# STUDIES ON
# ORGANO-PALLADIUM AND -PLATINUM COMPLEXES

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# ORGANO-PALLADIUM AND -PLATINUM COMPLEXES

By

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SCOPE AND CONTENTS:

Reaction of potassium tetrachloroplatinate with hexamethyl-(Dewar benzene) or 5-(1-substituted-ethyl)pentamethylcyclopentadienes (derived from the Dewar benzene), gave the pentamethylcyclopentadiene complex $\left[Pt(C_5Me_5H)Cl_2\right]$, the first chelating 1,3-diene complex to be reported. A mechanism for this reaction is proposed.

Other 1,3-diene-Pt(II) complexes were also obtained with some 5-substituted-pentamethylcyclopentadienes. The stereochemistries of these complexes were determined. The 5-vinylpentamethylcyclopentadiene platinum(II) complex underwent a hydrogen catalysed isomerisation reaction in which the isomer with the vinyl group <u>endo</u>- was transformed to that with the vinyl group <u>exo</u>- .

Reaction of palladium(II) with hexamethyl(Dewar benzene) or ligands derived from it did not give the pentamethylcyclopentadiene complex. Instead, on reaction with the corresponding cyclopentadienes, a series of 5-substituted-pentamethylcyclopentadiene complexes were obtained. 'H N.m.r. was used to determine their stereochemistries, and the geometry of the ligands in the complexes.

A "homocyclobutadiene" structure has been suggested for the above cyclopentadiene-Pd(II) and Pt(II) complexes to explain their stability and spectroscopic properties.

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# INTRODUCTION

# INTRODUCTION

Metals and their salts have long been used as catalysts in organic reactions. Reactions which commonly use transition metals and which are commercially important include hydrogenation of unsaturated organic compounds - olefins and acetylenes, isomerisation of olefins, polymerisation of olefins and acetylenes, etc. The role of organo-transition metal compounds as intermediates in such reactions is now being recognised.

Study of the formation, stability and reactions of the organometallic complexes, particularly those involving olefins and acetylenes, has thrown much light onto the mechanism of catalysis of organic reactions by transition metals. The transition metal provides a path of lower energy barrier for the reaction by its interaction with the reactants thereby causing suitable changes in the energy states and also by the arrangement of the reactants about the metal atom in a way most suitable for the reaction to proceed.

The greater understanding of organometallic chemistry has, in turn, stimulated much interest in homogeneous catalysis, which can be more efficient and convenient than heterogeneous catalysis where the reaction medium consists of two phases - a solid and a fluid phase.

The study of the complexes of olefins and acetylenes with transition metals is also interesting from the viewpoint of theoretical chemistry, since these complexes show new types of bonding and have provided challenges for the recent theories of bonding, including molecular orbital theory.

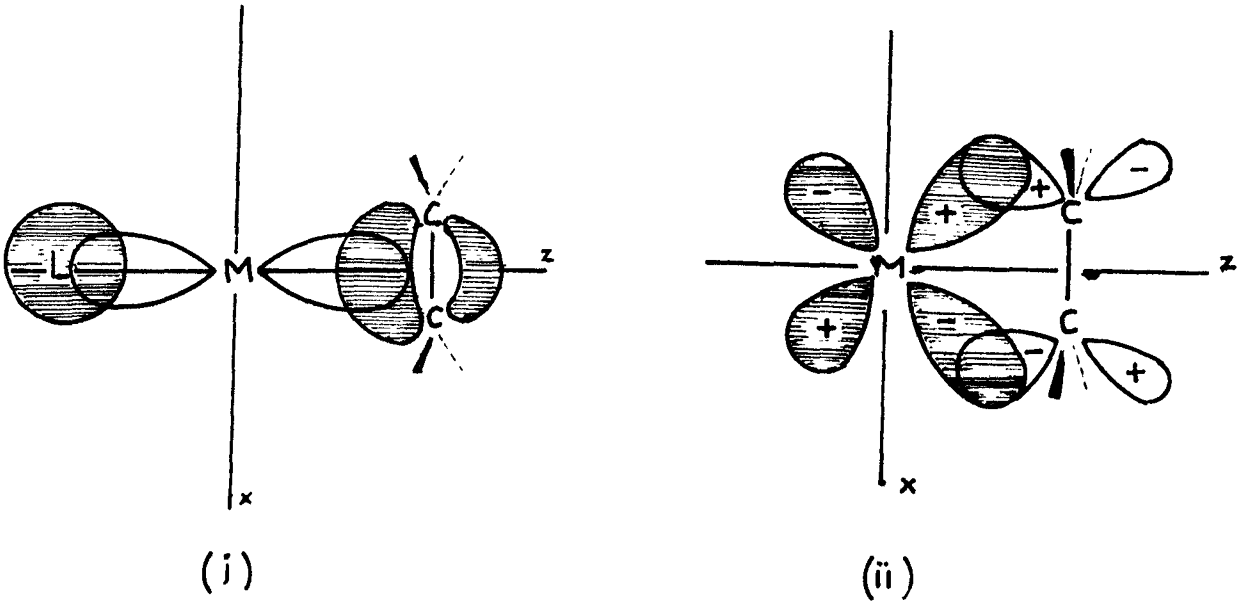
A brief discussion of the structure of and bonding in the various types of olefin-metal complexes is given in this introduction. Some of the relevant reactions of the complexes are also described.

I. Mono-olefin-metal complexes:

The first olefin-transition metal complex, $K\left[C_2H_4PtCl_3\right].H_20$, known as Zeise's salt, was prepared by Zeise in 1827[1]. Since then a very large number of olefin and acetylene complexes have been reported[2,3].

The currently accepted explanation of the bonding in the olefin-metal complexes was put forward by Chatt and Duncanson[4], who based their theory on the model proposed earlier by Dewar[5] to explain the bonding in olefin-$Ag^+$ complexes. This stimulated much research on the structures of the metal-olefin complexes[6].

The Dewar-Chatt-Duncanson approach was essentially to regard the bond between platinum and the olefin, in Zeise's salt, as consisting of two parts: (i) the formation of a $\sigma$-type bond by overlap of a vacant $5d6s6p^2$ hybrid orbital of Pt(II) with the $\pi$-orbitals of the olefin, and (ii) the formation of a $\pi$-type bond by overlap of the filled 5d orbitals of the metal with the olefin $\pi^*$-orbitals. The latter interaction could be strengthened if a 5d-6p hybrid, rather than a true 5d orbital was used. The situation is depicted in fig. 1.



(i) (ii)

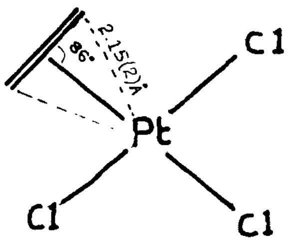
Fig. 1: Bonding in olefin complexes (e. g. Zeise's salt, $K[C_2H_4PtCl_3]$ (M=Pt, L=$Cl^-$)). Only one trans-ligand, L, is shown.

A necessary consequence of the Dewar-Chatt-Duncanson picture of bonding in olefin complexes is that by losing electron density from the bonding $\pi$-orbitals and having it returned to the antibonding $\pi^*$-orbitals, the olefinic C-C bond order will be decreased. This should be reflected as an increase in the C-C bond length and decrease in force constant and hence $\nu$(C=C) in the infrared. The magnitudes of these changes should be proportional to the strength of the metal-olefin bond, as defined by the amount of $\pi \rightarrow dsp^2$ and $\pi^* \leftarrow d_{(p)}$ interaction.

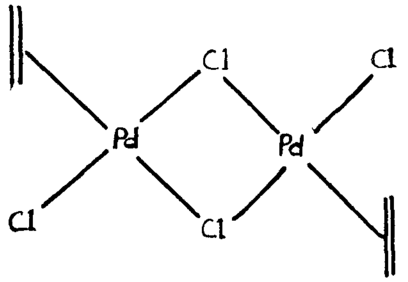
It has been observed that the $\nu_{C=C}$ is lowered by about 120 $cm^{-1}$ for various olefin complexes with platinum(II)[4,7]. The corresponding value of $\Delta\nu$(C=C) for palladium(II) is less, around 100 $cm^{-1}$ [8,9] and for silver (I) it is only about 60 $cm^{-1}$ [10]. An attempt to correlate $\Delta\nu$(C=C) with metal olefin bond strength was later given up[11]. It was realised that such correlations are at the best qualitative and could be used only as a rough guide to bond strength for a single olefin with different metals, because the C=C stretching vibrations are usually coupled to other modes, e.g. the in-plane $>CH_2$ scissoring motion in ethylene[12], and also the frequency is affected to varying degrees by the strain in the olefins[13] and the electronic effects due to the proximity of polar groups to the double bond. It has been suggested that for different olefins with a single metal, the metal-olefin stretching force constant serves as the best measure of the bond strength[7]. A normal coordinate analysis has indicated that bands at 408 (platinum) and 427 $cm^{-1}$ (palladium) are due to metal-ethylene stretches in Zeise's salt or its dimer and their palladium(II) analogues[12,7]. From this the force constants 2.25 and 2.14 mdynes/Å for platinum and palladium have been determined.

