36 Hz in $20^{\text{Ph}}$, and were unable to measure $J_{\text{Si,H}}$ for $20^{\text{Bu}}$.  

bbb Using 2D $^{29}\text{Si}^{-1}\text{H}$ HMBC NMR spectroscopy, we measured a magnitude for $J_{\text{Si,H}}$ of 36 Hz in $20^{\text{Ph}}$, and were unable to measure $J_{\text{Si,H}}$ for $20^{\text{Bu}}$.  

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Chapter 7

Reactions of Manganese Disilyl Hydride Complexes with Reagents Containing Unsaturated Polar Bonds

7.1 – Introduction to Chapter 7

Chapter 5 described the synthesis of manganese disilyl hydride complexes \([(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]\) (20\text{Ph}: R = Ph, 20\text{Bu}: R = \text{"Bu}), and reactions of 20\text{R} with ethylene to form silene hydride complexes \([(\text{dmpe})_2\text{MnH(RHSi=CHMe)}]\) (19\text{Ph,H}: R = Ph, 19\text{Bu,H}: R = \text{"Bu}). We proposed that these reactions could proceed via initial formation of a 5-coordinate silyl (17\text{R}) or a silylene hydride (16\text{R}2) intermediate, accessed from 20\text{R} by hydrosilane elimination, followed by (for 16\text{R}2) α-hydride elimination. In addition, Chapter 6 described reactions of 20\text{R} with H2 to form silyl dihydride complexes \([(\text{dmpe})_2\text{MnH}_2(\text{SiH}_2\text{R})]\) (18\text{R}), presumably proceeding via some silyl intermediate, 17\text{R}. Herein, we report the reactions of 20\text{Ph} with reagents containing unsaturated polar bonds, specifically diisopropylcarbodiimide and carbon dioxide, for comparison with the aforementioned reactivity involving apolar C=C bonds.

7.2 – Synthesis and Characterization of \([(\text{dmpe})_2\text{Mn}\{\kappa^2-\text{SiHR(N}^{\text{iPr}}\text{CHN}^{\text{iPr}}\}\}]\)

Disilyl hydride complexes \([(\text{dmpe})_2\text{MnH(SiH}_2\text{R})_2]\) (20\text{Ph}: R = Ph, 20\text{Bu}: R = \text{"Bu}) reacted with diisopropylcarbodiimide \{\text{C(N}^{\text{iPr}}\text{)}_2\} to form the manganese(I) amidinylsilyl complexes \([(\text{dmpe})_2\text{Mn}\{\kappa^2-\text{SiHR(N}^{\text{iPr}}\text{CHN}^{\text{iPr}}\}\}] (25\text{Ph,H}: R = \text{Ph, 25Bu,H}: R = \text{"Bu}); Scheme 7.1. These metallacycles feature a 5-membered M–Si–N–C–N ring, where one of the two hydrogen substituents originating from a silyl ligand in 20\text{R} is located on the central carbon atom of the \text{iPrNCN/iPr} unit. Complexes 25\text{R,H} are chiral at the metal centre and silicon, and in solution, two diastereomers were observed (in thermodynamic ratios}
of 2.8:1 and 2.3:1, respectively), with an NC(H)N signal at 7.58-7.70 ppm and an SiH signal at 5.50-6.26 ppm in the 1H NMR spectra, as well as a 29Si NMR peak between 81.1 and 87.1 ppm.

Scheme 7.1: Reactions of disilyl hydride complexes [(dmpe)2MnH(SiH2R)] (20Ph: R = Ph, 20Bu: R = "Bu) with diisopropylcarbodiimide to afford the amidinylsilyl complexes [(dmpe)2Mn{κ2-SiHR(NiPrCHNiPr)}] (25Ph,H: R = Ph, 25Bu,H: R = "Bu). Only one diastereomer of 25R,H is shown, as two canonical structures.

The 29Si NMR chemical shifts in 25R,H (vide supra) are comparable to those of base-stabilized silylene complexes, and a similarly high frequency resonance (65.4 ppm) has been used to suggest that the bonding environment in [Cp*(OC)2Mo{κ2-Si,N}-Si{p-tol}2{N(H)C6H4N}] (which contains a comparable M–Si–N–C–N metallacycle) involves a contribution from a base-stabilized silylene resonance structure. However, 29Si resonances at only slightly lower frequencies have also been reported for aminosilyl complexes such as [Cp*(OC)2Fe{SiMe2(NR2)}] (R = Me, "Pr, Ph; 29Si δ = 53-47 ppm).

X-ray quality crystals of amidinylsilyl complex 25Ph,H were obtained from a concentrated hexanes solution layered with hexamethyldisiloxane at –30 °C. The resulting structure contains disorder due to two overlapping diastereomers of 25Ph,H, and Figure 7.1 shows just one of these two components. At first glance, the X-ray crystal

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No EXSY NMR cross-peaks were observed to show chemical interchange between the two diastereomers of 25R,H (up to 60 °C). However, such an equilibrium was inferred by heating solutions starting with different ratios of the two isomers (obtained for preferential recrystallization), yielding solutions with consistent (i.e. thermodynamic) ratios.
structure and DFT calculations (25Bu,H was modelled with the "Bu group replaced by an Et group) indicate that the monoanionic \{κ²-SiHR(N\text{t}PrCHN\text{t}Pr)\} ligand can be described as a bidentate amidinylsilyl ligand, with Mn–Si distances of 2.347(1)-2.358(1) Å (calcd. 2.32 for 25R,H, with Mayer bond orders of 0.93-0.95), and Mn–N distances of 2.137(3)-2.141(3) Å (calcd. 2.12-2.13 for 25R,H, with Mayer bond orders of 0.58-0.59). The Mn–Si distances lie at the shorter end of the range observed for Mn(I) silyl complexes with dmpe co-ligands (e.g. 2.35-2.44 Å in 21a-d; Chapter 5), but are longer than those in related NHC-stabilized silylene hydride complexes (2.26-2.30 Å in 22a-d; Chapter 5). However, the two C–N distances in the metallacycle are more similar than would be expected for localized single and double bonds. The C–N bonds closer to silicon and manganese are 1.350(4)-1.350(5) Å (calcd. 1.34-1.35 Å for 25R,H, with Mayer bond orders of 1.23-1.25) and 1.296(6)-1.299(5) Å (calcd. 1.31 Å for 25R,H, with Mayer bond orders of 1.50), respectively; cf. 1.46 Å for a typical C–N single bond and 1.21 Å for a typical C–N double bond. Furthermore, the Si–N distances of 1.805(3)-1.813(3) Å (calcd. 1.82 Å for 25R,H, with Mayer bond orders of 0.69-0.74) are longer than those in free aminosilanes (1.70-1.76 Å). Together, these bond metrics suggest that 25R,H may be better described using a combination of the two resonance structures in Scheme 7.1; one with anionic aminosilyl and neutral imine donors on manganese (left), and the other with a neutral base-stabilized silylene and an anionic amido donor on manganese (right). Similar resonance structures have been employed to describe the bonding situation in a pair of M–Si–N–C–N metallacycles (M = Mo, Ru) where the N donor on the metal is part of a pyridine ring, as well as in related M–Si–O–C–E (E = O, N) metallacycles.
Figure 7.1: X-ray crystal structure of \([(\text{dmpe})_2\text{Mn}\{\kappa^2-\text{SiHPh(N}^\text{iPrCHN}^\text{iPr})\}] (25^\text{Ph,H})\) with ellipsoids at 50% probability. Most hydrogen atoms have been omitted for clarity. H(1) and H(7) were located from the difference map and refined isotropically. Two independent and essentially isostructural molecules were observed in the unit cell, only one of which is shown. Atom labels with an A suffix correspond to those without a suffix in the structure not shown. Bond distances (Å) and angles (deg): Mn(1)–Si(1) 2.347(1), Mn(1A)–Si(1A) 2.358(1), Mn(1)–N(1) 2.137(3), Mn(1A)–N(1A) 2.141(3), Si(1)–H(1) 1.44(5), Si(1A)–H(1A) 1.50(6), Si(1)–C(1) 1.934(4), Si(1A)–C(1A) 1.938(3), Si(1)–N(2) 1.815(3), Si(1A)–N(2A) 1.805(4), N(2)–C(7) 1.348(4), N(2A)–C(7A) 1.349(5), N(2)–C(11) 1.478(6), N(2A)–C(11A) 1.482(6), N(1)–C(7) 1.301(6), N(1A)–C(7A) 1.298(6), N(1)–C(8) 1.490(4), N(1A)–C(8A) 1.485(6), C(7)–H(7) 0.98(4), C(7A)–H(7A) 0.96(6), N(1)–Mn(1)–Si(1) 80.14(9), N(1A)–Mn(1A)–Si(1A) 79.45(9), Mn(1)–Si(1)–C(1) 136.4(1), Mn(1A)–Si(1A)–C(1A) 132.8(1), Mn(1)–Si(1)–H(1) 118(2), Mn(1A)–Si(1A)–H(1A) 120(2), Mn(1)–Si(1)–N(2) 100.5(1), Mn(1A)–Si(1A)–N(2A) 100.6(1), Si(1)–N(2)–C(7) 114.6(3), Si(1A)–N(2A)–C(7A) 115.1(3), Si(1)–N(2)–C(11) 126.2(2), Si(1A)–N(2A)–C(11A) 125.7(2), N(2)–C(7)–N(1) 123.9(3), N(2A)–C(7A)–N(1A) 123.3(3), C(7)–N(1)–Mn(1) 120.4(3), C(7A)–N(1A)–Mn(1A) 121.1(3), C(7)–N(1)–C(8) 114.0(3), C(7A)–N(1A)–C(8A) 113.8(3), C(11)–N(2)–C(7) 117.9(3), C(11A)–N(2A)–C(7A) 119.2(3), C(8)–N(1)–Mn(1) 125.5(2), C(8A)–N(1A)–Mn(1A) 125.1(3).
7.3 – Synthesis and Characterization of \textit{trans}--[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26)

Whereas the reactions of 20$^R$ with diisopropylcarbodiimide yielded structures in which the NCN unit remained intact, reactions with carbon dioxide afforded \textit{trans}--[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26; Scheme 7.2), in which one equivalent of CO$_2$ has been converted to CO. Synthesis of this carbonyl formate complex was accompanied by silane (H$_3$SiR) elimination and the formation of benzene-soluble byproducts thought to be polysiloxanes \{(SiHRO)$_n$, R = Ph or $^n$Bu\}, these byproducts gave rise to $^1$H NMR signals at 4.8-5.5 ppm in the SiH region, cumulatively integrating to a single SiH residue per equivalent of 26, and correlated to $^{29}$Si NMR signals ranging from –21 to –36 ppm (for R = Ph, further reactivity between the byproducts ensued). Such reactivity mirrors reported reactions of free silylenes with CO$_2$, which also yield polysiloxanes.

Scheme 7.2: Reaction of disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] (20$^{Ph}$: R = Ph, 20$^{Bu}$: R = $^n$Bu) with carbon dioxide to afford the formate complex \textit{trans}--[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26).

Compound 26 was obtained in pure form by sublimation to afford a 60 : 40 mixture of 26 and known \textit{trans}--[(dmpe)$_2$MnH(CO)] (\textit{trans}-27), the product of CO$_2$ elimination from the formate ligand, followed by re-exposure to CO$_2$ to re-form 26. In fact, 26 was only stable at room temperature under an atmosphere of CO$_2$, eliminating CO$_2$ slowly under argon (either as a solid or in solution) or under vacuum (approx. 2% conversion after 20 min.). DFT calculations afforded a ΔG of less than 0.1 kJ mol$^{-1}$ for this process at 298.15 K, reflecting the observed thermodynamic reversibility; to the best
of our knowledge, this is the first example of reversible CO$_2$ insertion/deinsertion into a manganese–hydride bond. 

NMR spectra of 26 feature a single $^{31}$P NMR environment at 68.3 ppm, and only five $^1$H NMR signals {four from the dmpe ligands between 1.23 and 1.90 ppm, and one (a pentet with $J_{31P-1H}$ of 2 Hz) for the formyl proton at 8.68 ppm}. Complex 26 also formed cleanly upon exposure of [(dmpe)$_2$MnH(=SiEt$_2$)] (16$^{E_2}$) to CO$_2$, whereas reaction of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with CO$_2$ only afforded 26 in low yield, accompanied by free dmpe and unidentified byproducts.

X-ray quality crystals of 26 were obtained from a concentrated toluene solution layered with hexamethyldisiloxane at $-30$ °C, and confirmed the expected octahedral geometry with trans-disposed carbonyl and κ$^1$-formate ligands (Figure 7.2). The equatorial dmpe ligands form a statistically perfect plane ($\sum$P–Mn–P = 359.98(4)-360.01(4)$^\circ$), the C–Mn–O angles are 172.23(5)-173.31(5)$^\circ$, and the various bonding parameters related to the terminal formate unit {Mn–O distances of 2.086(1)-2.096(1) Å, O–C distances of 1.266(2)-1.275(2) Å, O=C distances of 1.229(2)-1.237(2) Å, and Mn–O–C angles of 178.5(1)-179.3(1)$^\circ$} are all within the range previously observed for terminal manganese formate complexes.$^{211}$

$^{dd}$ For examples of irreversible CO$_2$ insertion into a terminal Mn–H bond, see refs. 170 and 527.
Figure 7.2: X-ray crystal structure of *trans*-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26), with ellipsoids drawn at 50% probability. H(1) was located from the difference map and refined isotropically. Most hydrogen atoms have been omitted for clarity. Two independent and essentially isostructural molecules are observed in the unit cell, one of which is shown. Atom labels with the A suffix correspond to atoms labels without a suffix in the structure not shown. Bond distances (Å) and angles (deg): Mn(1)–O(1) 2.096(1), Mn(1A)–O(1A) 2.086(1), Mn(1)–C(2) 1.751(1), Mn(1A)–C(2A) 1.742(1), O(1)–C(1) 1.275(2), O(1A)–C(1A) 1.266(2), C(1)–O(2) 1.229(2), C(1A)–O(2A) 1.237(2), C(1)–H(1) 0.97(2), C(1A)–H(1A) 0.98(2), C(2)–O(3) 1.191(2), C(2A)–O(3A) 1.175(2), C(2)–Mn(1)–O(1) 173.31(5), C(2A)–Mn(1A)–O(1A) 172.23(5), Mn(1)–C(2)–O(3) 178.5(1), Mn(1A)–C(2A)–O(3A) 179.3(1), Mn(1)–O(1)–C(1) 133.78(9), Mn(1A)–O(1A)–C(1A) 133.53(9), O(1)–C(1)–O(2) 128.8(1), O(1A)–C(1A)–O(2A) 128.9(1), O(1)–C(1)–H(1) 116(1), O(1A)–C(1A)–H(1A) 114(1), O(2)–C(1)–H(1) 115(1), O(2A)–C(1A)–H(1A) 117(1).

7.4 – Potential Pathways for Reactions of Disilyl Hydride Complexes with \{C(N^tPr)$_2$\} or CO$_2$

Reactions of the disilyl hydride complexes 20$^R$ with C(N$^t$Pr)$_2$ or CO$_2$ afforded [(dmpe)$_2$Mn{κ$^2$-SiHR(N$^t$PrCHN$^t$Pr)}] (25$^{Ph,H}$: $R$ = Ph, 25$^{Bu,H}$: $R$ = $^t$Bu) and [(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26), respectively (*vide supra*). These reactions (Scheme
7.3) could proceed via a 5-coordinate silyl species (17\textsuperscript{R}) or a silylene hydride complex (16\textsuperscript{R,H}), both of which have been shown to be accessible from 20\textsuperscript{R} through combined computational studies, high temperature \textsuperscript{1}H NMR spectroscopy, and trapping reactions with isonitriles and NHCs (Chapter 5).

The silylene hydride intermediates (16\textsuperscript{R,H}) present several plausible reaction pathways to the observed reaction products (Scheme 7.3). One possibility involves initial 2+2 cycloaddition of the Mn=Si double bond and a C=E (E = N\textsuperscript{i}Pr, O) bond to afford a metallacyclobutane intermediate A. This cycloaddition reaction could proceed either in a concerted or two-step process (via initial base coordination to the silicon centre), and similar mechanistic steps have been proposed for reactions of ruthenium silylene hydride complexes with RC≡N,\textsuperscript{343} RNCO,\textsuperscript{504} and MesNCS.\textsuperscript{505,528} Subsequent C–H bond-forming reductive elimination from A would then generate intermediate B, and isomerization would afford compound 25; the observed product \{R = Ph (25\textsuperscript{Ph,H}) or \textsuperscript{\textmu}Bu (25\textsuperscript{Bu,H})\} in reactions with \{C(N\textsuperscript{i}Pr)\textsubscript{2}\}.

It is also conceivable that intermediate B could be formed directly from 16\textsuperscript{R,H} and CE\textsubscript{2} via an outer sphere mechanism involving formal 2+3 cycloaddition of the Si=M–H unit across one of the C=E bonds. Such a process (either concerted or two-step), via a transition state with a M–Si–E–C–H ring system (analogous to C\textsuperscript{5}), has been suggested for reactions of ruthenium silylene complexes with MesNCO\textsuperscript{505,528} and CO\textsubscript{2},\textsuperscript{529} and a similar transition state was also suggested for the reaction of a tungsten silylene hydride complex with acetone.\textsuperscript{327}

An alternative route to compound 25 could involve CE\textsubscript{2} insertion into the Mn–H bond of a silylene hydride complex (16\textsuperscript{R,H}) to afford silylene formate or formamidinate \{HC(NR)\textsubscript{2}\} intermediate D, with subsequent cyclization (involving nucleophilic attack of the formate or formamidinate anion on the silylene).
Scheme 7.3: Potential pathways for the reactions of \([\text{dmpe}_2\text{MnH(SiH}_2\text{R})_2]\) (20\(^\text{Ph}\): R = Ph, 20\(^\text{Bu}\): R = \(^\alpha\text{Bu}) with E=C=E (E = N\(^\text{Pr},\) O). [Mn] = Mn(dmpe)_2. For some compounds, more than one isomer is likely to be accessible (e.g. \textit{cis} vs \textit{trans}, the presence/absence of an interaction between silicon and an adjacent hydride ligand, or coordination/lack of coordination of lone pairs on E to the metal centre), but for clarity, only one isomer is shown. Solid boxes indicate known complexes and intermediates.
The reactions of $^{20}R$ with $CO_2$ and $C(N^{i}\text{Pr})_2$ could also proceed via 5-coordinate silyl intermediates $^{17}R$ instead of silylene hydride intermediates $^{16}R^{H}$ (Scheme 7.3). In one such mechanism, intermediate D could be accessed directly from silyl intermediates $^{17}R$ via initial 2+3 cycloaddition of the Mn–Si–H moiety on silyl complexes $^{17}R$ across one of the E=C bonds {forming a delocalized M–Si–H–C–E ring system (E$^5$)}. This is analogous to mechanisms proposed by Whited et al. in the reaction of a ruthenium silylene hydride with $CO_2$, and computationally investigated (though discarded as higher in energy) by We and Lin et al. for the reactions of a tungsten silylene hydride complex with acetonitrile and acetone.

Alternatively, reactions of $^{17}R$ could involve initial $CO_2/C(N^{i}\text{Pr})_2$ coordination to afford manganese(III) intermediate F, followed by Si–E bond-forming reductive elimination to generate acyl intermediate G, which could then undergo oxidative addition of an Si–H bond across the metal centre to form previously mentioned metallacyclobutyl intermediate A. While 1,2-insertion reactions involving C(NR)$_2$ and silyl ligands typically form silylamidinate {R$_3$SiC(NR)$_2$} ligands, N–Si bond-formation has been observed in the reaction of [(C$_5$H$_4$N)(OC)CpFe(SiR$_3$)] with diisopropylcarbodiimide to generate a $-C(=N^{i}\text{Pr})N(^{i}\text{Pr})$SiR$_3$ ligand. Additionally, Tobita et al. proposed an equivalent mechanism for the reactions of ruthenium silylene hydride complexes with aldehydes (involving Si–O bond-forming 1,2-insertion of an $\eta^2$-aldehyde ligand into a metal–silyl bond). These two mechanistic proposals are reflected in our proposed transformation from intermediate F to G, while the latter report includes subsequent oxidative addition of the Si–H bond to form a metallacyclic structure analogous to intermediate A).

The above reaction pathways provide access to structure 25; the final product in reactions with carbodiimides. However, in the case of $CO_2$, further reactivity ensues to generate 26, where CO ligand formation is accompanied by polysiloxane \{(RHSiO)$_n$\} elimination; this reactivity bears some resemblance to the C–S bond cleavage observed upon reaction of [Cp*(CO)RuH{=SiHC(SiMe$_3$)$_3$}] with MesNCS.
One potential route to compound 26 involves cleavage of the O–C bond in A to afford intermediate H, containing a hydride and a neutral silaaldehyde ligand (O=SiHR; silaaldehyde complexes of Mn are unknown, but Tobita recently reported a stable W complex with a \(\eta^2\)-coordinated silaaldehyde ligand,\(^{338}\) and silanone complexes have been proposed as reactive intermediates in the generation of polysiloxanes\(^{534}\), followed by silaaldehyde elimination \{yielding a polsiloxane, (RHSiO)\(_n\}\) to afford compound 27 (cis or trans), which we have shown reversibly inserts CO\(_2\) to afford 26.

Two additional pathways could be envisaged to generate intermediate H, in both cases proceeding via intermediate I, which contains a siloxide (OSiH\(_2\)R) and a carbonyl ligand.

Firstly, the C(O)OSiR\(_3\) ligand in compound G could undergo \(\alpha\)-siloxide elimination to form I. To our knowledge, this type of reaction has not previously been proposed. However, it resembles the CNMes extrusion reaction observed for a C(NMes){SSiH\(_2\)C(SiMe\(_3\))\(_3\)} ligand on ruthenium.\(^{505,528}\) Furthermore, the reverse process (1,1-insertion involving a siloxy group and a carbonyl ligand) has been observed in the reaction of [(Me\(_3\)P)Re(OSi\(_t\)Bu)\(_3\)] with CO.\(^{535}\) Then compound H can be accessed from I by \(\beta\)-hydride elimination; \(\beta\)-hydride elimination from a siloxide ligand also has not been reported, but the reverse reaction (siloxide generating 1,2-insertion of a silanone into a metal hydride bond) has been proposed as a step in the catalytic disproportionation of siloxanes.\(^{536}\)

Alternatively, intermediate I could be accessed from F by Si–C bond-forming 1,2-insertion to generate silyl carboxylate (R\(_3\)SiCO\(_2\)) complex J, followed by CO extrusion. Reactions of silyl ligands with CO\(_2\) have been reported to form silyl carboxylate (R\(_3\)SiCO\(_2\)) complexes,\(^{537,538}\) and CO extrusion from some of these complexes has been observed to yield siloxide groups\(^{538}\) (DFT calculations have suggested that this step involves an outer-sphere migration of the SiR\(_3\) moiety from C to O).\(^{539}\)
Manganese disilyl hydride complexes $20^R$ reacted with $\text{E}=$Si=$\text{E}$ ($\text{E}=$ 'PrN or O) to generate manganese(I) amidinylsilyl ($25^R$) or formate ($26$) complexes. The former features a rare TM–Si–N–C–N 5-membered ring, and the latter was found to undergo reversible CO$_2$ dissociation to generate a manganese(I) hydride complex ($27$). This reactivity presumably proceeds via one of two potential intermediates discussed in Chapter 5 for the reactions of $20^R$ with ethylene; either a 5-coordinate silyl species ($17^R$) or a silylene hydride complex ($16^{R2}$). This work demonstrates the potential for manganese disilyl hydride complexes $20^R$ to be precursors to a wide variety of novel manganese-containing species.
Chapter 8

Catalytic Hydrosilylation of Ethylene

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8.1 – Introduction of Chapter 8

Chapters 4 and 5 showed that silyl, silylene, and silene complexes can be prepared from reactions of \([(\text{dmpe})_2\text{MnH(C}_2\text{H}_4)] (10)\) with hydrosilanes, in some cases followed by ethylene. Therefore, we decided to investigate the potential for 10 to catalyze ethylene hydrosilylation in combination with primary and secondary hydrosilanes. Alkene hydrosilylation is an industrially important transition metal-catalyzed process for alkylsilane production,\(^{381,382,384,385}\) and the most common olefin hydrosilylation catalyst used in industry is Karstedt’s catalyst, \([\text{Pt}_2\{\text{O(SiMe}_2\{\text{CH=CH}_2}\}_2\}_3]\).\(^{384}\) However, the development of catalytic systems based on first row transition metals such as manganese is of interest due to high abundance, low cost, reduced toxicity, and improved environmental compatibility.\(^{540}\) In this regard, manganese mediated hydrosilylation of polar unsaturated bonds has been well studied,\(^{541}\) but only a handful of manganese catalysts have been reported for alkene hydrosilylation.\(^{542}\)

The typical mechanism for alkene hydrosilylation (Chalk-Harrod mechanism; see Scheme 1.34 in Chapter 1) involves oxidative addition of a hydrosilane to generate a silyl hydride complex, followed by alkene coordination, C–H bond-forming 1,2-insertion, and finally Si–C bond-forming reductive elimination. However, in some cases alkene coordination is followed by C–Si bond-forming 1,2-insertion and then C–H bond-forming reductive elimination (modified Chalk-Harrod mechanism; see Scheme 1.34 in Chapter 1). Furthermore, catalytic cycles which proceed via a monosilyl complex rather
than a silyl hydride complex have been reported, including hydrosilylation reactions utilizing a cationic palladium(II) or cobalt(III) alkyl pre-catalyst.\textsuperscript{383,384}

\section*{8.2 – Catalytic Hydrosilylation of Ethylene}

At 60 °C, addition of 7 mol\% of \([\text{dmpe}]_2\text{MnH(C}_2\text{H}_4]\) (10) to primary or secondary hydrosilanes (\(\text{H}_3\text{SiPh}, \text{H}_3\text{Si}^{\text{tBu}}, \text{H}_2\text{SiPh}_2\) or \(\text{H}_2\text{SiEt}_2\)) in \(\text{C}_6\text{D}_6\) under ethylene (1.7 atm initial pressure) led to catalytic incorporation of one or two equivalents of ethylene into the Si–H bonds of the free hydrosilanes, leading to a mixture of new hydrosilanes (Table 8.1). The major products in reactions of secondary hydrosilanes were tertiary hydrosilanes (\(\text{HSiEtPh}_2\) or \(\text{HSiEt}_3\)), while reactions involving primary hydrosilanes first formed secondary hydrosilanes (\(\text{H}_2\text{SiEt}^{\text{tBu}}\) or \(\text{H}_2\text{SiEtPh}\)), followed by reaction with an additional equivalent of ethylene to generate the tertiary hydrosilane (\(\text{HSiEt}_3\)Ph or \(\text{HSiEt}_{2}^{\text{tBu}}\)) as the major product. Hydrosilylation reactions with \(\text{H}_3\text{Si}^{\text{tBu}}, \text{H}_2\text{SiPh}_2\), and \(\text{H}_2\text{SiEt}_2\) produced fewer byproducts than those with \(\text{H}_3\text{SiPh}\) (as noted in Table 8.1). Additionally, hydrosilylation with \(\text{H}_2\text{SiEt}_2\) progressed much more rapidly than that with \(\text{H}_2\text{SiPh}_2\). By contrast, no reactivity was observed when 10 was exposed to ethylene and the tertiary hydrosilanes \(\text{HSiEt}_3\) or \(\text{HSiEt}_{2}\); various other hydrosilylation catalysts exhibit higher activities than 10, especially precious metal catalysts,\textsuperscript{384,543} but the ability of 10 to selectively form tertiary but not quaternary hydrosilanes from ethylene is uncommon.\textsuperscript{\text{\textdegree\textdegree\textdegree}}

\textsuperscript{\text{\textdegree\textdegree\textdegree}} For examples of ethylene hydrosilylation selective for producing secondary hydrosilanes, see refs. 340 and 544. For examples of ethylene hydrosilylation selective for producing quaternary silanes, see refs. 251 and 545.
Table 8.1: Ratio of hydrosilane products (assigning the tertiary hydrosilane product a value of 100) observed by $^1$H NMR spectroscopy after hydrosilylation of ethylene catalysed by [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) pre-catalyst (7 mol%) with 1.7 atm ethylene (initially $n_{\text{silane}} \approx n_{\text{ethylene}}$; for reactions with H$_3$SiR, the headspace was re-filled with ethylene after 1 week) at 60 °C in C$_6$D$_6$ after 50 days (H$_3$SiPh), 25 days (H$_3$Si$n^\prime$Bu) or 6 days (H$_2$SiR$_2$).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>R/R’</th>
<th>Substrate</th>
<th>H$_2$SiEtR</th>
<th>HSiEtRR’</th>
<th>HSiViRR’</th>
<th>Unidentified$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$SiPh</td>
<td>Ph/Et</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>&lt; 5</td>
<td>20$^b$</td>
</tr>
<tr>
<td>H$_3$Si$n^\prime$Bu</td>
<td>$n^\prime$Bu/Et</td>
<td>0</td>
<td>&lt; 5</td>
<td>100</td>
<td>20</td>
<td>10$^c$</td>
</tr>
<tr>
<td>H$_2$SiPh$_2$</td>
<td>Ph/Ph</td>
<td>50</td>
<td>n.a.</td>
<td>100</td>
<td>&lt; 5</td>
<td>20</td>
</tr>
<tr>
<td>H$_2$SiEt$_2$</td>
<td>Et/Et</td>
<td>6</td>
<td>n.a.</td>
<td>100</td>
<td>11</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

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a. Relative amounts of unidentified SiH-containing silanes were determined assuming that they contain a single SiH proton.
b. At least seven unassigned SiH environments were observed.
c. Two unassigned SiH environments were observed.

Organic byproducts were observed during conversion of secondary to tertiary silanes, but not conversion of primary to secondary silanes. The major byproduct was a hydrosilane with a vinyl group (Vi) in place of an ethyl substituent (HSiEtViR, R = Et or $n^\prime$Bu or HSiPhViR, R = Et or Ph), accompanied by one or more unidentified SiH-containing silanes (Table 8.1). Vinyl silanes are commonly observed byproducts in olefin (e.g. H$_2$C=CHR) hydrosilylation, formed by β-hydride elimination from an M(CH$_2$CHR$\text{SiR}_3$) intermediate in the catalytic cycle,$^{546}$ and were an impetus for the initial proposal of a modified Chalk-Harrod catalytic cycle involving C–Si rather than C–H bond-forming 1,2-insertion from an alkene-coordinated silyl hydride intermediate.$^{382}$

During catalysis using primary and secondary hydrosilanes, a variety of manganese-containing complexes were observed by NMR spectroscopy, including disilyl hydride complexes (for reactions involving primarily hydrosilanes only), silylene hydride
complexes (for reactions involving secondary silanes only), silyl dihydride complexes, silene hydride complexes, and ethylene hydride complex 10. Furthermore, all of these classes of complex are catalytically active. For example, [(dmpe)$_2$MnH(Et$_2$Si=CHMe)] (19$_{Et^2}$) and [(dmpe)$_2$MnH(=SiEt$_2$)] (16$_{Et^2}$) are catalysts for ethylene hydrosilylation using secondary hydrosilanes, and [(dmpe)$_2$MnH(SiH$_2^n$Bu)$_2$] (20$_{Bu}$) and [(dmpe)$_2$MnH$_2$(SiH$_2^n$Bu)] (18$_{Bu}$) are active for ethylene hydrosilylation by H$_3$Si"Bu. Reactions involving 19$_{Et^2}$, 16$_{Et^2}$, and 20$_{Bu}$ rapidly generated distributions of Mn-containing species and hydrosilane products which are very similar to those formed when [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) was used as the pre-catalyst. By contrast, when 18$_{Bu}$ was employed, hydrosilylation proceeded at a slower rate, and even after 24 hours the dominant manganese-containing species was 18$_{Bu}$.

8.3 – Monitoring Ethylene Hydrosilylation by H$_3$Si"Bu Over Time

In order to monitor ethylene hydrosilylation reactions under conditions where ethylene concentration does not vary significantly during the course of the reaction, multiple aliquots from a stock solution of 10 and H$_3$Si"Bu in C$_6$D$_6$ were placed under a large excess of ethylene in a sealed 50 mL flask (initial pressure 1.7 atm, n$_{C2H4}$ ≈ 40 × n$_{silane}$) and heated at 60 °C for various time periods prior to analysis by NMR spectroscopy (Figure 8.1). Key observations were; (a) nearly complete conversion of the primary hydrosilane to secondary hydrosilane H$_2$SiEt"Bu was observed before any formation of the tertiary silane (HSiEt$_2^n$Bu) product or vinyl silane (HSiEtVi"Bu) byproduct, (b) during hydrosilylation by the primary hydrosilane H$_3$Si"Bu, the dominant metal-containing species was the SiH-containing silene hydride [(dmpe)$_2$MnH("BuHSi=CHMe)] (19$_{BuH}$), with small amounts of the disilyl hydride [(dmpe)$_2$MnH(SiH$_2^n$Bu)$_2$] (20$_{Bu}$), (c) after 13 hours, almost all H$_3$Si"Bu had been consumed, (d) from 13 to 18 hours, conversion of H$_2$SiEt"Bu to HSiEtVi"Bu proceeded rapidly with concurrent formation of the vinylsilane byproduct HSiEtVi"Bu (see below

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Silylene complexes were only observed during catalysis when most of the ethylene had been consumed.
for experiments to determine the manganese species present *between* 13 and 18 hours),
(e) after 18 hours, 10 was the dominant manganese species in solution {accompanied by
small amounts of the silene hydride [(dmpe)$_2$MnH("BuEtSi=CEtMe)] ($19^{Bu,Et}$) and the
silyl dihydride [(dmpe)$_2$MnH$_2$(SiHEt$^n$Bu)] ($18^{Bu,Et}$), and conversion of H$_2$SiEt$^n$Bu to
HSiEt$_2$"Bu now proceeded more slowly, and (f) after 12 days, > 99.5% of the H$_2$SiEt$^n$Bu
intermediate had been consumed yielding 81% HSiEt$_2$"Bu, 16% HSiEtVi"Bu, and 3% of
an unidentified SiH-containing byproduct (assuming that this species contains one SiH
proton), which is non-volatile at room temperature (5 mTorr); at this point, the only Mn-
containing species in the reaction mixture was [(dmpe)$_2$MnH(C$_2$H$_4$)] (10). Relative
amounts of the different hydrosilane and MnH-containing species in solution during
ethylene hydrosilylation by H$_3$Si$^n$Bu are plotted as a function of time in Figure 8.1.

Between 13 and 18 hours in Figure 8.1, conversion of H$_2$SiEt$^n$Bu to HSiEt$_2$"Bu
proceeded rapidly (to more than 50% conversion), and then slowed down dramatically, as
the resting state of the catalyst switched to [(dmpe)$_2$MnH(C$_2$H$_4$)] (10). However, during
secondary to tertiary hydrosilane conversion, [(dmpe)$_2$MnH("BuHSi=CHMe)] ($19^{Bu,H}$)
cannot be regenerated, indicating that a different manganese species may have spiked in
concentration *between* the 13 and 18 hour data points (this species is presumably
responsible for the rapid H$_2$SiEt$^n$Bu to HSiEt$_2$"Bu conversion observed during this time
period). Consequently, the reaction in Figure 8.1 was repeated and stopped after most but
not all of the primary hydrosilane had been consumed {the resulting mixture of
hydrosilanes and Mn-containing species in C$_6$D$_6$ was similar to that observed at 13 h in
Figure 8.1; i.e. mostly secondary hydrosilane H$_2$SiEt$^n$Bu and
[(dmpe)$_2$MnH("BuHSi=CHMe)] ($19^{Bu,H}$), with a small amount of the primary
hydrosilane, H$_3$Si$^n$Bu}. This mixture was then sealed under a near-stoichiometric
(relative to the hydrosilane) amount of ethylene in an NMR tube, and monitored by NMR
spectroscopy at 56 °C in 5 minute intervals (Figure 8.2).
Figure 8.1: SiH (left) and MnH (middle) regions of the $^1$H NMR spectra (298 K, 500 or 600 MHz) for the hydrosilylation of ethylene by $\text{H}_3\text{Si}^n\text{Bu}$ using $[(\text{dmpe})_2\text{MnH}($$\text{C}_2\text{H}_4$$)]$ (10) pre-catalyst (7 mol% relative to the hydrosilane) under ~1.7 atm of ethylene (initial, $n_{\text{C}_2\text{H}_4} \approx 40 \times n_{\text{silane}}$) in $\text{C}_6\text{D}_6$ and after various time intervals at 60° C. The x-axis corresponds to the bottom $^1$H NMR spectrum, and for clarity, each spectrum above that is shifted by 0.3 (SiH region) or 0.4 (MnH region) ppm to lower frequency. Right: graphs showing the ratio of (top) hydrosilanes (dark blue ♦ = $\text{H}_3\text{Si}^n\text{Bu}$; red ■ = $\text{H}_2\text{SiEt}^n\text{Bu}$; green ▲ = $\text{HSiEt}^2\text{nBu}$; purple × = $\text{HSiViEt}^n\text{Bu}$; light blue ✴ = unidentified SiH-containing silane) and (bottom) MnH-containing species {dark blue ♦ = $[(\text{dmpe})_2\text{MnH}($$\text{C}_2\text{H}_4$$)]$ (10); light blue × = $[(\text{dmpe})_2\text{MnH}($$\text{SiH}_2^n\text{Bu}$$)_2]$ (20$^{\text{Bu}}$); green ▲ = $[(\text{dmpe})_2\text{MnH}_2($$\text{SiHEt}^n\text{Bu}$$)]$ (18$^{\text{Bu,Et}}$); purple × = $[(\text{dmpe})_2\text{MnH}($$^n\text{BuHSi=CHMe}$$)]$ (19$^{\text{Bu,H}}$); red ■ = $[(\text{dmpe})_2\text{MnH}($$^n\text{BuEtSi=CHMe}$$)]$ (19$^{\text{Bu,Et}}$)} in these reactions, as measured by $^1$H NMR spectroscopy.
Figure 8.2: Graphs showing the ratio of (top) hydrosilanes (dark blue ♦ = H₃SiⁿBu; red ■ = H₂SiEtⁿBu; green ▲ = HSiEt₂ⁿBu; purple × = HSiViEtⁿBu; light blue ★ = unidentified SiH-containing silane) and (bottom) MnH-containing species {dark blue ♦ = [(dmpe)₂MnH(C₂H₄)] (10); red ■ = [(dmpe)₂MnH("BuEtSi=CHMe)] (19Bu,Et); green ▲ = [(dmpe)₂MnH₂(SiHeᵗBu)] (18Bu,Et); purple × = [(dmpe)₂MnH("BuEtSi=CHMe)] (19Bu,Et)} measured over time by ¹H NMR spectroscopy (in C₆D₆ at 56 °C) for the hydrosilylation of ethylene (initial, nC₂H₄ ≈ nₘsilane) by a mixture of hydrosilanes corresponding to the 13 h mark in Figure 8.1.

In Figure 8.2, consumption of remaining primary hydrosilane was complete after 10 minutes, followed by rapid secondary to tertiary hydrosilane conversion and a spike in the concentration of a new silene hydride complex, [(dmpe)₂MnH("BuEtSi=CHMe)] (19Bu,Et), while the concentrations of 19Bu,H (the resting state of the catalyst during primary to secondary hydrosilane conversion) and [(dmpe)₂MnH(C₂H₄)] (10) (the Mn-containing species dominant after the 18 h mark) diminished and increased, respectively.
Furthermore, a small amount (~12%) of the silyl dihydride complex [(dmpe)$_2$MnH$_2$(SiHEt$^n$Bu)] (18$^{Bu,Et}$) grew in over this time period, and vinylsilane (HSiViEt$^n$Bu) production was observed to accompany the formation of 10 and 18$^{Bu,Et}$. The slowdown in the rate of catalysis between 13 and 18 hours in Figure 8.1 can therefore be attributed to a change in the resting state of the catalyst, from more active silene hydride complexes 19$^{Bu,H}$ and 19$^{Bu,Et}$, to 10 and 18$^{Bu,Et}$, both of which are formed via vinylsilane elimination (vide infra), and re-enter the catalytic cycle slowly (18$^{Bu,Et}$ is particularly slow to enter the cycle; vide supra).

8.4 – Proposed Catalytic Cycles of Ethylene Hydrosilylation

A catalytic cycle (Scheme 8.1) can be envisaged based on the reaction pathways already proposed for (a) reaction of ethylene with disilyl hydride complexes 20$^R$ (formed in reactions of 10 with primary hydrosilanes; Chapter 5) to afford silene hydride complexes 19$^{R,H}$, and (b) reaction of ethylene with silylene hydride complexes 16$^{R2}$ (formed in reactions of 10 with secondary hydrosilanes; Chapter 4) to afford silene hydride complexes 19$^{R2}$. These reactions are identified with blue reaction arrows in Scheme 8.1. In the presence of free hydrosilane substrate, the catalytic cycle can be completed (green reaction arrows) by reaction of hydrosilanes with primary alkyl intermediate 23 (pathway 'a' in Scheme 8) or secondary alkyl intermediate 24 (pathway 'b' in Scheme 8.1); via oxidative addition followed by reductive elimination, or σ-bond metathesis. Energy minima for alkyl intermediates 23 and 24 were found to lie 46-67 kJ mol$^{-1}$ higher in energy than the respective silene hydride resting states, indicating their thermodynamic accessibility from complexes observed by NMR spectroscopy.

Alternatively, for conversion of primary to secondary hydrosilanes, the catalytic cycle in Scheme 8.1 can be completed by C–H bond-forming 1,2-insertion from intermediate 19$^{R,H}$ (pathway 'c', green reaction arrow) to generate silyl and silylene hydride species 17$^{R,Et}$ and 16$^{R,Et}$. Isomerization of 19$^{Bu,H}$ to 16$^{Bu,Et}$ has been observed in the absence of ethylene and hydrosilanes (Chapter 5), and this pathway is also thought to
be involved in the reactions of [(dmpe)$_2$MnH(RHSi=CHMe)] ($^{19}_{\text{R,H}}$) with ethylene to afford [(dmpe)$_2$MnH(REtSi=CHMe)] ($^{19}_{\text{R,Et}}$) in which an SiH group is converted to an SiEt group (Chapter 5). If pathway 'c' is involved in the catalysis, the resulting [Mn]SiHREt ($^{17}_{\text{R,Et}}$) complex must react with free H$_3$SiR to form [Mn]SiH$_2$R ($^{17}_{\text{R}}$) and eliminate H$_2$SiREt (likely via an unobserved disilyl hydride intermediate analogous to $^{20}_{\text{R}}$), given that the observed reactivity converts primary hydrosilanes to free secondary hydrosilanes prior to the formation of significant amounts of tertiary hydrosilane products. The accessibility of this reaction pathway is highlighted by the reaction of [(dmpe)$_2$MnH(=SiR$_2$)] (R = Ph ($^{16}_{\text{Ph2}}$) or Et ($^{16}_{\text{Et2}}$}) with excess H$_3$Si''Bu at 20 °C to afford [(dmpe)$_2$MnH(SiH$_2$''Bu)$_2$] ($^{20}_{\text{R}}$) and free H$_2$SiPh$_2$ or H$_2$SiEt$_2$, respectively. This reaction was complete in several hours (for $^{16}_{\text{Et2}}$) or minutes (for $^{16}_{\text{Ph2}}$).

Scheme 8.1: Proposed catalytic cycle for ethylene hydrosilylation by primary and secondary hydrosilanes. [Mn] = Mn(dmpe)$_2$. Only one isomer is shown for complexes 16 and 18. Boxes represent complexes observed by NMR spectroscopy during catalysis.
Unidentified SiH-containing byproducts \{formed in larger amounts in reactions with H\textsubscript{2}SiPh\textsubscript{2} and H\textsubscript{2}SiPh (after conversion to H\textsubscript{2}SiEtPh); Table 8.1\} may arise from reactions of 23 (or less likely 24) with hydrosilanes resulting in C–Si rather than C–H bond-formation to eliminate a disilylated organic product and generate manganese hydride intermediate [(dmpe)\textsubscript{2}MnH] (12), which can re-enter the proposed catalytic cycle (\textit{vide infra}) as shown in Scheme 8.1. This reactivity bears resemblance to that of [(dmpe)\textsubscript{2}MnEt] (13, which is an isomer of 10; see Chapter 3) with H\textsubscript{2}SiPh\textsubscript{2} to afford a 1:1 mixture of (a) [(dmpe)\textsubscript{2}MnH(=SiPh\textsubscript{2})] (16\textsubscript{Ph\textsubscript{2}}) and ethane, the products of C–H bond-forming oxidative addition / reductive elimination (or σ-bond metathesis) followed by α-hydride elimination, and (b) [(dmpe)\textsubscript{2}MnH\textsubscript{2}(SiHPh\textsubscript{2})] (18\textsubscript{Ph\textsubscript{2}}) and Ph\textsubscript{2}SiEtH, the products of C–Si bond-forming oxidative addition / reductive elimination (or σ-bond metathesis) to form [(dmpe)\textsubscript{2}MnH] (12), followed by oxidative addition of a second equivalent of H\textsubscript{2}SiPh\textsubscript{2} (see Chapter 4).

Pathways 'a', 'b' and 'c' described above (green reaction arrows in Scheme 8.1) generate the observed disilyl hydride (20\textsubscript{R}), silylene hydride (16) and silene hydride (19) complexes. However, they do not explain the formation of vinyl silane byproducts. These byproducts can be accessed by vinylsilane dissociation from intermediate \textsubscript{A}, forming low-coordinate hydride species 12, which can react with either of the available organic substrates: ethylene to form 10, or hydrosilanes to form silyl dihydride complexes (18); Scheme 8.1. While 10 reacts with primary or secondary hydrosilanes (but not tertiary hydrosilanes) to generate ethane and low-coordinate silyl species 17, complex 18 can slowly rejoin the catalytic cycle by H\textsubscript{2} elimination to afford 17. Support for this H\textsubscript{2} elimination process was obtained experimentally at elevated temperatures. For example, heating a solution of [(dmpe)\textsubscript{2}MnH\textsubscript{2}(SiH\textsubscript{2}Ph)] (18\textsubscript{Ph}) under D\textsubscript{2} at 70-80 °C overnight resulted in > 90% deuterium incorporation into the MnH environments, exclusively. Furthermore, reactions of 18\textsubscript{Bu} with \textsuperscript{t}BuNC, and [(dmpe)\textsubscript{2}MnD\textsubscript{2}(SiH\textsubscript{2}Ph)] (\textsubscript{d\textsubscript{2}}\textsubscript{18}\textsubscript{Ph}) with

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\textsuperscript{ggg} In hydrosilylation reactions with \textsubscript{d\textsubscript{4}}-ethylene, the vinyl byproducts contain fully deuterated vinyl groups, in keeping with the proposed pathway for their formation.
o-xylylNC, afforded [(dmpe)$_2$Mn(SiH$_2^n$Bu)(CN$^t$Bu)] (21d) and [(dmpe)$_2$Mn(SiH$_2$Ph)(CNXyl)] (21a), respectively, after 1 h at 75 °C.

In an effort to determine whether pathway 'a' (via primary alkyl intermediate 23), 'b' (via secondary alkyl intermediate 24), or 'c' (via a silene hydride complex with an SiH substituent; $^{19R,H}$) in Scheme 8.1 is operative, catalysis was carried out using $d_4$-ethylene; pathway 'a' would generate CD$_2$CD$_2$H groups, whereas pathways 'b' and 'c' would generate CHDCD$_3$ groups.\(^{hhh}\) Hydrosilylation of C$_2$D$_4$ by the secondary hydrosilane H$_2$SiEt$_2$ yielded $d_4$-HSiEt$_3$, primarily as HSiEt$_2$(CD$_2$CD$_2$H) (97%), with a minor amount of HSiEt$_2$(CDHCD$_3$) (3%), as determined by $^1$H, $^2$H, and $^{13}$C{$^1$H} NMR analysis (Appendix 2), indicating that pathway 'a' in Scheme 8.1 is dominant. By contrast, C$_2$D$_4$ hydrosilylation by H$_2$Si$^n$Bu under identical conditions yielded a solution containing 20% HSi$^n$Bu(CD$_2$CD$_2$H)$_2$, and 80% HSi$^n$Bu(CD$_2$CD$_2$H)(CDHCD$_3$); Appendix 2. Given that H$_2$SiEt$_2$ has been shown to react almost exclusively via pathway 'a' (affording a CD$_2$CD$_2$H substituent on silicon), and H$_2$Si$^n$BuEt can be expected to react analogously, this product distribution indicates that H$_2$Si$^n$Bu is converted to H$_2$Si$^n$BuEt primarily via pathway 'b' and/or 'c' (~77%), with a lesser contribution from pathway 'a' (~23%).

DFT calculations indicate that alkyl intermediates 23 and 24 are very similar in energy (within 5 kJ mol$^{-1}$). Therefore, the preferential reactivity of secondary silanes towards less hindered 23 (pathway 'a') may be sterically driven. By contrast, for conversion of primary to secondary hydrosilanes, where pathway 'b' and/or 'c' is dominant, it is not obvious why pathway 'b' would be preferred over pathway 'a'. Pathway 'c' is therefore a viable alternative, especially given that 'c' has been demonstrated (vide supra) in room temperature stoichiometric reactions involving silenes with a hydrogen substituent on silicon ($^{19R,H}$). Furthermore, it is notable that silenes ($^{19R,H}$) are the

\(^{hhh}\) Hydrosilylation reactions involving C$_2$D$_4$ (with either H$_2$Si$^n$Bu or H$_2$SiEt$_2$) proceeded to completion (i.e. complete consumption of the secondary hydrosilane reagent/intermediate) after 4 days at 60 °C, while analogous reactions using a higher pressure of C$_2$H$_4$ still contained 6-7% of the secondary hydrosilane (H$_2$SiEt$^n$Bu intermediate or H$_2$SiEt$_2$ reagent), suggestive of an inverse kinetic isotope effect.
dominant metal-containing species during the first phase of catalysis (conversion of primary to secondary hydrosilanes).

8.5 – Summary and Conclusions for Chapter 8

All of the silyl, silylene and silene complexes prepared in Chapters 4 and 5 were accessed via reactions of [(dmpe)₂MnH(C₆H₄)] (10) with hydrosilanes and/or ethylene. Therefore, ethylene hydrosilylation was investigated using 10 as a pre-catalyst, resulting in stepwise conversion of primary to secondary to tertiary hydrosilanes. Manganese complexes observed during catalysis include (a) disilyl hydride complexes (20R), (b) silylene hydride complexes (16), (c) silene hydride complexes (19), (d) silyl dihydride complexes (18), and (e) the ethylene hydride pre-catalyst (10). All of these species are catalytically active (although the silyl dihydride complexes 18 are significantly less active than the others), and a catalytic cycle is proposed on the basis of these observations, the aforementioned stoichiometric reactions, and hydrosilylation of d₄-ethylene. This catalytic cycle is unusual due to the involvement of silylene hydride and silene hydride complexes, potentially as on-cycle species. While the catalytic system discussed in this chapter displays very low activity relative to many previously reported catalysts, especially those containing precious metals, it is unusual in that it selectively forms tertiary but not quaternary hydrosilanes from ethylene, and utilizes a relatively inexpensive and environmentally benign metal centre.
Chapter 9

Synthesis of Manganese Hydride Complexes with Various Co-ligands
(not including Si-based co-ligands)

Portions of this chapter have been reprinted (adapted) with permission from Price, J. S.; Emslie, D. J. H.; Vargas-Baca, I.; Britten, J. F. [(dmpe)$_2$MnH(C$_2$H$_4$)] as a Source of a Low-Coordinate Ethyl Manganese(I) Species: Reactions with Primary Silanes, H$_2$, and Isonitriles, Organometallics 2018, 37, 3010-3023. Copyright 2018 American Chemical Society.

9.1 – Introduction to Chapter 9

As discussed in Chapter 3, Girolomi and Wilkinson’s ethylene hydride complex trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (trans-10)$^{120,172}$ could react with neutral reagents via either substitution of the ethylene ligand, or via initial isomerization to a 5-coordinate Mn(I) ethyl species [(dmpe)$_2$MnEt] (13).$^{547}$ Reactions of 10 with hydroxilane reagents (Chapters 4-5) yielded a variety of new manganese hydride complexes with different silicon-based ligands. Herein, we present the syntheses of additional manganese hydride complexes “(dmpe)$_2$MnHL” (L = neutral ligand) from 10 by exposure to neutral reagents from groups 13 (B, Al), 14 (Sn), and 15 (P), as well as H$_2$.

9.2 – Reaction of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] with H$_2$

Complex 10, trans-[(dmpe)$_2$MnH(C$_2$H$_4$)], has previously been reported to be unreactive with H$_2$ at room temperature.$^{120}$ However, we found that 10 does in fact react extremely slowly with H$_2$ at room temperature, and more rapidly at elevated temperatures (Scheme 9.1); [(dmpe)$_2$MnH(H$_2$)] (1) and ethane were formed over 5 days at 60 °C in benzene, in >95% purity (77% crude isolated yield), via initial isomerization of 10 to the 5-coordinate ethyl intermediate [(dmpe)$_2$MnEt] (13). When this synthesis was carried out in C$_6$D$_6$, significant deuterium incorporation was observed in the CH$_2$ and CH$_3$
environments of the dmpe ligands (consistent with Jones’ report that complex 11 undergoes H/D exchange between C₆D₆ and the dmpe ligands at elevated temperature).\(^{173}\)

\[ \text{Scheme 9.1: Synthesis of } [(\text{dmpe})₂\text{MnH(H}_2\text{)}] (11). \text{ 12 and 13 are unobserved intermediates.} \]

Complex 11 was previously prepared via the reaction of \([\{(\text{dmpe})₂\text{Mn(μ-AlH}_4\text{)}\}_₂]\) with water\(^{120}\) and it was determined spectroscopically that the dmpe ligands are arranged equatorially with the hydride ligand trans to dihydrogen.\(^{173}\) In this work, X-ray quality crystals of 11 (Figure 9.1 left) were obtained by recrystallization from a concentrated solution in hexanes at \(-30 °C\), confirming that the dmpe ligands lie in a plane, with the manganese atom displaced 0.15-0.16 Å from the plane. Unfortunately, we were unable to locate the hydride and dihydrogen ligands in the difference map. However, DFT calculations (ADF, gas-phase, all-electron, PBE, D3-BJ, TZ2P, ZORA) suggest that the equatorial belt of phosphorus donors is displaced towards the hydride ligand and away from the (bulkier) neutral axial donor (Figure 9.1 right),\(^{iii}\) analogous to the situation in 10 (Chapter 3, Figure 3.1).

The computationally determined H–H distance (1.017 Å, Mayer bond order of 0.40) of the H₂ ligand in 11 is consistent with the presence of a dihydrogen ligand (as opposed to two cis disposed hydride ligands, which generally feature longer than 1.6 Å of separation),\(^{548}\) as proposed by Jones on the basis of variable temperature NMR studies.\(^{173}\) This H–H distance lies between the two estimates reported by Jones on the basis of T₁ NMR measurements (assuming free dihydrogen rotation or not; 0.90(2) and 1.13(2) Å respectively),\(^{173}\) and is greater than those reported for other manganese dihydrogen

\(^{iii}\) Such a structure was obtained upon geometry optimization starting from coordinates with the dmpe ligands displaced towards either the H₂ or H ligands.
complexes (0.81-0.91 Å, determined from $T_1$ or $J_{\text{HD}}$ NMR studies), all of which are cationic.

**Figure 9.1:** Left: X-ray crystal structure of $[(\text{dmpe})_2\text{MnH(H}_2\text{)}]$ (11) with ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. H and H$_2$ ligands were not located from the difference map, and Mn is disordered over two positions, with only one conformation {51.5(1)%} shown; Mn(1A) is the Mn atom not shown in this conformation. Bond distances (Å) and angles (deg): Mn(1)–P(1) 2.1850(7), Mn(1A)–P(1) 2.2201(8), Mn(1)–P(2) 2.2000(6), Mn(1A)–P(2) 2.2032(7), Mn(1)–P(3) 2.2132(7), Mn(1A)–P(3) 2.1953(8), Mn(1)–P(4) 2.2143(6), Mn(1A)–P(4) 2.1907(7), $\Sigma$(P–Mn(1)–P) (cis) 358.96(4), $\Sigma$(P–Mn(1A)–P) (cis) 359.13(6). Right: geometry optimized (DFT calcd.) structure of $[(\text{dmpe})_2\text{MnH(H}_2\text{)}]$ (11).

9.3 – Reactions of trans-$[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4\text{)}]$ with Hydroboranes; Synthesis and Characterization of Borohydride Complexes of Manganese(I)

Exposure of trans-$[(\text{dmpe})_2\text{MnH(C}_2\text{H}_4\text{)}]$ (10) to the hydroborane reagents ‘HBR$_2$’ (BH$_3$·NMe$_3$, 9-BBN, or HBMes$_2$) at 60 °C (from 9-BBN or HBMes$_2$) or 90 °C (from BH$_3$·NMe$_3$) yielded the Mn(I) borohydride complexes $[(\text{dmpe})_2\text{Mn(μ-H)}_2\text{BR}_2]$ (28: R = H, 29: R$_2$ = C$_8$H$_{14}$, 30: R = Mes). Analytically pure samples were only obtained for 30 (34 % yield), while 28 was obtained in > 95 % purity (by NMR spectroscopy; 22 % yield) and pure samples of 29 were not obtained (solutions of > 95 % purity by NMR

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ji The NMe$_3$ adduct of BH$_3$ was used as a source of trihydroborane because free BH$_3$ (or, more specifically, the B$_2$H$_6$ dimer) is a pyrophoric and highly toxic gas.
spectroscopy were obtained by removing red crystals from a collection of yellow and red crystals obtained during recrystallization from hexanes at \(-30 \, ^\circ\text{C}\). The reaction with BH$_3$NMe$_3$ proceeded with ethylene elimination, whereas the reactions with 9-BBN and HBMe$_2$ afforded EtBR$_2$ byproducts (Scheme 9.2). Attempts to extend this reactivity to aluminum were unsuccessful; 10 reacted with DIBAL to produce an unidentified product, which proceeded to decompose at room temperature to numerous hydride containing products.

**Scheme 9.2:** Synthesis of borohydride Mn(I) complexes [(dmpe)$_2$Mn(μ-H)$_2$BR$_2$] (28: R = H, 29: R$_2$ = C$_8$H$_{14}$, 30: R = Mes).

In the synthesis of [(dmpe)$_2$Mn(μ-H)$_2$BH$_2$] (28), the observed ethylene byproduct suggests a simple substitution mechanism. By contrast, the EtBR$_2$ byproducts observed in reactions of 9-BBN or HBMe$_2$ with 10 indicate two possible mechanisms; i) ethylene substitution, followed by hydroboration of the released ethylene by a second equivalent of free HBR$_2$, \textit{kkk} or ii) initial isomerization of the ethylene hydride complex 10 to a 5-coordinate ethyl intermediate [(dmpe)$_2$MnEt] (13), which would react with one equivalent of HBR$_2$ (via either oxidative addition followed by C–B bond forming reductive elimination, or σ-bond metathesis) to generate an ethylborane (EtBR$_2$) and the 5-coordinate hydride complex [(dmpe)$_2$MnH] (12), to which a second equivalent of

\textit{kkk} Ethylene was found to insert into the B–H bond of free 9-BBN or HBMe$_2$ at room temperature, with 90% (9-BBN reaction) or 100% (HBMe$_2$ reaction) conversion to EtBR$_2$ after 1 h at 60 °C in C$_6$D$_6$ under an initial atmosphere of 1.7 atm ethylene.
hydroborane could coordinate. The former mechanism parallels that observed for reactions of 10 with BH$_3$·NMe$_3$ and phosphines (*vide infra*), whereas the latter is analogous to the reactions of 10 with H$_2$ (*vide supra*) or hydrosilanes (Chapters 4-5).$^{507,547}$

To determine which of these two mechanisms is active, we turned to deuterium labelling. In the reaction of two equivalents of DBMes$_2$ with 10, the former mechanism (ethylene substitution) would be expected to generate partially deuterated EtBMes$_2$ (with a single D incorporated into the β ethyl position) and [(dmpe)$_2$Mn(μ-D)(μ-H)BMes$_2$] ($d_1$-30), while the second mechanism {via [(dmpe)$_2$MnEt] (13)} would be expected to generate fully protonated EtBMes$_2$ and [(dmpe)$_2$Mn(μ-D)$_2$BMes$_2$] ($d_2$-30); Scheme 9.3. Monitoring this reaction by $^1$H and $^2$H NMR spectroscopy (Figure 9.2) revealed the latter set of products (the EtBMes$_2$ ethyl environments in the $^1$H NMR spectrum are a quartet and triplet, and the only signal in the $^2$H NMR is shifted to slightly lower frequency relative to the MnH$_2$BR$_2$ proton environment$^{111}$. The reactions of 10 with 9-BBN and HBMes$_2$ therefore proceed via a different mechanism than the reaction with BH$_3$·NMe$_3$. The reason for this difference is unclear but could suggest that the BH$_3$·NMe$_3$ adduct remains intact during the first step of the reaction with 10; this is also consistent with the more forcing conditions required to promote the reaction with BH$_3$·NMe$_3$, relative to 9-BBN or HBMes$_2$.

$^{111}$ The slight difference in δ for the MnD environment in the $^2$H NMR spectrum of $d_2$-30 and the MnH environment in the $^1$H NMR spectrum of 30 is due to isotope shift.
Scheme 9.3: Reaction of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with DBMes$_2$. Only one potential isomer of 13 and $d$-12 is shown.

Figure 9.2: Regions of the $^1$H NMR spectra (n = 1; 500 or 600 MHz, n = 2; 77 MHz) in C$_6$D$_6$ at 298 K containing the EtBMes$_2$ (left) and metal hydride/borohydride (right) environments for, from bottom to top, $^1$H NMR for the reaction of 2 DBMes$_2$ with 10 after heating overnight at 60 °C, $^2$H$^1$H NMR for the reaction of 2 DBMes$_2$ with 10 after heating overnight at 60 °C, $^1$H NMR for the reaction of 2 HBMes$_2$ with 10 after heating overnight at 60 °C, and $^1$H NMR for EtBMes$_2$. * is from an impurity in the C$_6$D$_6$ used.
In the syntheses of \([\text{dmpe}]_2\text{Mn}(\mu-\text{H})_2\text{BR}_2\] (29: \(R_2 = \text{C}_8\text{H}_{14}\), 30: \(R = \text{Mes}\)), an intermediate was observed by NMR spectroscopy (Figure 9.3), with a high-field \(^1\text{H}\) NMR signal (29: \(-13.1\) ppm 30: \(-13.0\) ppm). For the intermediate formed from the 9-BBN reaction, four \(^{31}\text{P}\) environments (57.8-85.8 ppm) and a sharp peak at \(-15.5\) ppm in the \(^{11}\text{B}\) NMR spectrum were observed, and the high-field \(^1\text{H}\) NMR peak was a broad singlet. In contrast, the intermediate formed from the \(\text{HBMes}_2\) reaction features a single sharp signal in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum at \(-4.0\) ppm, a broad \(^{11}\text{B}\) NMR environment at \(68.1\) ppm, and the high-field \(^1\text{H}\) NMR peak was an apparent triplet (\(J = 73.5\) Hz). These data suggest that these intermediates are not isostructural, and both contain hydride or borohydride ligands with (for the 9-BBN intermediate) a low-symmetry disphenoidal or (for the \(\text{HBMes}_2\) intermediate) a high-symmetry equatorial dmpe coordination environment. Furthermore, the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the intermediate generated from the 9-BBN reaction contained a small signal at \(-5.4\) ppm, and the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of the intermediate generated from the \(\text{HBMes}_2\) reaction contained a broad signal at 73.5 ppm; these suggest that each mixture contained a small amount of a complex isostructural to the major intermediate complex in the other reaction mixture.

![Figure 9.3](image_url)

**Figure 9.3:** Left: (boro)hydride region of the \(^1\text{H}\) NMR spectra, and right: \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra, for reactions of \(\text{trans-}[\text{dmpe}]_2\text{MnH}(\text{C}_2\text{H}_4)\] (10) with (bottom) 9-BBN or (top) \(\text{HBMes}_2\) before completion. * = peaks attributed to the dominant intermediate isomer, and † = peaks attributed to the minor intermediate isomer. \(\text{C}_6\text{D}_6\), 600 MHz, 298 K.
Attempts to isolate these intermediates were unsuccessful; when a limiting amount (1 equivalent) of 9-BBN was allowed to react with $\text{trans-}[(\text{dmpe})_2\text{MnH}(C_2\text{H}_4)]$ \textbf{(10)} at room temperature until complete consumption of the hydroborane (1 week), a mixture of starting material \textbf{10}, borohydride product \textbf{29}, and this intermediate were observed with a ratio of $1.3 : 0.5 : 2.0$ (assuming that the (boro)hydridic environment in the unidentified intermediate contains a single proton). Upon heating this mixture (with no free hydroborane present), the intermediate cleanly decomposed to a single unidentified hydride-containing complex (with a $^1\text{H}$ NMR pentet at $-11.9$ ppm, $J_{\text{H,P}}$ 55.4 Hz), not the borohydride complex $[(\text{dmpe})_2\text{Mn}(\mu-\text{H})_2\text{BC}_8\text{H}_{14}]$ \textbf{(29)}, suggesting that the intermediate contains a single equivalent of hydroborane. Furthermore, the reaction of \textbf{10} with DBMes$_2$ yielded an intermediate with the (boro)hydride environment fully replaced by deuterium, implying a structure where the hydrogen residual from the MnH environment in \textbf{10} no longer occupies a hydridic position. Therefore, possible identities of these intermediates would be $\sigma$-hydroborane complexes with \textit{cis}- or \textit{trans}- disposed ethyl ligands, $[(\text{dmpe})_2\text{MnEt(HBR)}_2]$ (Figure 9.4), which could be formed by coordination of free hydroborane to $[(\text{dmpe})_2\text{MnEt}]$ \textbf{(13)} in Scheme 9.3, with the reaction proceeding to form transient $[(\text{dmpe})_2\text{MnH}]$ \textbf{(12)} upon C–B bond forming reductive elimination of EtBR$_2$. However, it is unclear why the $^{31}\text{P}$ NMR chemical shifts for the high-symmetry products are so dissimilar to what is normally observed in dmpe complexes of Mn (usually $> 50$ ppm), or why the (boro)hydride $^1\text{H}$ NMR environment is an apparent triplet. No intermediate was observed in the reaction of \textbf{10} with BH$_3$·NMe$_3$, and perhaps its inaccessibility explains why that reaction proceeds via an alternative mechanism; \textit{vide supra}.

Figure 9.4: Potential structures of intermediates in the reaction of $\text{trans-}[(\text{dmpe})_2\text{MnH}(C_2\text{H}_4)]$ \textbf{(10)} with 9-BBN or HBMes$_2$. 

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Borohydride complexes [(dmpe)$_2$Mn(μ-H)$_2$BR$_2$] (28-30) yielded NMR spectra (Figure 9.5) featuring two $^{31}$P NMR signals consistent with a disphenoidal dmpe coordination geometry at Mn (62.6-88.6 ppm), and a single Mn$_2$BR$_2$ $^1$H environment (integrating to two protons) indicating chemical equivalence of the two bridging borohydride protons (28: –16.5 ppm, 29: –15.6 ppm, 30: –14.0 ppm). The single $^{11}$B NMR environments (28: 25.3 ppm, 29: 43.2 ppm, 30: 27.5 ppm) are located within the range associated with tetrahedral borate environments.$^{549,550}$ However, the moderate downfield shift in the $^{11}$B NMR environment for 28 relative to the bulk of tetrahydroborate complexes$^{551,552}$ is suggestive of some contribution from a boryl dihydride resonance structure. For [(dmpe)$_2$Mn(μ-H)$_2$BH$_2$] (28), a single environment (integrating to two protons) was located for the two terminal MnH$_2$BH$_2$ hydrides at 5.1 ppm. EXSY NMR spectroscopy did not provide evidence for chemical interchange between the bridging and terminal borohydride environments in 28 up to 339 K; this lies in contrast to the majority of tetrahydroborate complexes of transition metals, for which the bridging and terminal environments rapidly interchange.$^{553}$ In the case of [(dmpe)$_2$Mn(μ-H)$_2$BMes$_2$] (30), the NMR spectra are consistent with hindered rotation at the B–C bond, leading to magnetic inequivalence of the two sides of each mesityl ring.

![Figure 9.5: NMR spectra for borohydride complexes [(dmpe)$_2$Mn(μ-H)$_2$BR$_2$] (28: R = H, 29: R$_2$ = C$_8$H$_{14}$, 30: R = Mes) in $d_8$-toluene (28, 30) or C$_6$D$_6$ (29) at 298 K. From left to right, the MnH$_2$BR$_2$ region of the $^1$H NMR spectra (600 MHz), the $^{11}$B{$^1$H} NMR spectra (192 MHz), and the $^{31}$P{$^1$H} NMR spectra (243 MHz).](image-url)
In the $^{1}$H NMR spectra of $[(\text{dmpe})_{2}\text{Mn}(\mu-\text{H})_{2}\text{BR}_{2}]$ (28: $R = \text{H}$, 29: $R_{2} = \text{C}_{8}\text{H}_{14}$, 30: $R = \text{Mes}$), the MnH$_{2}$BR$_{2}$ and (for 28 only) MnH$_{2}$BH$_{2}$ signals are broad, and in the case of 28, they also feature unusual coupling patterns. However, upon decoupling the $^{11}$B nuclei these signals collapsed into sharp singlets. Furthermore, variable temperature (174-339 K) $^{1}$H NMR spectroscopy of $[(\text{dmpe})_{2}\text{Mn}(\mu-\text{H})_{2}\text{BH}_{2}]$ (28) shows that both the MnH$_{2}$BH$_{2}$ and MnH$_{2}$BH$_{2}$ signals transform from sharp singlets at low temperature to multiplets approaching the expected 1:1:1:1 quartet at high temperature due to coupling to $^{11}$B (Figure 9.6); the $^{10}$B satellites were not resolved, but could contribute the broadness of the signals. Together, this suggests that these borohydride signals are in the process of quadrupolar collapse due to the proximity of these environments to quadrupolar $^{11}$B.

**Figure 9.6:** Variable temperature (174-339 K) $^{1}$H NMR spectra of $[(\text{dmpe})_{2}\text{Mn}(\mu-\text{H})_{2}\text{BH}_{2}]$ (28) zoomed into the (left) terminal MnH$_{2}$BH$_{2}$ and (right) bridging MnH$_{2}$BH$_{2}$ regions in $d_{8}$-toluene at 500 MHz. Chemical shift scale refers to the spectrum at c. 178 K, and each additional spectrum above that is shifted to lower frequency by 0.1 ppm (MnH$_{2}$BH$_{2}$ region) or 0.4 ppm (MnH$_{2}$BH$_{2}$ region) for clarity.
X-ray crystal structures were obtained for borohydride complexes \textbf{28-30} (Figure 9.7), and in each case feature an octahedral environment around Mn composed of the two dmpe ligands (with a disphenoidal geometry) and a borohydride ligand (with two bridging hydrides, located from the difference map, occupying the remaining coordination sites on Mn, and the angles between the H(1)–Mn–H(2) and H(1)–B–H(2) planes ranging from 0.2-8.3°).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9_7.png}
\caption{X-ray crystal structures of [(dmpe)$_2$Mn(μ-H)$_2$BR$_2$] (28: R = H, 29: R$_2$ = C$_8$H$_{14}$, 30: R = Mes) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity. Hydrogen atoms on Mn and B were located from the difference map and refined isotropically. For 28, distances (Å) and angles (deg): Mn–B 2.170(4), Mn–H(1) 1.76(4), Mn–H(2) 1.78(4), B–H(1) 1.34(4), B–H(2) 1.31(4), B–H(3) 1.19(5), B–H(4) 1.18(4), H(1)–Mn–H(2) 75(2), H(1)–B–H(2) 109(2), θ{H(1)–Mn–H(2) plane to H(1)–B–H(2) plane} 8.3. For 29, distances (Å) and angles (deg): Mn–B 2.206(2), Mn–H(1) 1.71(2), Mn–H(2) 1.66(3), B–H(1) 1.31(2), B–H(2) 1.25(2), B–C(1) 1.624(2), B–C(5) 1.626(3), H(1)–Mn–H(2) 70(1), H(1)–B–H(2) 99(1), θ{H(1)–Mn–H(2) plane to H(1)–B–H(2) plane} 3.5. For 30, distances (Å) and angles (deg): Mn–B 2.245(3), Mn–H(1) 1.69(4), Mn–H(2) 1.72(4), B–H(1) 1.24(3), B–H(2) 1.19(4), B–C(1) 1.647(5), B–C(10) 1.647(6), H(1)–Mn–H(2) 65(2), H(1)–B–H(2) 97(2), θ{H(1)–Mn–H(2) plane to H(1)–B–H(2) plane} 0.2.}
\end{figure}
Description of the “R₂BH₂” moiety as a borohydride ligand (a single anionic ligand involving two 3-centre-2-electron bonds to Mn), as opposed to a boryl dihydride (three anionic ligands) or hydroborane hydride (an anionic hydride and neutral hydroborane) bonding motif, is supported by acute H₁─Mn─H₂ angles of 65(2)–75(2)° and high symmetry {B─H(1) and B─H(2) distances are statistically equivalent}, respectively. Furthermore, the relatively long Mn─B distances of 2.170(4)-2.245(3) Å are characteristic of complexes with significant B─Hₐₐ interactions (borohydride or σ-hydroborane complexes).

Complexes 29-30 are the first structurally characterized borohydride complexes of manganese with hydrocarbyl substituents on the borate ligand, and therefore allow a direct comparison of the effects that terminal hydride (28), alkyl (29), and aromatic (30) substituents on boron have on the “Mn(μ-H)₂B” core. Proceeding along this series from 28 to 30 (with increasing steric bulk at the boron centre), the Mn─B distances increase from 2.170(4) to 2.245(3) Å and the H─Mn─H angles decrease from 75(2) to 65(2)°. Furthermore, the Mn─P distances trans to the hydrogen atoms in the borohydride ligands (28: 2.193(1)-2.197(1) Å, 29: 2.2112(6)-2.2176(5) Å, 30: 2.215(1)-2.216(1) Å) are significantly shorter than to those perpendicular to the MnH₂ plane (28: 2.219(1)-2.229(1) Å, 29: 2.2433(5)-2.2463(5) Å, 30: 2.267(1)-2.268(1) Å).

In a borohydride complex with terminal hydrides on boron (e.g. 28), the terminal B─H distances would be expected to be shorter than the bridging B─H distances. The X-ray data for [(dmpe)₂Mn(μ-H)₂BH₂] (28) does appear to support this trend {d(B─H₈terminal) = 1.18(4)-1.19(5) Å, d(B─H₈bridging) = 1.31(4)-1.34(4) Å}, but large standard deviations in the bond distances prevent conclusions from being drawn. However, DFT calculations yielded a geometry optimized structure of 28 with B─H₈terminal distances (1.21-1.22 Å, Mayer bond order of 0.81) significantly shorter than the B─H₈bridging distances (1.32 Å, Mayer bond order of 0.55). Furthermore, significant Mayer bond orders were observed between Mn and both the boron atom (0.43) and bridging hydrides (0.48), though the
calculated structure does slightly underestimate the Mn–B distance (2.13 Å relative to 2.170(4) Å observed in the solid state).

Unlike the previously reported aluminum analogue [(dmpe)$_2$Mn(μ-H)$_2$AlH(μ-H)$_2$Mn(dmpe)$_2$],$^{120,172}$ 28 is monomeric {though with an isostructural ‘(dmpe)$_2$Mn(μ-H)$_2$E’ (E = Al, B) unit}. This difference is due to the inability of B to obtain a coordination number of 5, which would be required to access the dimeric structure. The observed monomeric structure is beneficial in terms being a potential precursor for applications in vapour-phase deposition; 28 sublimes at 80 °C (5 mTorr).

Borohydride complexes have been reported for many transition metals. While a number of borohydride complexes of divalent Mn(II) are known, the first (and, to our knowledge, only) monometallic, low-valent Mn(I) complexes with non-chelating borohydride ligands are [((Ar$_{Dipp}^2$NC)$_2$(OC)$_2$Mn(μ-H)$_2$BHR] (R = H, OSO$_2$CF$_3$; Figure 9.8), reported by Figueroa in 2017.$^{552}$ The Mn–B distances (2.170(4) to 2.245(3) Å) observed in complexes 28-30 are comparable to those in Figueroa’s borohydride complex [((Ar$_{Dipp}^2$NC)$_2$(OC)$_2$Mn(μ-H)$_2$BH(OSO$_2$CF$_3$)] (2.08(3)-2.142(7) Å),$^{553}$ as well as the dimetallic bridging BH$_4$ complex reported by Riera in 1993 (2.048(4) Å)$^{554}$ and a series of chelating borohydride complexes reported by Ghosh (2.137(4)-2.1817(19) Å),$^{555}$ Figure 9.8.

$^{553}$ The Mn–B distance was not reported for [((Ar$_{Dipp}^2$NC)$_2$(OC)$_2$Mn(μ-H)$_2$BH$_2$], and the atomic coordinates are not available through the CSD.
Figure 9.8: Structurally characterized borohydride complexes of Mn(I).

Exposure of [(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28) to D$_2$ (initial pressure of 1.7 atm) for 12 h at 90 °C led to 40 % deuterium incorporation into both the MnH$_2$BH$_2$ and MnH$_2$BH$_2$ environments, with HD and H$_2$ byproducts. This reaction (Scheme 9.4) may proceed by initial BH$_3$ dissociation to generate [(dmpe)$_2$MnH] (12), followed by reaction with D$_2$ to form [(dmpe)$_2$MnH(D$_2$)] ($d_2$-11a). Spectroscopic studies by Jones et al. have shown chemical exchange between the MnH and Mn(H$_2$) positions in 11.$^{173}$ This would allow [(dmpe)$_2$MnH(D$_2$)] ($d_2$-11a) to isomerize to [(dmpe)$_2$MnD(DH)] ($d_2$-11b), from which HD elimination would yield a deuterated analogue of 12 [(dmpe)$_2$MnD] ($d_1$-12), to which the free BH$_3$ could re-associate to form [(dmpe)$_2$Mn($\mu$-H)($\mu$-D)BH$_2$] ($d_1$-28). Subsequent cycles of these reactions {which involve initial elimination and subsequent association of partially deuterated free borane (in each case, via fully protonated 12), and in some cases HD in place of D$_2$} would allow step-wise deuterium incorporation.
Scheme 9.4: Potential mechanism for deuterium incorporation into [(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28) by D$_2$. Only one isomer of 12$_\text{d}_n$ is shown.

9.4 – Synthesis and Characterization of κ$^1$-dmpe Hydride Complexes of Manganese

$^1$H NMR spectra of solutions containing crude borohydride complexes 28-30 all contained a peak at −15.7 ppm, presumably from an identical hydride-containing complex. Closer inspection of these spectra revealed that there are actually two sets of NMR peaks with nearly overlapping MnH signals (0.03 ppm apart), which have been identified by NMR spectroscopy as [{{(dmpe)$_2$MnH}$}_2$($\mu$-dmpe)] (31) and [(dmpe)$_2$MnH(κ$^1$-dmpe)] (32); *vide infra*. For both complexes, the MnH peak is a pentet ($^2J_{\text{H,P}} = 49$ Hz) of doublets ($^2J_{\text{H,P}} = 13$ Hz) from coupling to two $^{31}$P environments; one with four equivalent P donors and the other with one (upon $^{31}$P decoupling, both signals became singlets). The larger coupling constant is comparable to that in Mn(I) hydride complexes where the hydride is located apical to an equatorial plane consisting of two dmpe ligands (e.g. 56.5 Hz in 10).$^{120}$ These data are consistent with pentaphosphino manganese(I) hydride complexes with trans hydride and either μ-dmpe or terminal κ$^1$-dmpe ligands (the additional dmpe ligand is presumably generated by decomposition of one or more of the products or intermediates).
The same mixture of pentaphosphino hydride complexes was independently prepared by the reaction of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with excess free dmpe either under inert atmosphere (overnight at 105 °C) or an atmosphere of H$_2$ (3 days at 60 °C), with either ethylene or ethane observed as the reaction byproduct, respectively (Scheme 9.5). While the former synthesis proceeded via ethylene elimination, the latter proceeded by initial reaction of 10 with H$_2$ to generate [(dmpe)$_2$MnH(H$_2$)] (11; vide infra, Scheme 9.1) and ethane, followed by substitution of H$_2$ by the free phosphine (Jones et al. have shown that the H$_2$ ligand in 11 is prone to substitution reactions by even very weak ligands such as N$_2$). Potentially due to the milder conditions required, the reaction under H$_2$ proceeded more cleanly.

Scheme 9.5: Synthesis (under inert atmosphere (red reaction arrow) or an atmosphere of H$_2$ (blue reaction arrows)) and purification of [(dmpe)$_2$MnH]$_2$(μ-dmpe)] (31) and [(dmpe)$_2$MnH(κ$^1$-dmpe)] (32) from trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10). Only one isomer of 31 and 32 is shown.
Washing the crude mixture with O(SiMe$_3$)$_2$, followed by recrystallization of the residual solid from a concentrated hexanes solution layered with O(SiMe$_3$)$_2$ at $-30$ °C, allowed for the isolation of dimetallic [{$(dmpe)_2$MnH$_2$}$_2$(μ-dmpe)] (31) as orange crystals (Scheme 9.5). The NMR spectra of 31 (Figure 9.9 bottom) indicate 2.5 equivalents of dmpe (5 P moieties) per MnH environment with two broad singlets at 78.9 and 26.5 ppm in the $^{31}$P{$_1^1$H} NMR spectrum; one for the κ$^2$-coordinated ligands, and one for the bridging ligand. For the bridging ligand, the alkyl region of the $^1$H NMR spectrum contains a single PCH$_3$ signal (a doublet with $^2$J$_{H,P}$ = 3.6 Hz, integrating to 6 × the MnH area) and a single PCH$_2$ signal (a multiplet, integrating to 2 × the MnH area). The apparent $C_{2v}$ symmetry of 31 indicates that the complex contains trans disposed hydride and bridging dmpe ligands (trans,trans-[$(dmpe)_2$MnH$_2$](μ-dmpe)]; trans,trans-31).

**Figure 9.9:** Alkyl (left) and hydride (middle) regions of the $^1$H NMR spectrum, and the full $^{31}$P{$_1^1$H} NMR spectrum (right) of (top) [{$(dmpe)_2$MnH(κ$^1$-dmpe)}] (32) and (bottom) [{$(dmpe)_2$MnH$_2$}$_2$(μ-dmpe)] (31) in C$_6$D$_6$ at 298 K (600 MHz). * and † represent PCH$_3$ environments from the κ$^1$- and chelating dmpe ligands, respectively.

Upon allowing complex 31 to sit in C$_6$D$_6$ at room temperature, a new set of NMR signals slowly appeared (immediately after recrystallization, they were present in the
baseline; approx. 5% relative to the major isomer), with a single Mn\textsubscript{H} \textsuperscript{1}H NMR environment at –11.7 ppm featuring a very complex coupling pattern, and five resolved \textsuperscript{31}P NMR environments (40.91-76.12 ppm). Due to the low symmetry of this product, these NMR signals have been tentatively assigned to an alternative isomer of \textsuperscript{31} with a disphenoidal arrangement of the chelating dmpe ligands; \textit{cis,cis-}[{(dmpe)\textsubscript{2}MnH}\textsubscript{2}(\mu-dmpe)] (\textit{cis,cis-31}).

By contrast, when the crude mixture of \textsuperscript{31} and \textsuperscript{32} was sublimed at 120 °C \textit{in vacuo}, monometallic [(dmpe)\textsubscript{2}MnH(\kappa\textsuperscript{1}-dmpe)] (\textsuperscript{32}) was isolated as a yellow powder. The NMR spectra of \textsuperscript{32} (Figure 9.9 top) indicate 3 equivalents of dmpe (6 P moieties) per Mn\textsubscript{H} environment. Two broad singlets (at 79.3 and 28.4 ppm), along with a sharp doublet ($J_{P,P} = 14$ Hz, –48.9 ppm), were observed in the \textsuperscript{31}P{\textsuperscript{1}H} NMR spectrum. One of the high-frequency signals is from the \kappa\textsuperscript{2}-coordinated ligands, and the other from the donor atom on the \kappa\textsuperscript{1}-coordinated phosphine. The low-frequency \textsuperscript{31}P{\textsuperscript{1}H} NMR signal is consistent (both in frequency and line sharpness) with a PR\textsubscript{3} environment which is not coordinated to a metal centre (cf. the \textsuperscript{31}P{\textsuperscript{1}H} signal from free dmpe is a sharp singlet at –48.1 ppm), and has therefore been attributed to the pendent phosphine on the \kappa\textsuperscript{1}-coordinated ligand. For the terminal dmpe ligand, the alkyl region of the \textsuperscript{1}H NMR spectrum contained two PCH\textsubscript{3} signals (both doublets with $2J_{H,P} = 3.8$ and 2.9 Hz, each integrating to 6 \times the Mn\textsubscript{H} area) and two PCH\textsubscript{2} signals (both multiplets, each integrating to 2 \times the Mn\textsubscript{H} area). These data, combined with apparent C\textsubscript{2v} symmetry, indicate that \textsuperscript{32} features \textit{trans} disposed hydride and \kappa\textsuperscript{1}-coordinated dmpe ligands; \textit{trans,trans-}[{(dmpe)\textsubscript{2}MnH(\kappa\textsuperscript{1}-dmpe)] (\textit{trans,trans-32}).

Spectroscopically pure samples of \textit{trans,trans-32} were not obtained, as the sublimed sample contained some minor impurities (including a low-symmetry species with a Mn\textsubscript{H} environment at –11.7 ppm, which may be an alternative isomer of \textsuperscript{32} with the chelating dmpe ligands forming a disphenoidal geometry). It is currently unclear whether sublimation of the crude reaction mixture only extracts complex \textsuperscript{32} already present in the mixture, or whether decomposition of \textsuperscript{31} occurs at the sublimation
temperature to generate additional 32. The volatility of compound 32 suggests that it could potentially be utilized as a precursor for vapour-phase deposition of Mn-containing thin films.

Upon recrystallization of reaction mixtures containing [{(dmpe)$_2$MnH}$_2$(μ-dmpe)] (31) from hexanes or O(SiMe$_3$)$_2$ at –30 °C, X-ray quality crystals were obtained for both the high- and low- symmetry isomers of 31. These structures (Figure 9.10) feature two octahedral Mn centres separated by a bridging dmpe ligand, with the remaining five coordination sites occupied by two chelating dmpe ligands and a hydride.

The X-ray crystal structure of 31 obtained from hexanes is consistent with the dominant isomer observed in solution by NMR spectroscopy (trans,trans-31; vide supra); Figure 9.10 left. Each octahedral Mn core is related to the other by an inversion centre. The Mn–P distances are 2.2055(4)-2.2138(4) Å for the two chelating dmpe ligands, which are significantly shorter than the Mn–P distance of 2.2331(4) Å to the bridging dmpe ligand, reflecting the higher trans influence of hydride vs. phosphine ligands.

In contrast to the structure of trans,trans-31, the X-ray crystal structure of 31 obtained from O(SiMe$_3$)$_2$ (Figure 9.10 right) features a disphenoidal coordination geometry of the two chelating dmpe ligands, and the bridging phosphine ligand is cis disposed to the hydride ligand (cis,cis-31). This structure could be the source of the NMR signals tentatively identified as a ‘minor isomer’ in solutions of 31 (vide supra). Unfortunately, poor crystal quality precluded any quantitative analysis of the bonding metrics in cis,cis-31.
Figure 9.10: X-ray crystal structures of (left) trans,trans-\([\{(\text{dmpe})_2\text{MnH}\}_2(\mu-\text{dmpe})]\) (trans,trans-31) and (right) cis,cis-\([\{(\text{dmpe})_2\text{MnH}\}_2(\mu-\text{dmpe})]\) (cis,cis-31) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity. Hydrogen atoms on Mn(1) were located from the difference map and refined isotropically {the hydride on Mn(2) in the cis,cis isomer was not located from the difference map and is not included in the figure or CIF}. For trans,trans-31, distances (Å) and angles (deg): Mn(1)–P(1) 2.2331(4), Mn(1)–P(2) 2.2138(4), Mn(1)–P(3) 2.2065(4), Mn(1)–P(4) 2.2114(4), Mn(1)–P(5) 2.2055(4), Mn(1)–H(1) 1.53(1), P(1)–Mn(1)–H(1) 174.8(6), Σ(P–Mn–P) (cis, equatorial) 355.02(2). For cis,cis-31, all dmpe ligands were disordered over two positions, and only the major conformation (84.3(2)% is shown. Due to poor quality data, bond metrics are not discussed.

9.5 – Reaction of trans-\([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) with HPPH₂

Heating 10 with an excess of HPPH₂ at 90 °C yielded the monometallic pentaphosphino hydride complex \([(\text{dmpe})_2\text{MnH}(\text{PHPH}_2)]\) (33), accompanied by
elimination of free ethylene (Scheme 9.6). This parallels the reaction of 10 with dmpe (vide supra), and presumably proceeded via straightforward ethylene substitution.

Scheme 9.6: Synthesis of [(dmpe)\textsubscript{2}MnH(PHPh\textsubscript{2})] (33).

The NMR spectra of 33 are very similar to those observed for the dominant species in solutions of complexes 31 and 32, and feature a single Mn\textsubscript{1}H \textsuperscript{1}H NMR environment at –14.08 ppm {a pentet ($^{2}J_{\text{H,P}} = 51$ Hz) of doublets ($^{2}J_{\text{H,P}} = 12$) due to coupling to two $^{31}$P environments} and two $^{31}$P NMR signals (Figure 9.11 bottom). While the terminal P\textsubscript{1}H environment was not immediately apparent in the \textsuperscript{1}H NMR spectrum, this was due to serendipitous overlap of both peaks of the doublet with larger aromatic \textsuperscript{1}H NMR signals. However, this signal was conclusively located at 7.28 ppm by \textsuperscript{1}H{$^{31}$P} (Figure 9.11 top) and $^{31}$P–\textsuperscript{1}H HMBC NMR spectroscopy. Furthermore, cooling a solution of 33 in d\textsubscript{8}-toluene led to temperature-dependent migration of \textsuperscript{1}H NMR signals, allowing the doublet to be resolved at 207 K (Figure 9.12). Very large $^{31}$P–\textsuperscript{1}H coupling constants were measured from \textsuperscript{1}H, $^{31}$P, and/or $^{31}$P–\textsuperscript{1}H HMBC NMR spectroscopy at both 298 K (288 Hz; Figure 9.11) and 207 K (282 Hz; Figure 9.12). The apparent $C_{2v}$ symmetry of 33 in solution suggests a geometry about Mn involving trans-disposed hydride and HPPH\textsubscript{2} ligands.
Figure 9.11: NMR spectra (C₆D₆) of [(dmpe)₂MnH(PHPh₂)] (33) at 298 K; aromatic (left) and hydride (middle) regions of the ¹H (bottom) and ¹H{³¹P} (top) NMR spectra (600 MHz), and ³¹P{¹H} (top right) and ³¹P (bottom right) NMR spectra (243 MHz).

Figure 9.12: NMR spectra (d₈-toluene, 500 MHz) of [(dmpe)₂MnH(PHPh₂)] (33) at 207 K; aromatic region of the ¹H (bottom left) and ¹H{³¹P} (top left) NMR spectra, and (right) the region of the ³¹P–¹H HMBC spectrum showing the cross-peak between the terminal PH signal and the major ³¹P environment.

Solutions of 33 contained a second set of ¹H NMR signals in very small concentrations (negligible upon initially dissolving, growing to ~10% after 4 days at
room temperature), including a Mn$^H$ environment (at –11.4 ppm) with a complex coupling pattern. This impurity could potentially be an alternative isomer of 33 with a disphenoidal dmpe arrangement, and cis disposed HPPH$_2$ and hydride ligands (similar to that observed for cis,cis-31; vide supra). Unfortunately, low concentrations and the broadness of the NMR signals prevented identification. Furthermore, complex 33 is unstable in solution and slowly decomposed to yield numerous unidentified products, as well as free HPPH$_2$, hindering attempts to obtain an analytically pure sample.

X-ray quality crystals of [(dmpe)$_2$MnH(PHPh$_2$)] (33) were obtained from a hexanes solution at –30 °C (Figure 9.13), and revealed an octahedral environment about the manganese centre composed of the two chelating dmpe ligands equatorially coordinated, and the hydride trans to the HPPH$_2$ ligand \{$\angle$H–Mn–P$_{\text{HPPh}_2}$ = 165(3)$^\circ$\} with Mn–P–C$_{\text{ipso}}$ angles of 122.9(1)-126.2(1)$^\circ$, and a Mn–P–H(1P) angle of 116(2)$^\circ$.

The Mn–P distances involving the chelating dmpe ligands in 33 \{2.2091(7) to 2.2255(7) Å\} are similar to those involving the chelating dmpe ligands in trans,trans-31. By contrast, the Mn–P$_{\text{PHPh}_2}$ distances of 2.2048(8)-2.206(2) Å in 33 are significantly shorter than the Mn–P$_{\nu1}$ distance of 2.331(4) Å in trans,trans-7, which is consistent with the expected greater degree of $\pi$-backdonation from the electron rich Mn(I) centre to a HPPH$_2$ ligand relative than to a trialkylphosphine ligand.

nnn The two phenyl substituents in 33 are tilted towards the axis formed by the Mn–H bond.
Figure 9.13: X-ray crystal structure of $[(\text{dmpe})_2\text{MnH(PHPh}_2\text{)}]$ (33) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity. Hydrogen atoms on Mn(1) and P(1) were located from the difference map and refined isotropically. The HPPh$_2$ ligand was disordered over two positions, and only the major conformer {86.8(2)\%} is shown.oo The HPPh$_2$ location in the minor conformation wasn’t located from the difference map.

Distances (Å) and angles (deg), where atoms with the ‘A’ suffix refer to those in the minor disordered HPPh$_2$ ligand analogous to those without that suffix: Mn(1)–P(1) 2.2048(8), Mn(1)–P(1A) 2.206(2), Mn(1)–P(2) 2.2195(7), Mn(1)–P(3) 2.2202(8), Mn(1)–P(4) 2.2255(7), Mn(1)–P(5) 2.2091(7), Mn(1)–H(1) 1.38(7), P(1)–H(1P) 1.35(5), P(1)–Mn(1)–H(1) 165(3), P(1A)–Mn(1)–H(1) 165(3), Mn(1)–P(1)–H(1P) 116(2), Mn(1)–P(1)–C(1) 126.2(1), Mn(1)–P(1A)–C(1A) 124.8(5), Mn(1)–P(1)–C(7) 122.9(1), Mn(1)–P(1A)–C(7A) 124.0(6), $\Sigma$(P–Mn–P) (cis, equatorial) 355.11(6).

Complexes 31 and 33 are, to our knowledge, the first pentaphosphino hydride complexes of manganese to be crystallographically characterized. Furthermore, the only previously reported spectroscopically characterized example, $[(\text{F}_3\text{P})_5\text{MnH}]$, differs significantly from an electronic standpoint (PF$_3$ is a poor σ-donor and strong π-acceptor, comparable to carbon monoxide).
9.6 – Reactions of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with Hydrotin Reagents

Exposure of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) to HSnPh$_3$ generated a dark pine-green solution containing a manganese(II)-stannyl complex identified as [(dmpe)$_2$MnH(SnPh$_3$)] (34; vide infra), along with ethylene and, presumably, additional unidentified products (Scheme 9.7). The $^1$H NMR spectrum of 34 featured five broad signals over a wide range of chemical shifts, characteristic of one or more paramagnetic complexes, suggesting oxidation of the metal centre. Unfortunately, attempts to purify complex 34 were unsuccessful because it is unstable under vacuum, decomposing to a number of species including SnPh$_4$. As well, reactions of 10 with HSn$^n$Bu$_3$ resulted in paramagnetic species (determined by $^1$H NMR spectroscopy), though no ethylene was formed, and attempts to identify the product(s) were unsuccessful. The reaction of 10 with stannyl hydride reagents clearly differs from the other reactions of 10 discussed in this work (including reactions with lighter group 14 hydrosilane reagents; Chapters 4-5) by involving 1-electron redox chemistry.

Scheme 9.7: Reaction of trans-[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) with HSnPh$_3$.

Large turquoise crystals of [(dmpe)$_2$MnH(SnPh$_3$)] (34) were obtained from toluene at \(-30 \, ^{\circ}C\) (Figure 9.14), and the structure was found to be octahedral about the manganese centre with a disphenoidal arrangement of the two chelating dmpe ligands, and cis disposed stannyl (–SnPh$_3$) and hydride ligands. While the metal hydride ligand lies exactly trans to a phosphine (\(\angle H\text{–}Mn\text{–}P(4) = 176(2)^{\circ}\)), the stannyl ligand is angled towards the hydride (\(\angle H\text{–}Mn\text{–}Sn = 71(2)^{\circ}\)) presumably due to steric repulsion from the methyl groups of one or more dmpe ligands.
Figure 9.14: X-ray crystal structure of \([(\text{dmpe})_2\text{MnH(SnPh}_3)]\) (34) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity. The hydrogen atom on Mn(1) was located from the difference map and refined isotropically. Distances (Å) and angles (deg): Mn(1)–Sn(1) 2.5944(7), Sn(1)–H(1) 2.52(5), Mn(1)–H(1) 1.47(5), Mn(1)–P(1) 2.259(1), Mn(1)–P(2) 2.235(1), Mn(1)–P(3) 2.240(1), Mn(1)–P(4) 2.247(1), P(1)–Mn(1)–Sn(1) 146.34(3), H(1)–Mn(1)–Sn(1) 71(2), H(1)–Mn(1)–P(4) 176(2), Mn(1)–Sn(1)–C(1) 117.11(9), Mn(1)–Sn(1)–C(7) 119.80(7), Mn(1)–Sn(1)–C(13) 122.21(9), P(2)–Mn(1)–P(3) 176.85(4).

The Mn–Sn distance in 34 of 2.5944(7) Å is within the range previously reported for manganese complexes with non-bridging Sn(IV) ligands; 2.446-2.693 Å, \(^{211}\) and significantly shorter than the two structurally characterized manganese stannyl hydride (or \(\eta^2\)-hydrostannane) complexes, \([(\text{OC})_2\text{Cp}^\text{Me}\text{MnH(SnPh}_3)]\) \{d(Mn–Sn) = 2.636(1) Å\} \(^{557}\) and \([(\text{OC})_3\text{Mn(μ-H)(μ-dppm)Mn(CO)}_3\text{(SnPh}_3)]\) \{d(Mn–Sn) = 2.6415(7) Å\} \(^{558}\). In contrast to \([(\text{OC})_2\text{Cp}^\text{Me}\text{MnH(SnPh}_3)]\), which was described as featuring an \(\eta^2\) hydrostannane ligand in the process of oxidative addition across a manganese centre \{d(Sn–H) = 2.16(4) Å, \(\angle\text{Sn–Mn–H} = 55(2)^\circ\}\) \(^{557}\), the bonding metrics in 34 \{d(Sn–H) = 2.52(5) Å, \(\angle\text{Sn–Mn–H} = 71(2)^\circ\}\) suggests that no significant interligand stannyl-hydride interaction is present. \([(\text{dmpe})_2\text{MnH(SnPh}_3)]\) (34) is, to our knowledge, the first reported example of a manganese(II) complex which contains both hydride and stannyl ligands.
However, the mechanism for the formation of 34 is unclear, it could not be isolated in pure form, and the mechanism of decomposition to form SnPh₄ remains obscure.

9.7 – Summary and Conclusions for Chapter 9

\( \text{trans-}[\text{dmpe}]_2\text{MnH(C}_2\text{H}_4]\) (10) has been shown to be a versatile precursor from which to access a variety of new manganese hydride complexes; the previously reported dihydrogen complex \([\text{dmpe}]_2\text{MnH(H}_2]\) (11), the borohydride complexes \([\text{dmpe}]_2\text{Mn}(\mu-\text{H})\text{BR}_2\] (28: \(R = \text{H}\), 29: \(R = \text{C}_8\text{H}_{14}\), 30: \(R = \text{Mes}\)), pentaphosphino hydride complexes \([\{(\text{dmpe})_2\text{MnH(PR}_3\}\}_n]\) (31: \(\text{PR}_3 = 0.5\ \text{dmpe}, n = 2\); 32: \(\text{PR}_3 = \kappa^1\)-dmpe, \(n = 1\); 33: \(\text{PR}_3 = \text{HPPh}_2\), \(n = 1\) ), and the stannyl hydride complex \([\text{dmpe}]_2\text{MnH(SnPh}_3\]\) (34). In some cases, these reactions proceeded by ethylene substitution, and in others via initial isomerization of 10 to \([\text{dmpe}]_2\text{MnEt}\) (13) followed by ethane or ethylborane elimination (the mechanism to form 34, however, remains unclear).

X-ray crystal structures were obtained for the borohydride complexes 28-30, and provided an opportunity to examine the effect that different terminal substituents on boron (H, alkyl, aromatic) have on structural parameters. Complexes 29-30 are the first examples of manganese borohydride complexes with hydrocarbyl substituents on boron, and complex 28 was shown to undergo H/D exchange under an atmosphere of D₂.

\[
[\{(\text{dmpe})_2\text{MnH}\}_2(\mu-\text{dmpe})]\ (31), [\{(\text{dmpe})_2\text{MnH}(\kappa^1-\text{dmpe})]\ (32), and [\{(\text{dmpe})_2\text{MnH(PPh}_3\}\] (33) were prepared, and 31 and 33 are the first pentaphosphino hydride complexes of manganese to be structurally characterized. Compound 31 features a dmpe ligand bridging between two well-separated Mn centres, and X-ray crystal structures were obtained for two isomers with an equatorial or disphenoidal arrangement of the chelating dmpe ligands on each metal centre.