In principle, the olefin could bond to the metal either perpendicular to the coordination plane (using the $d_{xz}$ orbital for the $\pi$-backbonding, as shown in fig. 1) or coplanar with it (using the $d_{yz}$ orbital for backbonding). In Zeise's salt and analogous complexes, the nonbonded interactions of the cis-ligands are expected to make the coplanar arrangement higher in energy than the perpendicular one.

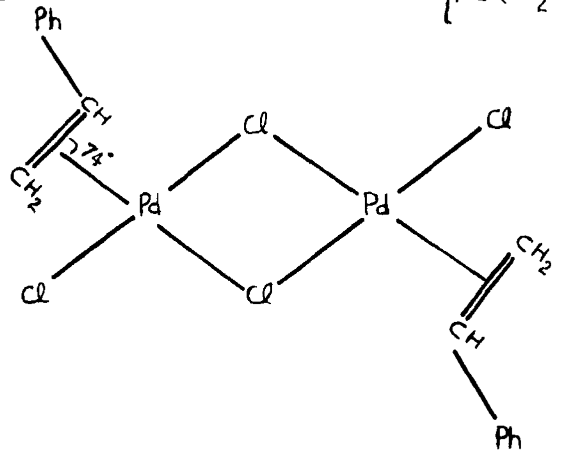
Crystal structure determinations on some ethylene-platinum (II) complexes[14-18] and $\left\{Pd(C_2H_4)Cl_2\right\}_2$[19] and $\left\{Pd(styrene)Cl_2\right\}_2$[20] show that the olefin was more or less perpendicular to the coordination plane of the metal with the C-C bond being nearly bisected by the plane. Deviations from 90° for the angle between the olefin-C-C axis and the metal-olefin axis have been observed[17,20]. Furthermore, in $\left\{Pd(styrene)Cl_2\right\}_2$, the $Pd_2Cl_4$ plane cuts the vinyl C-C axis nearer the terminal $-CH_2$ group in the ratio 0.92:0.40. This effect was attributed to steric and electronic causes, the latter arising from unsymmetrical electron density distribution in the vinyl group. These structure determinations did not conclusively establish a definite lengthening of the C-C bond.



$[Pt(C_2H_4)Cl_3]^-$ (Ref: 17)



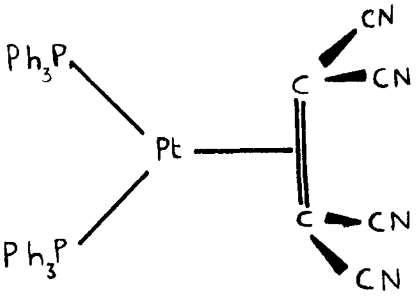
$\{Pd(C_2H_4)Cl_2\}_2$ ( Ref : 19)

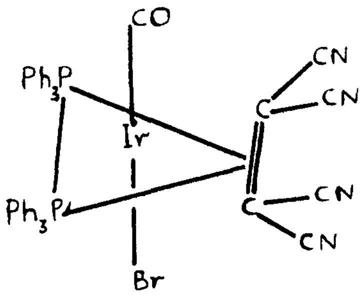


$\{Pd(Styrene)Cl_2\}_2$ ( Ref : 20)

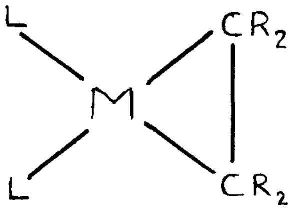
X-Ray structure determinations on olefin-metal complexes where the metal is formally in the zero-oxidation state showed that here the olefinic carbons were coplanar with the metal and the other ligands.

For example, in ethylenebis(triphenylphosphine)nickel[21,22] and tetracynoethylenebis(triphenylphosphine)platinum[23], the olefin C-C axis was almost coplanar with the coordination plane of the metal, the angle between them being only 12° and 8.3° respectively in the two cases. The C-C bonds were also reported to be slightly longer than that in the free ligands. Similarly, McGinnety and Ibers[24] described the structure of a tetracynoethylene(TCNE) iridium(I) complex as trigonal bipyramidal with the TCNE being regarded as a monodentate ligand in the equatorial plane. The olefinic C-C bond length (1.507(15)Å) was a little higher than that in TCNE (1.339 Å) itself. The cyno-groups in the TCNE complexes were no longer coplanar, but were bent away from the metal.

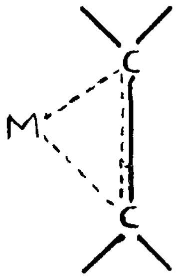




A number of workers have suggested that the olefin complexes of metals (Pt, Ni) formally in the zero oxidation state should be considered as square planar M(II) complexes with the olefin occupying two coordination sites (cis-) in a three membered metala-cyclopropane ring and they derive support from the observed increased C-C bond lengths and a comparison of the M-C bond lengths with those of the known M-C $\sigma$ bonds. A consideration of the bonding involved here, however, makes it clear that this valence bond description as a metala-cyclopropane is



equivalent to the representation, in molecular orbital terms, of these complexes as M(0) complexes with trigonal coordination about the metal, the unsaturated ligand occupying one coordination site. A convenient way to describe the bonding which avoids ambiguity and an implication of M-C $\sigma$-bonds is:



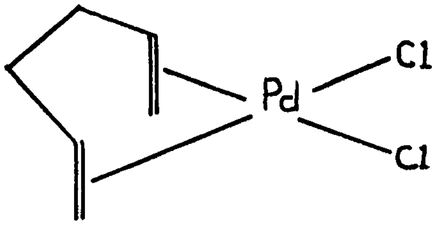
Recent nuclear magnetic resonance studies have indicated that the molecular orbital scheme of the olefin-metal bonding might be too rigid. Studies on single crystals of Zeise's salt have suggested that the ethylene molecule was undergoing large amplitude rotational oscillations about the platinum-olefin bond and the carbon-carbon double bond axis[25]. Similarly, in solution, in the complexes trans-dichloro(olefin) (2, 4, 6-trimethylpyridine)platinum, in which the 2- and 6-methyl groups on pyridine maintained the plane of the pyridine molecule perpendicular to the $PtCl_2$ plane, when the olefin was unsymmetrical (t-butylethylene, or styrene) the two methyls were magnetically inequivalent. Though at room temperature only one methyl signal was observed in the n. m. r., on cooling to $-50^o$ two signals were seen. The authors interpreted this as indicating rapid (on the magnetic resonance time scale) rotation of the olefin about its coordination axis[26].

Cramer[27-29] in his studies on ethylene-rhodium(I) complexes showed that a rotation about the $C_2H_4$-metal axis did occur and that the activation energy barrier for the rotation was 15 $kcal.mole^{-1}$. The low barrier was explained by invoking the intermediacy of a complex, in which the ethylene was coplanar with the metal and the other ligands and bonding occurred through the back-donation from olefin-$\pi^*$ to the metal $d_{yz}$ orbitals. Similar results have been obtained by Lewis and coworkers for olefin Pt(II) complexes[30,31]. A twisting about the C-C double bond also has been observed in these complexes. Such twisting has been observed with a number of complexes containing unsymmetrical olefins. The effect of twisting was to force the substituent on the double bond away from the metal[32-34]. In addition, a slight rotation about an axis perpendicular to both the metal-olefin bond and the olefinic double bond, which forced the substituted end of the double bond further away from the metal, has been observed[20,33].

II. Nonconjugated polyolefin complexes:

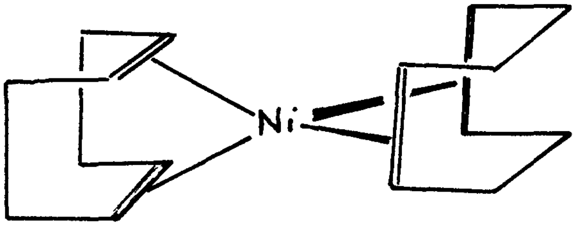
A number of nonconjugated diolefins and higher polyolefins exist in conformations which present the olefinic bonds in ideal arrangements for chelation to metal atoms. Examples of such ligands are 1,5-cyclooctadiene, norbornadiene and hexamethyl(Dewar benzene). The most common, thermodynamically most stable, diene complexes are those of 1,5-dienes, in particular 1,5-cyclooctadiene and dicyclopentadiene.

Structures for several 1,5-diene complexes have been reported[35-38], e.g.,



[Pd(1,5-hexadiene)$Cl_2$]
(Ref: 35)

In these $d^8$ complexes, the plane of the metal and the two chlorines attached to it was usually very nearly the bisector of the double bonds, and the coordination about the metal was square planar. $d^{10}$ Complexes with 1,5-cyclooctadiene have been shown to have tetrahedral stereochemistry about the metal[39-41], for example



Bis(1,5-cyclooctadiene)nickel (Ref: 41).

Diene complexes with metals in the zero oxidation state are known for nickel[42], palladium[43] and platinum[44].

The structure of a 1,4-diene complex dichloro(bicyclo [2, 2, 1] heptadiene)palladium,(dichloro(norbornadiene)palladium) has been determined[45]. Complexes of other 1,4-dienes[46] and of 1,6-dienes[47] have been reported.