Unlike the reactions of 10 with hydroboranes and phosphines, 10 reacted with HSnPh₃ to afford the divalent manganese complex \([\{(\text{dmpe})_2\text{MnH(SnPh}_3\}\] (34) via 1-electron oxidation. Compound 34 is the first manganese(II) stannyl hydride complex to
have been structurally characterized, and its structure features cis-disposed hydride and stannyl ligands without a significant Sn···H interligand interaction (in contrast to previously reported [(OC)$_2$MeCpMnH(SnPh$_3$)], for which such an interaction was observed).
Chapter 10

Future Directions

10.1 – Future Directions Pertaining to Vapour-phase Deposition of Mn-containing Thin Films

Chapter 2 includes solution-state reactions involving dialkylmanganese(II) complexes (1 and 2) or their Lewis base adducts (3-8) with H\textsubscript{2} or ZnEt\textsubscript{2}, which resulted in electroless deposition of elemental manganese or a Mn:Zn alloy, respectively. Furthermore, the 1:1 dmpe adducts of Mn(CH\textsubscript{2}EMe\textsubscript{3})\textsubscript{2} (E = C, Si; complexes 3 and 4) exhibited desirable properties for an ALD or CVD precursor. Because of this, future work in this area will include attempts to deposit Mn and Mn:Zn alloy films by ALD using complexes 3 or 4 in combination with H\textsubscript{2} or ZnEt\textsubscript{2} as a co-reactant.

Initial efforts in this direction will be to determine if the electroless deposition observed in Chapter 2 could be mirrored in an ALD-type experiment (which involves reactivity at a vapour-surface interface).\textsuperscript{ppp} If a thin film could successfully be deposited using these precursor/co-reactant combinations, it will be necessary to determine i) if the film growth is self-limiting, ii) the rate of film growth, iii) the chemical composition of the film, iv) which substrates the film could be deposited on (e.g. silica, H-terminated silicon, various metals), and v) the deposition temperature range for which ALD could be observed. Furthermore, additional co-reactants could be investigated for deposition of elemental thin films using the same dialkylmanganese(II) precursors (3 or 4). These could include other hydride sources such as hydrosilanes or hydroboranes, as well as other ethyl sources such as AlEt\textsubscript{3} or BEt\textsubscript{3}. This work will involve initial solution-state test

\textsuperscript{ppp} It cannot be assumed that reactivity at a surface-vapour interface will mimic that observed in solution. One reason for this is that upon absorption to a surface, the environment around the metal centre will be significantly different than in the free molecule (for example, by complete or partial phosphine dissociation from 3 or 4).
reactions similar to those described in section 2.5 for H₂ and ZnEt₂, and promising results will be followed up in a manner described above (i.e. attempts to deposit a film by ALD).

Other work in this area could involve determination if dialkylmanganese(II) complexes could be generic Mn-containing precursors for ALD of a variety of Mn-containing thin films. For example, reactions with H₂O, H₂S, NH₃, or HF could potentially yield various Mn-containing films (MnSₓ, MnOₓ, MnNₓ, or MnFx, respectively); Scheme 10.1. Deposition of Mn-containing films by ALD, with the exception of manganese oxide films, remains a relatively unexplored area of research (see section 1.2.8).

Scheme 10.1: Potential deposition of Mn-containing films using proton-source co-reactants. For example, E = O, S, N, or F, and x = 1 or 0.5.

Lastly, deposition of Mn-containing films by CVD using Mn(I) hydride complexes could be explored. Deposition of elemental manganese could be envisaged by the reactivity outlined in Scheme 10.2; initial dissociation of the neutral non-dmpe co-ligand (which, when free of the metal centre, would be neutral, volatile, and thermally stable) to generate the reactive intermediate [(dmpe)₂MnH] (12), which could decompose to form Mn(s) and volatile byproducts by dmpe dissociation and bimolecular H–H bond-forming reductive elimination. Some hydride complexes in this work have displayed promising physical properties (thermal stability and volatility) for acting as vapour-phase precursors, including [(dmpe)₂MnH(C₂H₄)] (10), [(dmpe)₂MnH(κ¹-dmpe)] (32) and
[(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28). The thermal stability and volatility of many other manganese hydride complexes reported in this work have yet to be determined. For hydride complexes which are determined to have these necessary (for CVD) physical properties, CVD experiments will be conducted and the resulting films will be analyzed as discussed above for ALD, with the exception of determination of self-limiting growth, which is not relevant for CVD.

**Scheme 10.2:** Potential CVD reactivity to obtain thin films of elemental manganese from manganese(I) hydride precursors. L represents a neutral, volatile ligand (e.g. HBR$_2$, PR$_3$). Only one isomer of all complexes are shown.

### 10.2 – Future Directions Pertaining to Dialkylmanganese(II) Chemistry

In 2010, the Cámpora group reported that the reaction of [(bipy)Mn(CH$_2$SiMe$_3$)$_2$] with a quarter equivalent of O$_2$ yielded the mixed valence species [{Mn$_2$(CH$_2$SiMe$_3$)$_3$(μ-O)(bipy)}]$_2$. It would be interesting to observe the differences in structure between this species and those produced by an analogous reaction of the dmpe and/or dmpm adducts of Mn(CH$_2$EMe$_3$)$_2$ (E = C, Me) discussed in Chapter 2. Exposure of some of the dialkylmanganese(II) complexes discussed in this work to trace oxygen led to a change in colour from yellow/orange/red to green (an excess of oxygen resulted in an exothermic conversion to a black powder), suggesting formation of a molecular higher valent alkyl species. In addition, similar chemistry could be explored with limiting and stoichiometric equivalents of other reagents such as S$_8$ or P$_4$.
10.3 – Future Directions Pertaining to the Structure of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10)

Chapter 3 highlighted that [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) is unusual for a 1$^{\text{st}}$ row transition metal complex in that it is observed in solution and the solid state as an alkene hydride complex, as opposed to an ethyl species (the product of 1,2-insertion). DFT calculations indicated that this is due to the unique steric environment provided by the two chelating dmpe ligands. A combination of these DFT calculations and trapping experiments showed that complex 10 is in equilibrium with the 5-coordinate ethyl complex [(dmpe)$_2$MnEt] (13), from which reactions with main group hydrides could proceed. Further work in this area could examine how altering the steric and electronic nature of both the phosphine and alkene ligands in complex 10 would affect the alkene hydride to ethyl equilibrium.

Initial work could be carried out computationally by comparing the difference in energy between these species (as well as the cis alkene hydride isomer) when different phosphine or alkene groups were used. It would be relatively simple to repeat the calculations described in Chapter 3 using input coordinates with, for example, CF$_3$ or phenyl groups in place of methyl group on the phosphine, a propyl linker in place of the ethylene linker on the phosphine, or a sterically bulky substituent could replace one of the hydrogen atoms on the alkene.

Experimentally, analogues of 10 with different alkene ligands can be prepared by H$_2$ substitution from [(dmpe)$_2$MnH(H$_2$)] (11), in a manner similar to Jones’ synthesis of 10 and a 1-pentene analogue of 10 (a in Scheme 10.3). Alternatively, such complexes could be prepared by exposing the silylene hydride complex [(dmpe)$_2$MnH(=SiEt$_2$)] (16$^{\text{Et}_2}$) to different terminal alkenes; preliminary results show that 16$^{\text{Et}_2}$ reacts with 3-trimethylsilylpropene and 1-octene to form the alkene hydride complexes trans-
In the reactions of terminal alkenes with $16^{\text{Et}2}$, no intermediate was observed spectroscopically to suggest the formation of a transient silene complex, however it is possible that this mechanism passes through an unobserved silene hydride intermediate in an analogous manner to the reactions of silene hydride complexes with multiple equivalents of ethylene (described in Chapter 5); \(b\) in Scheme 10.3. Presumably, similar reactivity would be observed from $[(\text{dmpe})_2\text{MnH}(\text{Et}_2\text{Si}=\text{CHMe})]$ (19\(^{\text{Et}2}\)), though there is no apparent benefit to using this higher-value complex as a reagent relative to using $16^{\text{Et}2}$ (c in Scheme 10.3).

**Scheme 10.3:** Potential routes (a-c) to the synthesis of derivatives of $[(\text{dmpe})_2\text{MnH} (\text{C}_2\text{H}_4)]$ (10) with different alkene ligands. Only one isomer of each complex is shown, R\(\neq\)H.

Lastly, attempts could be made to prepare the alkyne analogue of complex 10, to compare the structure and reactivity of this species to that of the alkene hydride complex reported in this work. A potential synthetic route could involve substitution of H\(_2\) from $[(\text{dmpe})_2\text{MnH}(\text{H}_2)]$ (11) by a free alkyne (a in Scheme 10.4). Alternatively, a pathway

\[^{999}\text{These complexes featured a } ^1\text{H NMR environment at } -13.05\text{ ppm (3-} \text{trimethylsilylpropene complex) or } -12.87\text{ ppm (1-octene complex) corresponding to the MnH environment. An X-ray crystal structure was obtained for the 3-} \text{trimethylsilylpropene analogue.}\]
can be envisaged analogous to the initial synthesis of \([(\text{dmpe})_2 \text{MnH} (\text{C}_2\text{H}_4)] (10)\) with a divinyl magnesium reagent in place of \(\text{MgEt}_2\) (b in Scheme 10.4).

**Scheme 10.4:** Potential routes (a-b) to the synthesis of \([(\text{dmpe})_2 \text{MnH} (\text{alkyne})]\) complexes. For route b, \(R' = \text{H}\).

### 10.4 – Future Directions Pertaining to DFT Calculations

In Chapters 4, 5, and 7, various mechanisms were proposed for the synthesis of a number of different manganese complexes, and in Chapter 8 a potential catalytic cycle for ethylene hydrosilylation was proposed. In some cases, DFT calculations were employed to demonstrate the thermodynamic accessibility of some of the proposed intermediates (as well as, in some cases, trapping studies and high temperature NMR spectroscopy). Furthermore, we gained some insight into the mechanism for ethylene hydrosilylation by deuterium labelling experiments. In all cases, however, multiple potential reaction pathways were proposed. DFT calculations can be employed to analyze each of the proposed reaction pathways (involving locating energy minima for all potential intermediates, potential energy profiles for each transformation, and transition states) to determine which of the proposed reaction pathways is of lowest energy for each case. Such knowledge could potentially allow for rational design of new reaction chemistry.

### 10.5 – Future Directions Pertaining to Manganese Silylene Hydride Complexes

The synthesis of silylene hydride complex \([(\text{dmpe})_2 \text{MnH} (=\text{SiEt}_2)] (16\text{Et}_2)\) required very mild reaction conditions (i.e. the reaction mixture could not be heated above
ambient temperature), and therefore took a full month before 100% conversion was observed. When heated above 30 °C, 16^Et decomposed to form a new complex tentatively identified as \((\text{dmpe})\{k^3-P(\text{Me})_2\text{CH}_2\text{CH}_2P(\text{Me})\text{CH}_2\text{SiEt}_2\}\text{MnH}_2\)], which features two hydride ligands and a tridentate bis(phosphine)-silyl ligand, by \(^1\text{H}\) NMR spectroscopy. Tilley et al. reported that an analogous structure was formed from the decomposition of \([\text{Cp}^*(\text{dmpe})\text{MoH}(=\text{SiR}_2)]\) (R = Me, Ph).\(^{226}\) Future work in this area could involve isolating and fully characterizing this species.

Chapter 5 discussed the use of DFT calculations, trapping experiments, and high temperature NMR spectroscopy to show the accessibility of base-free silylene hydride complexes with a hydrogen substituent on Si (\((\text{dmpe})_2\text{MnH}(=\text{SiHR})\); 16^RH) from disilyl hydride complexes \([(\text{dmpe})_2\text{MnH}(\text{SiH}_2\text{R})_2]\) (20^R). Further work in this field could involve isolation of these complexes; to date no manganese complexes with an electronically unstabilized terminal silylene ligand featuring a terminal SiH substituent have been isolated. Three potential routes to obtaining such complexes are shown in Scheme 10.5. First, reactivity could be envisaged where NHC-stabilized silylene hydride complexes featuring a terminal SiH substituent \([(\text{dmpe})_2\text{MnH}(=\text{SiHR}(\text{NHC}))]\) react with a reagent capable of abstracting the NHC; a in Scheme 10.5. Given that complexes 22 are presumably in an equilibrium with free NHC and the base-free silylene complex (see Chapter 5), reagents could be chosen which will preferentially react with free NHCs and added stoichiometrically to remove the free NHC from this equilibrium.\(^{226}\) The Fillipou group has used B(p-tol)_3 to obtain a base-free silylyne complex from an NHC-stabilized silylyne complex, with elimination of an NHC-borane adduct.\(^{349}\) Preliminary results in this area involved the reaction of excess BPh_3 with \([(\text{dmpe})_2\text{MnH}(=\text{SiH}^n\text{Bu}(\text{iPrNHC}))]\) (22b), which resulted in clean conversion to a single hydride-containing species and a byproduct tentatively identified by NMR spectroscopy as an adduct of BPh_3 and \((\text{iPrNHC}). Presumably, this reaction involved initial NHC abstraction to form the base-free silylene hydride complex \([(\text{dmpe})_2\text{MnH}(=\text{SiH}^n\text{Bu})]\)

\(^{226}\) Care should be taken not to add an excess of the abstraction reagent because it could potentially react with the highly reactive target base-free silylene hydride complex.
(16_{Bu,H}), which proceeded to react with a second equivalent of BPh$_3$ to form an as-yet unidentified species (2 equiv. of BPh$_3$ were consumed in the reaction).

Scheme 10.5: Potential routes to isolation of manganese complexes bearing electronically unstabilized terminal silylene ligands with a terminal SiH substituent; [(dmpe)$_2$MnH(=SiHR)] (16$_{R,H}$). Only one isomer is shown for all complexes.

A related pathway would be removal of free hydrosilane from a solution containing a disilyl hydride complex [(dmpe)$_2$MnH(SiH$_2$R)$_2$] (20$_R$), which is in equilibrium with a base-free silylene hydride complex and a free hydrosilane (Chapter 5); b in Scheme 10.5. A possible reagent for this is $i$PrNHC, which irreversibly reacts with free hydrosilanes (care must be taken not to add an excess of NHC, or it will form the NHC-stabilized silylene complex 22$_a$).$^{511}$ Alternatively, attempts can be made to form
such a complex directly from [(dmpe)$_2$MnH(C$_2$H$_4$)] (10), using very bulky primary hydrosilanes H$_3$SiR (e.g. R = ‘Bu, Mes, Dipp); c in Scheme 10.5. Perhaps the steric bulk will inhibit addition of a second equivalent of hydrosilane to the putative silyl intermediate [(dmpe)$_2$Mn(SiH$_2$R)] (17$^R$); the presumed intermediate in the reactions of 10 with H$_3$SiR (R = ‘Bu, Ph) in Chapter 5. This would allow the silyl intermediate to isomerize to a base-free silylene hydride complex [(dmpe)$_2$MnH(=SiHR)] in a manner similar to that observed in the reaction of 10 with secondary hydrosilanes (Chapter 4).  

Chapters 4, 6, and 7 include discussion of the reactions of silylene hydride complexes 16$^R$$_2$ with H$_2$, ethylene, CO$_2$, and diisopropylcarbodiimide (reactions of disilyl hydride complexes 20$^R$, which are in equilibrium with silylene hydride complexes, with H$_2$ and ethylene were also discussed in Chapters 5-6). Investigation of the reactivity of manganese silylene hydride complexes can be further expanded to additional reagents such as ketones and imines.

Reactions of silylene hydride complexes 16$^R$$_2$ with H$_2$ or (potentially) ethylene are proposed to proceed via a 5-coordinate silyl intermediate accessed by 1,1-insertion. The accessibility of this complex can be confirmed by trapping experiments with isonitriles, similar to how an isostructural complex was trapped from solutions of disilyl hydride complexes 20$^R$ (Chapter 5).

10.6 – Future Directions Pertaining to Manganese Silene Hydride Complexes

In the synthesis of [(dmpe)$_2$MnH(Ph$_2$Si=CHMe)] (19$^{Ph_2}$), an unidentified hydride-containing intermediate was observed by NMR spectroscopy. Identification of this

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It is also possible that the increased steric bulk in the primary hydrosilane reagent will inhibit reaction with 10 from occurring at all.
species (potentially via low temperature NMR spectroscopy) could provide corroboration for the proposed synthetic mechanism (Chapter 4).  

Chapter 5 also contained a discussion of the first spectroscopically observed transition metal silene hydride complexes featuring a hydrogen substituent on Si; 
\[(\text{dmpe})_2\text{MnH}(\text{RHSi=CHMe})\] (19R,H: R = "Bu, Ph). However, we were unsuccessful at obtaining X-ray quality crystals, so the literature currently contains no solid state structural characterization of these types of complexes. Future work in this area could involve preparing derivatives of 19R,H where the non-H substituent on Si is a group which would allow for easier crystallization. Use of different primary hydrosilanes in the initial synthesis of disilyl hydride complexes 20R (the precursors to 19R,H) should allow a family of such complexes to be prepared. Examples of R groups which may promote crystallization of 19R,H are Me, Pr, or p-PrPh (though it should be noted that H3SiMe and H3SiPr are gases at room temperature, and the latter is not commercially available).

To date, no spectroscopically or crystallographically observed silene complexes of transition metals have been reported which contain two hydrogen substituents on Si. Attempts to obtain such a complex could involve reactivity analogous to that presented in Chapter 5 but with SiH4 in place of a primary hydrosilane. This could initially yield a disilyl hydride complex \([(\text{dmpe})_2\text{MnH}((\text{SiH}_3)_2)]\) (20H) which could then react with ethylene to form the target silene hydride complex \([(\text{dmpe})_2\text{MnH}(\text{H}_2\text{Si=CHMe})]\) (19H2); Scheme 10.6. In addition, isolation or observation of a manganese silylene complex with two terminal SiH substituents (16H2) would be of interest in its own right. Such a complex would presumably be in equilibrium with the proposed disilyl hydride intermediate (and could potentially be observed at high temperature by NMR spectroscopy or trapped by NHC coordination; Scheme 10.6).

\[\text{cis-19}^{\text{Ph}_2}\] (see Chapter 5 for discussion of different possible isomers), which is kinetically more accessible but isomerizes to a lower-energy (observed) product over time.
Scheme 10.6: Potential routes for accessing a silene hydride complex or an NHC-stabilized silylene hydride complex with two terminal SiH substituents. Only one isomer is shown for all complexes.

Absent from this work is an investigation of the reactivity of manganese silene hydride complexes 19. This investigation could reflect what we have done for silylene hydride complexes, including what has been proposed for future directions in that field (see Chapter 7 or section 10.5). For example, reactions with various small molecules (e.g. ketones, alkynes, CO$_2$, C(N$'$Pr)$_2$, imines) could be carried out for silene hydrides with- and without- an SiH substituent.

10.7 – Future Directions Pertaining to Silyl Dihydride Complexes

Chapter 6 discussed the structures of silyl dihydride complexes [(dmpe)$_2$MnH$_2$(SiHR']) (18), which feature nonclassical silyl hydrosilane or silicate

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**uuu** With the exception of the stoichiometric reaction with ethylene or hydrosilanes, and the catalytic hydrosilylation of ethylene.
ligands. The strength of the Si–H interactions is commonly inferred from the Si–H distances. However, X-ray crystallography is notoriously inaccurate in locating hydrogen atoms. Therefore, in this work we turned to DFT calculations to analyze these distances. Future work in this field could involve obtaining neutron structures, for which accurate Si–H distances could be obtained (along with other key bonding metrics such as the Mn–H distances and Si–Mn–H angle).

The silyl dihydride complexes discussed in chapter 6 exist in solution as an equilibrium between multiple isomers, two of which (central and transHSi) were observed by NMR spectroscopy. The ratios of observed central : transHSi isomers ranged from 87 : 13 to 27 : 72. Further work in this field could involve investigating how the steric and electronic properties of the substituents on Si affect this equilibrium. Analogues of 18 could be prepared with various silicon substituents including hydrogen, halogens, or bulky aromatic groups (such as Dipp).

Lastly, Chapter 6 introduced $^{29}$Si$_{\text{edited}}$ $^1$H–$^1$H COSY NMR spectroscopy, which could be used for measuring the sign and magnitude of the $^{29}$Si–$^1$H coupling constants (by a modification of the Scherer method). This method was able to locate $^{29}$Si satellites with greater accuracy than standard $^1$H–$^1$H COSY spectroscopy (used by Scherer), and in some cases was able to locate signals which could not be located at all in the $^1$H–$^1$H COSY experiment. However, these experiments were very time-consuming, so further work in this area could involve optimizing the $^{29}$Si$_{\text{edited}}$ $^1$H–$^1$H COSY experiment (such as by applying a double quantum filter (dqf) sequence).

10.8 – Future Directions Pertaining to Reactions of Disilyl Hydride Complexes with CO$_2$ and C(N$^i$Pr)$_2$

Chapter 7 contained a discussion of the reactions of disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)] ($^{20}$R) with diisopropylcarbodiimide {C(N$^i$Pr)$_2$} to form the manganese(I) amidinylsilyl complexes [(dmpe)$_2$Mn{κ$^2$-SiHR(N$^i$PrCHN$^i$Pr)}] ($^{25}$R$^\text{H}$). Given the similarities between reactions of either $^{20}$R or silylene hydride complexes $^{16}$R$^2$
with either H\textsubscript{2}, ethylene, or CO\textsubscript{2}, which form isostructural products (Chapters 4-7), this chemistry can be expanded to determine if similar manganese(I) amidinylsilyl complexes could be formed from reactions of C(N\textsubscript{i}Pr)\textsubscript{2} and silylene hydride complexes. Furthermore, the reactivity of complexes 25\textsuperscript{R,H} towards a variety of small molecules can be investigated.

Reactions of CO\textsubscript{2} with disilyl hydride complexes 20\textsuperscript{R} or silylene hydride complex 16\textsuperscript{Et2} were shown to yield trans-[(dmpe)\textsubscript{2}Mn(CO)(κ\textsuperscript{1}-O\textsubscript{2}CH)] (26) with polysiloxane byproducts. In Chapter 7, the polysiloxane byproducts were only characterized by NMR spectroscopy, and further characterization would be useful. Examples of characterization techniques which could be employed are Gel Permeation Chromatography (for measuring molecular weight average and distribution) and IR spectroscopy (to obtain chemical information to supplement that provided by NMR spectroscopy).\textsuperscript{559} In addition, the polysiloxane byproduct formed from the reaction of [(dmpe)\textsubscript{2}MnH(SiH\textsubscript{2}Ph)] (20\textsuperscript{Ph}) and CO\textsubscript{2} {(SiHPhO)\textsubscript{n}} was observed to react with the free hydrosilane byproduct H\textsubscript{3}SiPh. This reaction bears further examination, as does characterization of this as-yet unidentified product. Lastly, formate complex 26 could be investigated for activity towards the catalytic hydrosilylation of CO\textsubscript{2} to form formoxysilanes. Though highly speculative, a potential catalytic cycle (Scheme 10.7) could involve i) O–Si bond-forming σ-bond metathesis (or oxidative addition followed by O–Si bond-forming reductive elimination) of 26 and free hydrosilane to generate the target formoxysilane (silyl formate) and [(dmpe)\textsubscript{2}MnH(CO)] (27), and ii) 1,2-insertion of a C=O bond in CO\textsubscript{2} into the Mn–H bond in 27 to reform complex 26. The second of these two steps has been observed in this work (Chapter 7).
Scheme 10.7: Potential catalytic cycle for hydrosilylation of CO\textsubscript{2} using \textit{trans} - [(dmpe)\textsubscript{2}Mn(CO)(κ\textsuperscript{1}-O\textsubscript{2}CH)] (26). For clarity, a tertiary hydrosilane is shown as feedstock, though this chemistry could also potentially apply to other hydrosilanes.

10.9 – Future Directions Pertaining to Catalytic Hydrosilylation

Chapter 8 includes discussion that [(dmpe)\textsubscript{2}MnH(C\textsubscript{2}H\textsubscript{4})] (10), and the various silicon-containing complexes prepared from reactions of 10 with hydrosilanes (in some cases followed by ethylene or H\textsubscript{2}), are all catalytically active towards the hydrosilylation of ethylene. A potential catalytic cycle was proposed which involves a number of unobserved intermediates. Further work in this area (aside from DFT calculations; section 10.4) can involve attempting to trap the proposed primary or secondary alkyl intermediates (23 or 24), perhaps by the reaction of silene hydride complexes (which are proposed to be in equilibrium with these intermediates) with nucleophiles which could coordinate to the metal centre. Additionally, the substrate scope could be expanded to other unsaturated reagents such as imines, ketones, and aldehydes.
10.10 – Future Directions Pertaining to Manganese Hydride Complexes with non-Si Co-ligands

Chapter 9 highlights reactions of complex \([(\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (10) with a variety of main group species to form new manganese hydride complexes “\((\text{dmpe})_2\text{MnHL}\)” (L = neutral ligand). However, many of the synthetic procedures are very low yielding and require optimization. In addition, many of these complexes require further spectroscopic or crystallographic characterization. This work was not carried out due to time constraints, but will be required prior to publication.

A variety of complexes reported in Chapter 9 have only been tentatively identified, and further characterization is required to confidently identify and understand them. These include intermediates in the reactions of 10 with 9-BBN or HBMes₂ (tentatively identified as cis and trans isomers of \([(\text{dmpe})_2\text{MnEt}(\text{HBR}_2)]\)), as well as ‘impurities’ in solutions of \([\{(\text{dmpe})_2\text{MnH}\}_2(\mu-\text{dmpe})]\) (31), \([(\text{dmpe})_2\text{MnH}(\kappa^1-\text{dmpe})]\) (32), and \([(\text{dmpe})_2\text{MnH}(\text{HPPh}_2)]\) (33) (which have been tentatively identified as isomers of these complexes with a disphenoidal arrangement of the chelating dmpe ligands). As well, attempts should be made to identify the as-yet unidentified product of the reaction of complex 10 with HSn”Bu₃ (including obtaining an X-ray crystal structure).

The reaction of complex 10 with HSnPh₃ to form \([(\text{dmpe})_2\text{MnH(SnPh}_3)]\) (34) is an unusual reaction (compared to reactions of 10 with other reagents in this thesis) in that it involves conversion to a divalent species. The mechanism for formation of 34, as well as the mechanism for its decomposition (under vacuum, 34 decomposes to form various species including SnPh₄) is currently unclear and work could be done to understand this. Furthermore, the source of the deep green colour of solutions containing 34 could be indicative of unusual electronic transitions and could be explored further.

vvv It is unclear at this point if the source of this colour is complex 34 or another species in solution.
Chapter 11

Experimental Methods

11.1 – General Details

11.1.1: Laboratory Equipment and Apparatus

An argon-filled MBraun UNIlab glove box equipped with a –30 °C freezer was employed for the manipulation and storage of all oxygen- and moisture-sensitive compounds. Air-sensitive preparative reactions were performed on a double-manifold high-vacuum line equipped with a two stage Welch 1402 belt-drive vacuum pump (ultimate pressure $1 \times 10^{-4}$ Torr) using standard techniques. The vacuum was measured periodically using a Kurt J. Lesker 275i convection enhanced Pirani gauge. Commonly utilized specialty glassware included thick walled flasks equipped with Teflon stopcocks, a swivel frit assembly, Wilmad-LabGlass LPV EPR tubes, Starna 1-Q-10/GS UV-Vis-NIR cells with spectrosil far-UV quartz windows (transparent from 170 nm to 2700 nm), quartz to pyrex graded seals and Teflon stopcocks, and J-Young or Wilmad-LabGlass LPV NMR tubes. A VWR Clinical 200 Large Capacity Centrifuge (with 28° fixed-angle rotors that hold 12 × 15 mL or 6 × 50 mL tubes, and in combination with VWR high-performance polypropylene conical centrifuge tubes) located within a glove box was used where indicated. Where indicated, a Branson 2510 ultrasonic bath was used to sonicate reaction mixtures. Residual oxygen and moisture was removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.

11.1.2: Solvents

Benzene, diethylether, pentane, octane, and hexamethyldisiloxane were purchased from Aldrich, hexanes, toluene, DME and THF were purchased from Caledon, and deuterated solvents were purchased from ACP Chemicals. Benzene, diethylether, DME THF, pentane, octane, hexamethyldisiloxane, hexanes and toluene were initially dried and distilled at atmospheric pressure from sodium/benzophenone (first eight solvents) or...
sodium (toluene). All solvents were stored over an appropriate drying agent (hexamethyldisiloxane, benzene, diethylether, toluene, $d_8$-toluene, $C_6D_6 = Na/Ph_2CO$; hexanes, pentane = Na/Ph$_2$CO/tetraglyme) and introduced to reactions or solvent storage flasks via vacuum transfer with condensation at $-78 \, ^{\circ}C$.

11.1.3: Starting Materials

Dmpe, dmpm, $H_3SiPh$, $H_3Si^{t}Bu$, $H_2SiEt_2$, $H_2SiPh_2$, $D_2$, 1,4-dioxane, tert-butyl isocyanide, o-xylyl isocyanide, $d_4$-ethylene, 1,3-diisopropylimidazolium chloride, potassium tert butoxide, trimethylsilylmethylmagnesium chloride solution (1.0 M in diethyl ether), ethylmagnesium chloride solution (2.0 M in diethyl ether), 2-mesitylmagnesium bromide solution (1.0 M in THF), CO$_2$, diisopropylcarbodiimide, BH$_3$∙NMe$_3$, 9-BBN, BF$_3$∙Et$_2$O, HPPh$_2$, LiAlH$_4$, LiAlD$_4$, DIBAL, HSnPh$_3$, and HSn$^{t}Bu_3$ were purchased from Sigma-Aldrich. Manganese dichloride, neopentyl chloride, and diethyl zinc (min. 95 % in Sure-Pak cylinder) were purchased from Strem Chemicals. Argon, ethylene, and hydrogen gas were purchased from PraxAir. 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene ($^{Me}$NHC) was obtained from Green Centre Canada. Bis(trimethylsilylmethyl)magnesium (0.25 equivalents of 1,4-dioxane was present in the product),$^{561}$ dineopentylmagnesium (0.8 equivalents of 1,4-dioxane was present in the product),$^{96}$ MgEt$_2$,$^{561}$ FBMes$_2$,$^{562}$ 1,3-diisopropylimidazol-2-ylidene ($^{iPr}$NHC),$^{563}$ HBMes$_2$,$^{564}$ and [(dmpe)$_2$MnH($C_2$H$_4$)] (1)$^{120,172}$ were prepared according to the literature. DBMes$_2$ was prepared in a manner analogous to HBMes$_2$, with LiAlD$_4$ in place of LiAlH$_4$.

11.1.4: Instrumentation and Analysis

Combustion elemental analyses were performed a) in house on a Thermo EA1112 CHNS/O analyzer {samples for elemental analysis (typically 1-4 mg) were packed and sealed in pre-weighed 3 × 6 mm smooth wall tin capsules inside the glovebox. After removal from the glovebox, these capsules were packed into 5 × 8 mm pressed aluminum capsules containing approximately 10 mg of V$_2$O$_5$}, b) by the London Metropolitan University in London, UK, or c) by Midwest Microlabs in Indianapolis, USA.
NMR spectroscopy was performed on Bruker AV200, DRX-500, AV-500, AV-600, and AV-700 spectrometers. Spectra were obtained at 298 K unless otherwise indicated. All $^1$H NMR spectra were referenced relative to SiMe$_4$ through a resonance of the protio impurity of the solvent used: C$_6$D$_6$ ($\delta$ 7.16 ppm) and $d_8$-toluene ($\delta$ 2.08 ppm, 6.97 ppm, 7.01 ppm, and 7.09 ppm). The $^2$H NMR spectra were referenced relative to the solvent used {C$_6$D$_6$ ($\delta$ 7.16 ppm)} or the C$_6$H$_5$D impurity in C$_6$H$_6$ ($\delta$ 7.15 ppm). Also, all $^{13}$C NMR spectra were referenced relative to SiMe$_4$ through a resonance of the $^{13}$C in the solvents: C$_6$D$_6$ ($\delta$ 128.06 ppm) and $d_8$-toluene ($\delta$ 20.43, 125.13, 127.96, 128.87, and 137.48 ppm). The $^{29}$Si NMR spectra were referenced using an external standard of hexamethyldisiloxane in CDCl$_3$ (6.53 ppm), the $^{31}$P NMR spectra were referenced using an external standard of 85% H$_3$PO$_4$ in D$_2$O (0.0 ppm), and the $^{11}$B NMR spectra were referenced using neat BF$_3$·Et$_2$O (0.0 ppm). Relative intensities of overlapping peaks were calculated, where appropriate, using the SOLA feature of Bruker Topspin 3.2. Relative concentrations of species were determined by integration of $^1$H NMR spectra, unless otherwise indicated.

$^1$H–$^1$H COSY NMR spectra (and variations thereof) used to measure $J_{\text{Si,H}}$ from the Scherer method (see Chapter 6) were performed on Bruker AV-500 instruments at the highest temperatures where all peaks are completely resolved. Spectral widths were chosen to ensure all peaks were encompassed. $^1$H–$^1$H{$^{31}$P} dqf COSY NMR spectroscopy required input of a $^{31}$P chemical shift to be used in calculating the frequency used for $^{31}$P decoupling; 75 ppm was used for all samples (of $^{18}$R, $^{18}$R$_2$, and $^{20}$R) because it was close to the $^{31}$P chemical shifts observed for these complexes. $^{29}$Si edited $^1$H–$^1$H COSY NMR spectroscopy required input of a transmitter frequency for the pulses on $^{29}$Si (calculated from the $^{29}$Si chemical shifts; $\delta_{\text{Si}}$) and an estimated $J_{\text{Si,H}}$ used to calculated the delay required to preferentially select, by polarization transfer, those protons interacting with $^{29}$Si (excluding all others). The former was chosen separately for each complex based on an average of the chemical shifts of the central and transHSi isomers. Determination of the latter involved starting with a ‘best guess’ determined from 1D $^1$H NMR spectra (usually the coupling constant between $^{29}$Si and a terminal SiH proton),
followed by repeatedly collecting a 1D slice of a $^1\text{H}--^{29}\text{Si}$ HSQC experiment varying in estimated $J_{\text{Si,H}}$, with the value leading to the greatest intensity of the cross-peak of interest being chosen for use in the 2D experiment. Pertinent parameters (optimized for each sample based on values which gave the best results for $^{29}\text{Si}$_edited $^1\text{H}--^1\text{H}$ COSY NMR experiments) used for all three COSY-type experiments (number of scans, experiment time, td1eff, td2eff, temperature, and for $^{29}\text{Si}$_edited $^1\text{H}--^1\text{H}$ COSY only, $\delta_{\text{Si}}$ and estimated $J_{\text{Si,H}}$) are available in the ESI to reference 510, as are symbolic pulse sequences used for $^1\text{H}--^1\text{H}$ dqf COSY and $^{29}\text{Si}$_edited $^1\text{H}--^1\text{H}$ COSY NMR experiments. For all COSY experiments, pulsed field gradients were used for coherence selection and artifact suppression.

Evans NMR measurements were conducted on the Bruker DRX-500 spectrometer in a manner described in the supporting information for ref. 565, and values are the average of two independent experiments. For 2, $\chi_{[\text{M(corr)}]}$ values above and below room temperature were collected using two different sets of samples; the values from 298 to 335 K were adjusted to give the same room temperature value by correcting the mass used from 8.3 to 8.6 mg, which is within the error of the mass balance.

Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone oil and mounted on either a SMART APEX II diffractometer with a 3 kW sealed-tube Mo generator and SMART6000 CCD detector or on a STOE IPDS II diffractometer with an image plate detector in the McMaster Analytical X-Ray (MAX) Diffraction Facility. A semi-empirical absorption correction was applied using redundant data. Raw data was processed using XPREP (as part of the APEX v2.2.0 software), and solved by either SHELXS-97 (direct)\textsuperscript{566} or SHELXT (intrinsic)\textsuperscript{567} methods. The structure was completed by difference Fourier synthesis and refined with full-matrix least-squares procedures based on $F^2$. In all cases, non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated in ideal positions and then updated with each cycle of refinement (with the exception of hydrogen atoms on Mn, Si, and sometimes C or P (see figure captions in each chapter for a complete list of these H atoms) which were
located from the difference map and refined isotropically}. Refinement was performed using Olex2.\textsuperscript{568}

Powder X-ray diffraction experiments were performed on a Bruker D8 Advance powder diffractometer with Cu K\textalpha radiation (\(\lambda = 0.154\) nm) operated at 40 kV and 40 mA. Powders were packed in 0.5 mm o.d. special glass (SG; wall thickness 0.01 mm) capillary tubes for X-ray diffraction (purchased from Charles Supper Co.) and sealed by inverting to submerge the open end in a pool of Apiezon H-grease within the glovebox. Calculated powder patterns were generated from the low-temperature single crystal data (for complexes 2-8) and a file downloaded from the Cambridge Crystallographic Database (for complex 1)\textsuperscript{99} using Mercury. Experimental powder diffractograms were generated and viewed using Gadds, Powdercell, Crystal Sleuth, Diffrac.eva, Topaz, and PANalytical HighScore.

UV/Vis spectra were obtained on a Cary 50 UV/Visible Spectrometer using 10 mM to 10 \(\mu\)M solutions in hexanes. Melting points were measured on a DigiMelt SRS MPA 160 melting point apparatus; between 1 and 2 mg of each sample was flame-sealed in a thin glass tube under an atmosphere of argon. X-Ray photoelectron spectra were collected on either a Thermo Scientific Thetaprobe or a K-Alpha (Thermo Scientific, E. Grinstead, UK) both of which are located at the University of Toronto. A monochromated Al K-Alpha was used with a spot size of 400 \(\mu\)m. An initial survey spectrum was collected at low energy resolution for composition, as well as the high energy resolution spectrum of the Zn 2p, Zn Aug, and Mn 2p regions.

IR spectra were performed on transmission mode on a Nicolet 6700 FT-IR spectrometer or a Bruker Tensor 27 IR spectrometer as a suspension in Nujol, or as a solution in hexanes or octane, in both cases using CaF\textsubscript{2} plates (for solution measurements, a liquid cell purchased from International Crystal Laboratories was used).

SQUID measurements were collected on a Quantum Design MPMS between 5 K and 300 K at applied fields ranging from 100 Oe (for most) to 10 000 Oe (for complexes...
Roughly 50 mg of sample was placed in a sealed sample rod assembly for transport of air-sensitive samples into the magnetometer (with the exception of 3, where between 2.9 and 3.4 mg of sample was placed in a flame-sealed glass capillary).

Thermal stability data was obtained by sealing approx. 10 mg of powder under argon in a flask with a Teflon valve. This flask was heated to the desired temperature for 24 hours and then cooled to room temperature for visual inspection as well as PXRD and/or $^1$H NMR spectroscopy. When ‘very little’ is used to describe the extent of decomposition, this indicates that the compound darkened in colour, but that decomposition was not observed by PXRD or $^1$H NMR spectroscopy.

11.1.5: DFT Calculations

All calculated structures were fully optimized with the ADF DFT package (SCM, versions 2014.05 to 2018.104). Calculations were conducted in the gas phase within the generalized gradient approximation using the 1996 Perdew-Burke-Ernzerhof exchange and correlation functional (PBE), using the scalar zeroth-order approximation (ZORA) for relativistic effects, and Grimme’s DFT-D3-BJ dispersion correction. Preliminary geometry optimizations were conducted with frozen cores corresponding to the configuration of the preceding noble gas (core = medium) using double-$\zeta$ basis sets with one polarization function (DZP), a Voronoi grid with an integration value of 5, and default convergence criteria for energy and gradients. These structures were further refined using all-electron triple-$\zeta$ basis sets with two polarization functions (TZ2P) and fine integration grids (Voronoi 7 or Becke verygood-quality).

Bond orders were calculated within the Mayer, Gopinathan-Jug, and Nalewajski-Mrozek formalisms. Visualization of the computational results was performed using the ADF-GUI (SCM) or Biovia Discovery Studio Visualizer. Electron density at the bond critical points were obtained using the BADER keyword. NBO analysis was carried out using nbo 6.0 within ADF 2014.5.
Bonding between the ‘(dmpe)$_2$MnR’ (R = H, Et) moiety and neutral ethylene in 10, isonitrile ligands in the two isomers of 14a-b, silylene ligands in 16$^{\text{Et2}}$, and silene ligands in 19$^{\text{Et2}}$ was analyzed in detail by fragment calculations (Ziegler-Rauk Energy Decomposition Analysis$^{580}$ and the ETS-NOCV method$^{577,581}$). In such calculations, fragments had structures as calculated in each optimized whole molecule. Relaxation (optimization) of the individual fragments yielded the preparation energy, i.e. the energetic cost of geometric distortion of the interacting fragments. BSSE values were not calculated, as their contribution is negligible for large interacting molecules.

Analytical frequency calculations$^{582}$ were conducted on all geometry optimized structures (including geometry optimized fragments) to ensure that the geometry optimization led to an energy minimum and to obtain thermodynamic parameters. In a handful of cases, slightly negative frequencies (frequency range from $-1$ to $-25$ cm$^{-1}$) were observed but were shown to be spurious imaginary frequencies using the SCANFREQ command.$^{583}$ In one case ($\text{transH}_2$-$18^{\text{Ph2}}$), the observed negative frequency ($-9$ cm$^{-1}$) was determined to be a dirty mode caused by low barrier rotation of the Mn–Si bond.

Transition states were optimized by minimizing energy gradients while ensuring that the Hessian had a negative eigenvalue for the normal coordinate that contains atomic motions consistent with the transformation (using the TransitionState subkey in the Geometry key block).

NMR coupling constants were calculated (using geometry optimized coordinates derived as discussed above) with the CPL program of the ADF package$^{584}$ from wave functions obtained by hybrid PBE0$^{585}$ (ZORA)$^{571}$ calculations using the TZ2P basis sets with additional steep basis functions (TZ2P-J). This method was benchmarked against published data calculated for nonclassical hydrosilane complexes. The literature results$^{241}$ were reproduced with acceptable accuracy for [(C$_3$H$_4$Me)MnH(SiHPh$_2$)(CO)$_2$] (our method: $-52$ Hz, literature calcd.: $-68$ Hz, literature expt.: $-63$ Hz$^{241}$), [Cp$_2$TiH(SiHPh$_2$)(PMe$_3$)] (our method: $-22$ Hz, literature calcd.: $-28$ Hz, literature expt.:
[28] Hz$^{238}$, and [Cp$_2$TiH(SiHClPh)(PM$_3$)] (our method: 19 Hz, literature calcd.: 23 Hz, literature expt.: 15 Hz$^{256}$).

All reported computational values in this work were for diamagnetic structures (obtained using restricted calculations).XXX Models of 16$^{Bu,H}$ and 17$^{Bu}$ were calculated with the $^n$Bu substituent replaced with an Et group and the two dmpe ligands were replaced with four PH$_3$ groups \{cis-17$^{Et;PH_3}$: cis-[(H$_3$P)$_4$Mn(SiH$_2$Et)], trans-17$^{Et;PH_3}$: trans-[(H$_3$P)$_4$Mn(SiH$_2$Et)], cis-16$^{Et,H;PH_3}$: cis-[(H$_3$P)$_4$MnH(=SiHEt)], trans-16$^{Et,H;PH_3}$: trans-[(H$_3$P)$_4$MnH(=SiHEt)]\}. The resulting minima were compared to those from two additional sets of calculations conducted to model potential paramagnetic structures using the UNRESTRICTED command$^{586}$ in conjunction with forcing two or four unpaired electrons (using the CHARGE command) and explicit occupation numbers (using the OCCUPATIONS command). Similar models were also obtained for various isomers of 13 and 18$^{Et;PH_3}$. In all cases resulting minima were >28 kJ mol$^{-1}$ higher in energy than the corresponding diamagnetic structure.$^{www}$ Paramagnetic minima of cis-17$^{Et;PH_3}$, trans-17$^{Et;PH_3}$, and cis-16$^{Et,H;PH_3}$ resulted in isostructural silyl complexes.

11.1.6: Additional Notes

All prepared complexes are air sensitive, and their products upon reaction with air are malodorous. Therefore, all syntheses were conducted under an atmosphere of argon.

11.2 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 2

Various data is available in the ESI to reference 565, including room temperature $^1$H NMR spectra of complexes 2-8, variable temperature $^1$H NMR spectra of complexes 2-5 and 7-8, variable temperature $^1$H NMR spectra used to obtain Evans measurements for 2,5, and 7, PXRD diffractograms of complexes 1-8, SQUID data tables and plots for complexes 2-8 (including fits to an exchange expression for 2 and 5-8), UV/Vis spectra $^{www}$ A single exception to this is an isomer of 13 with an equatorial arrangement of dmpe donors (13$^{trans}$); see Chapter 3.
of complexes 2-3 and 5-8, $^1$H NMR spectra and PXRD diffractograms for the results of reactions of 1-8 with H$_2$ or ZnEt$_2$, and XPS of solids deposited from the reactions of ZnEt$_2$ with 2 or 7. The identification numbers in reference 565 match those in this thesis. CSD 1450874-1450881 contain the supplementary crystallographic data for 2-7 and 9.

Bis(trimethylsilylmethyl)manganese(II) (1)$^{99}$ and [Mn(CH$_2$SiMe$_3$)(µ-CH$_2$SiMe$_3$)(PEt$_3$)$_2$] (9)$^{112}$ were prepared according to literature procedures.

$$\text{[}\text{Mn(CH}_2\text{CMe}_3\text{)(µ-CH}_2\text{CMe}_3\text{)}\text{]}_2\text{[Mn(µ-CH}_2\text{CMe}_3\text{)]}_2\text{Mn}] \quad (2)$$

MnCl$_2$ (2 g, 15.9 mmol) was suspended in 20 mL of diethyl ether. Mg(CH$_2$CMe$_3$)$_2$(1,4-dioxane)$_{0.8}$ (4.9 g, 20.7 mmol) was dissolved separately in 40 mL of diethyl ether and added dropwise to the MnCl$_2$ suspension over 20 minutes. The reaction was stirred at room temperature for four days with regular sonication. The resulting yellow/light brown suspension was centrifuged to remove MgCl$_2$, and the solvent was removed from the resulting solution in vacuo. Crude 2 was extracted into toluene forming a dark brown solution, and the solvent was again removed in vacuo. The remaining solid was recrystallized from hexanes (~ 10 mL) at –30 °C to afford large brown crystals. The mother liquors were then concentrated and maintained for several days at –30 °C to afford a 2$^{nd}$ batch of crystals; the total yield was 60 % (1.88 g). Note that on one occasion, a white solid was obtained rather than the expected dark brown solid. This solid was likely the Et$_2$O or 1,4 dioxane adduct of dineopentylmanganese(II), and was converted to pure 2 by extended exposure to dynamic vacuum. Compound 2 was found to sublime at 90 °C (5 mTorr) and to melt between 99 and 102 °C. X-ray quality crystals were obtained from hexanes at –30 °C. $^1$H NMR (C$_6$D$_6$, 500 MHz, 298 K): δ 32.6. $^1$H NMR (d$_8$-toluene, 500 MHz, 298 K): δ 28.2 $^1$H NMR (d$_8$-toluene, 500 MHz, 233 K): δ 14.9, 28.9, 65.9. Vis: $\lambda_{max}$ = 464 nm. Anal. Found (Calcd): C, 60.18 (60.90); H, 10.75 (11.24).

$$\text{[Mn(CH}_2\text{SiMe}_3\text{)]}_2\text{(dmpe)} \quad (3) \text{ and } \text{[}[\text{Mn(CH}_2\text{CMe}_3\text{)(µ-dmpe)}\text{]}_2\text{]} \quad (4)$$

The 1:1 dialkylmanganese(II):dmpe adducts were prepared according to literature procedures.$^{111}$ Complex 3 was purified by sublimation (60 °C at 5 mTorr) to a bright yellow powder,
and complex 4 was purified by recrystallization from hexanes to afford a white powder (4 also sublimed cleanly between 80 °C and 100 °C at 5 mTorr). X-ray quality crystals of 3 and 4 were obtained from hexanes at −30 °C. Complex 3: $^1$H NMR (C$_6$D$_6$, 500 MHz, 298 K): δ 20.6, 44.0, 58.1. $^1$H NMR (d$_8$-toluene, 500 MHz, 298 K): δ 20.6, 43.4, 56.4. $^1$H NMR (d$_8$-toluene, 500 MHz, 233 K): δ 26.2, 76 (v. broad). Anal. Found (Calcd): C, 44.16 (44.31); H, 10.36 (10.09). Complex 4: $^1$H NMR (C$_6$D$_6$, 500 MHz, 298 K): δ 25.2, 46.3, 59.1. $^1$H NMR (d$_8$-toluene, 500 MHz, 298 K): δ 25.1, 45.6, 56.5. $^1$H NMR (d$_8$-toluene, 500 MHz, 233 K): δ 30.6, 67 (v. broad). Anal. Found (Calcd): C, 56.02 (55.32); H, 11.11 (11.03).

$$\{\text{[Mn(CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)]}_2(\mu-\text{dmpe})\}$$ (5). Tetrametallic 2 (110 mg, 0.14 mmol) and dimetallic 4 (200 mg, 0.29 mmol) were dissolved in toluene. The solution was stirred overnight at room temperature, and then maintained at −30 °C for several days to obtain black crystals. The mother liquor was concentrated and maintained at −30 °C for several days to obtain a second batch of crystals, leading to a total yield of 92 % (279 mg). The product sublimed at 110 °C at 5 mTorr and melted with
some decomposition between 149 and 151.5 °C. $^1$H NMR ($C_6D_6$, 500 MHz, 298 K): $\delta$ 12.8, 26 (v. broad). $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 12.2, 25 (v. broad). $^1$H NMR ($d_8$-toluene, 500 HMe, 233 K): $\delta$ 4.0, 11.3, 31 (v. broad). Vis: $\lambda_{\text{max}}$ = 486 nm. Anal. Found (Caled): C, 57.06 (57.34); H, 11.23 (11.11).

[{$\text{Mn(CH}_2\text{SiMe}_3)(\mu-\text{CH}_2\text{SiMe}_3)$}_2(dmpm)] (7). A suspension of [{Mn($\mu$-CH$_2$SiMe$_3$)$_2$}]$_x$ (1) (119 mg, 0.52 mmol per Mn) in toluene (20 mL) was cooled to –78 °C. A solution of dmpm (180 mg, 1.3 mmol) in toluene (2 mL) was then added dropwise, and after stirring for 30 minutes at –78 °C and 1.5 hours at room temperature, the suspension turned to a clear orange solution. The solvent was then removed in vacuo and the solid was extracted with hexanes. After centrifuging to remove residual solid, the clear red hexanes solution was maintained at –30 °C for several days. The resulting red crystals were of X-ray quality. Crushing the crystals afforded a light pink powder (99 mg; 52 % yield). Complex 7 sublimed cleanly at 100 °C (5 mTorr) and melted without significant decomposition when heated rapidly to 176 °C (note: partial melting commenced at 160 °C). $^1$H NMR ($C_6D_6$, 500 MHz, 298 K): $\delta$ 3.1, 7.9, 15.5, 24 (v. broad). $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 3.1, 7.7, 15.4, 25 (v. broad). $^1$H NMR ($d_8$-toluene, 500 MHz, 233 K): $\delta$ 2.5, 8.4, 15.4, 25 (v. broad). Vis: $\lambda_{\text{max}}$ = 476 nm. Anal. Found (Caled): C, 42.24 (42.40); H, 9.86 (9.83).