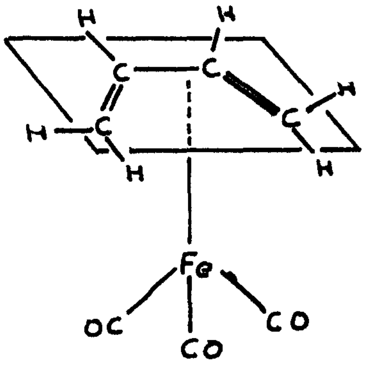
The bonding situation in complexes of nonconjugated di- and polyolefins, where there is no great interaction between the olefins can be regarded as similar to that in monoolefin complexes.

## III. Conjugated polyolefin complexes:

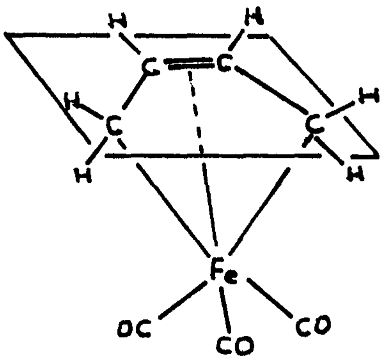
### A. 1,3-Diene complexes

Many 1,3-dienes and other conjugated polyolefins form complexes with a wide variety of transition metals, the most common being iron which, with some exceptions[48], does not form stable complexes with unconjugated dienes.

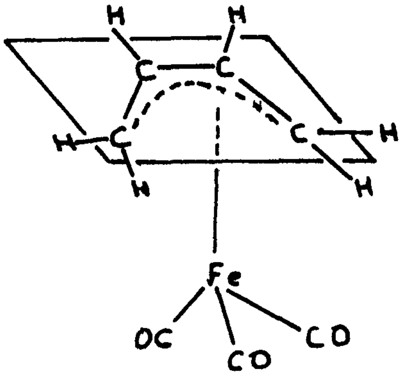
In the π-complexes of metals with conjugated dienes, the interaction between the olefinic bonds has to be taken into consideration. A molecular orbital treatment of tricarbonyl(butadiene)iron, in which the butadiene is present in the cisoid form, leads to the picture of bonding which, in valence bond terms, can be represented by the extremes A and B.



A



B

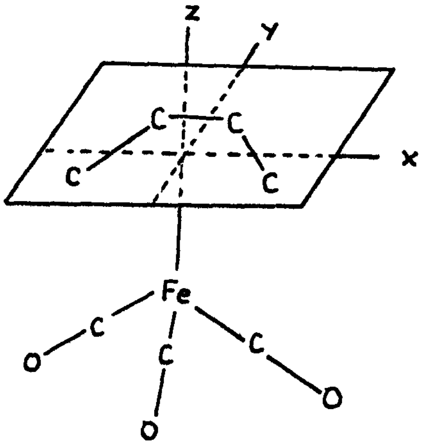


C

Representation A implies that the electrons are localised as in butadiene and that there is major bonding to the metal by the two low lying orbitals

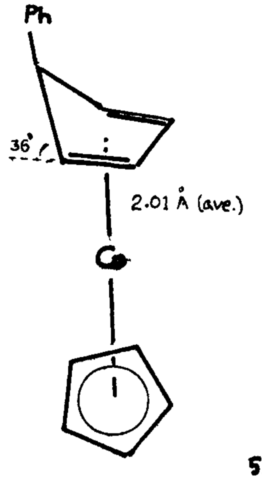
$\Psi_1$ and $\Psi_2$ of butadiene; representation B suggests that there is considerable localisation ($\sigma$-character) of bonding electrons between the metal and the terminal carbons of the butadiene with significant contribution to bonding from the third orbital $\Psi_3$. Representation C shows complete delocalisation of the butadiene electrons and is consistent with equal contributions from $\Psi_1$, $\Psi_2$ and $\Psi_3$.

The X-ray structure of butadiene iron tricarbonyl shows that the iron atom lies below the plane of the butadiene equidistant (2.1 Å) from the four carbons[49].

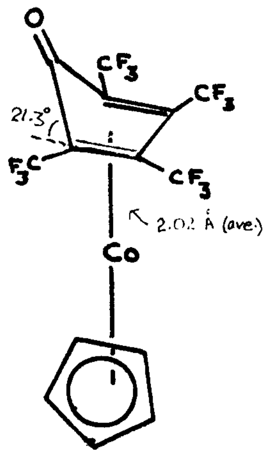


A comparison of the observed distances between the terminal carbons of a diene and the adjacent carbons of a substituent group (1.44-1.49Å) with the calculated distance for a $sp^2$ hybridised terminal carbon (1.48Å) and a $sp^3$ hybridised carbon atom (1.53-1.54Å) slightly favours structures A and C[50]. The $^{13}$C-H coupling constants of butadiene iron tricarbonyl are more consistent with sp$^2$ hybridised carbon than with sp$^3$ hybridisation[51].

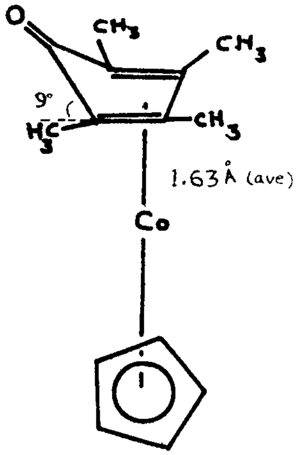
In complexes which contain a butadiene fragment in a cyclic ligand such as cyclopentadienes, cyclopentadienones, cyclohexadienes, the uncoordinated ring atoms are bent out of the plane of the diene carbons and away from the metal[52-56]; for example,



$[Co(C_5H_5)(C_5H_5Ph)]$[52]



$[Co(C_5H_5)[C_4(CF_3)_4CO]]$[53]



$[Co(C_5H_5)(C_4Me_4CO)]$[54]

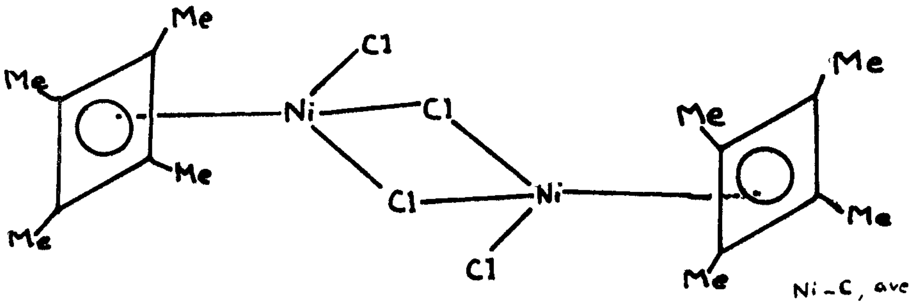
This suggests a degree of sp$^3$ character of the terminal carbon-metal bonds and thus in favour of B. As might be expected, the presence of electronegative substituents on the diene ligand increases the interaction of the metal with the $\Psi_3$ orbital of the butadiene unit and hence the sp$^3$ character of the terminal carbons. This is reflected by an increase in the bending of the ligand[57].

To summarise, it seems that the bonding of dienes cannot be simply represented by any one of the structures A, B or C.

## B. Cyclobutadiene complexes

Cyclobutadiene is an interesting ligand which is not known in the free state. However, Longuet-Higgins and Orgel, in 1956, predicted that it would be stable in the complexed form[58]. Many cyclobutadiene complexes are now known with Mo[59], Fe[60], Co[61], Ni[62], Pd[63, 64] and Pt[65].

The structure of dichloro(π-tetramethylcyclobutadiene)nickel has been determined by X-ray diffraction[62]. The cyclobutadiene was found to be square planar with the four carbons equidistant from the metal.



Ni-C, ave ·1997·2.047 Å

C-C of $C_4$-ring 1.40-1.45 Å

The M.O. treatment of the cyclobutadiene-metal system using the local symmetry $C_{4v}$ for the $C_4H_4M$ moiety leads to the suggestion that the degenerate orbitals $\Psi_2$ and $\Psi_3$ of symmetry E, of the square planar cyclobutadiene are the principal contributors to the stability of the metal-cyclobutadiene bond. In the free cyclobutadiene, if it were square planar, there would be an unpaired electron in each of the orbitals $\Psi_2$ and $\Psi_3$. The metal can provide two electrons in orbitals of the same symmetry and form two strong covalent bonds, thus neutralising the diradical character of the cyclobutadiene (see also Ref. 66).

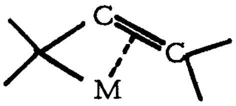
Trienes such as the arenes (benzene, etc.) and 1,3,5-cycloheptatriene form complexes with metals, analogous to the diene complexes considered above[67-69], as does cyclooctatetraene[70].