[{$\text{Mn(CH}_2\text{CMe}_3)(\mu-\text{CH}_2\text{CMe}_3)$}_2(dmpm)] (8). dmpm (220 mg, 1.61 mmol) was added to a solution of tetrametallic 2 (310 mg, 0.39 mmol) in a 4:1 mixture of hexanes and toluene (10 mL total). The reaction mixture was stirred for 24 hours after which time the solvent was removed in vacuo to give a brown powder (70 % yield). Both recrystallization over days at –30 °C from saturated hexanes, and slow evaporation of hexanes yielded thin red needles from which poor quality X-ray crystal structures could be obtained. The product sublimed between 100 and 120 °C at 5 mTorr and melted without decomposition between 161 and 165 °C. $^1$H NMR ($C_6D_6$, 500 MHz, 298 K): $\delta$ 8.1, 13.8, 21 (v. broad). $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 8.1, 13.8, 21 (v. broad).
broad). $^1$H NMR ($d_8$-toluene, 500 MHz, 233 K): $\delta$ 4.9, 11.4, 12.9, 19 (v. broad). Vis: $\lambda_{\text{max}}$ = 481 nm. Anal. Found (Calcd): C, 56.16 (56.60); H, 11.34 (11.02).

**Reactions with $H_2(g)$.** Approx. 10 mg of each complex was dissolved in approx. 0.6 mL of $C_6D_6$ (with the exception of $[\text{Mn(µ-CH}_2\text{SiMe}_3)_2]_{\infty}$, which was suspended in approx. 0.6 mL of $d_8$-toluene). The resulting solution (or suspension) was placed in a thick-walled NMR tube with a J-Young Teflon valve and was freeze-pump-thawed ($\times$ 3). The NMR tube was then placed under an atmosphere of hydrogen gas, cooled to –95 °C using a liquid nitrogen-acetone bath, sealed at this low temperature, and warmed to room temperature to provide approx. 1.7 atm of hydrogen gas. Reactions were then observed by $^1$H NMR spectroscopy as a function of time and temperature. Upon reaction completion, gases were removed by exposing to dynamic argon, and solutions were decanted. Shiny metallic mirrors on the walls of the NMR tubes were sonicated into around 2 mL of toluene (rarely, the mirrors were physically scratched into suspension). The resulting silver-black powder was then washed twice with 5 mL of toluene and once with 5 mL of hexanes, dried in vacuo, and examined by PXRD.

**Reactions with diethyl zinc.** These reactions were conducted in a manner analogous to those with $H_2$, with the following modifications: Approx. 10-15 mg of each manganese complex was used, and rather than addition of $H_2$, 1-3 equivalents of neat diethyl zinc was added to the solution (or suspension) in the NMR tube within the glovebox, and the Teflon valve was immediately closed to ensure that volatile reaction byproducts did not escape. The resulting silver mirrors were sonicated to yield silver-black powders (in most cases pyrophoric) which were examined by PXRD, as well as XPS in some cases.

**11.3 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 3**

Various data is available in the ESI to reference 547, including tables of calculated (for isomers of 10, isomers of 13, and isomers of 14a,b) and
crystallographically (for 10) determined bond lengths and angles, tables of bond orders, Hirshfeld charges, zero-point energies, and total bonding energies for calculated structures (isomers of 10, isomers of 13, and isomers of 14a,b), fragment interaction analyses for 10 and 14a,b, potential energy profiles for isomerizations of 10 and 13, and selected NMR spectra for 14a,b and 15. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 547 (X→Y) in the following manner; trans-10→1, cis-10→A, 11→5, 12→D, 13→B, 14→6, and 15→7. CSD 1846647 and 1846650-1846652 contain the supplementary crystallographic data for 10, 14a,b, and 15.

[(dmpe)_2MnH(C_2H_4)] (10) was prepared according to the literature.\(^{120}\)

[(dmpe)_2MnEt(CN^tBu)] (14a). An excess of tert-butyl isonitrile (250 mg, 3.01 mmol) was added to a solution of [(dmpe)_2MnH(C_2H_4)] (10) (129.8 mg, 0.34 mmol) in 10 mL of benzene. The reaction mixture was stirred in a sealed flask at 80 °C for 5 h, after which the solvent was removed \textit{in vacuo} leading to an orange oily solid. Recrystallization from hexamethyldisiloxane at –30 °C afforded 53.2 mg of yellow solid. Concentrating the mother liquor and allowing the solution to sit again at –30 °C afforded another 20.0 mg of the yellow solid, providing a combined yield of 46% (73.2 mg, 0.16 mmol). Upon dissolution in solution, the bulk of the sample was observed to be the \textit{trans} isomer, but a small amount of \textit{cis} isomer was observed in the baseline. To obtain NMR characterization of the \textit{cis} isomer, the reaction was carried out on a smaller scale (13.5 mg 10 and 24 mg CN^tBu) in approx. 0.6 mL of C_6D_6 at 50 °C for 1.5 h, which provided a 3 : 6 : 1 ratio of 10 : \textit{cis}-14a : \textit{trans}-14a, and was analyzed \textit{in situ} (with excess free isonitrile present). This ratio could be improved to 6 : 12 : 1 by removing the solvent \textit{in vacuo} and re-dissolving. X-ray quality crystals of \textit{trans}-14a were obtained from a saturated solution in pentane at –30 °C. \textit{cis}-14a (selected): \(^1\)H NMR (C_6D_6, 600 MHz, 298 K): δ 1.83 (t, 3H, \(^3\)J_{H,H} 8 Hz, CH_2CH_3), 1.54 (d, 3H, \(^2\)J_{H,P} 7 Hz, PCH_3), 1.47 (d, 3H, \(^2\)J_{H,P} 6 Hz, PCH_3), 1.29 (m, 6H, PCH_3), 1.28 (s, 9H, CNC(CH_3)_3), 1.14 (d, 3H, \(^2\)J_{H,P} 5 Hz, PCH_3), 1.04 (d, 3H, \(^2\)J_{H,P} 3 Hz, PCH_3), 0.22 (m, 1H, CH_2CH_3), –0.12 (m, 1H, CH_2CH_3). \(^1^3\)C\{\(^1\)H\} NMR (C_6D_6, 151 MHz, 298 K): δ 53.24 (m, PCH_2), 32.29 (s, CNC(CH_3)_3),
24.25 (s, PCH₃), 23.53 (d, 3J_C,P 10 Hz, CH₂CH₃), 23.32 (d, 1J_C,P 17 Hz, PCH₃), 22.22 (d, 1J_C,P 16 Hz, PCH₃), 19.51 (s, PCH₃), 17.25 (d, 1J_C,P 15 Hz, PCH₃), 14.25 (d, 1J_C,P 13 Hz, PCH₃), –2.47 (m, CH₂CH₃). ³¹P{¹H} NMR (C₆D₆, 243 MHz, 298 K): δ 81 (br. s, 1P), 74.43 (br. s, 1P), 61.58 (br. s, 2P). ¹H NMR (d₈-toluene 500 MHz, 207 K): δ 1.98 (t, 3H, 3J_H,H 7 Hz, CH₂CH₃), 1.60 (d, 3H, 2J_H,P 6 Hz, PCH₃), 1.51 (d, 3H, 2J_H,P 6 Hz, PCH₃), 1.30 (m, 3H, PCH₃), 1.27 (s, 9H, CNC(CH₃)₃), 1.26 (m, 3H, PCH₃), 1.08 (d, 3H, 2J_H,P 4 Hz, PCH₃), 1.01 (d, 3H, 2J_H,P 3 Hz, PCH₃), 0.92 (d, 3H, 2J_H,P 5 Hz, PCH₃), 0.88 (d, 3H, 2J_H,P 3 Hz, PCH₃), 0.26 (m, 1H, CH₂CH₃), xxx –0.11 (m, 1H, CH₂CH₃) ³¹C{¹H} NMR (d₈-toluene, 126 MHz, 207 K): δ 53.98 (s, CNC(CH₃)₃), 34.88 (m, PCH₂), 33.00 (m, PCH₂), 32.01 (s, CNC(CH₃)₃), 30.88 (m, PCH₂), 29.57 (m, PCH₂), 23.82 (d, 3J_C,P 11 Hz, CH₂CH₃), 23.51 (br. s, PCH₃), 22.94 (d, 1J_C,P 17 Hz, PCH₃), 22.05 (d, 1J_C,P 12 Hz, PCH₃), 21.50 (d, 1J_C,P 15 Hz, PCH₃), 18.97 (s, PCH₃), 16.28 (d, 1J_C,P 14 Hz, PCH₃), 13.94 (d, 1J_C,P 12 Hz, PCH₃), 12.45 (m, PCH₃), –2.66 (m, CH₂CH₃). ³¹P{¹H} NMR (d₈-toluene, 202 MHz, 207 K): δ 82.02 (s, 1P), 75.24 (s, 1P), 62.09 (s, 1P), 61.63 (s, 1P). ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 1.51 (m, 4H, PCH₂), 1.43 (m, 4H, PCH₂), 1.41 (t, 3H, 3J_H,H 8 Hz, CH₂CH₃), 1.40 (s, 12H, PCH₃), 1.29 (s, 12H, PCH₃), 1.12 (s, 9H, CNC(CH₃)₃), –0.47 (p of q, 2H, 3J_H,P 8 Hz, 3J_H,H 8 Hz, CH₂CH₃). ¹H NMR (C₆D₆, 151 MHz, 298 K): δ 205.95 (s, CNC(CH₃)₃), 53.79 (s, CNC(CH₃)₃), 32.62 (s, CNC(CH₃)₃), 32.12 (app. p, PCH₂), 24.63 (s, CH₂CH₃), 21.03 (s, PCH₃), 16.49 (s, PCH₃), 1.40 (p, 2J_C,P 17 Hz, CH₂CH₃). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 298 K): δ 74.66 (s). IR: ν(CN) (nujol, cm⁻¹) = 1915 (cis-14a), 1828 (trans-14a). ν(CN) (octane, cm⁻¹) = 1923 (cis-14a), 1829 (trans-14a). Anal. Found (Caled): C, 49.25 (48.82); H, 9.60 (9.92); N, 2.79 (3.00).

[(dmpe)₂MnEt(CNXyl)] (14b). 143.1 mg (0.37 mmol) of [(dmpe)₂MnH(C₂H₄)] (10) and 292.7 mg (2.23 mmol) of o-xyllyl isonitrile were dissolved in 10 mL of benzene. The reaction mixture was heated at 50-55 °C for 2 days, after which time the solvent was...

xxx ³¹P decoupling collapsed the multiplet to a doublet (2J_H,H = 11 Hz) of quartets (3J_H,H = 7 Hz), measured at 500 MHz.

yyy ³¹P decoupling collapsed the multiplet to a doublet (2J_H,H = 11 Hz) of quartets (3J_H,H = 7 Hz), measured at 500 MHz.
removed *in vacuo* to afford a dark brown oil. Attempts to recrystallize 14b from a variety of solvents failed to yield a pure product. However, X-ray quality crystals were obtained by recrystallization from toluene layered with hexanes at –30 °C which resulted in a green-brown oily residue with a small number of small bright orange crystals which could be picked out manually. To obtain NMR characterization of the *trans* isomer, the mother liquor from the aforementioned crystallization was maintained at –40 °C, yielding a green solid which contained *trans*-14b and 15 in a 1 : 6 ratio. To obtain NMR characterization of the *cis* isomer, the reaction was carried out on a smaller scale (17.7 mg 10 and 23.2 mg CNXyl) in C₆D₆ at 50 °C for 2.5 h, which provided a 7 : 1.25 : 1 : 2.5 ratio of 10 : *cis*-14b : *trans*-14b : 15, and was analyzed *in situ* (with excess free isonitrile present). *cis*-14b (selected): ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 6.95 (d, 2H, 3J_H,H 7 Hz, m), 6.76 (m, 1H, p), 2.52 (s, 6H, xylyl-CH₃), 1.92 (t, 3H, 3J_H,P 8 Hz, CH₂CH₃), 1.62 (m, 3H, PCH₂), 1.50 (d, 3H, 2J_H,P 6 Hz, PCH₃), 1.30 (m, 3H, PCH₃), 0.27 (m, 1H, CH₂CH₃). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 23.8 (CH₂CH₃), 21.11 (s, xylyl-CH₃), –1.3 (CH₂CH₃).

*trans*-14b: ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 6.93 (d, 2H, 3J_H,H 7 Hz, m), 6.71–6.82 (m, 8H) and p (5H), 2.33 (s, 6H, xylyl-CH₃), 1.54 (m, 8H, PCH₂), 1.37 (t, 3H, 3J_H,H 8 Hz, CH₂CH₃), 1.35 (s, 12H, PCH₃), 1.20 (m, 12H, PCH₃), –0.43 (p of q, 2H, 3J_H,P 8 Hz, 3J_H,H 8 Hz, CH₂CH₃). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 136.28 (i), 131.42 (s, o), 128.25 (m, m), 120.39 (s, p), 32.16 (m, PCH₂), 24.24 (m, CH₂CH₃), 21.20 (s, PCH₃), 20.81 (s, xylyl-CH₃), 16.27 (s, PCH₃), 3.37 (CH₂CH₃). ³¹P{¹H} (C₆D₆, 202 MHz, 298 K): δ 75.85 (s).

[(dmpe)Mn(CNXyl)₃{C(=NXyl)CEt(=NXyl)}] (15). The mixture of *trans*-14b and 15 (see synthesis of 14b) was then heated under vacuum at 140 °C for 2 hours. The resulting brown solid resisted further purification (approximately 90% pure by NMR spectroscopy). However, 15 was characterized by NMR spectroscopy and X-ray quality crystals were obtained by recrystallization of the crude mixture of *trans*-14b and 15 (see synthesis of 14b) from a dilute solution in hexanes at –30 °C. ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 7.04 (d, 2H, 3J_H,H 8 Hz, m), 6.73–6.82 {m, m (8H) and p (5H)}, 2.85 (q, 2H, 3J_H,H 8 Hz, CH₂CH₃), 2.47 (s, 12H, xylyl-CH₃), 2.44 (s, 12H, xylyl-CH₃), 1.99 (br. s, 6H,
xylyl-CH\textsubscript{3}), 1.64 (d, 6H, \textsuperscript{2}J\textsubscript{H,P} 8 Hz, PCH\textsubscript{3}), 1.34 (m, 4H, PCH\textsubscript{2}), 1.20 (d, 6H, \textsuperscript{2}J\textsubscript{H,P} 7 Hz, PCH\textsubscript{3}), 0.69 (t, 3H, \textsuperscript{4}J\textsubscript{H,H} 8 Hz, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}, 151 MHz, 298 K): \(\delta\) 179.44 (s, \textsubscript{C}CH\textsubscript{2}CH\textsubscript{3}), 156.33, 150.51, 134.13, 133.80, 133.11, 132.31, 131.01 (8 \times s, \textit{o} and \textit{i}), 128.06 (m, \textit{m}), 127.93 (m, \textit{m}), 125.47 (s, \textsubscript{p}), 123.57 (s, \textsubscript{p}), 121.62 (s, \textsubscript{p}), 120.20 (s, \textsubscript{p}), 31.38 (m, PC\textsubscript{H}\textsubscript{2}), 30.76 (m, PC\textsubscript{H}\textsubscript{2}), 26.68 (s, CH\textsubscript{2}CH\textsubscript{3}), 20.71 (s, xylyl-CH\textsubscript{3}), 20.39 (s, xylyl-CH\textsubscript{3}), 20.05 (s, xylyl-CH\textsubscript{3}), 19.14 (s, xylyl-CH\textsubscript{3}), 17.34 (d, \textsuperscript{1}J\textsubscript{C,P} 20 Hz, PCH\textsubscript{3}), 16.82 (d, \textsuperscript{1}J\textsubscript{C,P} 20 Hz, PCH\textsubscript{3}), 9.02 (s, CH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{31}P\{\textsuperscript{1}H\} (C\textsubscript{6}D\textsubscript{6}, 243 MHz, 298 K): \(\delta\) 66.15 (s, 1P), 53.90 (s, 1P).

11.4 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 4

Various data is available in the ESI to reference 507, including tables of calculated and crystallographically determined bond lengths and angles, bond orders, Hirshfeld charges, total bonding energies, Slater-type molecular orbitals involved in Mn–ligand interactions (not including interactions with dmpe), electrostatic potential diagrams, and fragment interaction analyses for calculated structures, and selected NMR spectra. The identification numbers in this chapter (X \rightarrow Y) of the thesis relate to those in reference 507 (X \rightarrow Y) in the following manner; 10 \rightarrow 1, 16\textsuperscript{Et}\rightarrow 2a, 16\textsuperscript{Ph}\rightarrow 2b, 17\textsuperscript{Et}\rightarrow A, 18\textsuperscript{Et}\rightarrow 3a, 18\textsuperscript{Ph}\rightarrow 3b, 19\textsuperscript{Et}\rightarrow 4a, and 19\textsuperscript{Ph}\rightarrow 4b. CSD 1529213-1529215 contain the supplementary crystallographic data for 16\textsuperscript{Et}, 16\textsuperscript{Ph}, and 19\textsuperscript{Ph}.

\[(\text{dmpe})_2\text{MnH(=SiEt}_2\text{)}\] (16\textsuperscript{Et}). An excess of H\textsubscript{2}SiEt\textsubscript{2} (734 mg, 8.32 mmol) was added to [(dmpe)\textsubscript{2}MnH(C\textsubscript{2}H\textsubscript{4})] (10) (463.1 mg, 1.78 mmol) in 30 mL of benzene. The reaction mixture was stirred in a sealed flask at room temperature for a month, turning from clear bright yellow to a clear vibrant red/brown solution and the solvent was removed \textit{in vacuo}. The resulting brown powder was dissolved in 2.5 mL of hexanes and a yellow residue was removed by centrifuging. Following this, the supernatant liquid was concentrated to 2 mL, and stored at –30 °C for two weeks resulting in brown crystals. Yield = 277 mg (52%). X-ray quality crystals were obtained by recrystallizing from a
dilute solution in hexanes at –30 °C. $^1$H NMR ($C_6D_6$, 600 MHz, 298 K): δ 1.88 (m, 4H, P($C_H2$)), 1.74 (m, 4H, P($C_H2$)), 1.34 (br. s, 12H, P($C_H3$)), 1.34 (q, 4H, $^3J_{H,H}$ 7.8 Hz, Si$CH_2$CH$_3$), 1.22 (br. s, 12H, P($C_H3$)), 1.09 (t, 6H, $^3J_{H,H}$ 7.9 Hz, Si$CH_2$CH$_3$), –10.46 (p, 1H, $^2J_{H,P}$ 51.4 Hz, Mn$H$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 151 MHz, 298 K): δ 34.63 (p, $^J_{C,P}$ 12.2 Hz, P($C_H2$)), 29.50 (br. s, P($C_H3$)), 29.35 (s, Si$C_H2$CH$_3$), 8.19 (s, Si$CH_2$CH$_3$). $^{29}$Si{$^1$H} NMR ($C_6D_6$, 119 MHz, 298 K): δ 365.30 (m). $^{31}$P{$^1$H} NMR ($C_6D_6$, 243 MHz, 298 K): δ 80.95 (s). Anal. Found (calcd.): C, 44.31 (43.44); H, 9.90 (9.80).

[(dmpe)$_2$MnH(=SiPh)$_2$] (16$^{Ph2}$). Three equivalents of H$_2$SiPh$_2$ (296.6 mg, 1.61 mmol) were added to [(dmpe)$_2$MnH($C_2H_4$)] (10) (201.3 mg, 0.52 mmol) in 25 mL of benzene. The solution was stirred at 60 °C for five days, turning from a clear bright yellow solution to a dark purple solution, and then the solvent was removed in vacuo. The resulting dark oil was washed with 5 mL hexanes and crystallized from 2 mL of toluene at –30 °C to get dark purple cubic single crystals of X-ray quality (88.4 mg). A further 32.1 mg could be obtained by cooling the hexanes mother liquors at –30 °C. In the solid state structure, the cis isomer (cis-16$^{Ph2}$) was obtained as a mixture with [(dmpe)$_2$MnH$_2$(SiHPh)$_2$] (18$^{Ph2}$), usually in ratios of roughly 1 : 1, due to the tendency to co-crystallize. In the case of the X-ray quality crystals, a ratio of 1 : 1 was confirmed both through XRD and $^1$H NMR data. Total yield of 23% of 16$^{Ph2}$ (45% if including 18$^{Ph2}$). In solution, 16$^{Ph2}$ exists as an equilibrium of a cis- and trans- isomer (in $C_6D_6$ at 298 K there is a 88 : 12 cis-16$^{Ph2}$: trans-16$^{Ph2}$ ratio). cis-16$^{Ph2}$: $^1$H NMR ($C_6D_6$, 500 MHz, 298 K): δ 7.81 (d of m, 4H, $^3J_{H,H}$ 6.3 Hz, o), 7.22 (t, 4H, $^3J_{H,H}$ 7.0 Hz, m), 7.17 (t, 2H, $^3J_{H,H}$ 7.0 Hz, p), 0-2.2 (series of broad signals from dmpe), –16.22 (s, 1H, Mn$H$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 151 MHz, 298 K): δ 156.81 (s, ipso), 134.83 (s, o), 127.14 (s, m), 126.00 (s, p), could not locate dmpe signals. $^{29}$Si{$^1$H} NMR ($C_6D_6$, 119 MHz, 298 K): δ 210.2. $^{31}$P{$^1$H} NMR ($C_6D_6$, 202 MHz, 298 K): δ 78.29(br. s), 69.11 (br. s). trans-16$^{Ph2}$: $^1$H NMR ($C_6D_6$, 500 MHz, 298 K): δ 7.50 (d of m, 4H, $^3J_{H,H}$ 6.6 Hz, o), 7.18 (t, 4H, $^3J_{H,H}$ 7.6 Hz, m), 7.07 (t, 2H, $^3J_{H,H}$ 7.4 Hz, p), 1.97 (br. s, 4H, P($C_H2$)), 1.69 (br. s, 4H, P($C_H2$)), 1.37 (s, 12H, P($C_H3$)), 1.17 (s, 12H, P($C_H3$)), –9.78 (p, 1H, $^2J_{H,P}$ 55.0 Hz, Mn$H$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 126 MHz, 298 K): δ 160.42 (s, ipso), 131.95 (s, o), 127.14
(s, p), 126.00 (s, m), 34.13 (m, P(\text{CH}_2)), 29.77 (m, P(\text{CH}_3)), 28.64 (s, P(\text{CH}_3)), 21.73 (m, P(\text{CH}_2)). \text{ }^{29}\text{Si}^1\text{H}\text{NMR (C}_6\text{D}_6, 119 \text{ MHz, 298 K): } \delta 285.1. \text{ }^{31}\text{P}^1\text{H}\text{NMR (C}_6\text{D}_6, 202 \text{ MHz, 298 K): } \delta 80.29 \text{ (br. s).} \text{ Anal. Found (calcd. based on 1:1 ratio of }^{16}\text{Ph}_2 :^{18}\text{Ph}_2 \text{ as observed by NMR for the sample submitted): C, 53.77 (53.43); H, 7.83 (8.22).}

[\text{(dmpe}_2\text{MnH}_2\text{(SiHEt}_2\text{)})] \text{ (18}^{\text{Et}_2}\text{). Method a) Approx. 15 mg of } [\text{(dmpe}_2\text{MnH(=SiEt}_2\text{)})] \text{ (16}^{\text{Et}_2}\text{) was dissolved in approx. 0.6 mL of C}_6\text{D}_6 \text{ and the solution was freeze/pump/thawed three times in an NMR tube with a J-young valve to remove dissolved argon. The NMR tube was then placed under 1 atm of H}_2 \text{ at } -95 \text{ °C, sealed, and warmed to room temperature. 100% conversion to } [\text{(dmpe}_2\text{MnH}_2\text{(SiHEt}_2\text{)})] \text{ (18}^{\text{Et}_2}\text{) was observed by }^1\text{H NMR after allowing the reaction mixture to sit at room temperature overnight (leading to a very pale clear yellow solution). Method b) An excess of H}_2\text{SiE}_t_2 \text{ (228 mg, 2.58 mmol) was added to } [\text{(dmpe}_2\text{MnH(C}_2\text{H}_4\text{)})] \text{ (10) (89 mg, 0.23 mmol) in 10 mL of benzene. The reaction mixture was freeze/pump/thawed in a 50 mL storage flask three times, and then was placed under 1 atm of H}_2 \text{ at } -95 \text{ °C, sealed, and warmed to room temperature. After stirring at 30-40 °C for one week, the clear bright yellow solution turned to a pale clear yellow solution. At this point, the solvent was removed } in \text{ vacuo and resulting pale yellow solid was recrystallized from a concentrated solution of hexanes at } -30 \text{ °C giving a pale yellow powder. Yield = 20 mg (19%). X-ray quality crystals (very pale yellow cubes) were obtained from pentane at } -30 \text{ °C, though a crystal structure could not be obtained due to severe disorder and/or twinning. In solution, 18}^{\text{Et}_2}\text{ exists as an equilibrium mixture of a central and transHSi isomer (in C}_6\text{D}_6 \text{ at 298 K there is a 78 : 22 ratio of isomers central-18}^{\text{Et}_2} : \text{ transHSi-18}^{\text{Et}_2}). \text{ central-18}^{\text{Et}_2}: \text{ }^1\text{H NMR (C}_6\text{D}_6, 600 \text{ MHz, 298 K): } \delta 4.97 \text{ (br. s, 1H, SiH), 0.4–1.7 (series of broad signals from dmpe and SiEt}_2\text{), } -12.67 \text{ (br. s, 2H, MnH}_2\text{Si),} \text{ }^{31}\text{P}^1\text{H}\text{NMR (C}_6\text{D}_6, 243 \text{ MHz, 298 K): broad pair of signals ranging from 65-80 ppm.} \text{ }^1\text{H NMR (d}_8\text{-toluene, 500 MHz, 224 K): } \delta 4.97 \text{ (br. s with }^{29}\text{Si sat., 1H, } J_{\text{H, Si}} 166 \text{ Hz, SiH), 0.4–1.9 (series of broad signals from dmpe and SiEt}_2\text{), } -12.71 \text{ (p, 2H, } J_{\text{H, P}} 23.3 \text{ Hz, MnH}_2\text{Si).} \text{ }^{29}\text{Si}^1\text{H}\text{NMR (d}_8\text{-toluene, 99 MHz, 224 K): } \delta 14.20. \text{ }^{31}\text{P}^1\text{H}\text{NMR (d}_8\text{-toluene, 202 MHz, 224 K): } \delta 75.19 \text{ (br. s, 2P), 71.69 (br. s, 2P). } \text{transHSi-18}^{\text{Et}_2}: \text{ }^1\text{H NMR (C}_6\text{D}_6, 600 \text{ MHz, 298 K): } \delta 5.20 \text{ (br. s, 1H, SiH), } -12.26
(br. s, 1H, Mn\(\text{H}_{\text{Si}}\)), 0.4–1.7 (series of broad signals from dmpe and SiEt\(_2\)), –12.28 (br. s, 1H, Mn\(\text{H}_{\text{Si}}\)), –14.23 (br. s, 1H, Mn\(\text{H}_{\text{Si}}\)). \(\text{\(^{31}\text{P}\{^1\text{H}\}}\) NMR (C\(_6\)D\(_6\), 243 MHz, 298 K): \(\delta\) 77.74. \(^1\text{H}\) NMR (d\(_8\)-toluene, 500 MHz, 224 K): \(\delta\) 5.26 (br. s with \(^{29}\text{Si}\) sat., 1H, \(^1\text{J}_{\text{H,Si}}\) 150 Hz, Si\(\text{H}\)), 0.4–1.9 (series of broad signals from dmpe and SiEt\(_2\)), –12.22 (p of d, 1H, \(^2\text{J}_{\text{H,P}}\) 52.5 Hz, Mn\(\text{H}_{\text{Si}}\)), –14.38 (m, 1H, Mn\(\text{H}_{\text{Si}}\)). \(\text{\(^{29}\text{Si}\}{^1\text{H}}}\) (d\(_8\)-toluene, 99 MHz, 224 K): \(\delta\) 23.78. \(\text{\(^{31}\text{P}\}{^1\text{H}}}\) (d\(_8\)-toluene, 202 MHz, 224 K): \(\delta\) 78.37 (br. s).

Anal. Found (calcd.): C, 43.46 (43.24); H, 10.10 (10.20). IR: \(\nu\)(SiH, MnH) (Nujol, cm\(^{-1}\))): 1877 (with shoulder to lower wavenumber), 2015. \(\nu\)(SiH, MnH) (hexanes, cm\(^{-1}\)): 1734, 1864, 2031 (with two shoulders to lower wavenumber).

\([\text{dmpe})_2\text{MnD}_2(\text{SiHEt}_2)]\) (d\(_2\)-18\(^{\text{E}2}\)) was prepared in a manner identical to that described above for 18\(^{\text{E}2}\) (method a) utilizing D\(_2\) in place of H\(_2\). 100% conversion was observed after one day at room temperature, including deuterium incorporation exclusively to the Mn-\(\text{H}_{\text{Si}}\) bridging position, and no incorporation of deuterium into the Si-\(\text{H}\) bond over time at room temperature. \(^1\text{H}\) NMR spectrum of d\(_2\)-18\(^{\text{E}2}\) (C\(_6\)D\(_6\)) is identical to that for 18\(^{\text{E}2}\) with no signals at –12.28, –12.67, or –14.23 ppm.

\([\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)]\) (18\(^{\text{Ph}2}\)): Method a) Approx. 15 mg of a mixture of \([\text{dmpe})_2\text{MnH} (=\text{SiPh}_2]\) (16\(^{\text{Ph}2}\)) and \([\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)]\) (18\(^{\text{Ph}2}\)) was dissolved in approx. 0.6 mL of C\(_6\)D\(_6\), and the solution was freeze/pump/thawed three times in an NMR tube with a J-young valve to remove dissolved argon. The NMR tube was then placed under 1 atm of H\(_2\) at –95 °C and sealed at this temperature. 100% conversion to \([\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)]\) (18\(^{\text{Ph}2}\)) was observed by \(^1\text{H}\) NMR spectroscopy after allowing the reaction mixture to warm to room temperature, leading to a pale yellow clear solution. Method b) \([\text{dmpe})_2\text{MnH}(\text{C}_2\text{H}_4)]\) (10) (133.7 mg, 0.35 mmol) was dissolved in 10 mL of benzene. To this bright yellow solution was added 192 mg (1.04 mmol) of H\(_2\)SiPh\(_2\) and the resulting mixture was placed in a 50 mL storage flask and freeze/pump/thawed three times before being placed under 1 atm of H\(_2\) at –95 °C. The flask was then sealed, and the mixture was heated at 60 °C for 5 days leading to a pale yellow clear solution. The solvent was removed \textit{in vacuo} and the resulting yellow oil was washed with 2 mL of
hexanes. The remaining yellow solid was dissolved in toluene and layered with hexanes or hexamethyldisiloxane (two different fractions) yielding a combined 136.2 mg (72% yield) of bright yellow crystals. $^{18}\text{Ph}_2$ exists as an equilibrium mixture of central and transHSi isomers ($298$ K, $C_6D_6$ or $d_2$-toluene) in a $87 : 13$ ratio. X-ray quality crystals of the dominant isomer (central-$^{18}\text{Ph}_2$) were prepared by recrystallization from toluene at $–30$ °C. central-$^{18}\text{Ph}_2$: $^1H$ NMR ($C_6D_6$, $500$ MHz, $298$ K): δ $8.17$ (d, $2H$, $^3J_{H,H}$ $5.6$ Hz, o), $7.87$ (d, $2H$, $^3J_{H,H}$ $6.1$ Hz, o), $7.41$ (t, $2H$, $^3J_{H,H}$ $6.6$ Hz, m), $7.28$ (t, $1H$, $^3J_{H,H}$ $6.6$ Hz, p), $7.24$ (t, $2H$, $^3J_{H,H}$ $6.8$ Hz, m), $7.15$ (t, $1H$, $^3J_{H,H}$ $6.6$ Hz, p), $6.62$ (app. t with $^{29}\text{Si}$ satellites, $1H$, $^3J_{H,P}$ $9.4$ Hz, $^1J_{H,Si}$ $177.8$ Hz, $\text{SiH}$), $1.47$ (br. s, $6H$, P($\text{CH}_3$)), $1.34$ (m, $4H$, P($\text{CH}_2$)), $1.08$ (m, $2H$, P($\text{CH}_2$)), $1.01$ (br. d, $^2J_{H,P}$ $5.3$ Hz, P($\text{CH}_3$)), $0.91$ (br. s, $2H$, P($\text{CH}_2$)), $0.89$ (br. s, $12H$, P($\text{CH}_3$)), $–12.40$ (m, $2H$, Mn$H$Si). $^{13}C\{^1H\}$ NMR ($C_6D_6$, $151$ MHz, $298$ K): δ $152.07$ (ipso), $151.63$ (ipso), $136.48$ (o), $136.05$ (o), $127.38$ (m), $127.22$ (m), $126.73$ (p), $35.08$ (P($\text{CH}_2$)), $32.42$ (P($\text{CH}_2$)), $30.74$ (P($\text{CH}_3$)), $23.82$ (P($\text{CH}_3$)), $23.47$ (P($\text{CH}_3$)), $21.42$ (P($\text{CH}_3$)). $^{29}\text{Si}\{^1H\}$ NMR ($d_8$-toluene, $119$ MHz, $298$ K): δ $10.01$. $^{31}\text{P}\{^1H\}$ NMR ($C_6H_6$, $202$ MHz, $298$ K): δ $78.30$ (v. broad m). Anal. Found (calcd.): C, 53.30 (53.33); H, 8.55 (8.39). IR: ν(SiH, MnH) (Nujol, cm$–1$): 1767, 1807, 1974. 

transHSi-$^{18}\text{Ph}_2$: aromatic and dmpe signals not resolved, δ $6.34$ (br. s, $1H$, Si$H$), $–11.43$ (p, $1H$, $^2J_{H,P}$ $55.4$ Hz, Mn$\text{H}$Si), $–12.75$ (br. s, $1H$, Mn$H$Si). $^{31}P\{^1H\}$ NMR ($C_6H_6$, $202$ MHz, $298$ K): δ $78.30$ (v. broad m). Anal. Found (calcd.): C, 53.30 (53.33); H, 8.55 (8.39). IR: ν(SiH, MnH) (Nujol, cm$–1$): 1767, 1807, 1974.

[(dmpe)$_2$MnD$_2$(Si$H$Ph$_2$)] ($d_2$-$^{18}\text{Ph}_2$): $d_2$-$^{18}\text{Ph}_2$ was prepared in a manner identical to that described above for $^{18}\text{Ph}_2$ (method a) utilizing $D_2$ in place of $H_2$. 100% conversion was achieved almost immediately upon warming to room temperature, including deuterium incorporation exclusively at the Mn$H$ environment, and no incorporation of deuterium into the terminal Si-$H$ bond. $^1H$ NMR spectra of $d_2$-$^{18}\text{Ph}_2$ are identical to those for $^{18}\text{Ph}_2$ with no signals at $–11.43$, $–12.40$, or $–12.75$ ppm. Also observed in solution is $^{18}\text{Ph}_2$ (as a residue from the starting solution of $^{16}\text{Ph}_2$ and $^{18}\text{Ph}_2$) at a ratio of $3 : 1$ $d_2$-$^{18}\text{Ph}_2$: $^{18}\text{Ph}_2$ which is identical to the portion of $^{16}\text{Ph}_2$: $^{18}\text{Ph}_2$ in the starting material used.

[(dmpe)$_2$MnH(Et$_2$Si=CHMe)] ($19\text{Et}_2$): [(dmpe)$_2$MnH(=SiEt$_2$)] ($16\text{Et}_2$) (55.1 mg, 0.12 mmol) was dissolved in 5 mL of benzene. The solution was freeze/pump/thawed
three times in a 50 mL storage flask, then placed under 1 atm of ethylene at –95 °C. The flask was sealed and warmed to room temperature, and after stirring for 3.5 h, the solution had turned from a clear red/brown solution to a clear light orange. Following this, solvent was removed in vacuo and the resulting orange oil was recrystallized from hexamethyldisiloxane at –30 °C to afford an orange solid (20.5mg, 35% yield). X-ray quality crystals were not obtained. $^1$H NMR indicates that samples of $^{19}$Et$_2$ contain 0.1 equivalents of hexamethyldisiloxane which could not be removed by exposure of the solid to vacuum. $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 1.79 (d, 3H, $^3$J$_{H,H}$ 7.2 Hz, Si=CHC$_3$H$_3$), 1.56 (m, 1C, P(CH$_2$)), 1.49 (d, 3H, $^2$H$_P$ 6.7 Hz, P(CH$_3$)), 1.45(m, 2C, P(CH$_2$)), 1.42 (d, 3H, $^3$J$_{H,H}$ 5.4 Hz, P(CH$_3$)), 1.34 (t, 3H, $^3$J$_{H,H}$ 7.9 Hz, SiCH$_2$CH$_3$), 1.31 (t, 3H, $^3$J$_{H,H}$ 7.8 Hz, SiCH$_2$CH$_3$), 1.28 (d, 3H, $^3$J$_{H,H}$ 5.5 Hz, P(CH$_3$)), 1.26 (d, 3H, $^3$J$_{H,H}$ 5.3 Hz, P(CH$_3$)), 0.95 (m, 1C, P(CH$_3$)), 0.96 (m, 9H, P(CH$_3$), 2H, SiCH$_2$CH$_3$), 0.80 (d of q, 1H, $^1$J$^1$H$_{H,H}$ 14.1 Hz, $^3$J$^2$H$_{H,H}$ 7.5 Hz, SiC$_2$H$_3$C), –0.02 (m, 1H, Si=C$_3$H$_7$C), –15.34 (br. s, 1H, Mn$^1$HSi). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 37.43 (t, 1C, $^1$J$^1$C,P 25.5 Hz, P(CH$_2$)), 35.34 (d of d, 1C, $^1$J$^1$C,P 19.9, 17.5 Hz, P(CH$_2$)), 33.47 (t, 1C, $^1$J$^1$C,P 16.8 Hz, P(CH$_2$)), 33.28 (d, 1C, $^1$J$^1$C,P 18.3 Hz, P(CH$_3$)), 32.94 (m, 1C, P(CH$_3$)), 28.04 (s, 1C, P(CH$_3$)), 26.50 (d, 1C, $^1$J$^1$C,P 10.4 Hz, P(CH$_3$)), 25.16 (s, 1C, P(CH$_3$)), 22.99 (m, 2C, P(CH$_3$) and Si=CHCH$_3$), 22.73 (m, 1C, P(CH$_3$)), 20.72 (s, 1C, P(CH$_3$)), 15.52 (s, 1C, P(CH$_3$)), 10.22 (s, 1C, SiCH$_2$CH$_3$), 10.05 (s, 1C, SiCH$_2$CH$_3$), 7.56 (m, 1C, SiCH$_2$CH$_3$), 5.15 (s, 1C, SiCH$_2$CH$_3$), –19.37 (s, 1C, Si=CHCH$_3$). $^{29}$Si{$^1$H} NMR (C$_6$D$_6$, 119 MHz, 298 K): δ –2.95. $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 243 MHz, 298 K): δ 79.32 (br. s, 1P), 70.74 (br. s, 1P), 67.68 (br. s, 1P), 65.54 (br. s, 1P). Anal. Found (calcd. with 0.1 equiv. O(SiMe$_3$)$_2$): C, 46.01 (45.90); H, 9.97 (10.11).

$^{[[\text{dmpe}]_2\text{MnH}(\text{Et}_2\text{Si}=\text{CD}_3\text{C})]}$ ($d_4$-19$^{\text{Et}_2}$): $d_4$-19$^{\text{Et}_2}$ was prepared by dissolving approx. 15 mg of $^{[[\text{dmpe}]_2\text{MnH}(=\text{SiEt}_2)]}$ (16$^{\text{Et}_2}$) in approx. 0.6 mL of C$_6$D$_6$. The solution was placed in an NMR tube fitted with a J-young valve and freeze/pump/thawed three times to remove dissolved argon. 1 atm of $d_4$-ethylene was then admitted into the NMR tube at –95 °C, which was sealed, warmed to room temperature, and left for two hours.
100% conversion was observed by $^1$H NMR spectroscopy, which shows peaks identical to those of to $^{19}_{\text{Et}2}$, but with no signals at 1.79 or –0.02 ppm.

$[(\text{dmpe})_2\text{MnH(Ph}_2\text{Si}=\text{CHMe})] (19^{\text{Ph}_2})$: A mixture of $[(\text{dmpe})_2\text{MnH} (=\text{SiPh})_2] (16^{\text{Ph}_2})$ and $[(\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)] (18^{\text{Ph}_2})$ (total of 126.4 mg, containing 0.12 mmol of $^{16}_{\text{Ph}_2}$) was dissolved in 20 mL of benzene. The dark purple solution was freeze/pump/thawed 3 times in a 50 mL storage flask, and then placed under 1 atm of ethylene at –95 °C. The flask was sealed, and upon thawing, the reaction mixture turned a bright clear orange indicative of complete conversion to an unidentified intermediate. Following five hours of stirring at room temperature, most of the intermediate had converted to the target complex ($^{19}_{\text{Ph}_2}$), and the residual intermediate was removed by removal of the solvent in vacuo and recrystallizing the resulting orange oil from hexanes. The orange powder which precipitated after leaving the solution at –30 °C for a week contained $[(\text{dmpe})_2\text{MnH(Ph}_2\text{Si}=\text{CHMe})] (19^{\text{Ph}_2})$ mixed with $[(\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)] (18^{\text{Ph}_2})$, which was present in the starting solution and did not react with ethylene. Yield = 81.2 mg (61% of $^{19}_{\text{Ph}_2}$). X-ray quality orange crystals were obtained from recrystallization in dilute hexanes at –30 °C. $^1$H NMR ($C_6D_6$, 600 MHz, 298 K): δ 8.05 (d, 2H, $^3J_{\text{H,H}}$ 8.0 Hz, o), 8.01 (d, 2H, $^3J_{\text{H,H}}$ 7.2 Hz, o), 7.16 (t, 2H, $^3J(1^1\text{H}-1^1\text{H})$ 7.6 Hz, m), 7.10 (t, 2H, $^3J(1^1\text{H}-1^1\text{H})$ 7.4 Hz, m), 7.05 (t of t, 1H, $^3J(1^1\text{H}-1^1\text{H})$ 7.2 Hz, $^4J_{\text{H,H}}$ 1.2 Hz, p), 7.00 (t of t, 1H, $^3J_{\text{H,H}}$ 7.5 Hz, $^4J_{\text{H,H}}$ 1.0 Hz, p), 2.14 (d, 3H, $^3J_{\text{H,H}}$ 7.4 Hz, Si=CHC$_3$), 1.72 (d, 3H, $^3J_{\text{H,H}}$ 5.4 Hz, P(C$_2$H$_2$)), 1.51 (d, 3H, $^3J_{\text{H,H}}$ 6.4 Hz, P(C$_2$H$_2$)), 1.47 (m, 2H, P(C$_2$H$_2$)), 1.36 (m, 2H, P(CH$_2$)), 1.35 (m, 2H, P(CH$_2$)), 1.30 (m, 2H, P(CH$_2$)), 1.14 (d, 3H, $^3J_{\text{H,H}}$ 5.5 Hz, P(CH$_3$)), 1.01 (d, 6H, $^3J_{\text{H,H}}$ 5.5 Hz, P(CH$_3$)), 0.94 (d, 3H, $^3J_{\text{H,H}}$ 5.0 Hz, P(CH$_3$)), 0.59 (d, 3H, $^3J_{\text{H,H}}$ 5.2 Hz, P(CH$_3$)), 0.54 (d, 3H, $^3J_{\text{H,H}}$ 5.6 Hz, P(CH$_3$)), 0.39 (m, 1H, Si=CHCH$_3$), –14.56 (m, 1H, MnH$_2$Si). $^{13}C(1^1\text{H})$ NMR ($C_6D_6$, 151 MHz, 298 K): 144.60 (s, ipso), 144.33 (s, ipso), 135.64 (s, o), 135.56 (s, o), 127.8 (p), 127.58 (s, m), 35.75 (m, P(CH$_2$)), 34.48 (app. t, $J_{\text{C,P}}$ 17.1 Hz, P(CH$_2$)), 33.68 (d, $J_{\text{C,P}}$ 18.9 Hz, P(CH$_3$)), 33.09 (m, P(CH$_2$)), 26.03 (d, $J_{\text{C,P}}$ 8.9 Hz, P(CH$_3$)), 25.66 (s, P(CH$_3$)), 24.21 (s, P(CH$_3$)), 23.36 (m, Si=CHCH$_3$), 22.64 (d, $J_{\text{C,P}}$ 14.4 Hz, P(CH$_3$)), 21.87 (d, $J_{\text{C,P}}$ 10.0 Hz, P(CH$_3$)), 21.12 (d, $J_{\text{C,P}}$ 21.1 Hz, P(CH$_3$)), 15.43 (s, P(CH$_3$)), –22.93 (s, Si=CHCH$_3$). $^{29}$Si ($C_6D_6$, 119 MHz,
298 K): –1.47 (d, \(J_{\text{Si,H}}^{31P}\{^1H\}) (C_6D_6, 243 MHz, 298 K): 78.31 (s), 69.14 (s), 66.52 (s), 62.72 (s). Anal. Found (calcd. based on 50:50 mixture observed for the submitted sample by \(^1H\) NMR): C, 54.42 (54.24); H, 8.46 (8.38).

\[[(\text{dmpe})_2\text{MnH}((\text{Ph}_2\text{Si})=\text{CDCD}_3)] \text{ (}d_4\text{-}19\text{Ph}_2\text{)}: \text{ } d_4\text{-}19\text{Ph}_2\text{} \text{ was prepared by dissolving approx. 15 mg of a mixture of } [(\text{dmpe})_2\text{MnH}=(\text{SiPh}_2)] \text{ (}16\text{Ph}_2\text{)} \text{ and } [(\text{dmpe})_2\text{MnH}_2(\text{SiHPh}_2)] \text{ (}18\text{Ph}_2\text{)} \text{ (3:1 ratio) in approx. 0.6 mL of C}_6\text{D}_6. \text{ The solution was placed in an NMR tube fitted with a J-young valve and freeze/pump/thawed three times to remove dissolved argon. 1 atm of } d_4\text{-ethylene } \text{ was admitted into the NMR tube at } -95 \degree \text{C, the tube was sealed, and the reaction mixture was warmed to room temperature. 100\% consumption of } 16\text{Ph}_2 \text{ was observed by } ^1\text{H NMR after 5 minutes at room temperature, producing } d_4\text{-}19\text{Ph}_2 \text{ and an unidentified intermediate which slowly converted into } d_4\text{-}19\text{Ph}_2; \text{ 95\% complete after 2 days. } ^1\text{H NMR spectroscopy of } d_4\text{-}19\text{Ph}_2 \text{ shows identical peaks to } 19\text{Ph}_2, \text{ but with no signals at 2.14 or 0.39 ppm. Also observed in solution is } 18\text{Ph}_2 \text{ residual from the starting solution.}

11.5 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 5

Various data for complex 20\(^R\) is available in the ESI to reference 547, including tables of calculated and crystallographically determined bond lengths and angles, bond orders, Hirshfeld charges, and total bonding energies for calculated structures, along with selected NMR spectra. Various data is also available of other complexes in this chapter in the ESI to reference 587, including tables of calculated and crystallographically determined bond lengths, bond orders, total bonding energies, Hirshfeld charges, and thermodynamic parameters for calculated structures, and selected NMR spectra. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 547 (X→Y) in the following manner; \textit{trans-}10→1, \textit{cis-}10→A, 12→D, 13→B, 16→2, 17→C, 18→3, and 20→4. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 587 (X→Y) in the following manner; 10→1, 12→A, 16→3, 17→2.
An excess of phenylsilane (770 mg, 7.12 mmol) was added to a solution of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) (543.7 mg, 1.41 mmol) in 30 mL of toluene. The reaction mixture was stirred in a 100 mL sealed flask at 60 °C for 4 h, after which time the solvent was removed in vacuo leading to a dark orange oil. Note that ethane is formed as a by-product in this reaction, so after 30 minutes, the reaction mixture was temporarily allowed to cool to room temperature and the excess gas was vented into the Schlenk line before continuing heating at 60 °C. Washing twice with 10 mL of hexanes produced a yellow solid, which was dissolved in 9 mL of toluene and residual solid was removed by centrifugation. Layering the resulting solution with 20 mL of hexanes and storing at –30 °C for days afforded large orange crystals of 20$^{\text{Ph}}$ with a yield of 63% (509.2 mg, 0.89 mmol). Note that on some occasions, instead of large orange crystals a yellow powder was obtained. X-ray quality crystals were obtained from a saturated solution of 20$^{\text{Ph}}$ in hexanes at –30 °C.

$^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 8.12 (d, 4H, $^3$J$_{H,H}$ 7 Hz, o), 7.31 (t, 4H, $^3$J$_{H,H}$ 7 Hz, m), 7.24 (t, 2H, $^3$J$_{H,H}$ 7 Hz, p), 5.31 (s with $^{29}$Si sat., 2H, $^1$J$_{H,\text{Si}}$ 158 Hz, SiH), 5.28 (s with $^{29}$Si sat., 2H, $^1$J$_{H,\text{Si}}$ 167 Hz, SiH), 1.50 (d, 6H, $^1$J$_{C,P}$ 6 Hz, PC$_3$), 1.39 (m, 2H, PC$_2$), 1.16 (m, 2H, PC$_2$), 1.03 (d, 6H, $^1$J$_{H,P}$ 5 Hz, PCH$_3$), 1.02 (m, 2H, PC$_2$), 0.98 (d, 6H, $^1$J$_{H,P}$ 6 Hz, PCH$_3$), 0.91 (m, 2H, PC$_2$), 0.91 (d, 6H, $^1$J$_{H,P}$ 3 Hz, PCH$_3$), –14.55 (p, 1H, $^2$J$_{H,P}$ 20 Hz, $^3$J$_{H,\text{Si}}$ –31 Hz, MnH).

$^{13}$C$_{^1}$H NMR (C$_6$D$_6$, 151 MHz, 298 K): $\delta$ 147.34 (s, i), 137.03 (s, o), 127.37 (s, m), 127.23 (s, p), 32.76 (m, PCH$_3$), 32.15 (m, PCH$_2$), 23.66 (d, $^1$J$_{C,P}$ 6 Hz, PCH$_3$), 23.62 (d, $^1$J$_{C,P}$ 6 Hz, PCH$_3$), 22.65 (d, $^1$J$_{C,P}$ 15 Hz, PCH$_3$), 22.55 (d, $^1$J$_{C,P}$ 16 Hz, PCH$_3$), 21.81 (d, $^1$J$_{C,P}$ 17 Hz, PCH$_3$), 17.25 (d, $^1$J$_{C,P}$ 25 Hz, PCH$_3$). $^{29}$Si$^{1}$H NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ –4.20 (m). $^{29}$Si NMR (d$_8$-toluene, 119 MHz, 298 K): $\delta$ –4.18 (t of m, $^1$J$_{\text{Si,H}}$

$^{zzz}$ Measured using $^{29}$Si$_{\text{edited}}$ $^1$H–$^1$H COSY NMR spectroscopy as described in Chapter 6.
[(dmpe)$_2$MnH(SiH$_2^n$Bu)$_2$] (20$^{Bu}$): An excess of $n$-butyl silane (293 mg, 3.32 mmol) was added to a solution of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) (503.2 mg, 1.31 mmol) in 25 mL of benzene. The reaction mixture was stirred in a 50 mL sealed flask at 60 °C for 2 days, after which the solvent was removed in vacuo leading to a yellow solid. Note that ethane is formed as a by-product in this reaction so after a few hours the reaction mixture was temporarily allowed to cool to room temperature and the excess gas was vented into the Schlenk line before continuing at 60 °C. Recrystallization in hexanes at –30 °C yielded 357.6 mg of 20$^{Bu}$, and removing the solvent in vacuo from the mother liquor and recrystallization of the residue in toluene at –30 °C yielded an additional 178.5 mg, for a total yield of 77% (536.1 mg, 1.01 mmol) of yellow powder.