IV. <u>$\pi$-Allyl complexes:</u>

An allyl group which may be considered as a 3-carbon ligand, can bond in three ways:

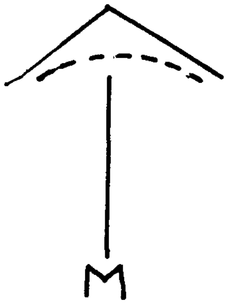
i) via a normal $\sigma$-bond $C=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-M$, as in $\sigma$-$C_3H_5Mn(CO)_5$[71]

ii) via a $\sigma$- and a $\pi$-bond

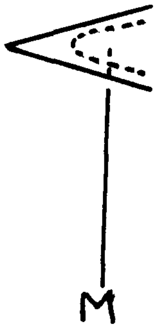


iii) via a donor-acceptor bond between the metal and a compcetely delocalised three centre $\pi$-electron system.

There are two extreme stereochemical situations of bonding for the case (iii), corresponding to dihedral angles of 180° and 90° between the plane of the 3 carbons of the allyl group, and the plane containing the metal and the remaining ligands. Bonding intermediate



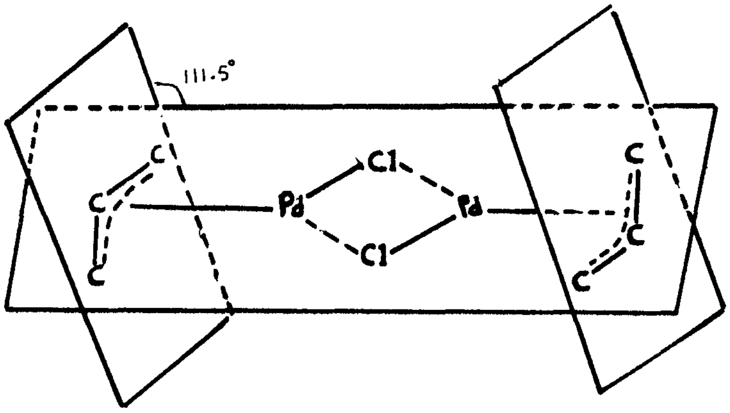
(a) dihedral angle 180°



(b) dihedral angle 90°

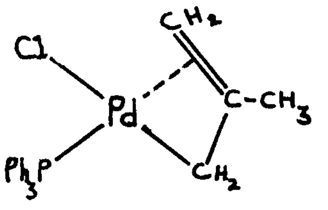
between these extremes is observed for transition metals, as seen from their crystal structures.

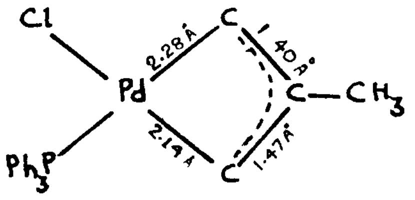
The structure of chloro(π-allyl)palladium dimer $\{Pd(\pi\text{-}C_3H_5)Cl\}_2$[72-74] is shown below.



The plane of the three allylic carbons intersected the plane formed by the $[PdCl]_2$ system at an angle of 111.5±0.9°, with the central carbons tipped away from the palladium. The $(PdCl)_2$ plane was nearer the two terminal carbons than the central carbons of the allyl groups. These trends are actually seen in all π-allylic complexes whose structures have been determined. A molecular orbital calculation involving both the conformations (a) and (b) for the allyl ligand predicted that the bonding energy would be maximised at a dihedral angle of $110^{\circ}$[75].

The σ, π -bonded allylic system has been found to occur in molecules such as





by X-ray and n.m.r. determinations[76-86].

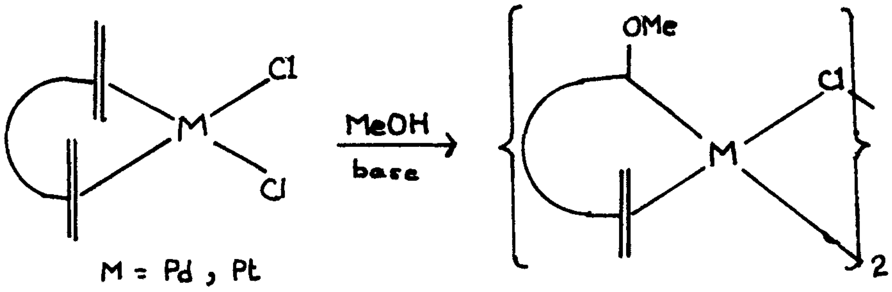
### V. Nucleophilic attack on π-complexed rings:

π-Complexed ligands become very susceptible to nucleophilic attack, especially if the metal is in a higher oxidation state. A good example of this reaction is in the oxidation of ethylene to acetaldehyde by the Wacker process using palladium catalyst[87]. The process, which is made catalytic by introducing cupric chloride, is represented by the equation:

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd^{0} + 2HCl$$

The key step in this process has been shown by kinetic studies to be the attack of the nucleophile (OH) at the metal followed by intramolecular nucleophilic attack on the coordinated olefin. Olefin Pt(II) complexes undergo similar reactions[88].

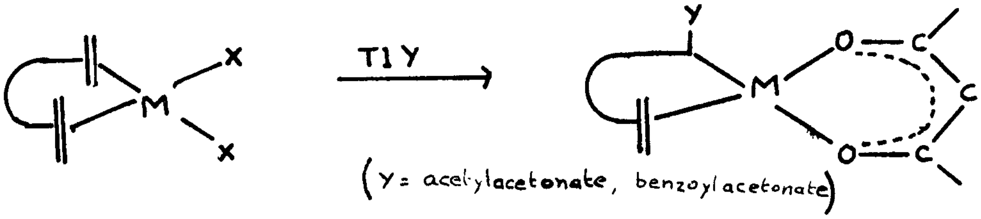
Diene complexes of palladium (II) and platinum (II) are highly susceptible to attack by various nucleophiles. Chatt obtained the complexes 1 by reacting $[\mathrm{M(diene)X_2}]$ (diene = 1,5-cyclooctadiene,(COD); dipentene(DPT); M = Pd, Pt; X = halogen) in methanol in the presence of a base[89,90]:



1

Stille and Morgan[91,92], who prepared the $\{$methoxynorbornenyl MCl$\}_2$ complexes, showed by n.m.r. studies that the methoxy group was in the exo-position. X-Ray structure determination on $\{\mathrm{Pt(DPD\text{-}OMe)Cl}\}_2$ (DPD = dicyclopentadiene) revealed the position of the methoxy group as exo-[93].

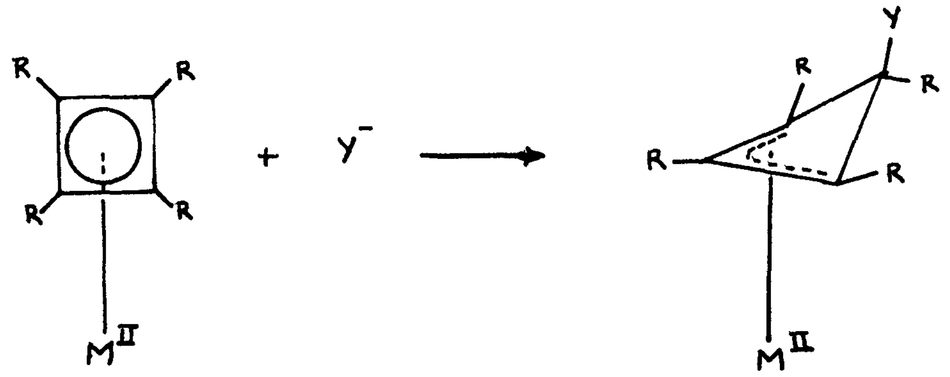
Similar reactions occur with acetylacetonate, benzoylacetonate, ethylacetoacetate, diethylmalonate and amines[94-96]



(Y= acetylacetonate, benzoylacetonate)

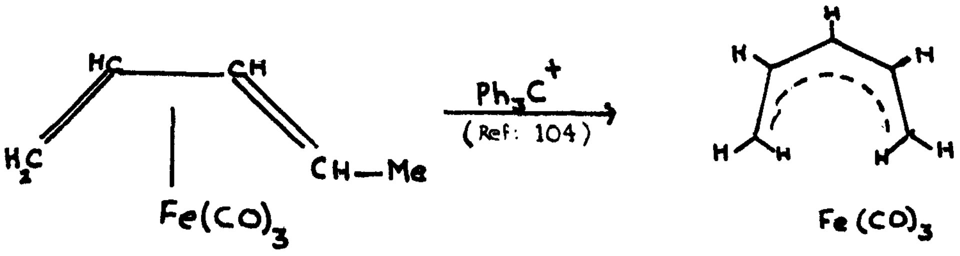
All these complexes revert to $\left[M(diene)X_2\right]$ on reaction with acid HX.

Cyclobutadiene complexes also undergo such nucleophilic attack[63, 64, 97-103]:



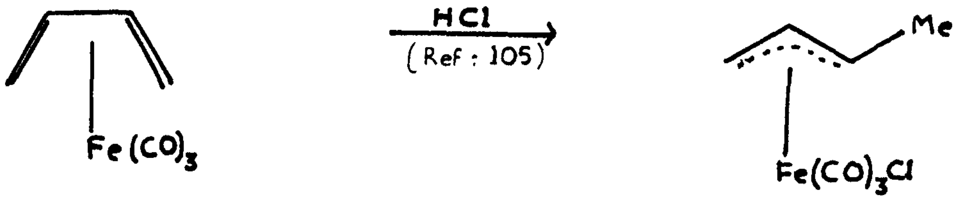
### VI. π-Polyenyl complexes:

The conjugated polyolefin complexes can undergo very similar reactions, but to give an essentially delocalised system with one more or one less carbon atom complexed to the metal:



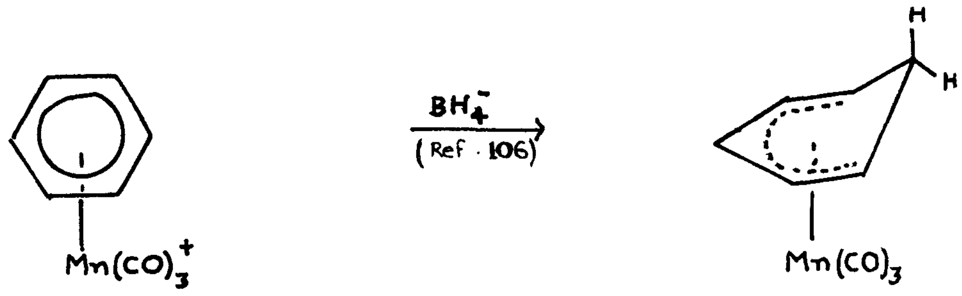
Tetrahapto-

Pentahapto- (  -dienyl)



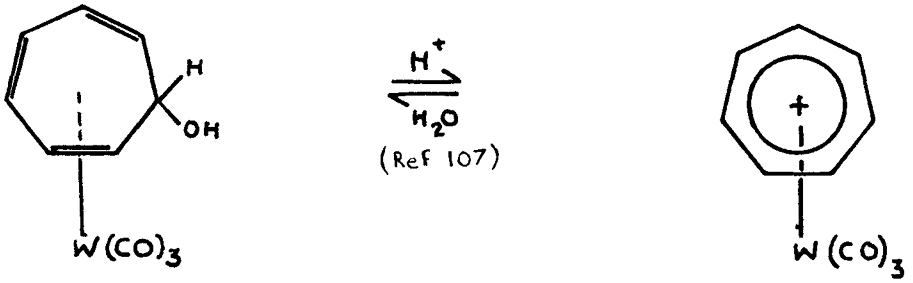
Tetrahapto-

Trihapto- (  -allyl)



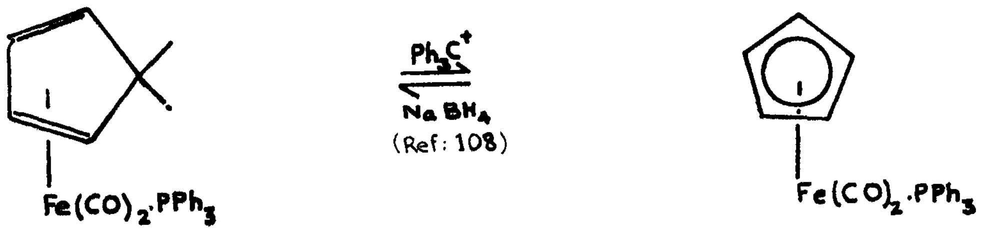
Hexahapto-

Pentahapto- ( -dienyl)



Hexahapto-

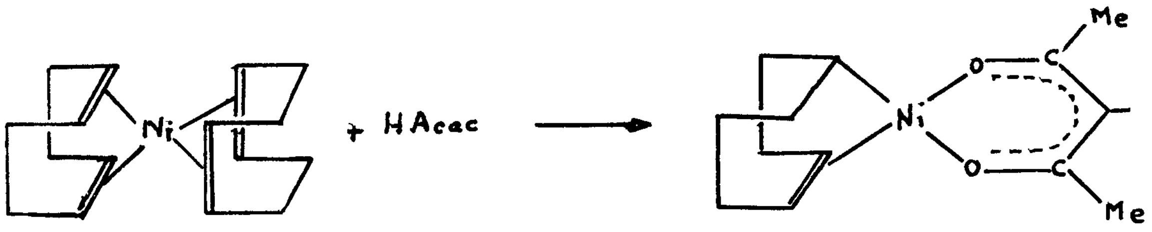
Heptahapto- ( -trienyl)



Tetrahapto-

Pentahapto- ( -dienyl)

It may be noted that most of these reactions leading to the π-enyl system are electrophilic in nature, since the metals here are in low oxidation states. This contrasts with the reaction of diene-M (II) complexes which undergo nucleophilic attack. A comparable case in nonconjugated olefin complexes is the reaction of acetylacetone with bis(cyclooctadiene)nickel[109].



The 5-carbon ligand cyclopentadienyl ($C_5H_5$) formed from cyclopentadiene is a very interesting one and has a broad chemistry, which started with the discovery of ferrocene, $Fe(C_5H_5)_2$, a 'sandwich' complex[110]. Cyclopentadienyl complexes are known for a wide variety of transition metals. The bonding of the $\pi$-cyclopentadienyl ligand has been discussed by Schustorovich and Dyatkina[111] and Cotton[111a].

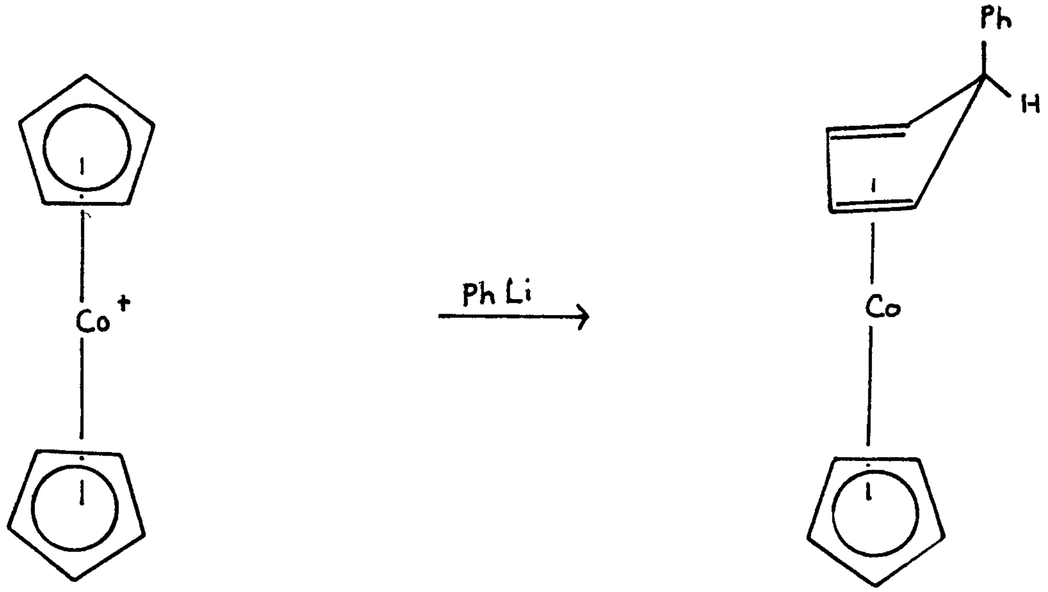
Palladium (II) and platinum (II) also form some monocyclopentadienyl complexes. Some examples are $\{Pt(C_5H_5)CO\}_2$[112,113], $[Pt(C_5H_5)(CO)I]$[112,113], $[Pt(C_5H_5)(\pi\text{-allyl})]$[114] and $[Pt(C_5H_5)_2]_2$(cyclooctatetraene)[114] for Pt (II). A Pt (IV) complex $[Pt(C_5H_5)Me_3]$[115] is also known. With palladium (II) a larger number of complexes have been prepared, particularly of the type $[Pd(\pi\text{-allyl})(C_5H_5)]$[116]. Other examples include $[Pd(C_5H_5)(C_4Ph_4)]^+Br^-$[117]

and $[Pd(C_5H_5)NO]$ [118]. The complexes $[Pd(C_5H_5)X]$, (X = Cl, Br), obtained by Jira and Smidt[119] as brown insoluble solids from $PdX_2$ and $C_5H_6$ in aqueous solution seem to be doubtful. Robinson and Shaw[120] and other workers were unable to obtain these. Recently some complexes of the type $[M(C_5H_5)(L)X]$ have been prepared for both palladium (II) and platinum (II), where L = triethyl- or triphenylphosphine and X = Br or I[121].