$^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 4.53 (m with $^{29}$Si sat., 2H, $^1$J$_{H, Si}$ 178 Hz, SiH), 4.36 (m with $^{29}$Si sat., 2H, $^1$J$_{H, Si}$ 159 Hz, SiH), 1.95 (m, 4H, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.67 (t of q, 4H, $^3$J$_{H, H}$ 7 Hz, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.47 (m, 2H, PCH$_2$), 1.40 (d, 6H, $^2$J$_{H, P}$ 6 Hz, PCH$_3$), 1.31 (d, 6H, $^2$J$_{H, P}$ 6 Hz, PCH$_3$), 1.22 (m, 4H, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.21 (m, 4H, PCH$_2$), 1.08 (t, 6H, $^3$J$_{H, H}$ 7 Hz, SiH$_2$CH$_2$CH$_2$CH$_2$H$_3$), 1.03 (d, 6H, $^2$J$_{H, P}$ 6 Hz, PCH$_3$), 0.97 (d, 6H, $^2$J$_{H, P}$ 4 Hz, PCH$_3$), 0.84 (m, 2H, PCH$_2$), –13.27 (t, 1H, $^2$J$_{H, P}$ 17 Hz, J$_{H, Si}$ –30 Hz, $^{13}$C$^{[4]H}$ NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 34.72 (s, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 33.94 (m, PCH$_2$), 30.12 (m, PCH$_2$), 27.12 (s, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 24.00 (d, $^1$J$_{C, P}$ 6 Hz, PCH$_3$), 23.96 (d, $^1$J$_{C, P}$ 6 Hz, PCH$_3$), 21.60 (s, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 20.55 (d, $^1$J$_{C, P}$ 13 Hz, PCH$_3$), 19.31 (d, $^1$J$_{C, P}$ 23 Hz, PCH$_3$), 17.97 (d, $^1$J$_{C, P}$ 15 Hz, PCH$_3$), 17.86 (d, $^1$J$_{C, P}$ 16 Hz, PCH$_3$), 14.53 (s, SiH$_2$CH$_2$CH$_2$CH$_2$CH$_3$). $^{29}$Si$^{[4]H}$ NMR (C$_6$D$_6$, 119 MHz, 298 K): δ 1.62 (p, $^2$J$_{Si, P}$ 23 Hz). $^{29}$Si NMR (C$_6$D$_6$, 119 MHz, 298 K): δ 1.63 (t of m, $^1$J$_{Si, H}$ 165 Hz). $^{31}$P$^{[4]H}$ (C$_6$D$_6$, 243 MHz, 298 K): δ 72.62 (s, 2P), 58.56 (s, 2P). Anal. Found (Caled): C, 45.17 (45.27); H, 10.39 (10.45).

aaaaa Measured using $^{29}$Si$_{edited}$ $^1$H–$^1$H COSY NMR spectroscopy as described in Chapter 6.
trans-$[(\text{dmpe})_2 \text{MnH}(\equiv \text{SiEt}^n\text{Bu})]$ (16Bu,Et). Approx. 15 mg of $[(\text{dmpe})_2 \text{MnH}(\text{SiH}^2\text{Bu})_2]$ (20Bu) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube, and this solution was freeze-pump-thawed ($\times$3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to –95 °C, sealed at this low temperature, and allowed to stand for 1-3 days at room temperature (until complete consumption of 20Bu). The solvent and free hydrosilane byproducts were then removed in vacuo (note that solvent and hydrosilanes must be removed before the H$_3$Si$^n$Bu is completely consumed by ethylene hydrosilylation; i.e. as soon as possible after 20Bu is consumed), and the resulting reddish/brown oil was dissolved in approx. 0.6 mL of C$_6$D$_6$.

This solution of 19Bu,H was allowed to stand at room temperature, with >65% conversion to 16Bu,Et after 1 week. The resulting clear, bronze solution contained impurities of 19Bu,Et and an unidentified MnH-containing species, as well as significant deuteration from solvent activation in the MnH and various alkyl environments. Characterization was performed by NMR spectroscopy in situ {spectra were collected after 18 ($^1$H and $^{31}$P{1H}), 14 (1D TOCSY and various 2D experiments), 17 (1D $^{29}$Si–HSQC), 11 ($^{13}$C{1H}), 16 ($^{29}$Si–1H HMBC), or 10 ($^{29}$Si{1H}) days}, and NMR spectra in C$_6$H$_6$ were conducted by removing the C$_6$D$_6$ in vacuo after 18 days of isomerization, and dissolving the resulting oil in C$_6$H$_6$. Selected NMR data are as follows; $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 1.90 (m, 4H, PC$_2$H$_2$), 1.75 (m, 4H, PC$_2$H$_2$), 1.46 (m, various $^n$Bu environments), 1.39 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.36 (s, 12H, PCH$_3$), 1.35 (q, 2H, $^3$J$_{H,H}$ 8.5 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.23 (s, 12H, PCH$_3$), 1.11 (t, 3H, $^3$J$_{H,H}$ 7.9 Hz, SiCH$_2$CH$_3$) 1.00 (t, 3H, $^3$J$_{H,H}$ 6.5 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), –10.48 (p, 1H, $^2$J$_{H,P}$ 51.2 Hz, MnH). $^2$H NMR (C$_6$H$_6$, 77 MHz, 298 K): 1.39 (br. s, alkyl), 1.28 (br. s, alkyl), 1.12 (br. s, alkyl), 0.98 (br. s, alkyl), 0.98 (br. s, alkyl), –10.54 (app. t, $^2$J$_{D,P}$ 7.8 Hz, MnD). $^{13}$C{1H} NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 38.04 (s, $^n$Bu environment), 34.65 (p, $^2$J$_{C,P}$ 12.3 Hz, PCH$_2$), 30.07 (s, SiCH$_2$CH$_3$), 29.53 (d, $^2$J$_{C,P}$ 8.9 Hz, PCH$_3$), 29.41 (s, PCH$_3$), 27.42 (s, $^n$Bu environment), 26.95 (s, $^n$Bu environment), 14.25 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 8.33 (s, SiCH$_2$CH$_3$). $^{29}$Si{1H} NMR (C$_6$D$_6$, 77 MHz, 298 K): δ 17.96 (s, $^{29}$Si).  

bbb All $^2$H NMR environments are due to room-temperature activation of the C$_6$D$_6$ solvent.
119 MHz, 298 K): δ 364.49 (m). $^{31}$P$^1$H NMR (C$_6$D$_6$, 243 MHz, 298 K): 80.50 (s, 2P), 80.35 (s, 2P).

**trans**-[(dmpe)$_2$MnH(=Si"Bu(CDHCD$_3$))] ($d_4$-$16$Bu,Et). $d_4$-$16$Bu,Et was prepared in a manner analogous to $16$Bu,Et, with $d_4$-ethylene in place of ethylene and a 4 day reaction time for the exposure of $20$Bu to C$_2$D$_4$ (with the headspace being evacuated and refilled with $d_4$-ethylene at the 2 day mark). Characterization was performed by NMR spectroscopy in situ, and NMR spectra in C$_6$H$_6$ were conducted by removing the C$_6$D$_6$ in vacuo and dissolving the resulting oil in C$_6$H$_6$. NMR data are consistent with those from $16$Bu,Et, with the following exceptions; no $^1$H NMR peak for the β ethyl environment (1.11 ppm in $16$Bu,Et), an isotopic shift in the $^1$H NMR peak for the α ethyl environment (singlet) to 1.29 ppm (cf. 1.35 ppm in $16$Bu,Et), and isotopic shifts of the α and β ethyl $^{13}$C NMR peaks to 29.4 and 7.5 ppm, respectively ($^1$H NMR collected at 600 MHz, $^{13}$C$^1$H NMR collected at 151 MHz, both at 298 K). $^2$H NMR (C$_6$H$_6$, 77 MHz, 298 K): δ 1.28 (s, 1D, SiCDHCD$_3$), 1.00 (s, 3D, SiCDHCD$_3$).

**trans**-[(dmpe)$_2$MnH(=SiHPh)] ($16$Ph,H). Approx. 15 mg of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] ($20$Ph) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube. NMR spectra were collected at 311, 322, and 333 K, with increasing concentrations of **trans**-[(dmpe)$_2$MnH(=SiHPh)] ($16$Ph,H) observed at higher temperatures (at 333 K, approx. 4% of the solution was **trans**-$16$Ph,H). Selected NMR data for **trans**-$16$Ph,H is as follows: $^1$H NMR (C$_6$D$_6$, 500 MHz, 333 K): δ 9.83 (s, 1H, =SiH), –9.01 (app. t, 1H, $^2$J$_{H,P}$ 54 Hz, MnH).

**trans**-[(dmpe)$_2$MnH(=SiH"Bu)] ($16$Bu,H). Approx. 15 mg of [(dmpe)$_2$MnH(SiH$_2$"Bu)$_2$] ($20$Bu) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube. NMR spectra were collected at 311, 322, and 333 K, with increasing concentrations of **trans**-[(dmpe)$_2$MnH(=SiH"Bu)] ($16$Bu,H) observed at higher temperatures (at 333 K, approx. 2% of the solution was **trans**-$16$Bu,H). Selected NMR data for **trans**-$16$Bu,H is as follows: $^1$H NMR (C$_6$D$_6$, 500 MHz, 333 K): δ 9.53 (s, 1H, =SiH), –9.60 (app. t, 1H, $^2$J$_{H,P}$ 51 Hz, MnH).
[(dmpe)$_2$MnH(PhHSi=CHMe)] (19$^{\text{Ph,H}}$). Approx. 15 mg of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (20$^{\text{Ph}}$) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube, and the solution was freeze-pump-thawed ($\times$3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to –95 °C, and sealed at this low temperature. After standing at room temperature for 24 h, the solvent and free hydrosilane byproducts were removed in vacuo and the resulting solid was dissolved in $d_8$-toluene. Characterization was performed by NMR spectroscopy in situ. The following NMR data encompasses signals from both observed isomers (which are in a 1 : 1 ratio); $^1$H NMR ($d_8$-toluene, 600 MHz, 298 K): δ 7.94 (d, 2H, $^3$J$_{\text{H,H}}$ 7.0 Hz, o), 7.88 (d, 2H, $^3$J$_{\text{H,H}}$ 6.9 Hz, o), 7.22 (t, 2H, $^3$J$_{\text{H,H}}$ 7.4 Hz, m), 7.16 (t, 1H, $^3$J$_{\text{H,H}}$ 6.2 Hz, p), 4.45 (br. s, 1H, SiH), 1.93 (d, 3H, $^3$J$_{\text{H,H}}$ 5.8 Hz, Si=C(H)C$_3$H$_3$), 1.92 (d, 3H, $^3$J$_{\text{H,H}}$ 4.5 Hz, Si=C(H)C$_3$H$_3$), 1.89 (d, 3H, $^2$J$_{\text{H,P}}$ 7.4 Hz, PH$_3$), 1.51 (d, 3H, $^2$J$_{\text{H,P}}$ 5.1 Hz, PH$_3$), 1.46 (d, 3H, $^2$J$_{\text{H,P}}$ 6.6 Hz, PH$_3$), 1.44 (d, 3H, $^2$J$_{\text{H,P}}$ 5.7 Hz, PH$_3$), 1.17 (m, 1H, Si=C(H)CH$_3$), 0.07 (m, 1H, Si=C(H)CH$_3$), –14.54 (br. s, 1H, MnH), –14.70 (br. s, 1H, MnH).

$^{31}$C{$^1$H} NMR ($d_8$-toluene, 151 MHz, 298 K): δ –20.95 (s, $^1$J$_{\text{C,H}}$ 140 Hz, Si=C(H)CH$_3$), –21.17 (s, Si=C(H)CH$_3$).

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 243 MHz, 298 K): δ 84.96, 83.81, 81.82, 74.95, 72.01, 70.48, 66.81, 63.30.

$^1$H NMR ($d_8$-toluene, 500 MHz, 213 K): δ 8.08 (d, 2H, $^3$J$_{\text{H,H}}$ 6.9 Hz, o), 8.02 (d, 2H, $^3$J$_{\text{H,H}}$ 7.2 Hz, o), 4.61 (s with $^{29}$Si sat., 1H, $^1$J$_{\text{H,SI}}$ 194.8 Hz, SiH$_3$), 4.61 (s with $^{29}$Si sat., 1H, $^1$J$_{\text{H,SI}}$ 194.8 Hz, SiH$_3$), 2.09 (m, 3H, Si=C(H)CH$_3$), 2.06 (m, 3H, Si=C(H)CH$_3$), 0.28 (m, 1H, Si=C(H)CH$_3$), 0.11 (m, 1H, Si=C(H)CH$_3$), –14.47 (m, 1H, MnH), –14.64 (m, 1H, MnH).

$^{13}$C{$^1$H} NMR ($d_8$-toluene, 126 MHz, 213 K): δ –21.63 (s, Si=C(H)CH$_3$), –21.85 (s, Si=C(H)CH$_3$).

$^{29}$Si NMR ($d_8$-toluene, 99 MHz, 213 K): δ –7.11, –17.42.

[(dmpe)$_2$MnH("BuHSi=CHMe)] (19$^{\text{Bu,H}}$). Approx. 15 mg of [(dmpe)$_2$MnH("BuH$_2$H$_2$Bu)$_2$] (20$^{\text{Bu}}$) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube, and this solution was freeze-pump-thawed ($\times$3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to –95 °C, sealed at this low temperature, and allowed to stand for 3 days at room temperature. The solvent and
free hydrosilane byproducts were then removed in vacuo and the resulting oil was dissolved in approx. 0.6 mL of C₆D₆. The reaction mixture was allowed to stand for 1 hour and the solvent was removed again in vacuo, yielding a red oil. The red oil was then dissolved in d₅-toluene and analyzed by NMR spectroscopy in situ, with two isomers present in solution (in a 1:1.9 ratio at room temperature). **Dominant isomer: **¹H NMR (d₅-toluene, 600 MHz, 298 K): δ 3.74 (d with ²⁹Si sat., 1H, ³J_H,P 17.8 Hz, ¹J_H,Si 192.2 Hz, SiH), 1.74 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.68 (d, 3H, ³J_H,H 7.5 Hz, Si=CH(CH₃)₂), 1.54 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.54-0.87 (various m, 8H, PCH₂), 1.43 (d, 3H, ²J_H,P 6.6 Hz, PCH₃), 1.32 (d, 3H, ²J_H,P 5.0 Hz, PCH₃), 1.23 (d, 3H, ²J_H,P 4.7 Hz, PCH₃), 1.22 (d, 3H, ²J_H,P 5.5 Hz, PCH₃), 1.11 (d, 3H, ²J_H,P 5.0 Hz, PCH₃), 1.01 (t, 3H, ³J_H,H 7.3 Hz, SiCH₂CH₂CH₂CH₃), 0.99-0.95 (m, 6H, PCH₃), 0.97 (m, 1H, SiCH₂CH₂CH₂CH₃), 0.84 (d, 3H, ²J_H,P 5.6 Hz, PCH₃), 0.78 (m, 1H, SiCH₂CH₂CH₂CH₃), –0.16 (m, 1H, Si=CH(CH₃)₂), –14.99 (br. s, 1H, MnH).

**¹³C{¹H} NMR (d₅-toluene, 151 MHz, 298 K):** δ 35.37 (app. t, J_C,P 24.7 Hz, PCH₂), 34.65 (m, PCH₂), 33.96 (d of d, ¹J_C,P 25.4 Hz, ²J_C,P 20.0 Hz, PCH₂), 32.96 (m, PCH₂), 32.16 (d, ¹J_C,P 19.0 Hz, PCH₃), 30.27 (s, SiCH₂CH₂CH₂CH₃), 28.07 (m, PCH₃), 26.77 (s, SiCH₂CH₂CH₂CH₃), 25.84 (d, ¹J_C,P 10.9 Hz, PCH₃), 24.30 (br. s, PCH₃), 22.10 (t, ³J_C,P 8.4 Hz, Si=CH(CH₃)₂), 21.82 (d, ¹J_C,P 13.9 Hz, PCH₃), 20.92 (m, PCH₃), 19.97 (m, PCH₃), 14.40 (s, SiCH₂CH₂CH₂CH₃), 12.86 (s, SiCH₂CH₂CH₂CH₃), 10.85 (m, PCH₃), –20.75 (s, ¹J_C,H 139 Hz, Si=CH(CH₃)₂).

**³¹P{¹H} NMR (d₅-toluene, 243 MHz, 298 K):** δ –16.98.

**Minor isomer: **¹H NMR (d₅-toluene, 119 MHz, 298 K): δ –17.86.

**¹³C{¹H} NMR (d₅-toluene, 151 MHz, 298 K):** δ 35.37 (app. t, J_C,P 24.7 Hz, PCH₂), 34.65 (m, PCH₂), 33.96 (d of d, ¹J_C,P 25.4 Hz, ²J_C,P 20.0 Hz, PCH₂), 32.96 (m, PCH₂), 32.16 (d, ¹J_C,P 19.0 Hz, PCH₃), 30.27 (s, SiCH₂CH₂CH₂CH₃), 28.07 (m, PCH₃), 26.77 (s, SiCH₂CH₂CH₂CH₃), 25.84 (d, ¹J_C,P 10.9 Hz, PCH₃), 24.30 (br. s, PCH₃), 22.10 (t, ³J_C,P 8.4 Hz, Si=CH(CH₃)₂), 21.82 (d, ¹J_C,P 13.9 Hz, PCH₃), 20.92 (m, PCH₃), 19.97 (m, PCH₃), 14.40 (s, SiCH₂CH₂CH₂CH₃), 12.86 (s, SiCH₂CH₂CH₂CH₃), 10.85 (m, PCH₃), –20.75 (s, ¹J_C,H 139 Hz, Si=CH(CH₃)₂). **²⁹Si NMR (d₅-toluene, 151 MHz, 298 K):** δ –19.68.
$^{13}C$ NMR ($d_8$-toluene, 119 MHz, 298 K): δ 146.12 (s, PCH$_2$), 128.14 (s, SiCH$_2$), 121.51 (d, $^3J_{C,P}$ 25.4 Hz, PCH$_2$), 32.96 (m, PCH$_2$), 30.34 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 26.70 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 25.95 (m, PCH$_3$), 24.07 (br. s, PCH$_3$), 23.87 (m, PCH$_3$), 23.72 (t, $^3J_{C,P}$ 7.5 Hz, Si=C(H)CH$_3$), 23.31 (m, PCH$_3$), 21.17 (m, PCH$_3$), –19.32 (s, $^1J_{C,H}$ 138 Hz, Si=CH$_3$).

$^{29}$Si NMR ($d_8$-toluene, 119 MHz, 298 K): δ –8.87.

$^{31}P$ NMR ($d_8$-toluene, 243 MHz, 298 K): δ 79.13 (s, 1P), 72.39 (s, 1P), 70.04 (s, 1P), 65.75 (s, 1P).

[(dmpe)$_2$MnH($^{19}$BuHSi=CD$_3$)] ($d_4$-$^{19}$BuH). $d_4$-$^{19}$BuH was prepared in a manner analogous to the first steps in the preparation of $d_4$-$^{19}$BuH, with NMR spectra taken immediately after re-dissolving in C$_6$D$_6$. $^1$H NMR data is consistent with that for $^{19}$BuH, though without peaks for the Si=C(H)CH$_3$ and Si=C(H)CH$_3$ environments (which are deuterated).

$^2$H NMR (C$_6$D$_6$, 77 MHz, 298 K): δ 1.85 (s, Si=C(D)CD$_3$ minor isomer), 1.69 (s, Si=C(D)CD$_3$ major isomer), –0.10 (br. s, Si=C(D)CD$_3$ both isomers).

[(dmpe)$_2$MnH(PhEtSi=CHMe)] ($^{19}$Ph,Et). 177.7 mg (0.311 mmol) of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] ($^{20}$Ph) was dissolved in 10 mL of benzene, and the solution was placed in a 50 mL storage flask and freeze-pump-thawed (×3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to –95 °C, and sealed at this low temperature. After stirring at room temperature for two days, the solvent was removed in vacuo and the resulting reddish-orange oil was recrystallized from a concentrated solution of hexamethyldisiloxane at –30 °C, yielding 20.6 mg (0.040 mmol, 13%) of a brown solid. Small impurities could not be removed, and the resulting complex decomposed slowly at room temperature (overnight at room temperature, a variety of hydride resonances appeared in the $^1$H NMR spectrum). $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 7.89 (d, 2H, $^3J_{H,H}$ 7.0 Hz, o), 7.22 (t, 2H, $^3J_{H,H}$ 7.2 Hz, m), 7.16 (t, 1H, $^3J_{H,H}$ 7.2 Hz, p), 1.88 (d, 3H, $^3J_{H,H}$ 7.3 Hz, Si=C(H)CH$_3$), 1.58 (d, 3H, $^3J_{H,P}$ 5.5 Hz, PCH$_3$), 1.56–1.09 (m, 6H, PCH$_3$), 1.51 (d, 3H, $^3J_{H,P}$ 6.7 Hz, PCH$_3$), 1.29 (d, 3H, $^3J_{H,P}$ 5.1 Hz, PCH$_3$), 1.24 (d, 3H, $^3J_{H,P}$ 4.6 Hz, PCH$_3$), 1.18 (t, 3H, $^3J_{H,H}$ 7.7 Hz, SiCH$_2$CH$_3$), 1.04 (m, 1H, PCH$_2$), 1.02 (m, 1H, SiCH$_2$CH$_3$), 0.97 (d, 3H, $^3J_{H,P}$ 4.6 Hz, PCH$_3$), 0.93 (d, 3H, $^3J_{H,P}$ 4.6 Hz, PCH$_3$).
4.9 Hz, PCH₃), 0.91 (m, 1H, PCH₂), 0.89 (d, 3H, ³J_H,P 5.5 Hz, PCH₃), 0.85 (m, 1H, SiCH₃(CH₃)), 0.54 (d, 3H, ³J_H,P 5.3 Hz, PCH₃), 0.18 (m, 1H, Si=C(H)CH₃), −14.89 (m, 1H, MnH). ¹³C¹{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 142.81 (s, i), 136.22 (s, o), 127.68 (s, p), 127.30 (s, m), 37.47 (t, J_C,P 25.0 Hz, PCH₂), 35.69 (d of d, ¹J_C,P 25.0 Hz, ³J_C,P 20.1 Hz, PCH₂), 33.59 (m, PCH₂), 33.59 (m, PCH₃), 32.98 (t of d, J_C,P 19.2 Hz, J_C,P 7.5 Hz, PCH₂), 28.30 (s, PCH₃), 26.14 (d, ¹J_C,P 10.3 Hz, PCH₃), 24.84 (s, PCH₃), 22.69 (s, Si=C(H)CH₃), 22.68 (d, ¹J_C,P 13.7 Hz, PCH₃), 21.12 (m, PCH₃), 20.64 (d, ¹J_C,P 14.9 Hz, PCH₃), 14.86 (s, PCH₃), 9.95 (s, SiCH₂CH₃), 9.56 (s, SiCH₂CH₃), −21.74 (s, ¹J_C,H 137 Hz, Si=C(H)CH₃). ²⁹Si NMR (C₆D₆, 119 MHz, 298 K): δ 0.72. ³¹P¹{¹H} NMR (C₆D₆, 243 MHz, 298 K): δ 79.17 (s, 1P), 68.61 (s, 1P), 65.65 (s, 2P). Low temperature (selected): ¹H NMR (d₈-toluene, 500 MHz, 213 K): δ 7.99 (d, 1H, ³J_H,H 6.4 Hz, o), 7.88 (d, 1H, ³J_H,H 6.6 Hz, o), 7.27 (t, 1H, ³J_H,H 6.8 Hz, m), 7.20 (t, 1H, ³J_H,H 6.8 Hz, m), 7.17 (m, 1H, p), 1.91 (d, 3H, ³J_H,P 6.7 Hz, Si=C(H)CH₃), 1.58 (d, 3H, ²J_H,P 4.2 Hz, PCH₃), 1.51 (d, 3H, ²J_H,P 5.8 Hz, PCH₃), 1.26 (m, 2H, SiCH₂CH₃), 1.19 (d, 3H, ²J_H,P 2.7 Hz, PCH₃), 0.55 (d, 3H, ²J_H,P 3.5 Hz, PCH₃), 0.18 (m, 1H, Si=C(H)CH₃), −14.91 (m, 1H, MnH). ²⁹Si NMR (d₈-toluene, 99 MHz, 213 K): δ 0.51. ³¹P¹{¹H} NMR (C₆D₆, 202 MHz, 203 K): δ 79.51 (app, q, ²J_P,P 29.9 Hz, 1P), 69.00 (s, 1P), 65.80 (m, 2P).

[(dmpe)₂MnH("BuEtSi=CHMe") (19BuEt)]. Approx. 15 mg of [(dmpe)₂MnH("BuHSi=CHMe")] (19BuH, >95% pure) was dissolved in approx. 0.6 mL of C₆D₆. The reaction mixture was freeze-pump-thawed (×3) in a J-young NMR tube, and then was placed under 1 atm of ethylene at −95 °C, sealed at this temperature, and warmed to room temperature. After standing at room temperature for 14 days, the resulting mixture contained primarily [(dmpe)₂MnH("BuEtSi=CHMe")] (19BuEt) and [(dmpe)₂MnH(C₂H₄)] (10), along with a series of small impurities including [(dmpe)₂MnH("BuHSi=CHMe")] (19BuH), and was analyzed by NMR spectroscopy in situ. Selected NMR data are as follows; ¹H NMR (d₈-toluene, 600 MHz, 298 K): δ 1.69 (d, 3H, ³J_H,H 6.0 Hz, Si=C(H)CH₃), 1.47 (d, 3H, ³J_H,H 6.7 Hz, PCH₃), 1.41 (m, 3H, PCH₃), 1.28 (m, 3H, SiCH₂CH₃), 1.27 (m, 6H, PCH₃), 1.15 (m, 3H, PCH₃), 0.96 (m, 3H, PCH₃), 0.95 (m, 3H, PCH₃), 0.94 (m, 3H, PCH₃), −0.11 (m, 1H, Si=C(H)CH₃), −15.33
(m, 1H, MnH]. $^{13}$C{$^1$H} NMR ($C_6D_6$, 151 MHz, 298 K): $\delta$ –19.28 (s, $^1J_{C,H}$ 137 Hz, Si=CH$_2$CH$_3$). $^{29}$Si NMR ($C_6D_6$, 119 MHz, 298 K): $\delta$ –6.45. $^{31}$P{$^1$H} NMR ($C_6D_6$, 243 MHz, 298 K): $\delta$ 65.45 (s, 1P), 67.57 (s, 1P), 70.66 (s, 1P), 79.26 (s, 1P).

[(dmpe)$_2$MnH($^{n}$BuEtSi=CDCD$_3$)] ($d_4$-$^{19}$Bu,$^{13}$Et). Approx. 15 mg of [(dmpe)$_2$MnH($^{n}$BuH)$_2$] ($^{20}$Bu) was dissolved in approx. 0.6 mL of $C_6D_6$. The reaction mixture was freeze-pump-thawed ($\times$3) in a J-young NMR tube, and then was placed under 1 atm of ethylene at –95 °C, sealed at this temperature, and warmed to room temperature. After standing at room temperature for 30 hours, the solvent and free hydrosilane byproducts were removed in vacuo. The resulting dark red/brown oil ($^{19}$Bu,$^{13}$H) was dissolved in approx. 0.6 mL of $C_6D_6$, and the resulting solution was freeze-pump-thawed ($\times$3) in a J-young NMR tube, placed under 1 atm of $d_4$-ethylene at –95 °C, sealed at this temperature, and warmed to room temperature where it was monitored over time by NMR spectroscopy. $^1$H NMR data was consistent with that for $^{19}$Bu,$^{13}$Et, though without peaks for the Si=C(H)CH$_3$ and Si=C(H)CH$_2$ environments (which are deuterated).

cis-[(dmpe)$_2$Mn(SiH$_2$Ph)(CNxylyl)] (cis-$^{21}$a). A slight excess of $o$-xylyl isocyanide (28.6 mg, 0.218 mmol) was added to a solution of 118.3 mg (0.207 mmol) [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] ($^{20}$Ph) in 10 mL of benzene. The reaction mixture was stirred overnight at room temperature in a sealed flask, after which the solvent was removed in vacuo. The resulting yellow solid was washed with hexanes and recrystallized from a concentrated solution of toluene at –30 °C, yielding 79.1 mg of bright orange crystals. A further 8.7 mg of orange crystals could be obtained by concentrating the mother liquor, layering with hexanes, and allowing to stand at –30 °C, for a total yield of cis-$^{21}$a of 87.8 mg (0.148 mmol, 71%). X-ray quality crystals were obtained by complete evaporation of toluene from a concentrated solution of cis-$^{21}$a at room temperature under argon. For elemental analysis, residual toluene was removed by heating at 50 °C for 2 h at 5 mTorr, resulting in a bright yellow powder. $^1$H NMR ($C_6D_6$, 600 MHz, 298 K): $\delta$ 8.05 (d of d, 2H, $^3J_{H,H}$ 7.2 Hz, $^4J_{H,H}$ 1.8 Hz, o), 7.07 (m, 2H, m), 7.06 (m, 1H, p), 6.87 (d, 2H, $^3J_{H,H}$ 7.4 Hz, xylyl-m), 6.76 (t, 1H, $^3J_{H,H}$ 7.4 Hz, xylyl-p), 5.05 (d of d with $^{29}$Si
sat., 1H, $^3J_{H,P}$ 19.2 Hz, $^3J_{H,P}$ 7.7 Hz, $^1J_{H,Si}$ 138.7 Hz, Si(H), 4.73 (m with $^{29}$Si sat., 1H, $^1J_{H,Si}$ 137.5 Hz, Si(H), 2.05 (s, 6H, xylyl-C$H_3$), 1.74 (d, 3H, $^2J_{H,P}$ 7.0 Hz, PCH$_3$), 1.68 (m, 1H, PCH$_3$), 1.64 (d, 3H, $^2J_{H,P}$ 6.5 Hz, PCH$_3$), 1.61–1.44 (m, 3H, PCH$_3$), 1.32 (d, 3H, $^2J_{H,P}$ 6.0 Hz, PCH$_3$), 1.23 (d, 3H, $^2J_{H,P}$ 6.0 Hz, PCH$_3$), 1.20 (d, 3H, $^2J_{H,P}$ 6.2 Hz, PCH$_3$), 1.18 (m, 2H, PCH$_3$), 1.18 (d, 3H, $^2J_{H,P}$ 4.4 Hz, PCH$_3$), 0.75 (m, 1H, PCH$_2$), 0.75 (m, 1H, PCH$_2$).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 151 MHz, 298 K): $\delta$ 149.06 (s, i), 137.34 (s, o), 134.02 (s, xylyl-i), 128.04 (s, xylyl-o), 128.04 (s, xylyl-m), 127.01 (s, p), 125.95 (s, m), 122.26 (s, xylyl-p), 33.79 (t of d, $^1J_{C,P}$ 20.2 Hz, $^2J_{C,P}$ 5 Hz, PCH$_2$), 32.48 (t, $^1J_{C,P}$ 19.9 Hz, PCH$_2$), 32.10 (m, PCH$_2$), 23.70 (m, PCH$_3$), 22.96 (m, PCH$_3$), 22.55 (d, $^1J_{C,P}$ 8.8 Hz, PCH$_3$), 21.53 (d of d, $^1J_{C,P}$ 20.8 Hz, $^2J_{C,P}$ 5 Hz, PCH$_3$), 20.66 (m, PCH$_3$), 20.35 (s, xylyl-C$H_3$), 20.22 (m, PCH$_3$), 19.82 (d, $^1J_{C,P}$ 26.4 Hz, PCH$_3$), 16.83 (d of d, $^1J_{C,P}$ 21.2 Hz, $^2J_{C,P}$ 4.6 Hz, PCH$_3$).

$^{29}$Si NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ 6.97.

$^{31}$P{$^1$H} NMR (C$_6$D$_6$, 243 MHz, 298 K): $\delta$ 74.77 (s, 2P), 64.51 (s, 1P), 55.54 (s, 1P).

Anal. Found (calcd.): C, 54.89 (54.63); H, 8.61 (8.15); N, 2.32 (2.36).

trans-[(dmpe)$_2$Mn(SiH$_2$Ph)(CNxylyl)] (trans-21a). Method a) Approx. 15 mg of cis-[(dmpe)$_2$Mn(SiH$_2$Ph)(CNxylyl)] (cis-21a) was dissolved in approx. 0.6 mL of C$_6$D$_6$, and this solution was placed in an NMR tube with a J-Young Teflon valve and heated at 80-90°C for 5 days. The resulting solution contained a mixture of cis-7a (51%) and trans-21a (49%), and was analyzed by NMR spectroscopy in situ. Method b) Approx. 15 mg of [(dmpe)$_2$MnD$_2$(SiH$_2$Ph)] ($d_2$-18$_{\text{Ph}}$) was dissolved in approx. 0.6 mL of C$_6$D$_6$. To the reaction mixture was added an excess (5 mg) of o-xylyl isocyanide. The reaction mixture was placed in an NMR tube with a J-Young Teflon valve and heated at 75 °C for one hour, and NMR characterization was performed in situ. The resulting solution contained a mixture of cis-21a (91%) and trans-21a (9%). Data for the trans isomer is presented below. $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 7.82 (d of d, 2H, $^3J_{H,H}$ 7.8 Hz, $^4J_{H,H}$ 1.3 Hz, o), 7.22 (t, 2H, $^3J_{H,H}$ 7.1 Hz, m), 7.16 (m, 1H, p), 6.85 (d, 2H, $^3J_{H,H}$ 7.1 Hz, xylyl-m), 6.71 (t, 1H, $^3J_{H,H}$ 7.5 Hz, xylyl-p), 4.42 (p with $^{29}$Si sat., 2H, $^3J_{H,P}$ 8.4 Hz, $^1J_{H,Si}$ 140.5 Hz, Si(H), 2.27 (s, 6H, xylyl-C$H_3$), 1.72 (m, 4H, PCH$_2$), 1.50 (m, 4H, PCH$_2$), 1.34
cis-[(dmpe)$_2$Mn(SiH$_2$Bu)(CNxylyl)] (cis-21b). An excess of o-xylyl isocyanide (78.6 mg, 0.599 mmol) was added to a solution of 145.2 mg (0.274 mmol) [(dmpe)$_2$MnH(SiH$_2$Bu)$_2$] (20$^{Bu}$) in 10 mL of benzene. The reaction mixture was stirred overnight at room temperature in a sealed flask, after which the solvent was removed in vacuo. The resulting orange solid was extracted with 2.5 mL of hexanes, and the resulting solution was stored at –30 °C, yielding 33.3 mg of cis-21b as an orange powder. Additional yield was obtained by dissolving the residual solid in toluene, layering with hexamethyldisiloxane, and letting stand at –30 °C to give an additional 22.7 mg (for a total yield of 56.0 mg, 0.098 mmol, 36%). X-ray quality crystals (bright orange diamonds) were obtained from a concentrated solution of toluene layered with hexamethyldisiloxane at –30 °C.

$^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 6.91 (d, 2H, $^3$J$_{H,H}$ 7.4 Hz, xylyl-m), 6.76 (t, 1H, $^3$J$_{H,H}$ 7.5 Hz, xylyl-p), 4.15 (m with $^{29}$Si sat., 1H, $^1$J$_{H,Si}$ 134.5 Hz, SiH$_2$), 3.99 (m with $^{29}$Si sat., 1H, $^1$J$_{H,Si}$ 133.8 Hz, SiH$_2$), 2.46 (s, 6H, xylyl-C$_2$H$_5$), 2.02 (t of t, 2H, $^3$J$_{H,H}$ 7.7 Hz, SiCH$_2$CH$_2$C$_2$H$_2$), 1.71 (m, 1H, PC$_2$H$_2$), 1.71 (d, 3H, $^2$J$_{H,P}$ 6.6 Hz, PC$_3$H$_3$), 1.68 (d, 3H, $^2$J$_{H,P}$ 6.4 Hz, PCH$_3$), 1.63 (t of q, 2H, $^3$J$_{H,H}$ 7.4 Hz, SiCH$_2$CH$_2$CH$_2$CH$_2$C$_2$H$_2$), 1.54 (m, 3H, PCH$_2$), 1.27 (d, 3H, $^2$J$_{H,P}$ 6.4 Hz, PCH$_3$), 1.23 (d, 3H, $^2$J$_{H,P}$ 5.9 Hz, PCH$_3$), 1.22 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_2$C$_2$H$_2$), 1.22 (m, 1H, PCH$_2$), 1.18 (m, 6H, PCH$_3$), 1.15 (m, 1H, PCH$_2$), 1.04 (m, 1H, PCH$_2$), 1.03 (d, 3H, $^2$J$_{H,P}$ 4.9 Hz, PCH$_3$), 1.02 (t, 3H, $^3$J$_{H,H}$ 7.3 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.77 (d, 3H, $^2$J$_{H,P}$ 4.7 Hz, PCH$_3$), 0.73 (m, 1H, PCH$_2$). $^{13}$C$^{'1}$H NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 134.66 (s, xylyl-i), 132.18 (s, xylyl-o), 128.41 (xylyl-m), 122.10 (s, xylyl-p), 35.55 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 33.87 (t of d, $^3$J$_{C,P}$ 19.8 Hz, $^5$J$_{C,P}$ 6.9 Hz, PCH$_2$), 32.88 (t of d, $^3$J$_{C,P}$ 23.5 Hz, $^5$J$_{C,P}$ 8.6 Hz, PCH$_2$), 32.53 (t, $^3$J$_{C,P}$ 18.9 Hz, PCH$_2$), 31.45 (t, $^3$J$_{C,P}$ 20.2 Hz, PCH$_2$), 27.08 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 23.93 (d of d, $^3$J$_{C,P}$ 13.0 Hz, $^3$J$_{C,P}$ 2.3 Hz, PCH$_3$), 23.39 (d of d, $^3$J$_{C,P}$ 8.4 Hz, $^3$J$_{C,P}$ 3.7 Hz, PCH$_3$),
trans-[(dmpe)$_2$Mn(SiH$_2$Bu)(CNxylyl)] (trans-21b). Approx. 15 mg of cis-[(dmpe)$_2$Mn(SiH$_2$Bu)(CNxylyl)] (cis-21b) was dissolved in approx. 0.6 mL of C$_6$D$_6$, and this solution was placed in an NMR tube with a J-Young Teflon valve and heated at 80-90 °C for 5 days. The resulting solution contained a mixture of cis-21b (56%) and trans-21b (44%), and was analyzed by NMR spectroscopy in situ. Data for the trans isomer is presented below.

$^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 6.87 (d, 2H, $^3J_{H,H}$ 7.3 Hz, xylyl-m), 6.72 (t, 1H, $^3J_{H,H}$ 7.4 Hz, xylyl-p), 3.58 (m with $^{29}$Si sat., 2H, $^1J_{H,Si}$ 135.5 Hz, SiCH$_2$), 2.31 (s, 6H, xylyl-C$_6$H$_3$), 1.92 (app. p, 2H, $^3J_{H,H}$ 7.5 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.67 (m, 4H, PCH$_3$), 1.65 (app. sextet, 2H, $^3J_{H,H}$ 8.7 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.50 (m, 4H, PCH$_3$), 1.42 (s, 12H, PCH$_3$), 1.31 (s, 12H, PCH$_3$), 1.07 (t, 3H, $^3J_{H,H}$ 7.3 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.69 (m, 2H, SiC$_6$H$_2$CH$_2$CH$_2$CH$_3$).

$^{13}$C{$^1$H} NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 134.29 (s, xylyl-i), 132.12 (s, xylyl-o), 128.48 (s, xylyl-m), 121.95 (s, xylyl-p), 37.05 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 32.80 (m, PCH$_3$), 27.35 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 22.39 (s, PCH$_3$), 21.18 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 20.61 (s, xylyl-CH$_3$), 20.42 (s, PCH$_3$), 14.63 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$).

$^{29}$Si NMR (C$_6$D$_6$, 119 MHz, 298 K): δ 0.24. $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 243 MHz, 298 K): δ 73.03.

cis-[(dmpe)$_2$Mn(SiH$_2$Ph)(CN'Bu)] (cis-21c). An excess of tert-butyl isocyanide (57.0 mg, 0.686 mmol) was added to a solution of 60.9 mg (0.107 mmol) [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (20$^{th}$) in 10 mL of benzene. The reaction mixture was stirred for an hour in a sealed flask at room temperature, after which the solvent was removed in vacuo. The resulting yellow solid was extracted with hexanes, and the resulting solution was stored at −30 °C, yielding 12.1 mg of cis-21c as a light yellow powder. Additional
yield was obtained by dissolving the residual solid in a minimal amount of toluene, layering with hexamethyldisiloxane, and storing at −30 °C to give an additional 15.8 mg (total yield of 27.9 mg, 0.051 mmol, 48 %). X-ray quality crystals (pale yellow) were obtained from a concentrated solution of toluene layered with hexamethyldisiloxane at −30 °C.  

\( ^1\text{H NMR (C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 600 MHz, 298 K)} \): \( \delta \) 8.14 (d of m, 2H, \( ^3\text{J}_{\text{H,H}}\) 7.6 Hz, o), 7.32 (t, 2H, \( ^3\text{J}_{\text{H,H}}\) 7.5 Hz, m), 7.21 (t, 1H, \( ^3\text{J}_{\text{H,H}}\) 7.3 Hz, p), 4.98 (d of d of d with 29Si sat., 1H, \( ^3\text{J}_{\text{H,P}}\) 16.2 Hz, \( ^3\text{J}_{\text{H,P}}\) 7.0 Hz, \( ^3\text{J}_{\text{H,P}}\) 3.4 Hz, \( ^1\text{J}_{\text{H,Si}}\) 136.9 Hz, SiH), 4.78 (q with 29Si sat., 1H, \( ^3\text{J}_{\text{H,P}}\) 7.8 Hz, \( ^1\text{J}_{\text{H,Si}}\) 138.2 Hz, SiH), 1.75 (m, 1H, PCH\(_2\)), 1.66 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 6.9 Hz, PCH\(_3\)), 1.63 (m, 1H, PCH\(_2\)), 1.53 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 7.0 Hz, PCH\(_3\)), 1.39 (m, 1H, PCH\(_2\)), 1.38 (m, 1H, PCH\(_2\)), 1.36 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 6.1 Hz, PCH\(_3\)), 1.30 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 6.1 Hz, PCH\(_3\)), 1.29 (m, 1H, PCH\(_2\)), 1.24 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 5.9 Hz, PCH\(_3\)), 1.17 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 5.9 Hz, PCH\(_3\)), 1.09 (m, 2H, PCH\(_2\)), 1.06 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 4.7 Hz, PCH\(_3\)), 1.02 (s, 9H, CNC(CH\(_3\))\(_3\)), 0.96 (m, 1H, PCH\(_2\)), 0.82 (d, 3H, \( ^2\text{J}_{\text{H,P}}\) 5.1 Hz, PCH\(_3\)).  

\( ^{13}\text{C\{^1\text{H}}\) NMR (C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 151 MHz, 298 K): \( \delta \) 152.01 (s, i), 137.30 (s, o), 126.95 (s, m), 125.64 (s, p), 54.62 (s, CNC(CH\(_3\))\(_3\)), 34.10 (t of d, \( \text{J}_{\text{C,P}}\) 21.5 Hz, \( \text{J}_{\text{C,P}}\) 5.5 Hz, PCH\(_2\)), 33.28 (t of d, \( \text{J}_{\text{C,P}}\) 22.8 Hz, \( \text{J}_{\text{C,P}}\) 7.9 Hz, PCH\(_2\)), 32.97 (t, \( \text{J}_{\text{C,P}}\) 20.3 Hz, PCH\(_2\)), 31.76 (s, CNC(CH\(_3\))\(_3\)), 30.89 (t, \( \text{J}_{\text{C,P}}\) 19.7 Hz, PCH\(_2\)), 24.39 (m, PCH\(_3\)), 23.78 (m, PCH\(_3\)), 23.19 (d, \( \text{J}_{\text{C,P}}\) 7.4 Hz, PCH\(_3\)), 22.08 (d of d, \( \text{J}_{\text{C,P}}\) 17.8 Hz, \( ^3\text{J}_{\text{C,P}}\) 5.7 Hz, PCH\(_3\)), 20.61 (d, \( \text{J}_{\text{C,P}}\) 13.9 Hz, PCH\(_3\)), 19.98 (d, \( \text{J}_{\text{C,P}}\) 23.8 Hz, PCH\(_3\)), 19.68 (d, \( \text{J}_{\text{C,P}}\) 21.8 Hz, PCH\(_3\)), 18.37 (d of d, \( \text{J}_{\text{C,P}}\) 19.5 Hz, \( ^3\text{J}_{\text{C,P}}\) 4.5 Hz, PCH\(_3\)).  

\( ^{29}\text{Si\{^1\text{H}}\) NMR (C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 119 MHz, 298 K): \( \delta \) 8.46 (m).  

\( ^{31}\text{P\{^1\text{H}}\) NMR (C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 243 MHz, 298 K): \( \delta \) 77.10 (s, 1P), 74.49 (s, 1P), 67.16 (s, 1P), 57.93 (s, 1P).  

Analy. Found (calcd.): C, 49.76 (50.64); H, 9.52 (8.87); N, 2.64 (2.57).

\textit{trans-}[\text{dmpe}]_2\text{Mn(SiH}_2\text{Ph}(\text{CN}_3\text{Bu})] \text{ (trans-21c).} \text{Approx. 15 mg of cis-}[\text{dmpe}]_2\text{Mn(SiH}_2\text{Ph}(\text{CN}_3\text{Bu})] \text{ (cis-21c) was dissolved in approx. 0.6 mL of d}_8\text{-toluene and this solution was placed in an NMR tube with a J-Young Teflon valve and heated at 65-80 °C for 10 days. The resulting solution contained a mixture of cis-21c (24%) and trans-21c (76%), and was analyzed by NMR spectroscopy \textit{in situ}. Data for the trans isomer is presented below.}  

\( ^1\text{H NMR (d}_8\text{-toluene, 600 MHz, 298 K):} \( \delta \) 7.73 (d of m, 2H, \( ^3\text{J}_{\text{H,H}}\) 6.7 Hz, o), 7.15 (t, 2H, \( ^3\text{J}_{\text{H,H}}\) 7.1 Hz, m), 7.09 (t, 1H, \( ^3\text{J}_{\text{H,H}}\) 6.5 Hz, p), 4.30 (p with}
cis-[(dmpe)₃Mn(SiH₂₉Bu)(CNBu)] (cis-21d). An excess of tert-butyl isocyanide (90 mg, 1.083 mmol) was added to a solution of 57.5 mg (0.108 mmol) of [(dmpe)₃MnH(SiH₂₉Bu)₂] (20Bu) in 10 mL of benzene. The reaction mixture was stirred in a sealed flask overnight at room temperature, after which the solvent was removed in vacuo. The resulting yellow solid was recrystallized from a concentrated solution of hexamethyldisiloxane at –30 °C, giving a yield of 19.8 mg of cis-21d (0.038 mmol, 35%). X-ray quality crystals were obtained from hexamethyldisiloxane at –30 °C. ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 4.12 (m with ²⁹Si sat., 1H, ¹H, J₁H,Si 131.7 Hz, SiH), 3.92 (m with ²⁹Si sat., 1H, ¹H, J₁H,Si 130.6 Hz, SiH), 2.12 (m, 2H, SiCH₂CH₂CH₂CH₂CH₃), 1.77 (s, 2H, ³J₁H,CH 7.4 Hz, SiCH₂CH₂CH₂CH₂CH₃), 1.75 (m, 1H, PCH₂), 1.65 (m, 1H, PCH₂), 1.61 (d, 3H, ³J₁H,PCH 6.8 Hz, PCH₃), 1.56 (m, 1H, PCH₂), 1.56 (d, 3H, ²J₁H,PCH 7.3 Hz, PCH₃), 1.53 (m, 1H, PCH₂), 1.36 (m, 1H, PCH₂), 1.29 (d, 3H, ²J₁H,PCH 6.0 Hz, PCH₃), 1.27 (d, 3H, ²J₁H,PCH 6.0 Hz, PCH₃), 1.23 (s, 9H, CNC(CH₃)₃), 1.23 (d, 3H, ²J₁H,PCH 4.9 Hz, PCH₃), 1.18 (d, 3H, ²J₁H,PCH 4.9 Hz, PCH₃), 1.17 (m, 2H, SiCH₂CH₂CH₂CH₂CH₃), 1.16 (t, 3H, ³J₁H,H 7.2 Hz, SiCH₂CH₂CH₂CH₂CH₃), 1.11 (d, 3H, ²J₁H,PCH 4.5 Hz, PCH₃), 1.01 (m, 1H, PCH₂), 0.99 (m, 1H, PCH₂), 0.85 (m, 1H, PCH₂), 0.84 (d, 3H, ²J₁H,PCH 4.7 Hz, PCH₃). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 54.44 (s, CNC(CH₃)), 35.98 (s, SiCH₂CH₂CH₂CH₂CH₃), 34.44 (t of d, J₁C,P 20.8 Hz, J₁C,P 6.2 Hz, PCH₂), 33.87 (t of d, J₁C,P 24 Hz, J₁C,P 8.1 Hz, PCH₂), 32.28 (d of d, J₁C,P 19.9 Hz, J₁C,P 18.1 Hz, PCH₂), 31.99 (s, CNC(CH₃)₃), 30.13 (t, J₁C,P 19.4 Hz, PCH₂), 27.51 (s, SiCH₂CH₂CH₂CH₂CH₃), 24.16 (m, PCH₃), 23.21 (d, J₁C,P 8.7 Hz, PCH₃), 22.06 (d of d, J₁C,P 17.9 Hz, J₁C,P 5.4 Hz, PCH₃), 20.20 (d of d, J₁C,P 12.4 Hz, J₁C,P 3.1 Hz, PCH₃), 19.12 (d, J₁C,P 5.0 Hz, SiCH₂CH₂CH₂CH₂CH₃), 18.16 (d, J₁C,P 24.9 Hz, PCH₃), 17.73 (d, J₁C,P 23.7 Hz, PCH₃), 17.27 (d of d, J₁C,P 19.3 Hz, J₁C,P 5.6 Hz, PCH₃), 14.76 (s,
SiCH$_2$CH$_2$CH$_2$CH$_3$). $^{29}$Si$_{^1}$H NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ 10.12 (m). $^{31}$P$_{^1}$H NMR (C$_6$D$_6$, 243 MHz, 298 K): $\delta$ 78.49 (s, 1P), 75.66 (s, 1P), 65.20 (s, 1P), 57.37 (s, 1P). Anal. Found (calcd.): C, 47.94 (47.99); H, 9.89 (9.97); N, 2.62 (2.67).