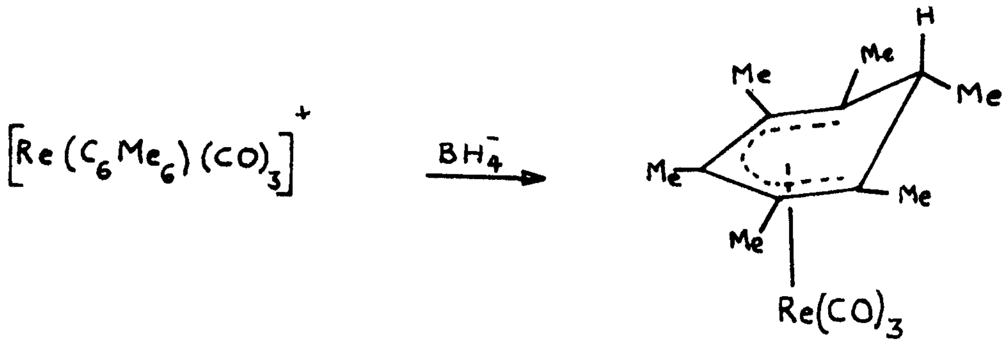
## VII. The Stereochemistry of Cyclopentadiene and Cyclohexadienyl complexes

Cyclopentadiene complexes such as $[Fe(C_5H_6)(CO)_2 . P\ Ph_3]$ [108] and cyclcohexadienyl complexes, e.g. $[Mn(C_6H_7)(CO)_3]$ [122] exhibit the interesting feature that in the infrared spectrum they show an intense low frequency C-H stretching band at ca. 2750 $cm^{-1}$. They also possess a reactive hydrogen which may readily be removed by oxidising agents (e.g. $H_2O_2/H^+$) or hydride abstracting reagents (e.g. $Ph_3C^+$). By using $LiAlD_4$ for the synthesis of such complexes it was shown that, in fact, the newly formed C-H bond was responsible for the low C-H stretching frequency[123].

Reaction of $[Co(C_5H_5)_2]^+$ with phenyllithium gave a compound which did not exhibit the low frequency C-H stretch. X-Ray structure determination[52,124] showed that the phenyl group had attacked from the least hindered side of the ring affording the non-planar exo-substituted product $\left[Co(C_5H_5)(C_5H_5Ph)\right]$.



This led to the assignment of the low frequency $\nu_{C-H}$ to the hydrogen in the exo-position. This has been verified in the rhenium complex obtained from the reduction of the hexamethylbenzene complex with borohydride[125]:



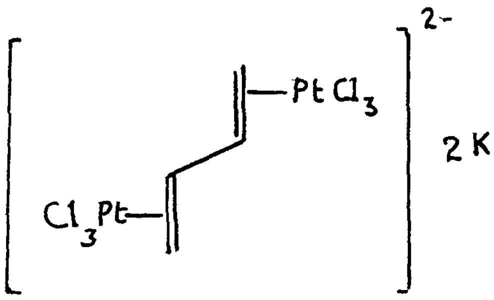
It showed the anomalous $\nu_{C-H}$ band at 2790 cm$^{-1}$ and a structure determination established the position of the hydrogen to be exo- to the ring.

Recently, Moseley et al.[126], have prepared the isomers of ($\pi$-cyclopentadienyl)($\pi$-pentamethylcyclopentadiene)-rhodium with the hydrogen endo- as well as exo-. Their infrared and mass spectroscopic studies as well as the reactivity of these complexes conclusively prove that the hydrogen in the exo- position in the cyclopentadiene caused the low $\nu_{C-H}$.

This is an invaluable criterion for determining the stereochemistry of cyclopentadiene (and cyclohexadienyl, etc.) complexes and has been useful in the present work.

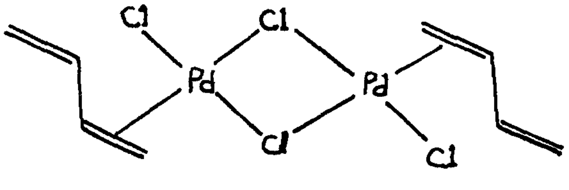
## VIII. Reactions of palladium (II) and platinum (II) with conjugated polyolefins:

Conjugated diolefins form $\pi$-allylic complexes with palladium (II), although platinum (II) forms true olefin complexes with these ligands. 1,3-Butadiene reacts with the dimeric complexes $\{PtX_2(PEt_3)\}_2$ (where X = halogen) to give the butadiene-bridged complexes $[(PEt_3)X_2Pt(C_4H_6)PtX_2(PEt_3)]$ in which butadiene coordinates to both platinum atoms[127]. The butadiene analogue of Zeise's salt, $K_2[Pt_2(C_4H_6)Cl_6]$ has been assigned the structure in which the butadiene in its transoid form coordinates to two platinums, from a study of its infrared spectrum[128].



Below -40°, palladium (II) forms a complex $\underline{2}$ with butadiene, in which only one double bond is complexed; above -20° this isomerises to the π-allylic complex $\underline{3}$

$$\{Pd(1\text{-pentene})Cl_2\}_2 + C_4H_6 \longrightarrow \underline{2} \longrightarrow \underline{3}$$



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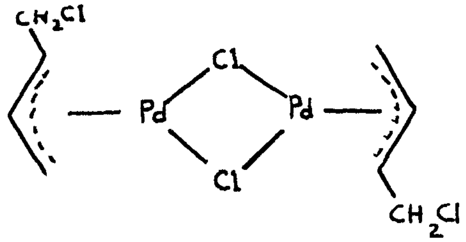
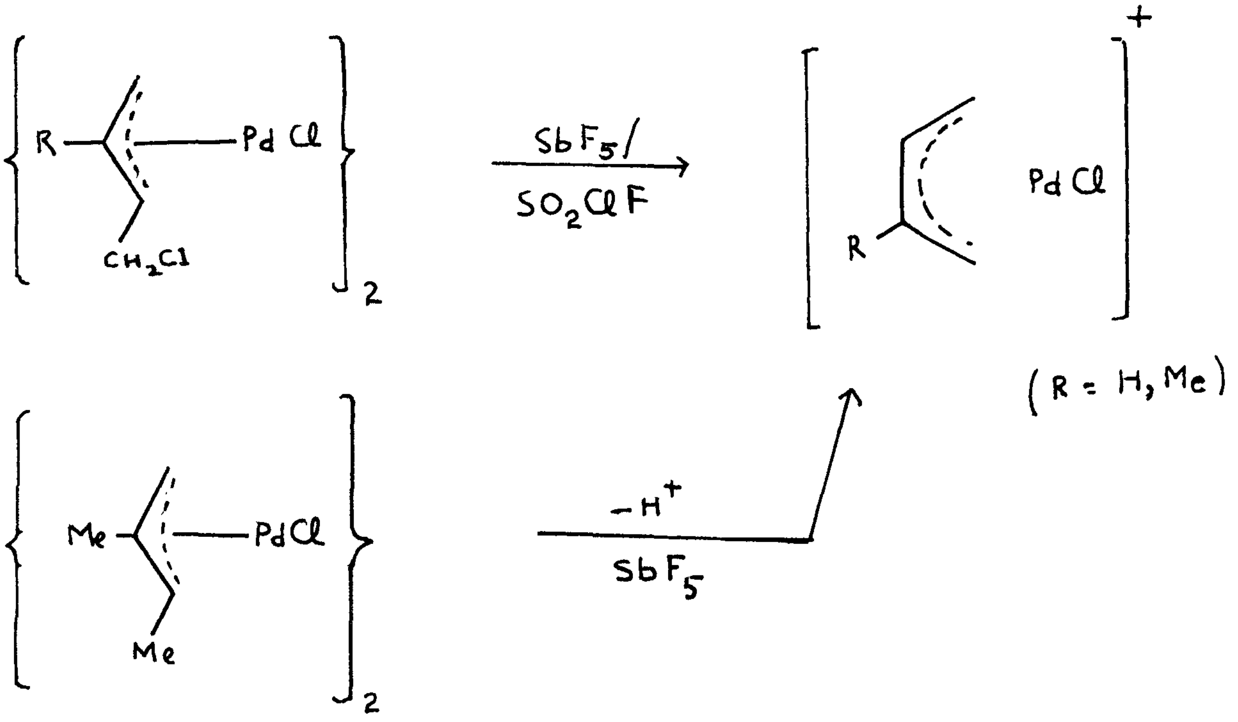


3

By contrast, 1,3-cyclooctadiene displaces pentene from $\{Pd(\text{pentene})Cl_2\}_2$ to give an olefin complex that is stable up to its melting point (110°)[129]. Both 1,3-cyclooctadiene and butadiene complexes show the presence of a free olefin ($\nu_{C=C}$ 1660 cm$^{-1}$) and one coordinated olefin ($\nu_{C=C}$ 1500 cm$^{-1}$), indicating that the ligands are truly monodentate. Displacement of benzonitrile from $Pd(PhCN)_2Cl_2$ by 1,3-cyclooctadiene leads exclusively to the formation of $[Pd(1,5\text{-cyclooctadiene})Cl_2]$[130].

Lukas and Kramer[131] have briefly reported obtaining cationic complexes of cisoid butadiene by reaction of 1-(chloromethyl)-allylpalladium chloride complexes with $SbF_5$ in $SO_2ClF$



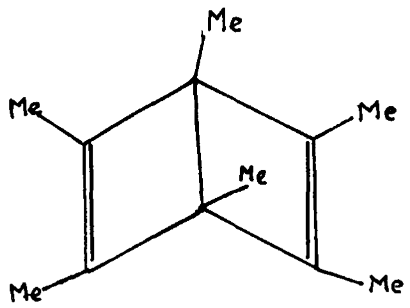
Cyclooctatetraene ($C_8H_8$) gives complexes such as $[Pd(C_8H_8)Cl_2]$ and $[Pt(C_8H_8)I_2]$. Infrared evidence[132] indicates that the cyclooctatetraene existed in these complexes in the tub form, and so is coordinated as a 1,5-diene.