-trans-[(dmpe)$_2$Mn(SiH$_2^n$Bu)(CN$_t^i$Bu)] (trans-21d). Method a) Approx. 15 mg of cis-[(dmpe)$_2$Mn(SiH$_2^n$Bu)(CN$_t^i$Bu)] (cis-21d) was dissolved in approx. 0.6 mL of C$_6$D$_6$ and this solution was placed in an NMR tube with a J-Young Teflon valve and heated at 80 °C for 20 days. The resulting solution contained mixture of cis-21d (47%) and trans-21d (53%), and was analyzed by NMR spectroscopy in situ. Method b) approx. 10 mg of [(dmpe)$_2$MnH$_2$(SiH$_2^n$Bu)] (18Bu) was dissolved in approx. 0.6 mL of C$_6$D$_6$. To the reaction mixture was added a large excess of $^t$BuN≡C. The reaction mixture was placed in an NMR tube with a J-Young Teflon valve and heated at 75 °C for one hour, and NMR characterization was performed in situ {the resulting solution contained mixture of cis-21d (82%) and trans-21d (18%)}. Data for the trans isomer is presented below.

$^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 3.60 (m with $^{29}$Si sat., 2H, $^1$J$_{H, Si}$ 131.4 Hz, SiH), 1.96 (p, 2H, $^3$J$_{H, H}$ 7.6 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.66 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.65 (m, 4H, PCH$_2$), 1.50 (s, 12H, PCH$_3$), 1.38 (m, 4H, PCH$_2$), 1.28 (s, 12H, PCH$_3$), 1.08 (t, 3H, $^3$J$_{H, H}$ 7.5 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.06 (s, 9H, CNC(CH$_3$)$_3$), 0.68 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_3$). $^{13}$C$_{^1}$H NMR (C$_6$D$_6$, 151 MHz, 298 K): $\delta$ 54.24 (s, CNC(CH$_3$)$_3$), 37.31 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 32.29 (s, PCH$_2$), 31.65 (s, CNC(CH$_3$)$_3$), 27.41 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 22.45 (m, PCH$_3$), 21.36 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 20.13 (m, PCH$_3$), 14.67 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$). $^{29}$Si NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ 2.51. $^{31}$P$_{^1}$H NMR (C$_6$D$_6$, 243 MHz, 298 K): $\delta$ 74.02 (s).

[(dmpe)$_2$MnH{=SiHPh($^{iP}$NHC)}] (22a). 1,3-diisopropylimidazolin-2-ylidene ($^{iP}$NHC) (84.7 mg, 0.556 mmol) was added to a solution of 95.1 mg (0.167 mmol) [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (20Ph) in 10 mL of benzene. The reaction mixture was placed in a 50 mL storage flask, sealed, and stirred overnight at room temperature, then overnight again at 55 °C. The solvent was then removed in vacuo and the resulting brownish/red powder was washed with hexanes. The remaining solid was extracted with pentane, and
the resulting solution was stored –30 °C. As well, the residual solid from the extraction was dissolved in a minimal amount of hexamethyldisiloxane and stored at –30 °C. Combining crystals from both batches provided a total yield of 14.4 mg (0.023 mmol, 14% yield) of \(22a\) as a red powder, though the product contained some unidentified impurities which were not removed. X-ray quality crystals (red blocks) were obtained from hexanes at –30 °C. Elevated temperature NMR analysis (signals are an average of the chemical shifts for 2 isomers): \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 330 K): \(\delta\) 7.51 (d, 2H, \(^3\)J\(_{\text{H,H}}\) 6.8 Hz, o), 7.05 (t, 2H, \(^3\)J\(_{\text{H,H}}\) 7.6 Hz, m), \(^7\)v (v. br. m, 2H, \(\text{CCH(CH}_3)_2\)), 6.97 (t, 1H, \(^3\)J\(_{\text{H,H}}\) 6.3 Hz, p), 6.31 (s, 2H, \(\text{CCH=CH}\)), 6.18 (br. s, 1H, SiH), 0.6-1.9 (many br. multiplets, 44H, dmpe and CH(CH\(_3\))\(_2\)), –12.54 (p, 1H, \(^2\)J\(_{\text{H,P}}\) 33.6 Hz, MnH). \(^{31}\)P\(^{\text{1}}\)H NMR (\(d_8\)-toluene, 202 MHz, 330 K): \(\delta\) 79.60 (m, 2P), 71.79 (s, 1P), 65.38 (s, 1P).

Room temperature NMR analysis (signals are in the process of decoalescing to two sets for the two observed isomers). Selected NMR signals are as follows; \(^1\)H NMR (\(d_8\)-toluene, 600 MHz, 298 K): \(\delta\) 7.55 (d, 2H, \(^3\)J\(_{\text{H,H}}\) 7.1 Hz, o), 7.08 (t, 2H, \(^3\)J\(_{\text{H,H}}\) 7.4 Hz, m), 7.00 (t, 2H, \(^3\)J\(_{\text{H,H}}\) 7.3 Hz, p), 6.80 (br. m, 1H, \(\text{CCH(CH}_3)_2\)), 6.24 (s, 2H, \(\text{CCH=CH}\)), 6.16 (br. s, 1H, SiH), 0.6-1.9 (many br. multiplets, 44H, dmpe and CH(CH\(_3\))\(_2\)), –12.43 (m, 1H, MnH minor isomer), –12.56 (m, 1H, MnH major isomer). \(^{13}\)C\(^{\text{1}}\)H NMR (\(d_8\)-toluene, 151 MHz, 298 K): \(\delta\) 135.66 (s, o), 127.06 (s, m), 116.47 (s, \(\text{CCH=CH}\)). \(^{31}\)P\(^{\text{1}}\)H NMR (\(d_8\)-toluene, 243 MHz, 298 K): \(\delta\) 79.92 (s, 1P, major isomer), 78.38 (s, 1P, major isomer), 78.38 (m, 2P, minor isomer), 73.75 (s, 1P, minor isomer), 71.14 (s, 1P, major isomer), 65.10 (s, 1P, major isomer), 64.42 (s, 1P, minor isomer). Low temperature NMR analysis (signals for two isomers could be observed in a 0.3 : 1 ratio). Selected NMR signals are as follows; Dominant isomer: \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 213 K): 8.77 (m, 1H, \(\text{CCH(CH}_3)_2\)), 7.68 (m, 2H, o), 7.20 (t, 2H, \(^3\)J\(_{\text{H,H}}\) 6.9 Hz, m), 7.10 (t, 1H, \(^3\)J\(_{\text{H,H}}\) 6.8 Hz, p), 6.26 (s, 1H, SiH), 6.09 (s, 1H, \(\text{HC=CH}\)), 5.86 (s, 1H, \(\text{HC=CH}\)), 5.76 (m, 1H, \(\text{CCH(CH}_3)_2\)), 1.84 (s, 3H, \(\text{PCCH}_3\)), 1.65 (m, 3H, \(\text{PCCH}_3\)), 1.47 (s, 3H, \(\text{PCCH}_3\)), 1.43 (s, 3H, \(\text{PCCH}_3\)), 1.39 (s, 3H, \(\text{PCCH}_3\)), 1.34 (s, 3H, \(\text{PCCH}_3\)), 1.30 (s, 3H, \(\text{CCH(CH}_3)_2\)), 1.20 (s, 3H, \(\text{CCH(CH}_3)_2\)), 1.20 (s, 3H, \(\text{PCCH}_3\)), 1.07 (s, 3H, \(\text{PCCH}_3\)), 0.82 (d, 3H, \(^3\)J\(_{\text{H,H}}\) 4.5 Hz, \(\text{CH(CH}_3)_2\)), 0.27 (d, 3H, \(^3\)J\(_{\text{H,H}}\) 3.8 Hz, \(\text{CH(CH}_3)_2\)), –12.47 (m, 1H, MnH). \(^{13}\)C\(^{\text{1}}\)H NMR (\(d_8\)-toluene, 126 MHz,
213 K): δ 156.34 (s, i), 135.39 (s, o), 127.02 (s, m), 116.58 (s, H=C=CH), 116.16 (s, H=C=CH), 49.69 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 47.95 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 37.08 (m, PC<sub>H</sub>), 35.30 (m, PC<sub>H</sub>), 34.00 (m, PC<sub>H</sub>), 33.90 (m, PC<sub>H</sub>), 29.52 (s, PC<sub>H</sub>), 27.74 (s, PC<sub>H</sub>), 26.10 (m, PC<sub>H</sub>), 25.33 (s, PC<sub>H</sub>), 23.66 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 23.24 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 22.54 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 21.96 (s, CH(CH<sub>3</sub>)<sub>2</sub>).

29Si NMR (d<sub>8</sub>-toluene, 99 MHz, 213 K): δ 24.11.

31P{1H} NMR (d<sub>8</sub>-toluene, 202 MHz, 213 K): δ 81.85 (t, <sup>2</sup>J<sub>P,P</sub> 27.2 Hz, 1P), 79.18 (s, 1P), 72.46 (d of d, <sup>2</sup>J<sub>P,P</sub> 41.9 Hz, <sup>2</sup>J<sub>P,P</sub> 20.9 Hz, 1P), 66.34 (m, 1P).

Minor isomer: 1H NMR (d<sub>8</sub>-toluene, 500 MHz, 213 K): δ 8.03 (m, 1H, C<sub>H</sub>(CH<sub>3</sub>)<sub>2</sub>), 7.68 (m, 2H, o), 7.19 (t, 2H, <sup>3</sup>J<sub>H,H</sub> 6.9 Hz, m), 7.08 (m, 1H, p), 6.37 (d with 29Si sat., 1H, <sup>3</sup>J<sub>H,P</sub> 19.0 Hz, <sup>1</sup>J<sub>H,Si</sub> 123.4 Hz, Si<sub>H</sub>), 5.59 (br. s, 1H, C<sub>H</sub>(CH<sub>3</sub>)<sub>2</sub>), 2.01 (s, 3H, PC<sub>H</sub>), 1.76 (m, 3H, PC<sub>H</sub>), 1.65 (m, 3H, PC<sub>H</sub>), 1.53 (d, 3H, <sup>3</sup>J<sub>H,H</sub> 3.2 Hz, PC<sub>H</sub>), 1.43 (s, 3H, PC<sub>H</sub>), 1.39 (s, 6H, PC<sub>H</sub>), 1.30 (s, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.12 (s, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.82 (s, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.75 (s, 3H, PC<sub>H</sub>), 0.42 (br. s, 3H, PC<sub>H</sub>), –12.32 (m, 1H, Mn<sub>H</sub>).

13C{1H} NMR (d<sub>8</sub>-toluene, 126 MHz, 213 K): δ 135.39 (s, o), 127.02 (s, m), 29.08 (s, PC<sub>H</sub>), 27.34 (m, PC<sub>H</sub>), 26.54 (m, PC<sub>H</sub>), 22.54 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 21.50 (m, PC<sub>H</sub>).

29Si NMR (d<sub>8</sub>-toluene, 99 MHz, 213 K): δ 22.21.

31P{1H} NMR (d<sub>8</sub>-toluene, 202 MHz, 213 K): δ 79.96 (t, <sup>2</sup>J<sub>P,P</sub> 30.9 Hz, 1P), 79.18 (s, 1P), 74.69 (d, <sup>2</sup>J<sub>P,P</sub> 40.8 Hz, 1P), 65.63 (s, 1P).

[(dmpe)<sub>2</sub>MnH{=SiH<sup>2</sup>Bu(Pr<sup>NHC</sup>)}) (22b). 1,3-diisopropylimidazolin-2-ylidene (Pr<sup>NHC</sup>) (70 mg, 0.460 mmol) was added to a solution of 104.1 mg (0.196 mmol) [(dmpe)<sub>2</sub>MnH(SiH<sup>2</sup>Bu)<sub>2</sub>] (20Bu) in 10 mL of benzene. The reaction mixture was placed in a 50 mL storage flask, sealed, and stirred for 1 hour at room temperature. Following this, half of the solvent was removed in vacuo, and the reaction mixture was stirred for 30 minutes at room temperature before the remainder of the solvent was removed in vacuo. This process was repeated (∙2): 10 more mL of benzene was added, the solution stirred for 30 minutes, half the solvent was removed in vacuo, the solution was stirred again for 30 minutes, and the remainder of the solvent was removed in vacuo leaving a red oil. Recrystallization from hexanes at –30 °C yielded 33.9 mg of 22b as a red powder, and the mother liquor was concentrated and allowed to stand at –30 °C yielding an additional 14.8 mg, for a combined yield of 48.7 mg (0.082 mmol, 42%). X-ray quality crystals
were obtained from hexanes at −30 °C. Elevated temperature NMR analysis (signals are the average of isomer chemical shifts): $^1$H NMR (d$_8$-toluene, 500 MHz, 333 K): $\delta$ 6.34 (s, 2H, $HC=CH$), 6.29 (br. s, 2H, $CH(CH_3)_2$), 5.18 (br. s, 1H, Si$H$), 2.0-0.9 (various br. signals, 50H, PCH$_2$, PCH$_3$, CH(CH$_3$)$_2$, and SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.90 (t, 3H, $^3J_{H,H}$ 7.1 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), −12.65 (br. s, 1H, Mn$H$). Room temperature NMR analysis (signals are in the process of decaoesing to two sets for the two observed isomers). Selected NMR signals are as follows; Dominant isomer: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 5.11 (br. s with $^{29}$Si sat., 1H, $^1J_{HSi}$ 112.6 Hz, Si$H$), 0.85 (br. s, 3H, PCH$_3$), −12.43 (m, 1H, Mn$H$). $^{13}$C NMR (d$_8$-toluene, 151 MHz, 298 K): $\delta$ 25.42 (m, PCH$_3$). $^{29}$Si$^1$H NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ 28.71. Minor isomer: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 5.43 (br. s with $^{29}$Si sat., 1H, $^1J_{HSi}$ 116.0 Hz, Si$H$), 0.56 (br. s, 3H, PCH$_3$), −12.62 (m, 1H, Mn$H$). $^{13}$C$^1$H NMR (d$_8$-toluene, 151 MHz, 298 K): $\delta$ 28.50 (m, PCH$_3$). $^{29}$Si$^1$H NMR (C$_6$D$_6$, 119 MHz, 298 K): $\delta$ 28.71. Indeterminate isomer or average signals not decaoesed yet: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 6.34 (br. s, 2H, $CH(CH_3)_2$), 6.22 (s, 2H, $HC=CH$), 2.20-0.98 (various br. signals, 47H, PCH$_2$, PCH$_3$, CH(CH$_3$)$_2$, and SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.95 (t, 3H, $^3J_{H,H}$ 7.1 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$). $^{13}$C$^1$H NMR (d$_8$-toluene, 151 MHz, 298 K): $\delta$ 116.66 (s, $HC=CH$), 49.55 (s, $CH(CH_3)_2$), 14.43 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$). $^{31}$P$^1$H NMR (C$_6$D$_6$, 243 MHz, 298 K): $\delta$ 80.49, 78.95, 78.43, 77.17, 76.72, 75.01, 65.08, 63.97. Low temperature NMR analysis (signals for two isomers could be observed in a 1.2 : 1 ratio). Dominant isomer: $^1$H NMR (d$_8$-toluene, 500 MHz, 197 K): $\delta$ 6.87 (m, 1H, CH($CH_3$)$_2$), 5.56 (m, 1H, CH($CH_3$)$_2$), 5.08 (br. s, 1H, $^3J_{H,H}$ 4.9 Hz, $^1J_{HSi}$ 119.5 Hz, Si$H$), 1.72 (d, 3H, $^2J_{H,P}$ 3.4 Hz, PCH$_3$), 1.68 (d, 3H, $^2J_{H,P}$ 4.2 Hz, PCH$_3$), 1.45 (br. s, 3H, PCH$_3$), 1.42 (br. s, 6H, PCH$_3$), 1.30 (br. s, 3H, PCH$_3$), 1.22 (d, 3H, $^3J_{H,H}$ 5.0 Hz, CH($CH_3$)$_2$), 1.03 (d, 3H, $^3J_{H,H}$ 5.3 Hz, CH($CH_3$)$_2$), 0.96 (t, 3H, $^3J_{H,H}$ 7.6 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.93 (m, 3H, CH($CH_3$)$_2$), 0.85 (d, 3H, $^3J_{H,H}$ 4.3 Hz, CH($CH_3$)$_2$), 0.78 (br. s, 3H, PCH$_3$), −12.40 (m, 1H, Mn$H$). $^{13}$C$^1$H NMR (d$_8$-toluene, 126 MHz, 197 K): $\delta$ 49.73 (s, CH($CH_3$)$_2$), 48.63 (s, CH($CH_3$)$_2$), 33.98 (m, PCH$_3$), 32.41 (m, PCH$_3$), 31.89 (s, PCH$_3$), 29.97 (m, PCH$_3$), 28.26 (s, PCH$_3$), 26.84 (br. s, PCH$_3$), 26.39 (m, PCH$_3$), 25.37 (m, PCH$_3$), 23.06 (s, CH($CH_3$)$_2$), 22.11 (s, CH($CH_3$)$_2$), 21.84 (s,
CH(CH₃)₂, 14.74 (s, SiCH₂CH₂CH₂CH₃). \(^{29}\)Si NMR (\(d₈\)-toluene, 99 MHz, 197 K): \(\delta\) 29.56. \(^{31}\)P\(^{1}\)H NMR (\(d₈\)-toluene, 202 MHz, 197 K): \(\delta\) 79.74 (m, 1P), 78.20 (m, 2P), 65.62 (s, 1P). Minor isomer: \(^1\)H NMR (\(d₈\)-toluene, 500 MHz, 197 K): \(\delta\) 7.17 (m, 1H, CH(CH₃)₂), 5.63 (m, 1H, CH(CH₃)₂), 5.40 (br. s, 1H, \(^3\)J\(_{H,H}\) 3.4 Hz, \(^1\)J\(_{H,Si}\) 124.8 Hz, SiH), 1.84 (br. s, 3H, PC₃H), 1.77 (br. s, 3H, PCH₃), 1.51 (br. s, 6H, PCH₃), 1.49 (br. s, 3H, PCH₃), 1.21 (d, 3H, \(^3\)J\(_{H,H}\) 5.0 Hz, CH(CH₃)₂), 0.93 (m, 3H, CH(CH₃)₂), 0.85 (d, 3H, \(^3\)J\(_{H,H}\) 4.3 Hz, CH(C₃H₃)₂), 0.50 (br. s, 3H, PC₃H), –12.59 (m, 1H, MnH). \(^{13}\)C\(^{1}\)H NMR (\(d₈\)-toluene, 126 MHz, 197 K): \(\delta\) 49.73 (s, CH(CH₃)₂), 48.85 (s, CH(CH₃)₂), 28.83 (m, PCH₃), 28.18 (m, PCH₃), 27.01 (m, PCH₃), 26.84 (br. s, PCH₃), 25.95 (m, PCH₃), 25.37 (m, PCH₃), 23.63 (s, CH(CH₃)₂), 22.26 (s, CH(CH₃)₂), 21.73 (s, CH(CH₃)₂), 20.49 (s, CH(CH₃)₂), 171.74 (s, NCN), 170.98 (s, NCN), 116.87 (s, H*=CH), 116.82 (s, H*=CH), 116.26 (s, H*=CH), 116.17 (s, H*=CH), 37.42 (s, one of SiCH₂CH₂CH₂CH₃), 28.51 (s, one of SiCH₂CH₂CH₂CH₃), 23.52 (s, CH(CH₃)₂), 23.47 (s, CH(CH₃)₂). Anal. Found (calcd.): C, 50.83 (50.49); H, 10.22 (10.00); N, 4.72 (4.71).

\(\text{[(dmpe)}_2\text{MnH\{=SiHPh}^{\text{MeNHC}}\}]\) (22c) 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene \(^{\text{MeNHC}}\) (37.2 mg, 0.300 mmol) was added to a solution of 101.0 mg (0.177 mmol) of \(\text{[(dmpe)}_2\text{MnH(SiH₂Ph)}_2\] (20\(^\text{Ph}\)) in 10 mL of benzene. The reaction mixture immediately turned orange and was stirred overnight at room temperature. Following this, the solvent was removed \textit{in vacuo} and the resulting solid was dissolved again in 10 mL of benzene and stirred again overnight at room temperature. The solvent was again removed \textit{in vacuo}, following which the resulting solid was washed with hexanes, then recrystallized from a concentrated solution of toluene layered with pentane.
at –30 °C, yielding 33.3 mg of 22c as a reddish-brown powder. The mother liquor was then concentrated and layered again at –30 °C in pentane, yielding an additional 14.6 mg for a total yield of 47.9 mg (0.082 mmol, 46%). X-ray quality crystals (red blocks) were obtained from a concentrated solution in toluene layered with pentane at –30 °C. Elevated temperature NMR analysis (one set of signals are the average of chemical shifts for the two cis isomers, and another are from the trans isomer, with a 15 : 1 ratio): 
cis-22c; \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 339 K): δ 7.98 (br. s, 2H, o), 7.17 (t, 2H, \(^3\)J\(_{\text{H,H}}\) 7.3 Hz, m), 7.07 (t, 1H, \(^3\)J\(_{\text{H,H}}\) 7.7 Hz, p), 6.06 (s with \(^{29}\)Si sat., 1H, \(^1\)J\(_{\text{H,SI}}\) 122.2 Hz, Si\(\text{H}\)), 3.45 (br. s, 6H, NCH\(_3\)), 1.31 (s, 6H, NCH\(_3\)), –12.60 (p, 1H, \(^2\)J\(_{\text{H,P}}\) 31.5 Hz, Mn\(\text{H}\)). All remaining \(^1\)H NMR signals could not be identified and range from 0.9 to 1.9 ppm. \(^{31}\)P\({\(^1\)H}\) NMR (\(d_8\)-toluene, 202 MHz, 333 K): δ 76.67 (br. s, 2P), 72.56 (br. s, 1P), 65.76 (br. s, 1P). 
trans-22c; \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 339 K): δ 7.81 (d, 2H, \(^3\)J\(_{\text{H,H}}\) 7.0 Hz, o), 7.13 (m, 2H, m), 7.03 (m, 1H, p), 5.84 (br. s, 1H, Si\(\text{H}\)), 3.23 (br. s, 6H, NCH\(_3\)), –14.92 (app. t, 1H, \(^2\)J\(_{\text{H,P}}\) 46.9 Hz, Mn\(\text{H}\)). All remaining \(^1\)H NMR signals could not be identified and range from 0.9 to 1.9 ppm. 

\(^{31}\)P\({\(^1\)H}\) NMR (\(d_8\)-toluene, 202 MHz, 333 K): δ 79.89 (s, 2P), 79.43 (s, 2P).

Room temperature NMR analysis (signals due to the cis isomers are in the process of decoalescing, and one set of sharp signals is observed due to the trans isomer; a 14 : 1 ratio is observed at room temperature between a sum of the two cis isomers and the trans isomer). Selected NMR signals are as follows; cis-22c (major isomer); \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 298 K): δ 8.24 (br. s, 2H, o), 7.23 (br. s, 2H, m), 7.12 (br. s, 1H, p), 6.08 (s with \(^{29}\)Si sat., 1H, \(^1\)J\(_{\text{H,SI}}\) 121.3 Hz, Si\(\text{H}\)), 3.24 (br. s, 6H, NCH\(_3\)), 1.22 (s, 6H, NCCH\(_3\)), 0.56 (br. s, 3H, PC\(_3\)), –12.56 (m, 1H, Mn\(\text{H}\)). All remaining \(^1\)H NMR signals could not be identified and range from 0.8 to 1.9 ppm. \(^{31}\)P\({\(^1\)H}\) NMR (\(d_8\)-toluene, 243 MHz, 298 K): δ 78.38 (br. s, 1P), 77.01 (br. s, 1P), 70.43 (br. s, 1P), 64.52 (br. s, 1P). cis-22c (minor isomer), \(^1\)H NMR (\(d_8\)-toluene, 500 MHz, 298 K): 7.77 (br. s, 2H, o), 6.08 (s with \(^{29}\)Si sat., 1H, \(^1\)J\(_{\text{H,SI}}\) 121.3 Hz, Si\(\text{H}\)), 3.70 (br. s, 6H, NCH\(_3\)), 1.22 (s, 6H, NCCH\(_3\)), –12.56 (m, 1H, Mn\(\text{H}\)). All remaining \(^1\)H NMR signals could not be identified and range from 0.8 to 1.9 ppm. \(^{31}\)P\({\(^1\)H}\) NMR (\(d_8\)-toluene, 243 MHz, 298 K): δ 78.38 (br. s, 1P), 77.01 (br. s, 1P), 72.58 (br. s, 1P), 64.52 (br. s, 1P). cis-22c (indeterminate or
both isomers): $^{13}$C$[^1]$H NMR ($d_8$-toluene, 151 MHz, 298 K): $\delta$ 126.83 (s, m), 126.01 (s, $p$), 124.28 (NCCCH$_3$), 33.96 (s, NCCCH$_3$), 7.87 (s, NCCH$_3$). $^{29}$Si$[^1]$H NMR ($d_8$-toluene, 119 MHz, 298 K): $\delta$ 24.29. $^{31}$P$[^1]$H NMR ($d_8$-toluene, 243 MHz, 298 K): $\delta$ 78.38 (br. s, 1P, major and minor isomers), 77.01 (br. s, 1P, major and minor isomers), 72.58 (br. s, 1P, minor isomer), 70.43 (br. s, 1P, major isomer), 64.52 (br. s, 1P, major and minor isomers), 72.58 (br. s, 1P, major and minor isomers), 70.43 (br. s, 1P, major isomer), 64.52 (br. s, 1P, major and minor isomers). trans-22c; $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 7.85 (t, 2H, $^3$J$\sub{H,H}$ 7.1 Hz, o), 7.17 (t, 2H, $^3$J$\sub{H,H}$ 7.5 Hz, m), 5.83 (app. t with $^{29}$Si sat., 1H, $^3$J$\sub{H,\text{Si}}$ 126.6 Hz, SiH), 3.18 (s, 6H, NCH$_3$), 1.71 (d, 6H, $^2$J$\sub{H,P}$ 4.4 Hz, PCH$_3$), 1.56 (d, 6H, $^2$J$\sub{H,P}$ 5.3 Hz, PCH$_3$), 1.47 (d, 6H, $^2$J$\sub{H,P}$ 5.0 Hz, PCH$_3$), 1.24 (d, 6H, $^2$J$\sub{H,P}$ 4.7 Hz, PCH$_3$), –14.88 (p, 1H, $^2$J$\sub{H,P}$ 49.3 Hz, MnH). All remaining $^1$H NMR signals could not be identified and range from 0.8 to 1.9 ppm. $^{13}$C$[^1]$H NMR ($d_8$-toluene, 151 MHz, 298 K): $\delta$ 138.32 (s, o), 126.60 (s, m), 38.34 (m, PCH$_3$), 32.89 (m, PCH$_3$), 24.43 (m, PCH$_3$), 23.52 (m, PCH$_3$). $^{31}$P$[^1]$H NMR ($d_8$-toluene, 243 MHz, 298 K): $\delta$ 79.84 (br. s, 2P), 78.71 (m, 2P). Low temperature NMR analysis (signals for the dominant cis, minor cis, and trans isomers could be observed in a 17 : 3 : 1 ratio). Selected NMR signals are as follows; cis-22c (major isomer); $^1$H NMR ($d_8$-toluene, 500 MHz, 197 K): $\delta$ 8.60 (s, 2H, o), 7.44 (t, 2H, $^3$J$\sub{H,H}$ 6.5 Hz, m), 7.27 (t, 1H, $^3$J$\sub{H,H}$ 7.9 Hz, p), 6.19 (s with $^{29}$Si sat., 1H, $^1$J$\sub{H,\text{Si}}$ 117.5 Hz, SiH), 3.25 (br. s, 3H, NCH$_3$), 2.80 (br. s, 3H, NCH$_3$), 2.08 (m, 3H, PCH$_3$), 1.90 (s, 3H, PCH$_3$), 1.80 (s, 3H, PCH$_3$), 1.47 (s, 3H, PCH$_3$), 1.39 (s, 3H, PCH$_3$), 1.23 (s, 3H, PCH$_3$), 1.19 (s, 3H, PCH$_3$), 0.9 (br. s, 6H, NCCCH$_3$), 0.61 (s, 3H, PCH$_3$), –12.47 (m, 1H, MnH). $^{13}$C$[^1]$H NMR ($d_8$-toluene, 126 MHz, 197 K): $\delta$ 171.12 (s, NCCN), 153.17 (s, i), 138.74 (s, o), 126.69 (s, m), 126.24 (s, p), 34.72 (m, NCCCH$_3$), 28.30 (m, PMCH$_3$), 26.75 (m, PCH$_3$), 26.39 (m, PCH$_3$), 24.90 (m, PCH$_3$), 23.35 (m, PCH$_3$), 7.70 (m, NCCCH$_3$), 7.47 (m, NCCCH$_3$). $^{29}$Si NMR ($d_8$-toluene, 99 MHz, 197 K): 24.72. $^{31}$P$[^1]$H NMR ($d_8$-toluene, 202 MHz, 197 K): $\delta$ 79.51 (br. s, 1P), 77.29 (br. s, 1P), 70.40 (m, 1P), 66.00 (br. s, 1P). cis-22c (minor isomer); $^1$H NMR ($d_8$-toluene, 500 MHz, 197 K): $\delta$ 7.88 (d, 2H, $^3$J$\sub{H,H}$ 6.8 Hz, o), 7.29 (t, 2H, $^3$J$\sub{H,H}$ 7.8 Hz, m), 7.13 (t, 1H, $^3$J$\sub{H,H}$ 6.9 Hz, p), 6.16 (s with $^{29}$Si sat., 1H, $^1$J$\sub{H,\text{Si}}$ 122.5 Hz, SiH), 4.41 (br. s, 3H, NCH$_3$), 3.09 (br. s, 3H, NCH$_3$), 1.93 (m, 3H, PCH$_3$), 1.83 (m, 3H, PCH$_3$), 1.53 (s, 3H, PCH$_3$), 1.52 (s, 3H, PCH$_3$), 1.47 (s, 3H, PCH$_3$). 337
PC\(\text{H}_3\), 1.40 (m, 3H, PCH\(\text{H}_3\)), 1.27 (s, 3H, PCH\(\text{H}_3\)), 1.13 (s, 3H, PCH\(\text{H}_3\)), −12.20 (m, 1H, MnH). \(^{13}\text{C}\{^1\text{H}\}\) NMR (\(\text{d}_8\)-toluene, 126 MHz, 197 K): \(\delta\) 135.67 (s, NCH\(\text{H}_3\)), 34.90 (m, NCH\(\text{H}_3\)), 28.30 (m, PCH\(\text{H}_3\)), 28.15 (m, PCH\(\text{H}_3\)), 25.87 (m, PCH\(\text{H}_3\)), 23.17 (m, PCH\(\text{H}_3\)). \(^{29}\text{Si}\) NMR (\(\text{d}_8\)-toluene, 99 MHz, 197 K): 23.17. \(^{31}\text{P}\{^1\text{H}\}\) NMR (\(\text{d}_8\)-toluene, 202 MHz, 197 K): \(\delta\) 80.04 (br. s, 1P), 78.15 (br. s, 1P), 73.59 (br. s, 1P), 66.15 (br. s, 1P).

trans-22c; \(^1\text{H}\) NMR (\(\text{d}_8\)-toluene, 500 MHz, 197 K): \(\delta\) 8.00 (d, 2H, \(^3J_{\text{H},\text{H}}\) 6.8 Hz, NCH\(\text{H}_3\)), 5.96 (m with \(^{29}\text{Si}\) sat., 1H, \(^1J_{\text{H},\text{Si}}\) 124.2 Hz, SiH), 3.12 (s, 3H, NCH\(\text{H}_3\)), 2.85 (s, 3H, NCH\(\text{H}_3\)), 1.75 (s, 6H, PCH\(\text{H}_3\)), 1.60 (s, 6H, PCH\(\text{H}_3\)), 1.27 (s, 3H, NCH\(\text{H}_3\)), 0.98 (s, 3H, NCH\(\text{H}_3\)), −14.57 (p, 1H, \(^2J_{\text{H},\text{P}}\) 48.9 Hz, MnH). \(^{13}\text{C}\{^1\text{H}\}\) NMR (\(\text{d}_8\)-toluene, 126 MHz, 197 K): \(\delta\) 138.17 (o), 123.55 (NCH\(\text{H}_3\)), 33.59 (m, NCH\(\text{H}_3\)), 32.76 (m, NCH\(\text{H}_3\)), 32.03 (PCH\(\text{H}_3\)). \(^{29}\text{Si}\) NMR (\(\text{d}_8\)-toluene, 99 MHz, 197 K): 16.63. \(^{31}\text{P}\{^1\text{H}\}\) NMR (\(\text{d}_8\)-toluene, 202 MHz, 197 K): \(\delta\) 81.54 (br. s, 2P), 79.67 (s, 2P).

Anal. Found (calcd.): C, 51.33 (51.19); H, 8.67 (8.76); N, 4.64 (4.78).

[(dmpe)\(_2\)MnH\{=SiH\(^n\)Bu(M\(^{\text{MeNHC}}\))\}] (22d). 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene (M\(^{\text{MeNHC}}\)) (50.6 mg, 0.407 mmol) was added to a solution containing 110.8 mg (0.209 mmol) of [(dmpe)\(_2\)MnH(SiH\(^n\)Bu\(_2\))] (20\(^\text{Bu}\)) in 10 mL of benzene. The reaction mixture immediately turned orange and was stirred overnight at room temperature. Following this, the solvent was removed in vacuo and the resulting red oil was dissolved again in 10 mL of benzene and stirred again overnight at room temperature. The solvent was again removed in vacuo, following which the resulting red oil was dissolved in hexanes. After a couple of minutes, a brown solid precipitated which contains a mixture of [(dmpe)\(_2\)MnH\{=SiH\(^n\)Bu(M\(^{\text{MeNHC}}\))\}] (22d) and M\(^{\text{MeNHC}}\), which could be removed by centrifugation. The mother liquor was allowed to stand at −30 °C for a month, yielding 20.9 mg (0.037 mmol, 18%) of pure [(dmpe)\(_2\)MnH\{=SiH\(^n\)Bu(M\(^{\text{MeNHC}}\))\}] (22d) as a very dark red solid. Elevated temperature NMR analysis (one set of signals are the average of chemical shifts for the two cis isomers, and another are from the trans isomer, with a 2 : 1 ratio): Selected NMR signals are as follows; cis-22d; \(^1\text{H}\) NMR (\(\text{d}_8\)-toluene, 500 MHz, 333 K): \(\delta\) 5.17 (s with \(^{29}\text{Si}\) sat., 1H, \(^1J_{\text{H},\text{Si}}\) 124.4 Hz, SiH), 3.71 (br. s, 6H, NCH\(\text{H}_3\)), 0.96 (m, 2H, SiCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 0.91 (t, 3H, \(^3J_{\text{H},\text{H}}\) 7.3 Hz, SiCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), −12.62 (p,
All remaining $^1$H NMR signals could not be identified and range from 0.6 to 1.8 ppm. $^{29}$Si NMR ($d_8$-toluene, 99 MHz, 333 K): $\delta$ 28.97. $^{31}$P{$^1$H} NMR ($d_8$-toluene, 202 MHz, 333 K): $\delta$ 75.90 (br. s). **trans-22d**: $^1$H NMR ($d_8$-toluene, 500 MHz, 333 K): $\delta$ 4.85 (m with $^{29}$Si sat., 1H, $^1J_{\text{H, Si}}$ 122.2 Hz, $^3J_{\text{H,H}}$ 3.9 Hz, SiH), 3.26 (br. s, 6H, NCH$_3$), 0.89 (t, 3H, $^3J_{\text{H,H}}$ 7.2 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.80 (m, 1H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.70 (m, 1H, SiCH$_2$CH$_2$CH$_2$CH$_3$), −15.07 (p, 1H, $^2J_{\text{H,P}}$ 48.4 Hz, MnH). All remaining $^1$H NMR signals could not be identified and range from 0.6 to 1.8 ppm. $^{29}$Si NMR ($d_8$-toluene, 99 MHz, 333 K): $\delta$ 22.75. $^{31}$P{$^1$H} NMR ($d_8$-toluene, 202 MHz, 333 K): $\delta$ 79.87 (br. s, 2P), 79.21 (br. s, 2P). Room temperature NMR analysis (signals due to the cis isomers are in the process of decalescing, and one set of sharp signals is observed due to the trans isomer; a 2 : 1 ratio is observed at room temperature between the sum of the two cis isomers and the trans isomer). Selected NMR signals are as follows; **cis-22d**: $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 5.18 (br. s, 1H, SiH), 3.70 (s, 6H, NCH$_3$), 1.29 (s, 6H, NCCN$_3$), 0.95 (t, 3H, $^3J_{\text{H,H}}$ 7.3 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), −12.54 (p, 1H, $^2J_{\text{H,P}}$ 33.3 Hz, MnH). $^{13}$C{$^1$H} NMR ($d_8$-toluene, 126 MHz, 298 K): $\delta$ 172.49 (s, NCCN), 124.34 (s, NCCN), 36.06 (s, one of SiCH$_2$CH$_2$CH$_2$CH$_3$), 34.22 (s, NCCN), 14.55 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 27.74 (s, one of SiCH$_2$CH$_2$CH$_2$CH$_3$), 26.04 (s, one of SiCH$_2$CH$_2$CH$_2$CH$_3$), 7.96 (s, NCCN). $^{29}$Si{$^1$H} NMR ($d_8$-toluene, 99 MHz, 298 K): $\delta$ 28.66. $^{31}$P{$^1$H} NMR ($d_8$-toluene, 202 MHz, 298 K): $\delta$ 78 (br. m, 1P), 74.80 (br. s, 1P), 67.05 (br. s, 1P), 65.49 (br. s, 1P). **trans-22d**: $^1$H NMR ($d_8$-toluene, 500 MHz, 298 K): $\delta$ 4.87 (s with $^{29}$Si sat., 1H, $^1J_{\text{H, Si}}$ 121.7 Hz, $^3J_{\text{H,H}}$ 6.5 Hz, SiH), 3.23 (s, 3H, NCH$_3$), 3.20 (s, 3H, NCH$_3$), 1.58 (d, 6H, $^2J_{\text{H,P}}$ 4.2 Hz, PCH$_3$), 1.54 (d, 6H, $^2J_{\text{H,P}}$ 4.9 Hz, PCH$_3$), 1.49 (d, 6H, $^2J_{\text{H,P}}$ 5.1 Hz, PCH$_3$), 1.46 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 1.40 (d, 6H, $^2J_{\text{H,P}}$ 4.3 Hz, PCH$_3$), 1.35 (s, 3H, NCCN), 1.26 (s, 3H, NCCN), 0.93 (m, 2H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.93 (t, 3H, $^3J_{\text{H,H}}$ 7.2 Hz, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.83 (m, 1H, SiCH$_2$CH$_2$CH$_2$CH$_3$), 0.72 (m, 1H, SiCH$_2$CH$_2$CH$_2$CH$_3$), −14.98 (p, 1H, $^2J_{\text{H,P}}$ 48.1 Hz, MnH). $^{13}$C{$^1$H} NMR ($d_8$-toluene, 126 MHz, 298 K): $\delta$ 175.86 (s, NCCN), 124.46 (s, NCCN), 123.66 (s, NCCN), 36.52 (s, SiCH$_2$CH$_2$CH$_2$CH$_3$), 35.17 (m, PCH$_3$), 33.71 (s, NCCN), 33.63 (s, NCCN), 33.54 (m, PCH$_3$), 32.84 (m, PCH$_3$), 27.71 (s,
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\[ \text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3, 26.40 \text{ (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 24.23 \text{ (s, PCH}_3), 24.13 \text{ (s, PCH}_3), 14.55 \text{ (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 8.10 \text{ (s, NCCCH}_3), 7.65 \text{ (s, NCCCH}_3). \]

\[ ^{29}\text{Si}^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 99 MHz, 298 K): } \delta \text{ 22.44.} \]

\[ ^{31}\text{P}^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 202 MHz, 298 K): } \delta \text{ 80.63 (m, 2P), 79.84 (m, 2P). Low temperature NMR analysis (signals for the two cis isomers and the trans isomer could be observed in a 1 : 1 : 1 ratio). Selected NMR signals are as follows; cis-22d (includes both cis isomers); }^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 500 MHz, 207 K): } \delta \text{ 5.39 (d with }^{29}\text{Si} \text{ sat., 1H, }^{3}\text{J}_{\text{H,P}} \text{ 13.3 Hz, }^{1}\text{J}_{\text{H,Si}} \text{ 127.0 Hz, SiH}) \text{ 5.14 (br. s with }^{29}\text{Si} \text{ sat., 1H, }^{3}\text{J}_{\text{H,H}} \text{ 6.5 Hz, }^{1}\text{J}_{\text{H,Si}} \text{ 122 Hz, SiH}). \]

\[ ^{13}\text{C}^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 126 MHz, 207 K): } \delta \text{ 171.27 (s, NCC), 124.58 (NCC), 123.39 (s, NCC), 34.41 (s, NCCCH}_3), 33.56 (s, NCCCH}_3), 29.31 (s, PCH}_3), 28.41 (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 28.41 (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 28.41 (s, PCH}_3), 28.18 (s, PCH}_3), 28.07 (s, PCH}_3), 27.88 (s, PCH}_3), 27.46 (m, PCH}_3), 26.78 (m, PCH}_3), 25.89 (s, PCH}_3), 24.15 (s, PCH}_3), 21.02 (s, PCH}_3), 14.96 (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 14.93 (s, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 7.91 (s, NCCCH}_3), 7.48 (s, NCCCH}_3). \]

\[ ^{29}\text{Si} \text{ NMR (}d_8\text{-toluene, 99 MHz, 207 K): } \delta \text{ 79.5 (1P), 78.67 (br. s, 1P), 77.28 (br. s, 1P), 76.40 (br. s, 1P), 74.45 (br. s, 1P), 73.12 (d, }^{2}\text{J}_{\text{P,P}} \text{ 33.2 Hz, 1P), 66.97 (br. s, 1P), 65.04 (br. s, 1P). trans-22d; }^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 500 MHz, 207 K): } \delta \text{ 4.99 (br. s with }^{29}\text{Si} \text{ sat., 1H, }^{3}\text{J}_{\text{H,H}} \text{ 6.5 Hz, }^{1}\text{J}_{\text{H,Si}} \text{ 116 Hz, SiH}) \text{ 3.06 (s, 3H, NCCCH}_3), 3.01 (s, 3H, NCCCH}_3), 1.76 (s, 6H, PCH}_3), 1.72 (s, 6H, PCH}_3), 1.63 (s, 6H, PCH}_3), 1.47 (s, 6H, PCH}_3), 1.15 (s, 3H, NCCCH}_3), 1.03 (t, 3H, }^{3}\text{J}_{\text{H,H}} \text{ 7.0 Hz, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 0.98 (m, 2H, SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 0.96 (s, 3H, NCCCH}_3), \]

\[ -14.67 (p, 1H, }^{2}\text{J}_{\text{H,P}} \text{ 46.6 Hz, MnH}). \]

\[ ^{13}\text{C}^{1}\text{H} \text{ NMR (}d_8\text{-toluene, 126 MHz, 207 K): } \delta \text{ 174.12 (s, NCC), 124.21 (s, NCC), 123.18 (s, NCC), 33.28 (s, PCH}_3), 33.15 (s, NCCCH}_3), \]
32.19 (s, PCH₃), 28.41 (s, SiCH₂₂H₂CH₂H₂), 24.08 (s, PCH₃), 23.29 (s, PCH₃), 15.03 (s, SiCH₂₂H₂CH₂H₂), 7.88 (s, NCCCH₃), 7.48 (s, NCCCH₃). ²⁹Si NMR (d₈-toluene, 99 MHz, 207 K): δ 22.71. ³¹P{¹H} NMR (d₈-toluene, 202 MHz, 207 K): δ 80.35 (m, 2P), 79.40 (m, 2P). Indeterminate: ¹³C{¹H} NMR (d₈-toluene, 126 MHz, 207 K): δ 36.97 (s), 36.83 (s), 36.36 (s), 35.07 (s), 32.10 (s), 27.14 (s), 26.52 (s). Anal. Found (calcd.): C, 48.72 (48.75); H, 9.65 (9.78); N, 4.80 (4.94).

**Reaction of [(dmpe)₂MnH{=SiHₙBu(PrNHC)}] (22b) with ethylene.** Approx. 15 mg of [(dmpe)₂MnH{=SiHₙBu(PrNHC)}] (22b) was dissolved in approx. 0.6 mL of C₆D₆, and the solution was freeze-pump-thawed (×3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to –95 °C, and sealed at this low temperature. The solution was then monitored over time at room temperature by ¹H NMR spectroscopy in situ; after 24 h, complete consumption of 22b was observed and the reaction mixture contained approx. 1% 10, 72% 19Bu,H, 23% 19Bu,Et, and 4% of an unidentified MnH-containing species.

11.6 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 6

Various data is available in the ESI to reference 507, including selected NMR spectra of 18R₂. Various data is available in the ESI to reference 510, including selected NMR spectra (for 18R), selected IR spectra, symbolic pulse sequences and parameters used for new COSY-type NMR experiments, tables of calculated and crystallographically determined bond lengths and angles, bond orders, Hirshfeld charges, and total bonding energies for calculated structures and PH₃ analogues. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 507 (X→Y) in the following manner; 10→1, 16Ph₂→2b, 16Et₂→2a, 18Ph₂→3b, 18Et₂→3a. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 510 (X→Y) in the following manner; 10→1, 18Ph₂→3a, 18Et₂→3b, 18Ph→4a, 18Bu→4b, 20Ph→2a, and
$^{20}\text{Bu} \rightarrow 2\text{b}$. CSD 1529216 and 1896287-1896288 contain the supplementary crystallographic data for $18^{\text{Ph}_{2}}$, $18^{\text{Ph}}$, and $18^{\text{Bu}}$.

Syntheses and selected characterization data for $18^{\text{Ph}_{2}}$ and $18^{\text{Et}_{2}}$ can be found in section 11.4.

$[\text{(dmpe)}_{2}\text{MnH}_{2}(\text{SiH}_{2}\text{Ph})] \ (18^{\text{Ph}})$. 209.5 mg (0.367 mmol) of $[\text{(dmpe)}_{2}\text{MnH}(\text{SiH}_{2}\text{Ph})_{2}] \ (20^{\text{Ph}})$ was dissolved in 10 mL of benzene. The reaction mixture was freeze/pump/thawed in a 50 mL storage flask three times, and then was placed under 1 atm of $\text{H}_{2}$ at $-95$ °C, sealed, and warmed to room temperature. After stirring at room temperature for 2 days, the solvent was removed in vacuo. The resulting yellow solid was recrystallized from a concentrated solution of hexanes at $-30$ °C giving a yellow powder which was dried in vacuo; 111.1 mg. Concentrating the mother liquor and leaving it at $-30$ °C yielded an additional 20.9 mg of $18^{\text{Ph}}$, for a total yield of 132.0 mg (0.284 mmol, 77 %). X-ray quality crystals were obtained from hexanes.

$\text{^{1}H NMR} \ (\text{d}_{8}-\text{toluene}, \text{600 MHz, 298 K}): \delta 8.00 \ (\text{br. s, 2H, o-ph}), 7.29 \ (t, 2H, \text{^{3}J}_{\text{H,H}} 7.4 \text{ Hz, m-ph}), 7.18 \ (t, 1H, \text{^{3}J}_{\text{H,H}} 7.1 \text{ Hz, p-ph}), 5.45 \ (\text{br. s, 2H, SiH}), 1.5–0.9 \ (\text{br. singlets, 32H, PC}_{\text{H}_{3}} \text{ and PC}_{\text{H}_{2}})$, $-12.54 \ (\text{br. s, 1H, MnH})$.

$\text{^{13}C\{^{1}H\} NMR} \ (\text{d}_{8}-\text{toluene, 151 MHz, 298 K}): \delta 135.83 \ (\text{s, o-ph}), 127.28 \ (\text{s, m-ph}), 126.82 \ (\text{s, p-ph}), 33.13 \ (\text{br. s})$.

$\text{^{31}P\{^{1}H\} NMR} \ (\text{d}_{8}-\text{toluene, 202 MHz, 298 K}): \delta 76.69 \ (\text{br. s})$. central-$18^{\text{Ph}}$: $\text{^{1}H NMR} \ (\text{d}_{8}-\text{toluene, 500 MHz, 186 K}): \delta 8.37 \ (\text{d, 2H, \text{^{3}J}_{\text{H,H}} 7.2 \text{ Hz, o-ph}}), 7.49 \ (t, 2H, \text{^{3}J}_{\text{H,H}} 7.2 \text{ Hz, m-ph}), 7.34 \ (t, 1H, \text{^{3}J}_{\text{H,H}} 7.0 \text{ Hz, p-ph}), 6.10 \ (\text{s with ^{29}Si sat., 1H, \text{^{1}J}_{\text{Si,}} 171.4 \text{ Hz, SiH}}), 6.02 \ (\text{t with ^{29}Si sat., 1H, \text{^{3}J}_{\text{H,P}} 9.5 \text{ Hz, \text{^{1}J}_{\text{Si,}} 175.6 \text{ Hz, SiH}}), 0.8-1.5 \ (\text{various m, 8H, PC}_{\text{H}_{2}})$, 1.39 (d, 6H, $^{2}J_{\text{H,P}} 2.9 \text{ Hz, PC}_{\text{H}_{3}}$), 1.30 (s, 6H, PC$_{3}$), 0.96 (s, 6H, PC$_{3}$), 0.74 (s, 6H, PC$_{3}$), $-12.83 \ (\text{m, 2H, MnH})$. $\text{^{13}C\{^{1}H\} NMR} \ (\text{d}_{8}-\text{toluene, 126 MHz, 207 K}): \delta 151.39 \ (\text{s, i-ph}), 135.59 \ (\text{s, o-ph}), 127.30 \ (\text{s, m-ph}), 127.04 \ (\text{s, p-ph}), 33.44 \ (\text{m, PC}_{\text{H}_{2}})$, 32.35 (m, PC$_{2}$), 30.13 (t, $J_{\text{C,P}} 15 \text{ Hz, PC}_{\text{H}_{2}}$), 22.56 (s, PC$_{3}$), 22.30 (d, $^{2}J_{\text{C,P}} 16 \text{ Hz, PC}_{\text{H}_{3}}$), 21.57 (m, PC$_{3}$). $^{29}\text{Si\{^{1}H\} NMR} \ (\text{d}_{8}-\text{toluene, 119 MHz, 226 K}): \delta -15.73 \ (\text{s})$. $^{31}\text{P\{^{1}H\} NMR} \ (\text{d}_{8}-\text{toluene, 202 MHz, 186 K}): \delta 73.98 \ (\text{br. s, 2P}), 72.38 \ (\text{br. s, 2P})$. $\text{transHSi}^{18^{\text{Ph}}}$: $\text{^{1}H NMR} \ (\text{d}_{8}-\text{toluene, 500 MHz, 186 K}): \delta 8.15 \ (\text{d, 2H, \text{^{3}J}_{\text{H,H}} 7.1 \text{ Hz, o-ph}}), 7.40 (t, 2H, $^{3}J_{\text{H,H}} 7.1 \text{ Hz,
[(dmpe)₂MnH₂(SiH₂₇Bu)] (18Bu). 108.9 mg (0.205 mmol) of [(dmpe)₂MnH(SiH₂₇Bu)]₂ (20Bu) was dissolved in 10 mL of benzene. The reaction mixture was freeze/pump/thawed in a 50 mL storage flask three times, and then was placed under 1 atm of H₂ at −95 °C, sealed, and warmed to room temperature. After stirring at room temperature for 3 days, the solvent was removed in vacuo. The resulting yellow solid was recrystallized from a concentrated solution of hexanes at −30 °C and dried in vacuo to afford a yellow powder. Yield = 41.6 mg (0.094 mmol, 46 %). X-ray quality crystals were obtained from a dilute solution in hexanes at −30 °C. ¹H NMR (d₈-toluene, 600 MHz, 298 K): δ 4.65 (br. s, 2H, SiH), 1.76 (p, 2H, ³J₃H, 7.6 Hz, SiH₂CH₂CH₂CH₂CH₃), 1.58 (s, 2H, ³J₃H, 7.4 Hz, SiH₂CH₂CH₂CH₂CH₃), 1.34 (br. s, 8H, PCH₃), 1.23 (br. s, 24H, PCH₃), 1.04 (t, 3H, ³J₃H, 7.3 Hz, SiH₂CH₂CH₂CH₂CH₃), 0.89 (br. s, 2H, SiH₂CH₂CH₂CH₂CH₃), −12.54 (br. s, 2H, MnH). ¹³C{¹H} NMR (d₈-toluene, 151 MHz, 298 K): δ 33.24 (br. s, PCH₃), 32.86 (s, SiH₂CH₂CH₂CH₂CH₃), 27.07 (s, SiH₂CH₂CH₂CH₂CH₃), 14.60 (s, SiH₂CH₂CH₂CH₂CH₃). ³¹P NMR (d₈-toluene, 243 MHz, 298 K): δ 76.51 (s). central-18Bu: ¹H NMR (d₈-toluene, 500 MHz, 207 K): δ 5.39 (s with ²⁹Si sat., 1H, ¹J₁₂H, 160.4 Hz, SiH), 5.24 (s with ²⁹Si sat., 1H, ¹J₁₂H, 168.4 Hz, SiH), 2.01 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), 1.77 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), 1.41 (s, 6H, PCH₃), 1.40 (m, 2H, PCH₂), 1.36 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), 1.26 (s, 6H, PCH₃), 1.21 (m, 2H, PCH₂), 1.18 (s, 6H, PCH₃), 1.18 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), 1.18 (t, 3H, ³J₃H, 7.4 Hz, SiH₂CH₂CH₂CH₂CH₃), 0.99 (m, 2H, PCH₂), 0.88 (m, 2H, PCH₂), 0.79 (s, 6H, PCH₃), −12.75 (m, 2H, MnH). ¹³C{¹H}
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NMR (d₈-toluene, 126 MHz, 207 K): δ 33.46 (m, PCH₂), 32.37 (m, PCH₂), 32.37 (s, SiH₂CH₂CH₂CH₂CH₃), 30.48 (m, PCH₃), 27.49 (s, SiH₂CH₂CH₂CH₂CH₃), 27.49 (s, SiH₂CH₂CH₂CH₂CH₃), 22.64 (s, PCH₃), 22.25 (m, PCH₃), 15.04 (s, SiH₂CH₂CH₂CH₂CH₃).