The only chelating 1, 3-diene complexes with palladium(II) which were known at the beginning of this work were the cyclobutadiene complexes, which are prepared from the reaction with substituted diphenylacetylenes[63, 64]. A tetraphenylcyclobutadiene platinum(II) complex has recently been reported[65].

## IX. Reactions of transition metal complexes with Dewar benzenes:

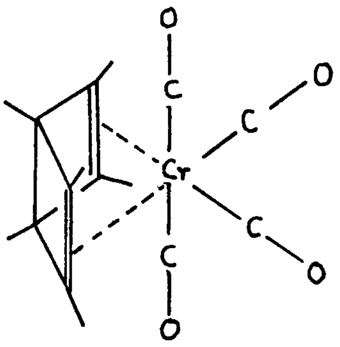
Dewar benzenes and the other non-planar valence isomers of benzene have been known since 1962[133]. The preparation of the isomers in general is rather difficult. The unsubstituted ones are thermally unstable too[134].

The discovery by Schäfer[135] that hexamethyl (Dewar benzene) HMDB (4) could be readily obtained from the bicyclotrimerisation of 2-butyne with aluminium trichloride, initiated much work on this compound. HMDB is thermally quite stable. The presence of only methyl groups in the compound makes structural studies by proton magnetic resonance very convenient.



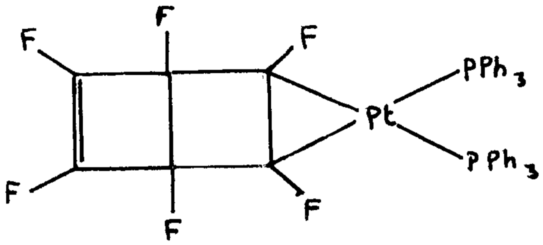
(4)

Dewar benzenes form complexes with metals by functioning as chelating dienes, similar to norbornadiene, to which they bear a structural resemblance. Thus, HMDB complexes have been prepared for $Cr^0$, $Mo^0$ and $W^0$ [136,137]. The proton magnetic resonance spectra suggested that the bicyclic structure was retained in these complexes. This was confirmed by an X-ray study of the chromium-tetracarbonyl complex[138].

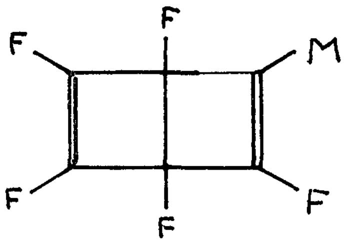


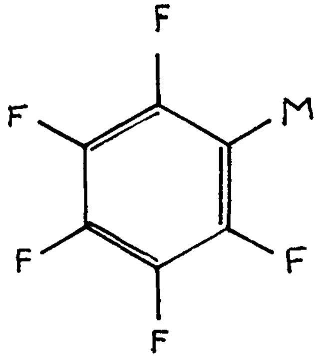
The Rh(I) complex of HMDB was obtained by the reaction of the bis(ethylene) rhodium(I) chloride dimer[139-140] with HMDB. Dichlorobis(benzonitrile)palladium, $Pd(PhCN)_2Cl_2$, gave the complex $Pd(HMDB)Cl_2$[141]. The platinum complex has now been prepared from the reaction of HMDB with Zeise's dimer, $\{Pt(C_2H_4)Cl_2\}_2$, in benzene solution (present work[142]) or with sodium tetrachloroplatinate in ethanol[143]. The palladium complex of the unsubstituted Dewar benzene has also been reported[144].

In some complexes Dewar benzene does not act as a chelating diene. Thus complexes of Pd and Pt[145, 146] are known in which the ligand has lost one hydrogen, but retained the para-bonded bicyclic structure, and bonds as an allylic moiety. The reaction of $Pt(PPh_3)_4$ with hexafluoro (Dewar benzene) gives a complex, which has been assigned the unsymmetrical structure involving a metalacyclopropane ring, from a study of its $^{19}F$ n.m.r. spectrum[147].



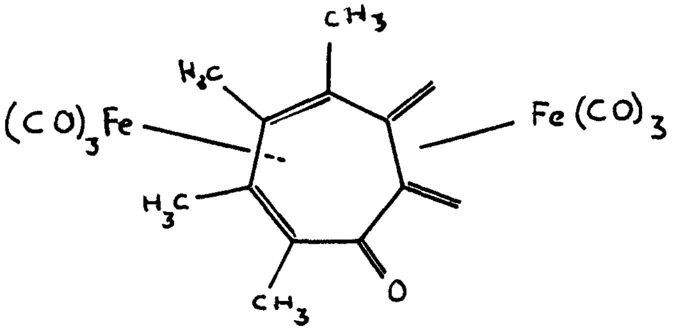
In its reaction with some anionic metal complexes, hexafluoro (Dewar benzene) gives complexes where a vinylic fluorine has been displaced by a metal and the para bond is retained. The double bonds are not involved in bonding in these complexes[148]. Some aromatised products, the pentafluorophenyl complexes, are also obtained in the reaction.





; [M = Re(CO)$_5$]

In some reactions the bicyclic structure of the Dewar benzene is not retained and some interesting rearrangements take place. Thus, in its reaction with $Fe_2(CO)_9$, hexamethyl (Dewar benzene) afforded a complex for which structure 5 was proposed[149].



(5)

The reaction with "rhodium trichloride trihydrate" in methanol is very remarkable. A ring contraction reaction took place here to give a quantitative yield of dichloro(π-pentamethylcyclopentadienyl)rhodium dimer[150]. Iridium trichloride also gave a similar product, although much less easily and in much lower yield ( 10%). The stoichiometry of the reaction was found to be

$$MCl_3 \cdot xH_2O + C_6Me_6 + 2MeOH \longrightarrow \frac{1}{2}\left\{C_5Me_5MCl_2\right\}_2 + MeCH(OMe)_2 + HCl + xH_2O$$

The intermediacy of 5(1-substituted ethyl)pentamethylcyclopentadiene was later established in this reaction.

This has been found to be the most convenient route to the pentamethylcyclopentadienylrhodium and -iridium complexes. An extensive chemistry has been developed for these organorhodium and -iridium complexes.

### X. The present work:

The work described in this thesis is on the reaction of hexamethyl (Dewar benzene) and ligands derived from it with palladium and platinum chlorides. Since rhodium and iridium chlorides lead to the pentamethylcyclopentadienyl system in their reaction with HMDB, it was considered probable that similar reactions might also occur in the cases of palladium and platinum and afford a new system of complexes with these metals. The chemistry of cyclopentadienyl palladium(II) and -platinum(II) is not very extensive since not many such complexes are known.

Indeed the reaction with platinum led to the ring contraction of HMDB, but instead of giving a cyclopentadienyl complex, it afforded a pentamethylcyclopentadiene platinum complex, the first chelating 1, 3-diene platinum(II) complex to be reported. Palladium(II) did not give the pentamethylcyclopentadiene on reaction with HMDB, or ligands derived from it, but gave a new series of 5-substituted pentamethylcyclopentadiene palladium complexes. Apart from the cyclobutadiene complexes, these are the only known chelating 1, 3-diene Pd(II) and Pt(II) complexes. Some 5-substituted pentamethylcyclopentadiene platinum(II) complexes were also obtained during the course of the work.

From their stability and spectroscopic properties, a "homocyclobutadiene" structure has been suggested for these complexes.

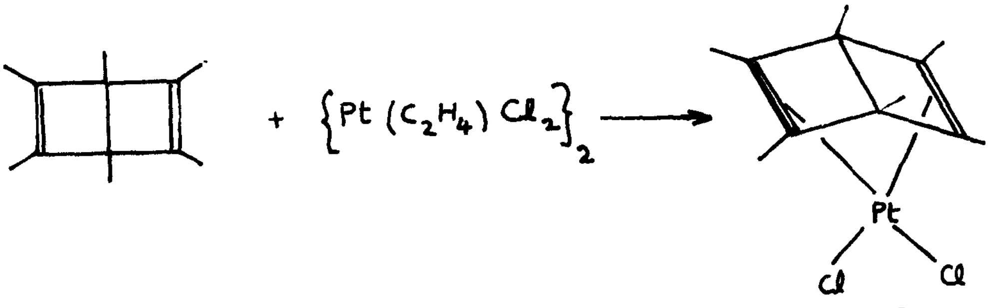
# RESULTS AND DISCUSSION

## RESULTS AND DISCUSSION

### I. Reaction of hexamethyl (Dewar benzene) with platinum chlorides:

### 1) Dichloro(hexamethylbicyclo [2, 2, 0] hexadiene)platinum, (6)

The reaction of Zeise's dimer, $\{Pt(C_2H_4)Cl_2\}_2$ with hexamethylbicyclo [2, 2, 0] hexadiene, (hexamethyl (Dewar benzene), HMDB ) in benzene gave the complex 6 in 83% yield. The 'H n.m.r. spectrum ($CDCl_3$) showed two resonances, at τ 8.13 (12H, olefinic methyls, $J_{Pt-H}$ = 35 Hz) and 8.86 (6H, bridgehead methyls, $J_{Pt-H}$ = 4.4 Hz) as required for a symmetric complex. The coupling of even the bridgehead methyl protons to $^{195}Pt$ is noteworthy.