²⁹Si{¹H} NMR (d₈-toluene, 119 MHz, 207 K): δ –22.00.

³¹P{¹H} NMR (d₈-toluene, 243 MHz, 205 K): δ 74.06 (br. s, 2P), 72.05 (br. s, 2P).

transHSi⁻¹⁸Bu⁻¹:¹H NMR (d₈-toluene, 500 MHz, 207 K): δ 4.72 (s with ²⁹Si sat., 2H, ¹J₅,H 151.7 Hz, Si₅H), 1.92 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), 1.69 (m, 2H, ³J₅,H 7.3 Hz, SiH₂CH₂CH₂CH₂CH₃), 1.56 (br. s, 4H, PCH₂), 1.36 (s, 12H, PCH₃), 1.26 (br. s, 4H, PCH₂), 1.12 (s, 12H, PCH₃), 1.12 (t, 3H, ³J₅,H 7.3 Hz, SiH₂CH₂CH₂CH₂CH₃), 0.99 (m, 2H, SiH₂CH₂CH₂CH₂CH₃), –11.25 (p, 1H, ²J₅,P 51.5 Hz, Mn₅H), –13.28 (p, 1H, ²J₅,P 23.0 Hz, Mn₅HSi). ¹³C{¹H} NMR (d₈-toluene, 126 MHz, 207 K): δ 33.46 (s, SiH₂CH₂CH₂CH₂CH₃), 32.37 (m, PCH₂), 27.62 (s, SiH₂CH₂CH₂CH₂CH₃), 27.49 (s, PCH₃), 22.82 (s, SiH₂CH₂CH₂CH₂CH₃), 20.78 (s, PCH₃), 14.91 (s, SiH₂CH₂CH₂CH₂CH₃).

²⁹Si{¹H} NMR (d₈-toluene, 119 MHz, 207 K): δ –6.91. ³¹P{¹H} NMR (d₈-toluene, 243 MHz, 205 K): 77.48 (s).


Anal. Found (calcd.): C, 43.39 (43.24); H, 9.94 (10.20).

[(dmpe)₂MnD₂(SiH₂R)] (d₂⁻¹₈Ph: R = Ph, d₂⁻¹₈Bu: R = nBu). Roughly 10 mg of the manganese-containing precursor used to synthesize the fully protonated complexes {for ¹₈Ph [(dmpe)₂MnH(SiH₂Ph)₂] (20⁻¹₈Ph) and for ¹₈Bu [(dmpe)₂MnH(SiH₂nBu)₂] (20⁻¹₈Bu)} was dissolved in roughly 0.6 mL of C₆D₆. The reaction mixture was freeze/pump/thawed in a J-young NMR tube three times, and then was placed under 1 atm of D₂ at –95 °C, sealed, and warmed to room temperature and then allowed to sit at room temperature for the reaction times required to prepare the protio analogues. The deuterated complexes were isolated from free hydrosilane byproducts on the NMR scale by removing the solvent and hydrosilane in vacuo, and used without further purification. NMR spectra of d₂⁻¹₈Ph and d₂⁻¹₈Bu differ from the protonated analogues by the absence of peaks in the ¹H NMR spectra corresponding to the MnH environments.
11.7 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 7

Tables of calculated and crystallographically determined bond lengths and angles, tables of bond orders, Hirshfeld charges, and total bonding energies for calculated structures and selected NMR spectra for $^{25}\text{Ph,H}$, $^{25}\text{Bu,H}$, and $^{26}$ can be found in Appendix 1. Crystal structures in this chapter have not yet been submitted to the CSD.

$[(\text{dmpe})_2\text{Mn}{\kappa}^2\text{SiHPh(N}^i\text{PrCHN}^i\text{Pr})] \ (^{25}\text{Ph,H})$. An excess of diisopropylcarbodiimide {C(N$^i$Pr)$^2$} (67 mg, 0.531 mmol) was added to a solution containing 60.4 mg (0.106 mmol) of $[(\text{dmpe})_2\text{MnH(SiH}_2\text{Ph})_2] \ (^{20}\text{Ph})$ in 8 mL of benzene. The reaction mixture was stirred in a sealed flask at 65 °C for two days, leading to a bright red solution which turned a clear orange upon cooling to room temperature. The solvent was then removed in vacuo. The resulting orange solid was recrystallized from a concentrated solution of hexanes layered with hexamethyldisiloxane at –30 °C giving a yield of 55.8 mg (0.095 mmol, 90%). X-ray quality crystals were obtained from a saturated solution of $^{25}\text{Ph,H}$ in hexanes layered with hexamethyldisiloxane at –30 °C.

**Dominant isomer:** $^1\text{H NMR (C}_6\text{D}_6$, 600 MHz, 298 K): $\delta$ 8.09 (d, 2H, $^3J_{H,H}$ 6.8 Hz, o), 7.67 (s with shoulders, 1H, NC(H)N), 7.34 (t, 2H, $^3J_{H,H}$ 7.6 Hz, m), 7.24 (t, 1H, $^3J_{H,H}$ 7.3 Hz, p), 6.26 (d of d with $^{29}\text{Si}$ sat., 1H, $^3J_{H,P}$ 17.9 Hz, $^3J_{H,P}$ 8.0 Hz, $^1J_{H,Si}$ 136.5, SiH), 3.45 (septet, 1H, $^3J_{H,H}$ 6.8 Hz, CγH(CH$_3$)$_2$), 2.91 (septet, 1H, $^3J_{H,H}$ 6.6 Hz, CβH(CH$_3$)$_2$), 1.99 (m, 1H, PVC$_2$), 1.83–1.37 (m, 6H, PVC$_2$), 1.47 (d, 3H, $^4J_{H,P}$ 6.2 Hz, PCH$_3$), 1.45 (d, 3H, $^3J_{H,P}$ 5.5 Hz, PCH$_3$), 1.39 (d, 3H, $^3J_{H,P}$ 4.3 Hz, PCH$_3$), 1.33 (d, 3H, $^3J_{H,P}$ 3.1 Hz, PCH$_3$), 1.17 (m, 9H, PCH$_3$), 1.06 (d, 3H, $^3J_{H,H}$ 6.7 Hz, CH(CH$_3$)$_2$), 1.02 (d, 3H, $^3J_{H,H}$ 6.8 Hz, CH(CH$_3$)$_2$), 0.99 (d, 3H, $^3J_{H,H}$ 6.7 Hz, CH(CH$_3$)$_2$), 0.94 (d, 3H, $^3J_{H,H}$ 6.5 Hz, CH(CH$_3$)$_2$), 0.78 (m, 1H, PCH$_2$), 0.73 (d, 3H, $^3J_{H,P}$ 4.7 Hz, PCH$_3$). $^{13}\text{C}^1\text{H NMR (C}_6\text{D}_6$, 151 MHz, 298 K): }$ $\delta$ 159.93 (s, N(C(H)N)), 153.11 (s, ipso), 137.37 (s, o), 127.01 (s, m), 126.66 (s, p), 59.53 (d, $^4J_{C,P}$ 8.7 Hz, C$_2$H(CH$_3$)$_2$), 50.08 (s, C$_2$(CH$_3$)$_2$), 35.24 (m, PCH$_2$), 29.90 (d, $^1J_{C,P}$ 16.6 Hz, PCH$_3$), 29.11 (d of d, $^1J_{C,P}$ 26.5 Hz, $^3J_{C,P}$ 15.7 Hz, PCH$_2$), 26.96 (m, PCH$_3$), 26.12 (s, CH(CH$_3$)$_2$), 24.46 (s, CH(CH$_3$)$_2$), 24.37 (s, PCH$_3$), 24.34 (s,
CH(CH₃)₂, 24.26 (s, CH(CH₃)₂), 23.87 (s, PCH₃), 23.73 (d, ¹J_C,P 4.8 Hz, PCH₃), 20.51 (m, PCH₃), 13.40 (d, ¹J_C,P 11.8 Hz, PCH₃).

³²Si{¹H} NMR (C₆D₆, 119 MHz, 298 K): δ 81.11 (m).

³¹P{¹H} NMR (C₆D₆, 243 MHz, 298 K): δ 74.49 (s, 1P), 72.09 (s, 1P), 66.19 (s, 1P), 55.10 (s, 1P). Minor isomer: ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 8.22 (d, 2H, ³J_H,H 7.8 Hz, o), 7.70 (s, 1H, NC(H)N), 7.37 (t, 2H, ³J_H,H 7.4 Hz, m), 7.24 (t, 1H, ³J_H,H 7.2 Hz, p), 6.23 (d of d with ²⁹Si sat., 1H, ³J_H,P 27.6 Hz, ³J_H,P 9.5 Hz, ¹J_H,Si 140.1, SiH), 3.48 (septet, 1H, ³J_H,H 6.8 Hz, CH(CH₃)₂), 3.07 (septet, 1H, ³J_H,H 6.7 Hz, CH(CH₃)₂), 1.94–0.72 (many multiplets, 8H, PCH₂), 1.72 (d, 3H, ³J_H,P 6.0 Hz, PCH₃), 1.53 (d, 3H, ³J_H,P 4.9 Hz, PCH₃), 1.32 (3H, PCH₃), 1.28 (d, 3H, ³J_H,P 4.2 Hz, PCH₃), 1.24 (d, 3H, ³J_H,P 2.9 Hz, PCH₃), 1.24 (d, 3H, ³J_H,P 2.8 Hz, PCH₃), 1.08 (d, 3H, ³J_H,P 5.3 Hz, PCH₃), 1.04 (d, 3H, ³J_H,H 6.9 Hz, CH(CH₃)₂), 1.03 (d, 3H, ³J_H,H 6.9 Hz, CH(CH₃)₂), 1.01 (d, 3H, ³J_H,H 6.8 Hz, CH(CH₃)₂), 0.88 (d, 3H, ³J_H,H 6.5 Hz, CH(CH₃)₂), 0.77 (d, 3H, ³J_H,P 4.2 Hz, PCH₃).

¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 159.93 (s, NC(H)N), 153.11 (s, ipso), 137.68 (s, o), 127.37 (s, m), 126.66 (s, p), 59.39 (d, ⁴J_C,P 8.3 Hz, CH(CH₃)₂), 50.02 (s, C(CH₃)₂), 36.32 (m, PCH₂), 34.28 (d of d, ¹J_C,P 25.0 Hz, ³J_C,P 13.4 Hz, PCH₂), 32.40 (m, PCH₂), 30.45 (d, ¹J_C,P 10.7 Hz, PCH₂), 26.54 (m, PCH₂), 26.35 (s, PCH₃), 26.16 (s, CH(CH₃)₂), 24.95 (s, PCH₃), 24.64–24.19 (m, CH(CH₃)₂), 24.12 (s, PCH₃), 22.06 (d, ¹J_C,P 10.0 Hz, PCH₃), 21.26 (m, PCH₃), 13.62 (m, PCH₃).

²⁹Si{¹H} NMR (C₆D₆, 119 MHz, 298 K): δ 81.11 (m).

³¹P{¹H} NMR (C₆D₆, 243 MHz, 298 K): δ 72.09 (s, 2P), 69.03 (s, 1P), 56.00 (s, 1P). Anal. Found (calcd.): C, 51.09 (51.01); H, 9.28 (9.08); N, 4.74 (4.76).

[(dmpe)₂Mn{κ²-SiH₆Bu(N¹PrCHN¹Pr)}] (25Bu,H). An excess of diisopropylcarbodiimide {C(N¹Pr)₂} (165 mg, 1.307 mmol) was added to a solution containing 135.5 mg (0.255 mmol) of [(dmpe)₂Mn(SiH₆Bu₂)] (20Bu) in 10 mL of benzene. The reaction mixture was stirred in a sealed flask overnight at room temperature, after which the solvent was removed in vacuo. The resulting orange solid was recrystallized from a concentrated solution of 25Bu,H in hexanes giving a yield of 35.3 mg (0.062 mmol, 24%). X-ray quality crystals could not be obtained. Dominant isomer: ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 7.58 (s, 1H, NC(H)N), 5.50 (d of d with
29Si sat., 1H, \( ^3J_{\text{H,P}} 24.2\) Hz, \( ^3J_{\text{H,H}} 6.8\) Hz, \( \text{CH} \{(\text{CH}_3)_2\} \), 3.09 (septet, 1H, \( ^3J_{\text{H,H}} 6.7\) Hz, \( \text{CH} \{(\text{CH}_3)_2\} \), 0.9-2.1 (various m, 8H, PCH\( \text{H}_2\)), 1.95 (m, 2H, SiHCH2CH\( \text{H}_2\)CH2CH3), 1.65 (m, 2H, SiHCH2CH\( \text{H}_2\)CH2CH3), 1.45 (d, 3H, \( ^2J_{\text{H,P}} 5.8\) Hz, PCH\( \text{H}_3\)), 1.44 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, PCH\( \text{H}_3\)), 1.38 (d, 3H, \( ^2J_{\text{H,P}} 4.9\) Hz, PCH\( \text{H}_3\)), 1.32 (d, 3H, \( ^2J_{\text{H,P}} 3.9\) Hz, PCH\( \text{H}_3\)), 1.24 (d, 3H, \( ^2J_{\text{H,P}} 2.5\) Hz, PCH\( \text{H}_3\)), 1.21 (d, 3H, \( ^3J_{\text{H,H}} 6.8\) Hz, CH\( \{(\text{CH}_3)_2\} \), 1.18 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, (PCH\( \text{H}_3\)), 1.18 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.13 (m, 5H, SiHCH2CH\( \text{H}_2\)CH2CH3 and SiHCH2CH\( \text{H}_2\)CH2CH3), 1.11 (d, 3H, \( ^2J_{\text{H,P}} 4.2\) Hz, PCH\( \text{H}_3\)), 0.97 (d, 3H, \( ^3J_{\text{H,H}} 6.9\) Hz, CH\( \{(\text{CH}_3)_2\} \), 0.86 (d, 3H, \( ^2J_{\text{H,P}} 4.4\) Hz, PCH\( \text{H}_3\)), 0.83 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \), 1.18 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, (PCH\( \text{H}_3\)), 1.18 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.13 (m, 5H, SiHCH2CH\( \text{H}_2\)CH2CH3 and SiHCH2CH\( \text{H}_2\)CH2CH3), 1.11 (d, 3H, \( ^2J_{\text{H,P}} 4.2\) Hz, PCH\( \text{H}_3\)), 0.97 (d, 3H, \( ^3J_{\text{H,H}} 6.9\) Hz, CH\( \{(\text{CH}_3)_2\} \), 0.86 (d, 3H, \( ^2J_{\text{H,P}} 4.4\) Hz, PCH\( \text{H}_3\)), 0.83 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.18 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, (PCH\( \text{H}_3\)), 1.18 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.13 (m, 5H, SiHCH2CH\( \text{H}_2\)CH2CH3 and SiHCH2CH\( \text{H}_2\)CH2CH3), 1.11 (d, 3H, \( ^2J_{\text{H,P}} 4.2\) Hz, PCH\( \text{H}_3\)), 0.97 (d, 3H, \( ^3J_{\text{H,H}} 6.9\) Hz, CH\( \{(\text{CH}_3)_2\} \), 0.86 (d, 3H, \( ^2J_{\text{H,P}} 4.4\) Hz, PCH\( \text{H}_3\)), 0.83 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.18 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, (PCH\( \text{H}_3\)), 1.18 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.13 (m, 5H, SiHCH2CH\( \text{H}_2\)CH2CH3 and SiHCH2CH\( \text{H}_2\)CH2CH3), 1.11 (d, 3H, \( ^2J_{\text{H,P}} 4.2\) Hz, PCH\( \text{H}_3\)), 0.97 (d, 3H, \( ^3J_{\text{H,H}} 6.9\) Hz, CH\( \{(\text{CH}_3)_2\} \), 0.86 (d, 3H, \( ^2J_{\text{H,P}} 4.4\) Hz, PCH\( \text{H}_3\)), 0.83 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \)), 1.18 (d, 3H, \( ^2J_{\text{H,P}} 5.7\) Hz, (PCH\( \text{H}_3\)), 1.18 (d, 3H, \( ^3J_{\text{H,H}} 6.6\) Hz, CH\( \{(\text{CH}_3)_2\} \))
trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O₂CH)] (26). Method a.) 128.1 mg (0.224 mmol) of 
[(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (20$^{Ph}$) was dissolved in 10 mL of benzene. The reaction mixture 
was freeze/pump/thawed in a 50 mL storage flask three times, placed under 1 atm of CO$_2$
 at room temperature, and then sealed. After stirring at room temperature overnight, the 
solvent was removed in vacuo and the resulting solid was sublimed at 80 °C at 5 mTorr. 
The sublimed solid was dissolved in approx. 0.6 mL of C$_6$D$_6$, and the reaction mixture 
was freeze/pump/thawed in an NMR tube with a J-young vale three times, before again 
being placed under 1 atm of CO$_2$ and sealed. NMR characterization was done in situ 
under an atmosphere of CO$_2$ because removal of CO$_2$ (and also removal of solvent) led to 
partial decomposition to form [(dmpe)$_2$MnH(CO)] (27). X-ray quality crystal were 
obtained by washing the crude (pre-sublimation) solid with hexamethyldisiloxane, then 
recrystallizing the solid residue from a concentrated solution of 26 in toluene layered 
with hexamethyldisiloxane at −30 °C. Methods b-d.) Approx. 10 mg of 
[(dmpe)$_2$MnH(SiH$_2$"Bu)$_2$] (20$^{Bu}$), [(dmpe)$_2$MnH(=SiEt)$_2$]) (16$^{Et}$), or 
[(dmpe)$_2$MnH(C$_2$H$_4$)] (10) was dissolved in approx. 0.6 mL of C$_6$D$_6$. The resulting 
solutions were then placed in a thick-walled NMR tube with a J-Young Teflon valve and 
was freeze-pump-thawed (×3). The NMR tubes were then placed under an atmosphere of 
carbon dioxide, sealed, and allowed to sit for 1.5h (b), 1.25h (c), or overnight (d). The 
resulting mixtures (b-d) were analyzed in situ without purification, leading to 100% 
conversion to complex 27 and a polysiloxane byproduct. $^1$H NMR (C$_6$D$_6$, 600 MHz, 
298 K): δ 8.68 (p, 1H, $^4$J$_{H,P}$ 1.8 Hz, OC(H)O), 1.90 (m, 4H, PCH$_2$), 1.36 (m, 4H, PCH$_2$),
1.26 (s, 12H, PC₆H₃), 1.23 (s, 12H, PC₆H₃). $^{13}$C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 167.93 (s, O₇C(H)O), 30.94 (p, J₇C,P 11.6 Hz, P₇C₃H₂), 17.95 (m, P₇C₃H₃), 15.54 (s, P₇C₃H₃).

$^{31}$P{¹H} NMR (C₆D₆, 243 MHz, 298 K): δ 68.33 (s).

11.8 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 8

Selected NMR spectra are available in the ESI to reference 587. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 587 (X→Y) in the following manner: 10→1, 12→A, 16→3, 17→2, 18→5, 19→6, 20→4, 21→7, 23→D, 24→F, and A→E.

Catalytic hydrosilylation of ethylene (used for obtaining hydrosilylation data except those in Figures 8.1 or 8.2). 12-21 mg of hydrosilane, and sufficient precatalyst (10 or, for H₃SiBu hydrosilylation either 10, 20Bu, or 18Bu or, for H₂SiEt₂ hydrosilylation either 10 or 16Et₂) to yield a 15 : 1 (silane : [Mn]) molar ratio, were dissolved in approx. 0.6 mL of C₆D₆, placed in a J-young NMR tube, and the solution was freeze-pump-thawed (×3). The resulting solution was placed under an atmosphere of ethylene gas, cooled to −95 °C, and sealed at this low temperature. NMR analysis was conducted in situ after intervals at 60 °C, and if the ethylene concentration in solution became low, the freeze-pump-thaw/addition of ethylene process described above was repeated.

Catalytic hydrosilylation of ethylene (used for obtaining data in Figure 8.1). A single stock solution was prepared containing 177 mg (2.01 mmol) of H₃SiBu and 45 mg (0.12 mmol) of [(dmpe)₂MnH(C₄H₄)] (10) in 10 mL C₆D₆. Aliquots (approx. 0.6 mL) of this stock solution were placed in separate 50 mL storage flasks, and were freeze-pump-thawed (×3). The resulting solutions were placed under an atmosphere of ethylene gas, cooled to −95 °C, and sealed at this low temperature. Each flask was heated at 60 °C for a given time period, then cooled to room temperature and the headspace was replaced with argon. NMR spectra were obtained for the resulting solutions, as well as distilled (5 mTorr, 298 K) products.
Catalytic hydrosilylation of ethylene (used for obtaining data in Figure 8.2). A single aliquot generated as described above (for hydrosilylation of ethylene to obtain data in Figure 8.1) taken after 11 h was placed in a J-young NMR tube. The resulting solution was freeze-pump-thawed (×3), placed under an atmosphere of ethylene gas, cooled to –95 °C, and sealed at this low temperature. Reaction progress was monitored *in situ* by NMR spectroscopy at 56 °C without cooling to room temperature.

**Catalytic hydrosilylation of d₄-ethylene.** 22-29 mg of hydrosilane (either H₃SiⁿBu or H₂SiEt₂), and sufficient [(dmpe)$_2$MnH(C₂H₄)] (10) to produce a 15 : 1 (silane : [Mn]) ratio (6.4-8.5 mg) were dissolved in approx. 0.6 mL C₆D₆. These solutions were placed in separate 50 mL storage flasks, and were freeze-pump-thawed (×3). The resulting solutions were placed under approx. 0.5 atm of d₄-ethylene, cooled to –95 °C, and sealed at this low temperature. Each flask was heated at 60 °C for 4 days, then cooled to room temperature and the headspace was replaced with argon. NMR spectra were obtained for the resulting solutions, as well as distilled (5 mTorr, 298 K) products.

**Reactions of silylene hydride complexes with H₃SiⁿBu.** Approx. 15 mg of silylene hydride complex [((dmpe)$_2$MnH(=SiEt₂)) (16$^{Et}$₂) or a mixture of [((dmpe)$_2$MnH(=SiPh₂)] (16$^{Ph}$₂) with [((dmpe)$_2$MnH₂(SiHPh₂)] (18$^{Ph}$₂) was dissolved in approx. 0.6 mL of C₆D₆. An excess of free H₃SiⁿBu (approx. 20 mg) was added, and the resulting solution was analyzed by NMR spectroscopy. Complete conversion of the silylene hydride complex to [(dmpe)$_2$MnH(SiH₂ⁿBu)] (20$^{Bu}$) was observed immediately (for 16$^{Ph}$₂), or after a few hours (for 16$^{Et}$₂), with a change in solution colour to pale-yellow.

**HSiViEt₂.**

**¹H NMR (C₆D₆, 600 MHz, 298 K):** δ 6.08 (d of d of d, 1H, $^3$J$_{H,H}$ 20.2 Hz, $^3$J$_{H,H(SiH)}$ 14.7 Hz, $^3$J$_{H,H(H)}$ 3.0 Hz, SiCH=CH₂), 5.98 (d of d, 1H, $^3$J$_{H,H}$ 14.6 Hz, $^2$J$_{H,H}$ 4.1 Hz, SiCH=CH₂), 5.79 (d of d, 1H, $^3$J$_{H,H}$ 20.1 Hz, $^2$J$_{H,H}$ 4.1 Hz, SiCH=CH₂), 4.12 (app. sextet with $^{29}$Si sat., 1H, $^3$J$_{H,H}$ 3.2 Hz $^1$J$_{H,Si}$ 183.6 Hz, SiH), 0.975 (m, 6H, SiCH₂CH₃), 0.59 (q of d, 4H, $^3$J$_{H,H}$ 8.0 Hz, $^3$J$_{H,H(SiH)}$ 3.4 Hz, SiCH₂CH₃).

**¹³C{¹H} NMR**
(C₆D₆, 151 MHz, 298 K): δ 134.61 (s, SiCH=CH₂), 134.24 (s, SiCH=CH₂), 8.23 (s, SiCH₂CH₃), 3.29 (s, SiCH₂CH₃). ²⁹Si NMR (C₆D₆, 119 MHz, 298 K): −10.03.

H₂SiEt²Bu. ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 3.88 (app. p with ²⁹Si sat., 1H, ³Jₜ,ₜ 6.6 Hz, ¹Jₛ,ₚ 183.6 Hz, SiH), 1.31 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.29 (m, 2H, SiCH₂CH₂CH₂CH₃), 0.98 (t, 3H, ³Jₜ,ₜ 7.9 Hz, SiCH₂CH₃), 0.85 (t, 3H, ³Jₜ,ₜ 7.1 Hz, SiCH₂CH₂CH₂CH₃), 0.58 (q of t, 2H, ³Jₜ,ₜ 7.4 Hz, ³Jₜ,ₚₚ 3.6 Hz, SiCH₂CH₂CH₂CH₃), 0.56 (q of t, 2H, ³Jₜ,ₜ 7.9 Hz, ³Jₜ,ₚₚ 3.8 Hz, SiCH₂CH₃). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 27.96 (s, SiCH₂CH₂CH₃), 26.27 (s, SiCH₂CH₂CH₂CH₃) 13.95 (s, SiCH₂CH₂CH₂CH₃), 9.34 (s, SiCH₂CH₃), 8.86 (s, SiCH₂CH₂CH₂CH₃), 1.65 (s, SiCH₂CH₃). ²⁹Si NMR (C₆D₆, 119 MHz, 298 K): −25.6.

HSiEt²Bu. Selected NMR data are as follows; ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 3.93 (septet with ²⁹Si sat., 1H, ³Jₜ,ₜ 3.1 Hz ¹Jₛ,ₚ 177.1 Hz, SiH), 1.33 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.33 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.00 (t, 6H, ³Jₜ,ₜ 7.9 Hz, SiCH₂CH₃), 0.90 (t, 3H, ³Jₜ,ₜ 6.7 Hz, SiCH₂CH₂CH₂CH₃), 0.58 (m, 2H, SiCH₂CH₂CH₂CH₃), 0.57 (q of d, 4H, ³Jₜ,ₜ 7.9 Hz, ³Jₜ,ₚₚ 3.2 Hz, SiCH₂CH₃). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 27.26 and 26.74 (two s, SiCH₂CH₂CH₂CH₃ and SiCH₂CH₂CH₂CH₃), 14.02 (s, SiCH₂CH₂CH₂CH₃), 10.69 (s, SiCH₂CH₂CH₂CH₃), 8.50 (s, SiCH₂CH₃), 3.20 (s, SiCH₂CH₃). ²⁹Si NMR (C₆D₆, 119 MHz, 298 K): −2.94 (d, ¹Jₜ,ₚ 179.0 Hz).

HSiViEt²Bu. Selected NMR data are as follows; ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 6.11 (d of d of d, 1H, ³Jₜ,ₜ 20.3 Hz, ³Jₜ,ₚₚ 14.8 Hz, ³Jₜ,ₜ,ₜ 3.3 Hz, SiCH=CH₂), 5.99 (d of d, 1H, ³Jₜ,ₜ 14.8 Hz, ²Jₜ,ₜ 4.1 Hz, SiCH=CH₂), 5.81 (d of d, 1H, ³Jₜ,ₜ 20.2 Hz, ²Jₜ,ₜ 4.0 Hz, SiCH=CH₂), 4.16 (app. sextet with ²⁹Si sat., 1H, ³Jₜ,ₜ 3.3 Hz ¹Jₜ,ₚ 183.8 Hz, SiH). ¹³C{¹H} NMR (C₆D₆, 151 MHz, 298 K): δ 134.98 (s, SiCH=CH₂), 134.12 (s, SiCH=CH₂), 27.06, 26.59, 11.11 (3 s, three of the "Bu environments), 8.32 (s, SiCH₂CH₃), 3.70 (s, SiCH₂CH₃). ²⁹Si NMR (C₆D₆, 119 MHz, 298 K): −12.06.
HSiViPh₂. Selected NMR data are as follows; $^1$H NMR (C₆D₆, 600 MHz, 298 K): δ 6.36 (d of d of d, 1H, $^3$Jₕ,ₕ 20.1 Hz, $^3$Jₕ,ₕ(SiH) 14.3 Hz, $^3$Jₕ,ₕ(SiH) 3.0 Hz, SiCH=CH₂), 6.06 (d of d, 1H, $^3$Jₕ,ₕ 14.3 Hz, $^2$Jₕ,ₕ 3.6 Hz, SiCH=CH₂), 5.85 (d of d, 1H, $^3$Jₕ,ₕ 20.1 Hz, $^2$Jₕ,ₕ 3.6 Hz, SiCH=CH₂), 5.33 (d, 1H, $^3$Jₕ,ₕ 2.9 Hz, SiH).

HSiViEtPh. Selected NMR data are as follows; $^1$H NMR (C₆D₆, 600 MHz, 298 K): δ 6.20 (d of d of d, 1H, $^3$Jₕ,ₕ 20.1 Hz, $^3$Jₕ,ₕ(SiH) 14.6 Hz, $^3$Jₕ,ₕ(SiH) 3.1 Hz, SiCH=CH₂), 6.01 (d of d, 1H, $^3$Jₕ,ₕ 14.8 Hz, $^2$Jₕ,ₕ 3.7 Hz, SiCH=CH₂), 5.83 (d of d, 1H, $^3$Jₕ,ₕ 20.1 Hz, $^2$Jₕ,ₕ 3.7 Hz, SiCH=CH₂), 4.70 (q, 1H, $^3$Jₕ,ₕ 3.3 Hz, SiH). $^{29}$Si NMR (C₆D₆, 119 MHz, 298 K): −15.88.

d₄-HSiEt₃ [isotopomer HSiEt₂(–CD₂CD₂H)]. Selected NMR data are as follows; $^1$H NMR (C₆D₆, 600 MHz, 298 K): δ 3.89 (p with $^{29}$Si sat., 1H, $^3$Jₕ,ₕ 3.2 Hz, $^1$Jₕ,ₛ 177.5 Hz, SiH), 0.98 (t, 6H, $^3$Jₕ,ₕ 8.0 Hz, SiCH₂CH₃), 0.93 (br. s, 1H SiCD₂CD₂H), 0.54 (q of d, 4H, $^3$Jₕ,ₕ 7.9 Hz, $^3$Jₕ,ₕ 3.2 Hz, SiCH₂CH₃). $^2$H NMR (C₆D₆, 77 MHz, 298 K): δ 0.90 (d, 2D, $^2$Jₕ,ᵢ 2.0 Hz, SiCD₂CD₂H), 0.46 (d, 2D, $^3$Jₕ,ᵢ 0.8 Hz, SiCD₂CD₂H). $^{13}$C{¹H} NMR (C₆D₆, 176 MHz, 298 K): δ 8.43 (s, SiCH₂CH₃), 7.64 (p, $^1$Jₕ,ᵢ 19 Hz, SiCD₂CD₂H), 2.79 (s, SiCH₂CH₃), 1.83 (p, $^1$Jₕ,ᵢ 18 Hz, SiCD₂CD₂H).

d₅-HSiEt₃ [isotopomer HSiEt₂(–CDHCD₂)]. Selected NMR data are as follows; $^{13}$C{¹H} NMR (C₆D₆, 176 MHz, 298 K): δ 2.11 (t, $^1$Jₕ,ᵢ 18 Hz, SiCDHCD₂).

d₆-HSiVi₂Bu [isotopomer HSiBu(–CD₂CD₂H)(–CDHCD₂)]. Selected NMR data are as follows; $^1$H NMR (C₆D₆, 600 MHz, 298 K): δ 3.93 (q with $^{29}$Si sat., 1H, $^3$Jₕ,ₕ 3.2 Hz, $^1$Jₕ,ₛ 177 Hz, SiH), 1.33 (m, 2H, SiCH₂CH₂CH₃), 1.33 (m, 2H, SiCH₂CH₂CH₃), 0.95 (br. s, 1H, SiCD₂CD₂H), 0.90 (t, 3H, $^3$Jₕ,ₕ 6.7 Hz,
SiCH₂CH₂CH₂CH₃, 0.58 (m, 2H, SiCH₂CH₂CH₂CH₃), 0.52 (br. s, 1H, SiCD₂CD₂H). ²H NMR (C₆D₆, 77 MHz, 298 K): δ 0.92 (d, 2D, ²J₂H, 2 Hz, SiCD₂CD₂H), 0.91 (d, 3D, ³J₂H, 0.8 Hz, SiC₂D₂H), 0.49 (s, 2D, SiCD₂CD₂H), 0.49 (d, 1D, ²J₃H, 2 Hz, SiC₂D₂H).

₁³C {¹H} NMR (C₆D₆, 176 MHz, 298 K): δ 27.27 and 26.74 (two s, SiCH₂CH₂CH₂CH₃), 14.0 (s, SiCH₂CH₂CH₂CH₃), 10.67 (s, SiCH₂CH₂CH₂CH₃), 7.73 (p, ¹J₁₁₃H 19 Hz, SiCD₂CD₂H), 7.43 (ap. p, ¹J₃₃H 19 Hz, SiCD₂CD₂H), 2.47 (t, ¹J₁₁₃H 18 Hz, SiC₂D₂H), 2.22 (m, ¹J₃₃H 19 Hz, SiCD₂CD₂H).

₂⁹HSiEt₂Bu {isotopomer HSiBu(--CD₂CD₂H)₂}. Selected NMR data are as follows; ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 3.92 (t with ²⁹Si sat., 1H, ³J₂H, 3.2 Hz, ¹J₁₁₃H 177 Hz, SiH), 1.33 (m, 2H, SiCH₂CH₂CH₂CH₃), 1.33 (m, 2H, SiCH₂CH₂CH₂CH₃), 0.95 (br. s, 2H, SiCD₂CD₂H), 0.90 (t, 3H, ³J₂H 6.7 Hz, SiCH₂CH₂CH₂CH₃), 0.58 (m, 2H, SiCH₂CH₂CH₂CH₃). ²H NMR (C₆D₆, 77 MHz, 298 K): δ 0.92 (d, 4D, ²J₂H, 2 Hz, SiCD₂CD₂H), 0.49 (s, 4D, SiCD₂CD₂H). ¹³C {¹H} NMR (C₆D₆, 176 MHz, 298 K): δ 27.27 and 26.74 (two s, SiCH₂CH₂CH₂CH₃ and SiCH₂CH₂CH₂CH₃), 14.0 (s, SiCH₂CH₂CH₂CH₃), 10.67 (s, SiCH₂CH₂CH₂CH₃), 7.73 (p, ¹J₁₁₃H 19 Hz, SiCD₂CD₂H), 2.22 (m, ¹J₃₃H 19 Hz, SiCD₂CD₂H).

₃⁹HSiViEt₄Bu {isotopomer HSiBu(--CDHCD₂) (--CD=CD₂)}. Selected NMR data are as follows; ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 4.16 (q with ²⁹Si sat., 1H, ³J₂H, 3.3 Hz, ¹J₁₁₃H 184 Hz, SiH). ²H (C₆D₆, 77 MHz, 298 K): δ 6.09 (s, SiCD=CD₂), 5.96 (s, SiCD=CD₂), 5.78 (s, SiCD=CD₂). ¹³C {¹H} (C₆D₆, 176 MHz, 298 K): δ 3.00 (t, ¹J₃₃H 18.4 Hz, SiC₂D₂H).

[(dmpe)₂MnH₂(SiHEtPh)] (18Ph₄Et). 18Ph₄Et was observed spectroscopically while monitoring ethylene hydrosilylation by H₂SiPh using 10. Selected NMR data are as follows (assignments are tentative, multiple isomers present); ¹H NMR (C₆D₆, 600 MHz, 298 K): δ 8.17 (d, ³J₁₁₃H 6 Hz, o), 8.12 (br. s, o), 7.87 (d, ³J₁₁₃H 7 Hz, o), 7.81 (br. s, o), 6.62 (app. t, ³J₁₁₃H 19 Hz, SiH), 5.69 (br. s, SiH), −11.59 (p, ²J₂₃H 53.7 Hz, MnH), −12.50 (br. s, MnH), −12.68 (br. s, MnH), −13.44 (br. s, MnH).
[(dmpe)$_2$MnH$_2$(SiHEt$^n$Bu)] (18$^{Bu,Et}$). 18$^{Bu,Et}$ was observed spectroscopically while monitoring ethylene hydrosilylation by H$_3$Si$^n$Bu using 10. Selected NMR data are as follows; $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): $\delta$ 4.98 (br. s, 1H, SiH), –12.66 (br. s, 2H, MnH).

11.9 – Synthetic Procedures and Characterization Pertaining to the Work of Chapter 9

Tables of calculated and crystallographically determined bond lengths and angles, along with bond orders, total bonding energies, and Hirshfeld charges for 11 are available in the ESI to reference 547. The identification numbers in this chapter of the thesis (X→Y) relate to those in reference 547 (X→Y) in the following manner; trans-10→1, cis-10→A, 11→5, 12→D, 13→B, 16→2, 17→C, and 18→3. CSD 1846649 contains the supplementary crystallographic data for 11 (other crystal structures in this chapter in this chapter have not been submitted to the CSD yet).

[(dmpe)$_2$MnH(H$_2$)] (11). 98.7 mg (0.26 mmol) of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) was dissolved in 10 mL of benzene, and the resulting solution was placed in a sealed flask and freeze-pump-thawed (×3). The flask was placed under an atmosphere of hydrogen gas at –95 °C using a liquid nitrogen-acetone bath, sealed at this temperature, and warmed to room temperature to provide approx. 1.7 atm of hydrogen gas for reactivity. After stirring at 60 °C for 5 days, the solvent was removed in vacuo and the resulting solid was extracted with pentane. Removal of the pentane in vacuo yielded a crude pale yellow powder with >95% purity by NMR (77% isolated yield; 70.4 mg, 0.20 mmol). Recrystallization from a concentrated solution in pentane at –30 °C yielded 48.7 mg of pure 11 (0.14 mmol, 52%). NMR data matches that previously reported via a different synthetic route (with $^{31}$P $\delta$ = 82 ppm). X-ray quality crystals were obtained from a concentrated solution of 11 in hexanes at –30 °C.

$^{ccc}$ The $^{31}$P chemical shift matches that reported in ref. 173, but not ref. 120.
\textbf{[(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28).} BH$_3$·NMe$_3$ (23.8 mg, 0.33 mmol) was added to a solution of 127.0 mg (0.33 mmol) of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) in 30 mL of toluene, and the resulting solution was stirred at 90 °C for two days (with the solution turning from bright yellow to dark purple/black within an hour). The solvent was then removed \textit{in vacuo}, and resulting black solid was dissolved in a minimal amount of hexanes and allowed to sit at –30 °C for a few days yielding a purple powder with some impurities. Purification by sublimation (5 mTorr, 80-85 °C) and recrystallization from a concentrated solution in hexanes yielded a combined 27.0 mg of purple solid (0.07 mmol, 22 %). X-ray quality crystals were obtained from a solution in hexanes at –30 °C.

$^1$H NMR (\textit{d$_8$-toluene, 600 MHz, 298 K}): $\delta$ 5.08 (m, 2H, B$H$), 1.69 (m, 2H, PCH$_2$), 1.60 (m, 6H, PCH$_3$), 1.43 (m, 6H, PCH$_3$), 1.34 (m, 4H, PCH$_2$), 1.16 (m, 2H, PCH$_2$), 0.97 (d, 6H, $^2$J$_{H,P}$ 5.8 Hz, PCH$_3$), 0.71 (d, 6H, $^2$J$_{H,P}$ 5.2 Hz, PCH$_3$), –16.52 (m, 2H, MnH). $^{11}$B$^{1}$H) NMR (\textit{d$_8$-toluene, 192 MHz, 298 K}): $\delta$ 25.30 (s).

$^{13}$C$^{1}$H) NMR (\textit{d$_8$-toluene, 151 MHz, 298 K}): $\delta$ 33.48 (m, PCH$_2$), 32.78 (m, PCH$_2$), 29.12 (m, PCH$_3$), 23.25 (m, PCH$_3$), 21.82 (s, PCH$_3$), 20.21 (PCH$_3$). $^{31}$P$^{1}$H) NMR (\textit{d$_8$-toluene, 243 MHz, 298 K}): $\delta$ 88.56 (s, 2P), 72.54 (s, 2P).

\textbf{Reaction of [(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28) with D$_2$.} Approx. 10 mg of [(dmpe)$_2$Mn($\mu$-H)$_2$BH$_2$] (28) was dissolved in approx. 0.6 mL of C$_6$D$_6$, and the resulting solution was placed in a J-young NMR tube and freeze/pump/thawed ×3. After cooling to –95 °C, D$_2$ was allowed to flow into the J-young NMR tube and the valve was sealed to this temperature. After heating at 90 °C for 12 h, the resulting solution was analyzed by NMR spectroscopy \textit{in situ}. $^1$H NMR data matches that for 28, with 40% reduction in the relative intensity of both the MnH and BH environments.
Figure 11.1: [(dmpe)$_2$Mn(μ-H)$_2$BC$_8$H$_{14}$] (29) with C atom labels used in the NMR list.

[(dmpe)$_2$Mn(μ-H)$_2$BC$_8$H$_{14}$] (29). 73.7 mg (0.60 mmol) of 9-BBN (purified by two successive recrystallizations from concentrated solutions in DME at –30 °C) was added to a solution of 116 mg (0.30 mmol) of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) in 20 mL of benzene, and the resulting solution was stirred at 90 °C overnight (with the solution turning from bright yellow to dark brown). The solvent was then removed in vacuo, and the resulting black solid was dissolved in a minimal amount of hexanes. Allowing this solution to stand at –30 °C yielded a mixture of yellow and red crystals; the former were [(dmpe)$_2$MnH]$_2$ (μ-dmpe)] (31) while the latter was [(dmpe)$_2$Mn(μ-H)$_2$BC$_8$H$_{14}$] (29). Both sets of crystals were X-ray quality. Picking out red crystals with tweezers allowed isolation of 29 in > 99 % purity. $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 2.29 (app. nonet, 2H, $^2$J$_{H,H}$ 6.0 Hz, CH$_2$(C)), 2.13 (m, 8H, CH$_2$(B)), 1.86 (m, 2H, CH$_2$(C)), 1.67 (m, 2H, PCH$_2$), 1.55 (m, 6H, PCH$_3$), 1.40 (s, 6H, PCH$_3$), 1.36 (br. s, 2H, CH(A)), 1.27 (m, 2H, PCH$_2$), 1.23 (d, 6H, $^2$J$_{H,P}$ 5.2 Hz, PCH$_3$), 1.17 (m, 4H, PCH$_2$), 0.72 (d, 6H, $^2$J$_{H,P}$ 4.7 Hz, PCH$_3$), –15.55 (br. s, 2H, MnH). $^{11}$B$^{'1}$H NMR (C$_6$D$_6$, 192 MHz, 298 K): δ 43.19 (s).

$^{13}$C$^{'1}$H NMR (C$_6$D$_6$, 151 MHz, 298 K): δ 36.96 (m, CH(A)), 35.94 (m, PCH$_2$), 35.39 (s, CH$_2$(B)), 34.32 (s, CH$_2$(B)), 31.25 (m, PCH$_2$ and PCH$_3$), 25.00 (s, CH$_2$(C)), 24.91 (m, PCH$_3$), 23.80 (s, PCH$_3$), 20.79 (s, PCH$_3$). $^{31}$P$^{'1}$H NMR (C$_6$D$_6$, 243 MHz, 298 K): δ 85.08 (s, 2P), 70.11 (s, 2P).

[(dmpe)$_2$Mn(μ-H)$_2$BMes$_2$] (30). 172.0 (0.69 mmol) of HBMes$_2$ was added to a solution of 132.1 mg (0.34 mmol) of [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) in 20 mL of toluene, and the resulting solution was stirred at 60 °C for two days (turning from bright yellow to

$^{	ext{dddd}}$ Number of moles based on a 9-BBN monomer.
dark purple). The solvent was then removed in vacuo, and the resulting purple solid was washed with 10 mL of hexanes, 3 mL of toluene, and dissolved in 12 mL of toluene. The toluene solution was layered with 3 mL of hexanes and stored for days at –30 °C, after which 48.8 mg of a very dark purple solid (both crystals and powder) had crystallized. To obtain a higher yield, the solvent was removed in vacuo from the mother liquor, and the resulting solid dissolved in 2 mL of THF which was allowed to sit for days at –30 °C yielded an additional 22.0 mg of purple crystals (combined yield of 70.8 mg, 0.12 mmol, 34 %). X-ray quality crystals were obtained from a solution in C₆D₆ at 60 °C.

\[ ^1\text{H} \text{ NMR (} d_8 \text{-toluene, 600 MHz, 298 K):} \delta 6.92 (s, 2H, m-C₃H₃), 6.61 (s, 2H, p-C₃H₃), 2.84 (s, 6H, o-C₃H₃), 2.26 (s, 6H, o-C₃H₃), 2.23 (s, 6H, p-C₃H₃), 1.51 (m, 2H, PC₂H₂), 1.38 (m, 6H, PC₃H₃), 1.26 (d, 6H, \^J_{H,P} 5.4 Hz, PCH₃), 1.08 (m, 6H, PCH₃), 0.70 (m, 6H, PCH₃), 0.65 (d, 6H, \^J_{H,P} 4.8 Hz, PCH₃), –13.98 (br. s, 2H, MnH). \]

\[ ^{11}\text{B} \{^1\text{H}\} \text{ NMR (} d_8 \text{-toluene, 192 MHz, 298 K):} \delta 27.46. \]

\[ ^{13}\text{C} \{^1\text{H}\} \text{ NMR (} d_8 \text{-toluene, 151 MHz, 298 K):} \delta 153.3 (i), 140.72 (s, o), 140.20 (s, o), 133.59 (s, p) 129.1 (m), 128.7 (m), 37.10 (m, PCH₂), 31.93 (m, PCH₂), 27.50 (s, o-C₃H₃), 27.40 (s, PCH₃), 25.24 (s, o-C₃H₃), 24.75 (m, PCH₃), 21.24 (m, PCH₃), 21.12 (s, p-C₃H₃), 20.0 (PCH₃). \]

\[ ^{31}\text{P} \{^1\text{H}\} \text{ NMR (} d_8 \text{-toluene, 243 MHz, 298 K):} \delta 85.82 (s, 2P), 62.61 (s, 2P). \text{ Anal. Found (calcd.):} C, 59.38 (59.42); H, 9.37 (9.31). \]

\[ [(\text{dmpe})_2\text{Mn(μ-D)}_2\text{BMes}_2] \ (d_2-30). \text{ 11.7 mg (0.03 mmol) of [(dmpe)_2MnH(C}_2\text{H}_4)] \ (10) and 15.3 mg (0.06 mmol) of DBMes}_2 \text{ were dissolved in approx. 0.6 mL of C}_6\text{D}_6. \text{ The resulting solution was heated overnight at 60 °C, and analyzed by NMR spectroscopy in situ.} \]

\[ ^1\text{H} \text{ NMR (C}_6\text{D}_6, 77 MHz, 298 K): \delta –14.09 (s, 2D, MnD). \]

\text{EtBC}_8\text{H}_{14}. \text{ Approx. 10 mg of HBC}_8\text{H}_{14} \text{ was dissolved in approx. 0.6 mL of C}_6\text{D}_6, \text{ and the resulting solution was placed in a J-young NMR tube and freeze/pump/thawed ×3. After cooling to –95 °C, ethylene was allowed to flow into the J-young NMR tube and the valve was sealed to this temperature. After heating at 60 °C for 1 h, the resulting solution was analyzed by NMR spectroscopy in situ.} \]

\[ ^1\text{H} \text{ NMR (C}_6\text{D}_6, 600 MHz, 298 K): \]

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\[ \delta \ 1.84 \text{ (m, 6H, C}_8H_{14}) , \ 1.76 \text{ (br. s, 2H, C}_8H_{14}) , \ 1.65 \text{ (m, 4H, C}_8H_{14}) , \ 1.35 \text{ (q, 2H, }^{3}J_{H,H} \ 7.6 \text{ Hz, CH}_2CH_3) , \ 1.17 \text{ (m, 2H, C}_8H_{14}) , \ 1.08 \text{ (t, 3H, }^{3}J_{H,H} \ 7.6 \text{ Hz, CH}_2CH_3). \]  

\[ ^{11}B\{^{1}H\} \]  

\[ \text{NMR (C}_6D_6, 192 \text{ MHz, 298 K) : } \delta \ 87.41 \text{ (s). } \]  

\[ ^{13}C\{^{1}H\} \]  

\[ \text{NMR (C}_6D_6, 151 \text{ MHz, 298 K) : } \delta \ 33.39 \text{ (s), 31.13 \ (br. s), 23.63 \ (s), 20.23 \ (br. s), 8.41 \ (s).} \]  

EtBMes\textsubscript{2}. Approx. 10 mg of HBMes\textsubscript{2} was dissolved in approx. 0.6 mL of C\textsubscript{6}D\textsubscript{6}, and the resulting solution was placed in a J-young NMR tube and freeze/pump/thawed ×3. After cooling to –95 °C, ethylene was allowed to flow into the J-young NMR tube and the valve was sealed to this temperature. After heating at 60 °C for 1 h, the resulting solution was analyzed by NMR spectroscopy in situ. \[ ^{1}H \]  

\[ \text{NMR (C}_6D_6, 600 \text{ MHz, 298 K) : } \delta \ 6.74 \text{ (s, 4H, m), 2.23 \ (s, 12H, o-CH}_3), \ 2.15 \text{ (s, 6H, p-CH}_3), \ 1.93 \text{ (q, 2H, }^{3}J_{H,H} \ 7.5 \text{ Hz, CH}_2CH_3), \ 1.15 \text{ (t, 3H, }^{3}J_{H,H} \ 7.5 \text{ Hz, CH}_2CH_3). \]  

\[ ^{11}B\{^{1}H\} \]  

\[ \text{NMR (C}_6D_6, 192 \text{ MHz, 298 K) : } \delta \ 84.02 \text{ (br. s). } \]  

\[ ^{13}C\{^{1}H\} \]  

\[ \text{NMR (C}_6D_6, 151 \text{ MHz, 298 K) : } \delta \ 139.13 \text{ (s), 138.34 \ (s), 128.98 \ (s), 26.55 \ (br. s), 22.91 \ (s), 21.18 \ (s), 9.38 \ (s).} \]  

Intermediates in the synthesis of 29. Method a) 3.6 mg of 9-BBN (0.030 mmol)\textsuperscript{mm} and 11.3 mg of [(dmpe)\textsubscript{2}MnH(C\textsubscript{2}H\textsubscript{4})] (10) (0.029 mmol) were dissolved in approx. 0.6 mL of C\textsubscript{6}D\textsubscript{6} and the resulting mixture was left for 7 days at room temperature and analyzed in situ by NMR spectroscopy indicating a 1.3 : 1.0 : 2.1 ratio of 10 : 29 : intermediates (region of the \[ ^{1}H \] NMR spectrum shown in Figure 9.3). Method b) 6.5 mg of 9-BBN (0.05 mmol)\textsuperscript{ee} and 10.3 mg of [(dmpe)\textsubscript{2}MnH(C\textsubscript{2}H\textsubscript{4})] (10) (0.27 mmol) were dissolved in approx. 0.6 mL of C\textsubscript{6}D\textsubscript{6} and the resulting mixture was left for 3 days at room temperature and analyzed in situ by \[ ^{1}H \] NMR spectroscopy indicating a 0.4 : 1.0 : 0.6 ratio of 10 : 29 : intermediates (region of the \[ ^{31}P\{^{1}H\} \] NMR spectrum shown in Figure 9.3). A major (>95%) and minor (<5%) intermediate were both observed in solution. Selected NMR data for the major species are as follows: \[ ^{1}H \]  

\[ \text{NMR (C}_6D_6, 600 \text{ MHz, 298 K) : } \delta \ 2.68 \text{ (m, 1H), 2.60 \ (m, 1H), 2.46 \ (m, 4H), 2.05 \ (m, 1H), 0.53 \ (m, 1H), 0.31 \ (m, 1H), –1.44 \ (br. s, 1H), –13.14 \ (br. s, 1H, MnH). \]  

\[ ^{11}B \]  

\[ \text{NMR (C}_6D_6, 192 \text{ MHz, 298 K) : } \delta \ –15.49 \text{ (s). } \]  

\[ ^{31}P\{^{1}H\} \]  

\[ \text{NMR (C}_6D_6, 243 \text{ MHz, 298 K) : } \delta \ 85.83 \text{ (s, 1P), 76.47 \ (s, 1P), 64.94 \ (s).} \]  

\textsuperscript{ee} Number of moles based on a 9-BBN monomer.
Selected NMR data for the minor species are as follows: $^{31}\text{P}\{^1\text{H}\}$ NMR ($C_6D_6$, 243 MHz, 298 K): $\delta$ –5.64 (s).

**Intermediates in the synthesis of 30.** 13.0 mg of HBMes$_2$ (0.052 mmol) and 10.0 mg of $[(\text{dmpe})_2\text{MnH}(C_2H_4)]$ (10) (0.026 mmol) were dissolved in approx. 0.6 mL of $C_6D_6$ and the resulting mixture was placed in an NMR tube with J-young valve and heated for 1.5 h at 60 °C. The resulting solution was analyzed *in situ* by NMR spectroscopy indicating a 1.4 : 1.0 : 0.6 ratio of 10 : 30 : intermediates. A major (>95%) and minor (<5%) intermediate were both observed in solution. Selected NMR data for the major species are as follows: $^1\text{H}$ NMR ($C_6D_6$, 600 MHz, 298 K): 4.12 (app. t, 2H, $J$ 2.2 Hz), 1.96 (q, 2H, $^3J_{\text{H,H}}$ 7.1 Hz), –13.03 (t, 1H, $J_{\text{H,P}}$ 73.7 Hz, Mn$^\text{H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR ($C_6D_6$, 243 MHz, 298 K): $\delta$ –4.01 (s). Selected NMR data for the minor species are as follows: $^{31}\text{P}\{^1\text{H}\}$ NMR ($C_6D_6$, 243 MHz, 298 K): $\delta$ 73.27 (br. s).

**Reaction of $[(\text{dmpe})_2\text{MnH}(C_2H_4)]$ (10) with DIBAL:** 18 mg (0.05 mmol) of $[(\text{dmpe})_2\text{MnH}(C_2H_4)]$ (10) was dissolved in approx. 0.6 mL $C_6D_6$. To this solution was added 24 mg (0.17 mmol) of DIBAL, and the resulting solution was analyzed by NMR spectroscopy *in situ*. Complete consumption of 10 was observed immediately, and the hydride-free product began decomposing to various hydride-containing products within 30 minutes, many of which themselves decomposed to further hydride-containing decomposition products.

$[(\text{dmpe})_2\text{MnH}]_2(\mu-\text{dmpe})$ (31) and $[(\text{dmpe})_2\text{MnH}(\kappa_1-\text{dmpe})]$ (32). Method a) 135.8 mg (0.35 mmol) of $[(\text{dmpe})_2\text{MnH}(C_2H_4)]$ (10) was dissolved in 10 mL toluene, then added to 149.6 mg (1.00 mmol) of dmpe dissolved in 10 mL of toluene. The resulting solution was sealed in a 50 mL thick-walled storage flask and stirred overnight at 105 °C, after which the solvent was removed *in vacuo*. Recrystallization from a concentrated solution of hexanes at –30 °C yielded 12.3 mg of a waxy yellow solid, and removing the solvent from the mother liquor *in vacuo* and recrystallizing the resulting solution from concentrated hexamethyldisiloxane at –30 °C yielded an additional 39.6 mg of yellow powder. The combined solids were then heated under vacuum at 75 °C.
for 5 h to remove unreacted 10, resulting in 19.8 mg of 31 and 32 in a 1 : 20 ratio. A small sample (~10 mg) of [{(dmpe)$_2$MnH}$]$_2$[μ-dmpe)] (31) was isolated from 32 by washing a crude mixture of 31 and 32 with hexamethyldisiloxane, followed by recrystallization from a concentrated solution in hexanes layered with hexamethyldisiloxane at –30 °C, and the product was characterized by NMR spectroscopy. A small sample of [{(dmpe)$_2$MnH(κ$_1$-dmpe)}] (32) was isolated from 31 by sublimation from a crude mixture of 31 and 32 at 120 °C (5 mTorr), and the product was characterized by NMR spectroscopy. Method b) 13 mg (0.03 mmol) of [{(dmpe)$_2$MnH(C$_2$H$_4$)}] (10) and 11 mg (0.07 mmol) of dmpe were dissolved in approx. 0.6 mL of C$_6$D$_6$ and placed in a J-young NMR tube. The resulting solution was freeze/pump/thawed ×3. After cooling to –95 °C, H$_2$ was allowed to flow into the J-young NMR tube and the valve was sealed to this temperature. Heating the sealed solution at 60 °C for 3 days resulted in quantitative conversion of 10 to 31 and 32 in a 1 : 8 ratio, and the products were analyzed in situ by NMR spectroscopy. X-ray quality crystals of trans,trans-31 were obtained from a solution of 31 and 29 in hexanes at – 30 °C, and X-ray quality crystal of cis,cis-31 were obtained from a solution of 31 in hexamethyldisiloxane at –30 °C. Selected NMR data for trans,trans-31 are as follows: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 1.66 (m, 8H, PCH$_2$-chelating), 1.50 (m, 8H, PCH$_2$-chelating), 1.48 (s, 24H, PCH$_3$-chelating), 1.36 (s, 24H, PCH$_3$-chelating), 1.30 (br. s, 4H, PCH$_2$-κ$^1$), 1.02 (d, $^2$J$_{HP}$ 3.5 Hz, 12H, PCH$_3$-κ$^1$), –15.74 (p of d, 2H, $^2$J$_{HP}$ 48.8 Hz, $^2$J$_{HP}$ 12.5 Hz, MnH). $^{31}$P{$^1$H} NMR (C$_6$D$_6$, 243 MHz, 298 K): δ 79.60 (s, 4P, chelating P), 27.16 (s, 1P, κ$^1$-P). Selected NMR data for the complex tentatively identified as cis,cis-31 are as follows: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ –11.66 (m, MnH). Selected NMR data for 32 are as follows: $^1$H NMR (C$_6$D$_6$, 600 MHz, 298 K): δ 1.62 (m, 4H, PCH$_2$-chelating), 1.47 (m, 4H, PCH$_2$-chelating), 1.45 (s, 12H, PCH$_3$-chelating), 1.38, (m, 2H, MnP(Me)$_2$CH$_2$CH$_2$PMe$_2$), 1.34 (s, 12H, PCH$_3$-chelating), 1.28 (m, 2H, MnP(Me)$_2$CH$_2$CH$_2$PMe$_2$), 0.96 (d, 6H, $^2$J$_{HP}$ 3.8 Hz, MnP(PCH$_3$)$_2$CH$_2$CH$_2$PMe$_2$), 0.89 (d, 6H, $^2$J$_{HP}$

Different batches of syntheses resulted in varying 31 : 32 ratios, ranging from 5 : 3 to 1 : 20.
2.8 Hz, MnP(Me)\(_2\)CH\(_2\)CH\(_2\)P(PC\(_3\)H\(_3\))\(_2\)), –15.72 (p of d, 1H, \(^2J\)\(_{H,P}\) 48.8 Hz, \(^2J\)\(_{H,P}\) 12.9 Hz, Mn\(H\)). \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 151 MHz, 298 K): δ 38.09 (s, MnP(Me)\(_2\)CH\(_2\)C\(_2\)H\(_2\)PMe\(_2\)), 34.33 (p, \(^1J\)\(_{C,P}\) 11.9 Hz, P\(_C\)H\(_2\)-chelating), 32.02 (s, P\(_C\)H\(_3\)-chelating), 26.50 (d of d, \(^1J\)\(_{C,P}\) 13.4 Hz, \(^2J\)\(_{C,P}\) 7.3 Hz, MnP(Me)\(_2\)CH\(_2\)CH\(_2\)PMe\(_2\)), 24.84 (d, \(^1J\)\(_{C,P}\) 9.4 Hz, MnP(P\(_C\)H\(_3\))\(_2\)CH\(_2\)CH\(_2\)PMe\(_2\)), 24.62 (s, P\(_C\)H\(_3\)-chelating), 13.95 (d, \(^1J\)\(_{C,P}\) 16.0 Hz, MnP(Me)\(_2\)CH\(_2\)CH\(_2\)P(P\(_C\)H\(_3\))\(_2\)).\(^{31}\)P\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 243 MHz, 298 K): δ 79.31 (s, chelating P), 28.40 (s, MnP(Me)\(_2\)CH\(_2\)CH\(_2\)PMe\(_2\)), –48.90 (d, \(^3J\)\(_{P,P}\) 14.1 Hz, MnP(Me)\(_2\)CH\(_2\)CH\(_2\)PMe\(_2\)).

**Synthesis of [(dmpe)\(_2\)MnH(PHPh\(_2\))] (33):** 199.0 mg (0.52 mmol) of [(dmpe)\(_2\)MnH(C\(_2\)H\(_4\))] (10) was dissolved in 20 mL of toluene and placed in a 50 mL storage flask. To this solution was added 192.8 mg (1.04 mmol) of HPPh\(_2\). The reaction mixture was stirred at 90 °C for 2 days to form a dirty brownish solution, and the solvent was then removed in vacuo. The brown solid was dissolved in a minimal amount of hexanes and residual solid was removed by centrifugation. After allowing to sit for a week at –30 °C, very dark yellow (X-ray quality) crystals were formed of 33 (57 mg, 0.11 mg, 20%) in >95 % purity. Selected NMR spectra are as follows: \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz, 298 K): δ 7.54 (app. t, 4H, \(^3J\)\(_{H,H}\) 7.9 Hz, \(^3J\)\(_{H,P}\) 7.3 Hz, o), 7.28 (d of m, 1H, \(^1J\)\(_{H,P}\) 284 Hz, P\(H\)), 7.02 (t, 4H, \(^3J\)\(_{H,H}\) 7.3 Hz, m), 6.95 (t, 2H, \(^3J\)\(_{H,H}\) 7.4 Hz, p), 1.52 (m, 8H, P\(_C\)H\(_2\)), 1.29 (s, 12H, P\(_C\)H\(_3\)), 1.27 (s, 12H, P\(_C\)H\(_3\)), –14.08 (p of d, 1H, \(^2J\)\(_{H,P}\) 50.7 Hz, \(^2J\)\(_{H,P}\) 11.4 Hz, Mn\(H\)). \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 151 MHz, 298 K): δ 149.06 (d, \(^1J\)\(_{C,P}\) 15.6 Hz, i), 131.71 (d, \(^2J\)\(_{C,P}\) 9.3 Hz, o), 127.05 (s, p), 33.36 (p, \(^1J\)\(_{C,P}\) 12.0 Hz, P\(_C\)H\(_2\)), 31.06 (s, P\(_C\)H\(_3\)), 21.46 (s, P\(_C\)H\(_3\)). \(^{31}\)P\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 243 MHz, 298 K): δ 79.34 (s, 4P, dmpe), 63.12 (s, 1P, PHPh\(_2\)).

**Synthesis of [(dmpe)\(_2\)MnH(SnPh\(_3\))] (34):** Method a) 111.4 mg (0.29 mmol) of [(dmpe)\(_2\)MnH(C\(_2\)H\(_4\))] (10) was dissolved in 10 mL of benzene. To this solution was added 215.0 mg (0.61 mmol) of HSnPh\(_3\) dissolved in 7 mL of benzene. The combined (17 mL) solution began turning green within a few minutes of stirring at room temperature. This solution was stirred overnight at room temperature, followed by
overnight again at 60 °C, forming a clear, pine green solution. The solvent was removed
in vacuo to yield a light green solid, which slowly turned white upon continued exposure
to vacuum (the white solid was identified by NMR spectroscopy as SnPh₄). X-ray quality
crystals (large turquoise blocks) were obtained by dissolving the light green solid in a
minimal amount of toluene and allowing the resulting solution to sit at –30 °C for a week.
A yield was not obtained because the complex was unstable upon exposure to vacuum.

Method b) 11.1 mg (0.03 mmol) of [(dmpe)₂MnH(C₂H₄)] (10) and 20.2 mg (0.06 mmol)
of HSnPh₃ were dissolved in approx. 0.6 mL of C₆D₆. The resulting solution was heating
at 65 °C overnight, and analyzed by NMR spectroscopy in situ. Selected NMR data
tentatively assigned as arising from 34 are as follows: $^1$H NMR (C₆D₆, 600 MHz,

Reaction of [(dmpe)₂MnH(C₂H₄)] (10) with HSn°Bu₃: 17.9 mg (0.05 mmol) of
[(dmpe)₂MnH(C₂H₄)] (10) and 25.7 mg (0.09 mmol) of HSn°Bu₃ were dissolved in
approx. 0.06 mL of C₆D₆, and the resulting solution was heated overnight at 60 °C, and
the resulting dark orange solution was analyzed by NMR spectroscopy in situ. Selected
NMR data tentatively assigned as arising from a paramagnetic Mn-containing species are
as follows: $^1$H NMR (C₆D₆, 600 MHz, 298 K): δ 4.01 (br. s), –1.15 (br. s), –3.67 (br. s),
–9.01 (br. s), –13.23 (br. s).
Appendix 1

Supplementary Information Related to Chapter 7

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</table>
Figures Showing Calculated Structures

**Figure A.1:** Calculated structures of, from left to right, two isomers of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHPh(N}^i\text{PrCHN}^i\text{Pr})\}]$ ($25^{\text{Ph,H}}$) and two isomers of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHEt(N}^i\text{PrCHN}^i\text{Pr})\}]$ ($25^{\text{Et,H}}$).

**Figure A.2:** Calculated structures of, from left to right, trans-$[(\text{dmpe})_2\text{Mn(CO)}(\kappa^1\text{-O}_2\text{CH})]$ (26) and trans-$[(\text{dmpe})_2\text{MnH(CO)}]$ (27).
Figures Showing Superimposed Calculated and X-ray Structures

**Figure A.3:** Superimposed calculated (red) and X-ray (blue and green) structures of, from left to right, [(dmpe)$_2$Mn{$κ^2$-SiHPh(N$^i$PrCHN$^i$Pr)}] (25$^{Ph,H}$) and trans-[(dmpe)$_2$Mn(CO)($κ^1$-O$_2$CH)] (26). The two X-ray structures in each figure are from two independent and essentially isostructural molecules in the unit cell.

### Tables of Calculated and Crystallographically Determined Bond Lengths, Mayer Bond Orders, and Angles

**Table A.1:** Selected Distances (Å) (and Mayer Bond Orders) for DFT Calculated or XRD Structures of $κ^2$-amidinylsilyl Complexes 25$^{R,H}$.

<table>
<thead>
<tr>
<th>Complex (L = dmpe)</th>
<th>Mn-Si</th>
<th>Mn-N</th>
<th>Si-N</th>
<th>Si-H</th>
<th>Si-C</th>
<th>NC-N$_{Si}$</th>
<th>NC-N$_{Mn}$</th>
<th>C$_{Pr}$-N$_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[L$_2$Mn[$κ^2$-$\text{SiHPh}(\text{N}^i\text{PrCHN}^i\text{Pr})]$]</td>
<td>2.32 (0.95)</td>
<td>2.12 (0.59)</td>
<td>1.82 (0.74)</td>
<td>1.53 (0.74)</td>
<td>1.93 (0.81)</td>
<td>1.35 (1.23)</td>
<td>1.31 (1.50)</td>
<td>1.47, 1.48 (0.89, 0.92)</td>
</tr>
<tr>
<td>(25$^{Ph,H}$) isomer 1 (DFT)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[L$_2$Mn[$κ^2$-$\text{SiHPh}(\text{N}^i\text{PrCHN}^i\text{Pr})]$]</td>
<td>2.32 (0.93)</td>
<td>2.12 (0.58)</td>
<td>1.82 (0.74)</td>
<td>1.53 (0.75)</td>
<td>1.93 (0.80)</td>
<td>1.34 (1.24)</td>
<td>1.31 (1.50)</td>
<td>1.47, 1.48 (0.90, 0.92)</td>
</tr>
<tr>
<td>(25$^{Ph,H}$) isomer 2 (DFT)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>[L$_2$Mn[$κ^2$-$\text{SiHPh}(\text{N}^i\text{PrCHN}^i\text{Pr})]$]</td>
<td>2.347(1), 2.358(1)</td>
<td>2.137(3), 2.141(3)</td>
<td>1.805(3), 1.813(3)</td>
<td>1.45(4), 1.47(5)</td>
<td>1.934(4), 1.939(3)</td>
<td>1.350(4), 1.350(5)</td>
<td>1.296(6), 1.299(5)</td>
<td>1.480(5), 1.492(4)</td>
</tr>
<tr>
<td>(25$^{Ph,H}$) (XRD)</td>
<td></td>
<td></td>
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<tr>
<td>[L$_2$Mn[$κ^2$-$\text{SiHPh}(\text{N}^i\text{PrCHN}^i\text{Pr})]$]</td>
<td>2.32 (0.95)</td>
<td>2.13 (0.59)</td>
<td>1.83 (0.70)</td>
<td>1.54 (0.75)</td>
<td>1.94 (0.67)</td>
<td>1.34 (1.25)</td>
<td>1.31 (1.50)</td>
<td>1.47, 1.48 (0.90, 0.93)</td>
</tr>
<tr>
<td>(25$^{Ph,H}$) isomer 1 (DFT)</td>
<td></td>
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<tr>
<td>[L$_2$Mn[$κ^2$-$\text{SiHPh}(\text{N}^i\text{PrCHN}^i\text{Pr})]$]</td>
<td>2.32 (0.93)</td>
<td>2.13 (0.59)</td>
<td>1.83 (0.69)</td>
<td>1.53 (0.75)</td>
<td>1.94 (0.67)</td>
<td>1.34 (1.24)</td>
<td>1.31 (1.50)</td>
<td>1.47, 1.48 (0.90, 0.92)</td>
</tr>
<tr>
<td>(25$^{Ph,H}$) isomer 2 (DFT)</td>
<td></td>
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<td></td>
<td></td>
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</tbody>
</table>

*The X-ray structure of 25$^{Ph,H}$ includes two independent and essentially isostructural structures in the asymmetric unit and the range of listed values encompasses these two structures.*
Table A.2: Selected Angles (°) for DFT Calculated or XRD Structures of κ²-amidinylsilyl Complexes 25^{R,H}.

<table>
<thead>
<tr>
<th>Complex (L = dmpe)</th>
<th>Mn–Si–R</th>
<th>Si–Mn–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHPh}(N^\text{iPr}CHN^\text{iPr})}]^{(25\text{Ph,H})}) isomer 1 (DFT)</td>
<td>H: 118.9, C: 136.5, N: 100.3</td>
<td>80.9</td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHPh}(N^\text{iPr}CHN^\text{iPr})}]^{(25\text{Ph,H})}) isomer 2 (DFT)</td>
<td>H: 119.5, C: 134.7, N: 100.7</td>
<td>80.5</td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHPh}(N^\text{iPr}CHN^\text{iPr})}]^{(25\text{Ph,H})}) (XRD)</td>
<td>H: 118(2), 119(2), C: 132.8(1), 136.4(1), N: 100.5(1), 100.6(1)</td>
<td>79.40(9), 80.13(8)</td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHEt}(N^\text{iPr}CHN^\text{iPr})}]^{(25\text{Et,H})}) isomer 1 (DFT)</td>
<td>H: 121.1, C: 129.1, N: 100.5</td>
<td>80.8</td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHEt}(N^\text{iPr}CHN^\text{iPr})}]^{(25\text{Et,H})}) isomer 2 (DFT)</td>
<td>H: 121.2, C: 128.6, N: 100.6</td>
<td>80.4</td>
</tr>
</tbody>
</table>

a. The X-ray structure of 25^{Ph,H} includes two independent and essentially isostructural structures in the asymmetric unit and the range of listed values encompasses these two structures.

Table A.3: Selected Angles (°) and Distances (Å) (and Mayer Bond Orders) for DFT Calculated \{or XRD\} Structures of Formate Complex 26.\(^a\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mn–C</th>
<th>Mn–O</th>
<th>O–C(_{Mn})</th>
<th>O(_{Mv})–C</th>
<th>O–C(_{isoaw})</th>
<th>C–Mn–O</th>
<th>Mn–O–C</th>
<th>O–C–O</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[\text{dmpe})_2\text{Mn}(CO)(\kappa^1\text{-O})^{(26)}CH)]</td>
<td>1.73 (1.65)</td>
<td>2.10 (0.48)</td>
<td>1.19 (1.86)</td>
<td>1.29 (1.33)</td>
<td>1.24 (1.65)</td>
<td>171.3</td>
<td>129.6</td>
<td>128.7</td>
</tr>
<tr>
<td>(26)</td>
<td>1.74(1), 2.086(1), 1.175(2), 1.266(2), 1.275(2)</td>
<td>1.191(2), 1.229(2), 1.237(2), 1.237(2)</td>
<td>172.23(5), 133.53(9), 133.78(9), 128.8(1), 128.9(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| trans-[\text{dmpe})_2\text{Mn}(CO)(\kappa^1\text{-O})^{(26)}CH)] | 1.73 (1.65) | 2.10 (0.48) | 1.19 (1.86) | 1.29 (1.33) | 1.24 (1.65) | 171.3 | 129.6 | 128.7 |
| (26) | 1.74(1), 2.086(1), 1.175(2), 1.266(2), 1.275(2) | 1.191(2), 1.229(2), 1.237(2), 1.237(2) | 172.23(5), 133.53(9), 133.78(9), 128.8(1), 128.9(1) |

a. The X-ray structure of 26 includes two independent and essentially isostructural structures in the asymmetric unit and the range of listed values encompasses these two structures.

Tables of Total Bonding Energies and Thermodynamic Parameters for Calculated Structures

Table A.4: Total bonding energy (E), Enthalpy (H), Entropy (S), and Gibbs Free Energy (G) at 298 K for DFT Calculated Structures of κ²-amidinylsilyl Complexes 25^{R,H}.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E (kJ mol(^{-1}))</th>
<th>H (kJ mol(^{-1}))</th>
<th>S (kJ mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHPh}(N^\text{Pr}CHN^\text{Pr})}]^{(25\text{Ph,H})}) isomer 1</td>
<td>−46182.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHPh}(N^\text{Pr}CHN^\text{Pr})}]^{(25\text{Ph,H})}) isomer 2</td>
<td>−46181.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHEt}(N^\text{Pr}CHN^\text{Pr})}]^{(25\text{Et,H})}) isomer 1</td>
<td></td>
<td>−42722.45</td>
<td></td>
</tr>
<tr>
<td>([\text{dmpe})_2\text{Mn}{\kappa^2\text{-SiHEt}(N^\text{Pr}CHN^\text{Pr})}]^{(25\text{Et,H})}) isomer 2</td>
<td></td>
<td>−42720.65</td>
<td></td>
</tr>
</tbody>
</table>

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Table A.5: Total bonding energy (E), Enthalpy (H), Entropy (S), and Gibbs Free Energy (G) at 298 K for DFT Calculated Structures of Formate Complex 26, and Products of CO₂ Abstraction from 26.

<table>
<thead>
<tr>
<th>Complex</th>
<th>E (kJ mol⁻¹)</th>
<th>H (kJ mol⁻¹)</th>
<th>S (J mol⁻¹ K⁻¹)</th>
<th>G (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[(dmpe)₂Mn(CO)(κ₁-O₂CH)] (26)</td>
<td>-29386.52</td>
<td>-28137.27</td>
<td>813.70</td>
<td>-28379.88</td>
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<td>trans-[(dmpe)₂MnH(CO)] (27)</td>
<td>-27089.63</td>
<td>-25893.17</td>
<td>765.5339</td>
<td>-26121.42</td>
</tr>
<tr>
<td>CO₂</td>
<td>-2231.96</td>
<td>-2192.90</td>
<td>219.8315</td>
<td>-2258.44</td>
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</table>

Tables of Hirshfeld Charges for Calculated Structures

Table A.6: Hirshfeld Charges for DFT Calculated Structures of κ²-amidinylsilyl Complexes 25.

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<tr>
<th>Complex</th>
<th>Mn</th>
<th>Si</th>
<th>Nᵣ</th>
<th>Nᵣ</th>
<th>Hᵣ</th>
<th>Nᵣ(C)</th>
<th>Nᵣ(C)</th>
<th>Cᵣ</th>
<th>Cᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(dmpe)₂Mn{κ²-SiHPh(NᵣPr)CHNᵣPr}] (25ᵣᵣ) isomer 1</td>
<td>-0.225</td>
<td>0.192</td>
<td>-0.117</td>
<td>-0.098</td>
<td>-0.104</td>
<td>0.042</td>
<td>0.066</td>
<td>-0.087</td>
<td>0.014, 0.021</td>
</tr>
<tr>
<td>[(dmpe)₂Mn{κ²-SiHPh(NᵣPr)CHNᵣPr}] (25ᵣᵣ) isomer 2</td>
<td>-0.225</td>
<td>0.191</td>
<td>-0.116</td>
<td>-0.100</td>
<td>-0.103</td>
<td>0.042</td>
<td>0.064</td>
<td>-0.089</td>
<td>0.015, 0.022</td>
</tr>
<tr>
<td>[(dmpe)₂Mn{κ²-SiHEt(NᵣPr)CHNᵣPr}] (25ᵣᵣ) isomer 1</td>
<td>-0.227</td>
<td>0.195</td>
<td>-0.117</td>
<td>-0.100</td>
<td>-0.108</td>
<td>0.041</td>
<td>0.064</td>
<td>-0.160</td>
<td>0.014, 0.023</td>
</tr>
<tr>
<td>[(dmpe)₂Mn{κ²-SiHEt(NᵣPr)CHNᵣPr}] (25ᵣᵣ) isomer 2</td>
<td>-0.226</td>
<td>0.195</td>
<td>-0.118</td>
<td>-0.100</td>
<td>-0.106</td>
<td>0.041</td>
<td>0.065</td>
<td>-0.160</td>
<td>0.015, 0.023</td>
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</table>

Table A.7: Hirshfeld Charges for DFT Calculated Structure of Formate Complex 26.

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<tr>
<th>Complex</th>
<th>Mn</th>
<th>Cᵣ(CO)</th>
<th>Oᵣ(CO)</th>
<th>Oᵣ(CO)</th>
<th>Oᵣ(C)</th>
<th>Oᵣ(C)</th>
<th>Oᵣ(C)</th>
<th>Oᵣ(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[(dmpe)₀Mn(CO)(κ₁-O₂CH)] (26)</td>
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<td>0.000</td>
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Tables of Crystal Data and Crystal Structure Refinement

**Table A.8:** Crystal and structure refinement data for [(dmpe)$_2$Mn{k$^2$-SiHPh(N$i$PrCHN$i$Pr)}] ($25^{ph,H}$).

<table>
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<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
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<td>MnHSiPh_CD1</td>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{25}$H$</em>{53}$MnN$_2$P$_4$Si</td>
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<td>Formula weight</td>
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<td>Temperature/K</td>
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<td>Crystal system</td>
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<td>Space group</td>
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<td>b/Å</td>
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<tr>
<td>c/Å</td>
<td>18.7841(7)</td>
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<td>$\rho_{calc}$/g/cm$^3$</td>
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<tr>
<td>Radiation</td>
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<td>2Θ range for data collection/°</td>
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<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<td>Data/restraints/parameters</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>Final R indexes [I$&gt;$2σ (I)]</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å$^{-3}$</td>
<td>2.14/-2.24</td>
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</table>
Table A.9: Crystal and structure refinement data for trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26).

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<td>Crystal size/mm$^3$</td>
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<td>Radiation</td>
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<td>2Θ range for data collection/°</td>
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<td>Independent reflections</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>Final R indexes [all data]</td>
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Selected NMR Spectra for Complexes 25$^{R,H}$ and 26

Figure A.4: $^1$H NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHPh(N}^\text{iPrCHN}^\text{iPr}\}\}]$ (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (600 MHz, 298 K).

Figure A.5: Expanded aromatic region of the $^1$H NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHPh(N}^\text{iPrCHN}^\text{iPr}\}\}]$ (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.6: Expanded SiH region of the $^1$H NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiHPh(N$i^*$PrCHN$i^*$Pr)} ($^{25}$Ph,$^1$H)] (25$^{25}$Ph,$^1$H) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.7: Expanded SiH region of the $^1$H{${}^{31}$P} NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiHPh(N$i^*$PrCHN$i^*$Pr)}] (25$^{25}$Ph,$^1$H) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.8: Expanded N(CHMe₂) region of the $^1$H NMR spectrum of [(dmpe)$_2$Mn{$^2$-SiHPh(N'iPrCHN'iPr)}] (25$^{\text{PhH}}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.9: Expanded high frequency alkyl region of the $^1$H NMR spectrum of [(dmpe)$_2$Mn{$^2$-SiHPh(N'iPrCHN'iPr)}] (25$^{\text{PhH}}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.10: Expanded low frequency alkyl region of the $^1$H NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiHPh(N$i$PrCHN$i$Pr)}] ($^{25\text{Ph,H}}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.11: $^{13}$C{$^1$H} NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiHPh(N$i$PrCHN$i$Pr)}] ($^{25\text{Ph,H}}$) in C$_6$D$_6$ (151 MHz, 298 K).
Figure A.12: Expanded aromatic region of the $^{13}$C{^1}H NMR spectrum of [(dmpe)$_2$Mn{κ$_2$-SiHPh(N$i$PrCHN$i$Pr)}] ($^{25}$Ph$_2^H$) in C$_6$D$_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.13: Expanded N(CHMe$_2$) region of the $^{13}$C{^1}H NMR spectrum of [(dmpe)$_2$Mn{κ$_2$-SiHPh(N$i$PrCHN$i$Pr)}] ($^{25}$Ph$_2^H$) in C$_6$D$_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.14: Expanded high frequency alkyl region of the $^{13}$C{$^{1}$H} NMR spectrum of $\text{[(dmpe)$_2$Mn{$^{2}$-SiHPh(N$_{\text{iPrCHN$_{\text{iPr}$)}}}$)]} (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.15: Expanded low frequency alkyl region of the $^{13}$C{$^{1}$H} NMR spectrum of $\text{[(dmpe)$_2$Mn{$^{2}$-SiHPh(N$_{\text{iPrCHN$_{\text{iPr}$)}}}$)]} (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.16: $^{29}$Si{$^1$H} NMR spectrum of \([\text{(dmpe)}_2\text{Mn}\{\kappa^2-\text{SiHPh(N}^\text{iPrCHN}^\text{iPr)}\}] (25^{\text{Ph,H}})\) in C$_6$D$_6$ (119 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.17: $^{29}$Si–{$^1$H} HMBC NMR spectrum of \([\text{(dmpe)}_2\text{Mn}\{\kappa^2-\text{SiHPh(N}^\text{iPrCHN}^\text{iPr)}\}] (25^{\text{Ph,H}})\) in C$_6$D$_6$ (119 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.18: Expanded aromatic region of the $^{29}\text{Si}^1\text{H}$ HMBC NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHPh(N}^i\text{PrCN}^i\text{Pr)}\}]$ (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (119 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.19: $^{31}\text{P}^1\text{H}$ NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2\text{-SiHPh(N}^i\text{PrCN}^i\text{Pr)}\}]$ (25$^{\text{Ph,H}}$) in C$_6$D$_6$ (243 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.20: $^1$H NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiH$^\text{Bu}$Bu(N$i^\text{Pr}$CH$i^\text{Pr}$)] (25$^\text{Bu,H}$) in C$_6$D$_6$ (600 MHz, 298 K).

Figure A.21: Expanded NC(H)N region of the $^1$H NMR spectrum of [(dmpe)$_2$Mn{κ$^2$-SiH$^\text{Bu}$Bu(N$i^\text{Pr}$CH$i^\text{Pr}$)] (25$^\text{Bu,H}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.22: Expanded SiH region of the $^1$H NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2$-
SiH$^n\text{Bu}(N^i\text{PrCHN}^i\text{Pr})\}]$ (25$^{Bu,H}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks
from the dominant and minor isomers, respectively.

Figure A.23: Expanded SiH region of the $^1$H$^{^{31}P}$ NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2$-
SiH$^n\text{Bu}(N^i\text{PrCHN}^i\text{Pr})\}]$ (25$^{Bu,H}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks
from the dominant and minor isomers, respectively.
Figure A.24: Expanded N(CHMe₂) region of the ¹H NMR spectrum of [(dmpe)₂Mn{κ²-SiH₆Bu(NⁱPrCHNⁱPr)}] (25Bu₆H) in C₆D₆ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.25: Expanded high frequency alkyl region of the ¹H NMR spectrum of [(dmpe)₂Mn{κ²-SiH₆Bu(NⁱPrCHNⁱPr)}] (25Bu₆H) in C₆D₆ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.26: Expanded low frequency region of the $^1$H NMR spectrum of $\text{[(dmpe)}_2\text{Mn}\{\kappa^2\text{-SiH}^{\text{Bu}}\text{Bu}(N'^{\text{Pr}}\text{PrCHN}'\text{Pr})\}]$ (25$^{\text{Bu,H}}$) in C$_6$D$_6$ (600 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.27: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{[(dmpe)}_2\text{Mn}\{\kappa^2\text{-SiH}^{\text{Bu}}\text{Bu}(N'^{\text{Pr}}\text{PrCHN}'\text{Pr})\}]$ (25$^{\text{Bu,H}}$) in C$_6$D$_6$ (151 MHz, 298 K).
Figure A.28: Expanded high frequency alkyl region of the $^{13}C\{^1H\}$ NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2-\text{SiH}^n\text{Bu}(N^i\text{PrCHN}^i\text{Pr})\}]$ (25$^{Bu,H}$) in $C_6D_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.29: Expanded middle frequency alkyl region of the $^{13}C\{^1H\}$ NMR spectrum of $[(\text{dmpe})_2\text{Mn}\{\kappa^2-\text{SiH}^n\text{Bu}(N^i\text{PrCHN}^i\text{Pr})\}]$ (25$^{Bu,H}$) in $C_6D_6$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.30: Expanded low frequency alkyl region of the $^{13}{\text{C}}^{1}{\text{H}}$ NMR spectrum of $\left[\left(\text{dmpe}\right)_{2}\text{Mn}\{\kappa^{2}-\text{SiH}^{\text{Bu}}\text{Bu(N'PrCHN'Pr)}\}\right]$ (25$^{\text{Bu,H}}$) in C$_{6}$D$_{6}$ (151 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.31: $^{29}\text{Si}^{1}{\text{H}}$ NMR spectrum of $\left[\left(\text{dmpe}\right)_{2}\text{Mn}\{\kappa^{2}-\text{SiH}^{\text{Bu}}\text{Bu(N'PrCHN'Pr)}\}\right]$ (25$^{\text{Bu,H}}$) in C$_{6}$D$_{6}$ (119 MHz, 298 K).
Figure A.32: $^{29}$Si–^1^H HSQC NMR spectrum of [(dmpe)$_2$Mn{$\kappa^2$-SiH$^n$Bu(N$i$PrCHN$i$Pr)}] (25$^{Bu,H}$) in C$_6$D$_6$ (119 MHz, 298 K).

Figure A.33: Expanded SiH region of the $^{29}$Si–^1^H HSQC NMR spectrum of [(dmpe)$_2$Mn{$\kappa^2$-SiH$^n$Bu(N$i$PrCHN$i$Pr)}] (25$^{Bu,H}$) in C$_6$D$_6$ (119 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.
Figure A.34: $^{31}$P/$^1$H NMR spectrum of [(dmpe)$_2$Mn($^\kappa^2$-SiH$^8$Bu(N$i^i$PrCHN$i^i$Pr))] ($^{25}$Bu,$^H$) in C$_6$D$_6$ (243 MHz, 298 K). A and B represent peaks from the dominant and minor isomers, respectively.

Figure A.35: $^1$H NMR spectrum of trans-[(dmpe)$_2$Mn(CO)($^\kappa^1$-O$_2$CH)] (26) in C$_6$D$_6$ (600 MHz, 298 K).
Figure A.36: Expanded formyl region of the $^1$H NMR spectrum of trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (600 MHz, 298 K).

Figure A.37: Expanded alkyl region of the $^1$H NMR spectrum of trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (600 MHz, 298 K).
Figure A.38: $^{13}\text{C}^{1\text{H}}$ NMR spectrum of \textit{trans-}[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (151 MHz, 298 K).

Figure A.39: Expanded formyl region of the $^{13}\text{C}^{1\text{H}}$ NMR spectrum of \textit{trans-}[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (151 MHz, 298 K).
Figure A.40: Expanded alkyl region of the $^{13}\text{C}$-$^1\text{H}$ NMR spectrum of trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (151 MHz, 298 K).

Figure A.41: $^{31}\text{P}$-$^1\text{H}$ NMR spectrum of trans-[(dmpe)$_2$Mn(CO)(κ$^1$-O$_2$CH)] (26) in C$_6$D$_6$ (243 MHz, 298 K).
Appendix 2

Supplementary Information Related to Chapter 8

Figures in this chapter have been reprinted (adapted) from Price, J. S.; Emslie, D. J. H. Interconverstion and reactivity of manganese silyl, silylene, and silene complexes, Chem. Sci. 2019, Advance Articles, DOI: 10.1039/C9SC04513A. Published by The Royal Society of Chemistry.

**Figure B.1:** NMR spectra \{298 K, C₆D₆, 600 (¹H), 77 (²H), 151 (¹³C{¹H}), or 175 (¹³C{¹H})-uDEFT and DEPTq) MHz\} for reaction mixtures from catalytic hydrosilylation of H₂SiEt₂ by ethylene or d₄-ethylene using [(dmpe)₂MnH(C₂H₄)] (10) as a precatalyst (7 mol% catalyst load, 4 days at 60 °C, n_{ethylene} \approx 40 \times n_{H₂SiEt₂}, initial pressure of C₂H₄ and C₂D₄ are c. 1.7 and 1.0 atm, respectively). Left: various regions of, from bottom to top, the ²H, ²H{¹H}, and ¹H NMR spectra of the reaction involving d₄-ethylene, and the ¹H NMR spectrum of the reaction involving protonated ethylene (unknown hydrosilane...
byproduct not shown). Right: the ethyl region of, from bottom to top, the uDEFT $^{13}$C\{\textsuperscript{1}H\}, DEPTq $^{13}$C\{\textsuperscript{1}H\}, and $^{13}$C\{\textsuperscript{1}H\} NMR spectra of the reaction involving $d_4$-ethylene, and the $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of the reaction involving protonated ethylene. * represents peaks tentatively assigned to the ethyl environments of HSiViEt\textsubscript{2}. In all cases (except the $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of the reaction involving protonated ethylene), NMR spectra were collected after vacuum distillation to remove manganese-containing species. Top: hydrosilane product distribution from hydrosilylation of ethylene (1\textsuperscript{st} row) or $d_4$-ethylene (2\textsuperscript{nd} row) by H\textsubscript{2}SiEt\textsubscript{2}.

**Analysis of Figure B.1 (Hydrosilylation of $d_4$-ethylene with H\textsubscript{2}SiEt\textsubscript{2})**

The $^2$H NMR spectrum of $d_4$-HSiEt\textsubscript{3} included 2 peaks at 0.90 (–CD\textsubscript{2}CD\textsubscript{2}H) and 0.46 (–CD\textsubscript{2}CD\textsubscript{2}H) ppm in a 2 : 1.9 ratio, with coupling constants to a single $^1$H environment of 2.0 Hz (2-bond) and 0.8 Hz (3-bond), respectively. The slight deviation from the expected 2 : 2 ratio is presumably due to the presence of a small amount of the minor (3\%) isotopomer HSiEt\textsubscript{2}(–CDHCD\textsubscript{3}) \{the major (97\%) isotopomer is HSiEt\textsubscript{2}(–CD\textsubscript{2}CD\textsubscript{2}H)\}. Furthermore, the $^1$H NMR spectrum contained a pentet at 3.89 ppm ($^3$J\textsubscript{H,H} = 3.2 Hz) due to the SiH environment (from coupling to four Et\textsubscript{a} protons, isotopically shifted 0.005 ppm upfield) and a broad singlet at 0.93 ppm due to the –CD\textsubscript{2}CD\textsubscript{2}H environment (isotopically shifted by 0.05 ppm upfield relative to the fully protonated Et\textsubscript{b} protons), along with two signals from the two environments in the fully protonated –CH\textsubscript{2}CH\textsubscript{3} substituents. The $^{13}$C\{\textsuperscript{1}H\} NMR spectrum features an isotopically shifted 1:2:3:2:1 pentet ($^1$J\textsubscript{C,D} = 19 Hz) for the –CD\textsubscript{2}CD\textsubscript{2}H environment, with 1-bond coupling to two deuterium atoms (at 7.64 ppm relative to 8.43 ppm for the analogous singlet from the –CH\textsubscript{2}CH\textsubscript{3} environment). Furthermore, an isotopically shifted –CD\textsubscript{2}CD\textsubscript{2}H environment was observed as a 1:2:3:2:1 pentet ($^1$J\textsubscript{C,D} = 18 Hz) in the $^{13}$C\{\textsuperscript{1}H\} DEPTq and uDEFT NMR spectra (at 1.83 ppm relative to 2.79 ppm for the analogous –CH\textsubscript{2}CH\textsubscript{3} environment). Also present in the $^{13}$C\{\textsuperscript{1}H\}-uDEFT NMR spectrum was a 1:1:1 triplet ($^1$J\textsubscript{C,D} = 18 Hz) at 2.11 ppm from the –CDHCD\textsubscript{3} environment of the minor isotopomer; the similar intensity of the 1:1:1 triplet from a small amount of HSiEt\textsubscript{2}(–CDHCD\textsubscript{3}) to the
1:2:3:2:1 pentet from the dominant isotopomer HSiEt$_2$–CD$_2$CD$_2$H is due to a combination of (for the former environment) a more concentrated signal (triplet vs. pentet), shorter relaxation time, and presence of NOE signal enhancement due to the adjacent $^1$H environment. No signal was observed for the –CDHCD$_3$ environment in the minor isotopomer, presumably because it would be spread into a septet, have longer relaxation time, and no NOE signal enhancement due to no adjacent $^1$H environments.

**Figure B.2:** NMR spectra \{298 K, C$_6$D$_6$, 600 ($^1$H), 77 ($^2$H), 151 ($^{13}$C{$^1$H}), or 175 ($^{13}$C{$^1$H})-uDEPT and DEPTq MHz\} for reaction mixtures from catalytic hydrosilylation of H$_3$Si$i^6$Bu by ethylene or $d_4$-ethylene using [(dmpe)$_2$MnH(C$_2$H$_4$)] (10) as a precatalyst (7 mol% catalyst load, 4 days at 60 °C, $n_{\text{ethylen}} \approx 40 \times n_{\text{H3SiBu}}$, initial pressure of C$_2$H$_4$ and C$_2$D$_4$ are c. 1.7 and 1.0 atm, respectively). Left: various regions of, from bottom to top, the $^2$H, $^2$H{$^1$H}, and $^1$H NMR spectra of the reaction involving $d_4$-ethylene, and $^1$H NMR spectrum of the reaction involving ethylene (unknown hydrosilane byproduct not shown). Right: the ethyl region of, from bottom to top, the uDEFT $^{13}$C{$^1$H}, DEPTq
\( ^{13}\text{C} \{^1\text{H}\} \), and \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectra of the reaction involving \( d_4\)-ethylene, and the \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectrum of the reaction involving protonated ethylene. * indicate peaks tentatively assigned to the ethyl environments of HSiViEt\(^n\)Bu. NMR spectra were collected after Vacuum distillation removed manganese-containing species. Top: hydrosilane product distribution from hydrosilylation of ethylene (1\textsuperscript{st} row) or \( d_4\)-ethylene (2\textsuperscript{nd} row) by H\(_3\)Si\(^n\)Bu. The \( ^{13}\text{C} \{^1\text{H}\} \) NMR spectrum of the reaction involving protonated ethylene was from a reaction mixture allowed to react for 8 days.

*Analysis of Figure B.2 (Hydrosilylation of \( d_4\)-ethylene with H\(_3\)Si\(^n\)Bu)*

The \(^{2}\text{H}\) NMR spectrum included multiplets at 0.91-0.92 ppm and 0.48-0.50 ppm in a 3 : 2 ratio for the beta and alpha ethyl environments, respectively, of the deuterated ethyl substituents in \( d_8\)-HSiEt\(^n\)Bu. Both multiplets were formed from two overlapping signals from the two potential isotope distributions. The two peaks, at 0.92 and 0.91 ppm, which compose the \( \beta \) multiplet, were both doublets with coupling of 2 and 0.8 Hz, to a single proton environment in a \( -\text{CD}_2\text{CD}_2\text{H} \) (2-bond coupling) or \( -\text{CDHCD}_3 \) (3-bond coupling) substituent, respectively. The multiplet for the alpha environment appears to be an overlapping singlet (from the \( -\text{CD}_2\text{CD}_2\text{H} \) environment) and doublet (from the \( -\text{CDHCD}_3 \) environment, due to 2-bond coupling to \(^1\text{H}\)), though a coupling constant for the latter could not be accurately determined. Given that one ethyl environment is nearly exclusively \( -\text{CD}_2\text{CD}_2\text{H} \), the observed relative integrations are consistent with a 1 : 5 ratio of \( -\text{CD}_2\text{CD}_2\text{H} : -\text{CDHCD}_3 \) isotope distributions in the other ethyl group. The \(^1\text{H}\) NMR spectrum contained an apparent quartet from the Si\(^\text{H} \) environment in \( d_8\)-HSiEt\(^n\)Bu, with a 1:3.4:4.1:1.7 pattern (\(^2J_{\text{H,H}} = 3.2\) Hz). This is consistent with overlapping 1:3:3:1 quartet (3.93 ppm) and 1:2:1 triplet (3.92 ppm) signals from the Si\(^\text{H} \) environments of the two isotopomers HSi(\( -\text{CD}_2\text{CD}_2\text{H} \))\(^n\)Bu (with three alpha protons) and HSi(\( -\text{CD}_2\text{CD}_2\text{H} \))^\(_2\)^\(^n\)Bu (with two alpha protons) in a 5 : 1 ratio (which would theoretically yield an apparent quartet with a 1:3.5:4.0:1.5 coupling pattern), which is also consistent with the \(^{2}\text{H}\) NMR integrations (and isotopically shifted upfield from the analogous signal in fully protonated HSiEt\(_2\)^\(^n\)Bu by 0.01 and 0.02 ppm, respectively). Also present in the \(^1\text{H}\)
NMR spectrum were two broad singlets at 0.95 and 0.52 ppm from the proton environments in the –CD₂CD₂H and –CDHCD₃ environments, respectively, in both cases isotopically shifted upfield from the respective fully protonated ethyl environments by 0.05 ppm. Signals from both isotopomers were observed in the ¹³C{¹H} NMR spectrum. The major signal in the β ethyl region was a 1:2:3:2:1 pentet at 7.73 ppm (¹J_D,C = 19 Hz, isotopically shifted upfield by 0.77 ppm from the fully protonated ethyl environment in HSiEt₂ⁿBu) due to the –CD₂CD₂H environment, and in the uDEFT ¹³C{¹H} spectrum, small spikes in the noise just to the right of this peak (and overlapping with the right portion of the peak) were observed which could be from the –CDHCD₃ environment, though it is small due to being more spread out (a septet) and lacking an adjacent ¹H environment (meaning that in addition to having a longer relaxation time, no NOE enhancement would be observed). The alpha ethyl environment is dominated by a 1:1:1 triplet (¹J_C,D = 18 Hz) at 2.47 ppm from the –CDHCD₃ environment (isotopically shifted upfield by 0.73 ppm from the fully protonated ethyl environment in HSiEt₂ⁿBu), with a multiplet just to the right which is consistent with two nearly-overlapping pentets at 2.22 and 2.20 ppm (¹J_C,D = 19 Hz) from the –CD₂CD₂H environments in the two isotopomers (isotopically shifted by 0.98 and 1.0 ppm, respectively, from the fully protonated ethyl environment in HSiEt₂ⁿBu). An additional 1:1:1 triplet at 3.00 ppm is from the –CDHCD₃ environment in the partially deuterated HSiEtViⁿBu byproduct.
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