6

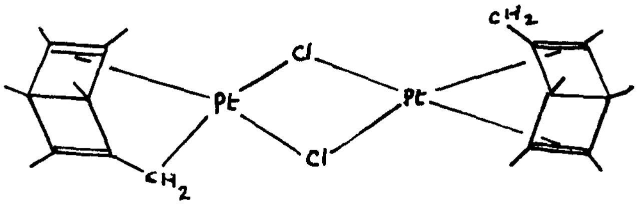
The osmometric molecular weight (in chloroform), although a little high (17%), is in favour of a monomer. The Pt-Cl stretching frequencies (318 and 337 $cm^{-1}$, Table 2) in the far infrared are in the region of terminal Pt-Cl stretches[154, 155] and thus exclude a dimeric structure involving bridging chlorines.

The reaction of HMDB with $\{Pt(C_2H_4)Cl_2\}_2$ also produced ca. $\frac{1}{2}$ mole of hexamethylbenzene (HMB) per mole of <u>6</u> formed. Since HMDB is quite stable to isomerisation under the reaction conditions, the metal must play an important role in the formation of HMB. Metal catalysed interconversions between the valence isomers of benzenes have recently attracted considerable attention[141, 151, 152].

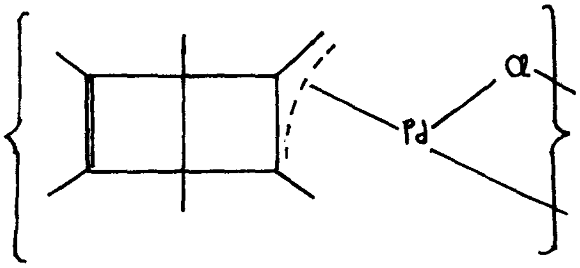
The complex <u>6</u> has also been obtained from sodium tetrachloroplatinate in ethanol[143]. It is similar to the palladium complex, $[Pd(HMDB)Cl_2]$[141], but is more stable. Evidence for stronger bonding of the diene to the metal comes from the infrared spectrum of <u>6</u> which shows the presence of a coordinated double bond at 1515 $cm^{-1}$. This is observed at 1532 $cm^{-1}$ for $[Pd(HMDB)Cl_2]$ and compares with a value of 1680 $cm^{-1}$ for $\nu_{C=C}$ in HMDB itself.

As expected, the complex <u>6</u> was also less labile than $[Pd(HMDB)Cl_2]$. No reaction was observed with pyridine over 2 days at 25°. Only a trace (5%) of HMB was formed when <u>6</u> was heated at 70° for 2 hours in chloroform. The palladium complex, by contrast, decomposed rapidly in chloroform at 33° to give HMB in a reaction that was catalysed by palladium chloride. Addition of palladium chloride (as the bisbenzonitrile complex) to a solution of 6 in chloroform did not catalyse this decomposition; HMB (50%) was observed after 192 hours at 25° both in the presence and the absence of catalyst. On heating the complex 6 above 76°, HMB sublimed out. Decomposition to HMB also occurred on irradiation of a solution by ultraviolet light or on treating a methanolic solution with acid (hydrogen chloride). Decomposition in chloroform solution was not catalysed to any detectable extent by acid. On reaction with triphenylphosphine in $CDCl_3$, HMDB was liberated quantatively. Complex 6 did not seem to react with iodine.

Reaction of 6 with base in methanolic solution gave a yellow complex, which was simultaneously prepared by Shaw[143]. The crystal structure determination of this complex by Mason[143] showed it to be a dehydro-hexamethyl (Dewar benzene) complex:

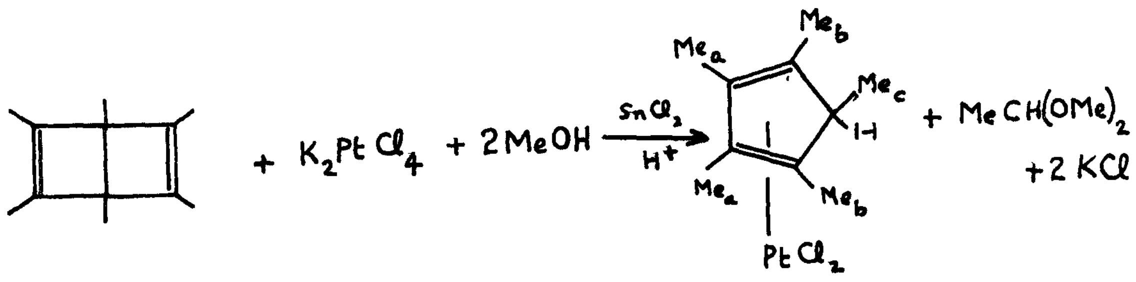


Analogous reaction with the palladium complex has also been found, by Shaw and coworkers, to proceed with deprotonation, but to give an allylic complex[145].



2) Dichloro(pentamethylcyclopentadiene)platinum, (7)

When HMDB was heated with potassium tetrachloroplatinate in dilute methanolic hydrochloric acid in the presence of a trace of tin(II)chloride as catalyst[153] the product (78%) was dichloro(pentamethylcyclopentadiene)platinum, (7). The mother liquor from the reaction mixture contained 1, 1-dimethoxyethane.



7

The complex 7 was identified by analysis, molecular weight and spectroscopic measurements. The n.m.r. spectrum (figure 3) showed resonances at τ 6.65 (1 H, q, $J_{H\text{-}Me}$ 6.5), 7.78 (6 H, $Me_a$, $J_{Pt\text{-}H}$ 38), 8.54 (6 H, $Me_b$, $J_{Pt\text{-}H}$ 10) and 9.04 (3 H, d, J = 6.5 Hz). The molecular weight corresponded to that for the monomer and the far infrared spectrum (Table 2) showed it to have only terminal Pt-Cl bonds[154,155]. Further, there was no $\nu_{C=C}$ band due to an uncoordinated double bond. The complex showed only a band at 1490 cm$^{-1}$ due to a coordinated double bond. These data support the formulation of complex 7 as a chelating 1, 3-diene complex of Pt(II), the first one of its kind.

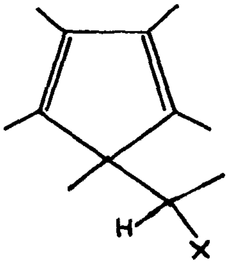
Moseley, et al.[126], have prepared both the exo- H and endo- H isomers of cyclopentadienyl(pentamethylcyclopentadiene)-rhodium; the former showed an intense $\nu_{CH}$ band at 2730 cm$^{-1}$ in the i. r., due to the exo- hydrogen, while the endo- H isomer did not. Similar observations have been reported for a number of related systems[156,157]. The complex 7 did not show an anomalously low frequency $\nu_{CH}$ band ($<$2800 cm$^{-1}$). It is, therefore, concluded that 7 had an endo- hydrogen on the sp$^3$ carbon. Some of the reactions of the complex, to be discussed in a later section, also support this stereochemistry.

The identical complex, and none of the exo- H isomer was obtained from pentamethylcyclopentadiene and $\{Pt(C_2H_4)Cl_2\}_2$; therefore 7 is the thermodynamically stable product and the exo- H isomer is not favoured, presumably for steric reasons.

The high field position of the resonance due to the exo-bridgehead methyl (~9 τ), as will be shown later, is quite characteristic for the exo- position of this substituent.

3) Mechanism of formation of complex 7:

The formation of the cyclopentadiene complex 7 occurs most easily in the presence of acid. Hydrogen chloride, for example, is known to react with HMDB to give 5-(1-chloroethyl)pentamethylcyclopentadiene,[158] (8, X=Cl):



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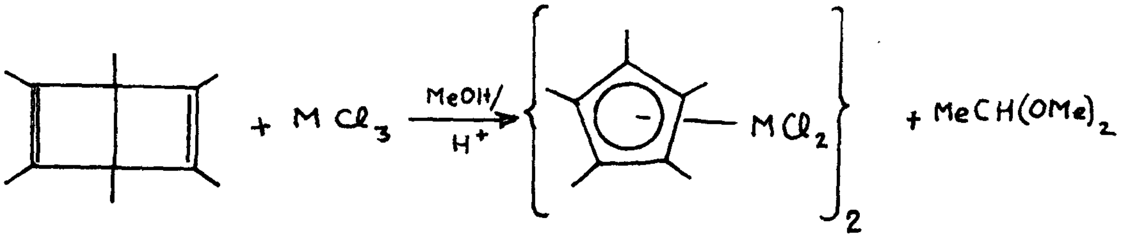
It has been observed that this chloro-compound in methanol, in the presence of a metal complex, is readily transformed into the methoxy-compound (8, X=OMe). This latter compound is regarded as the direct precursor of the pentamethylcyclopentadiene complex, (7). The formation of acetaldehyde dimethyl acetal ($MeCH(OMe)_2$) as a by-product in the synthesis of 7 from HMDB supports this. Further, the complex

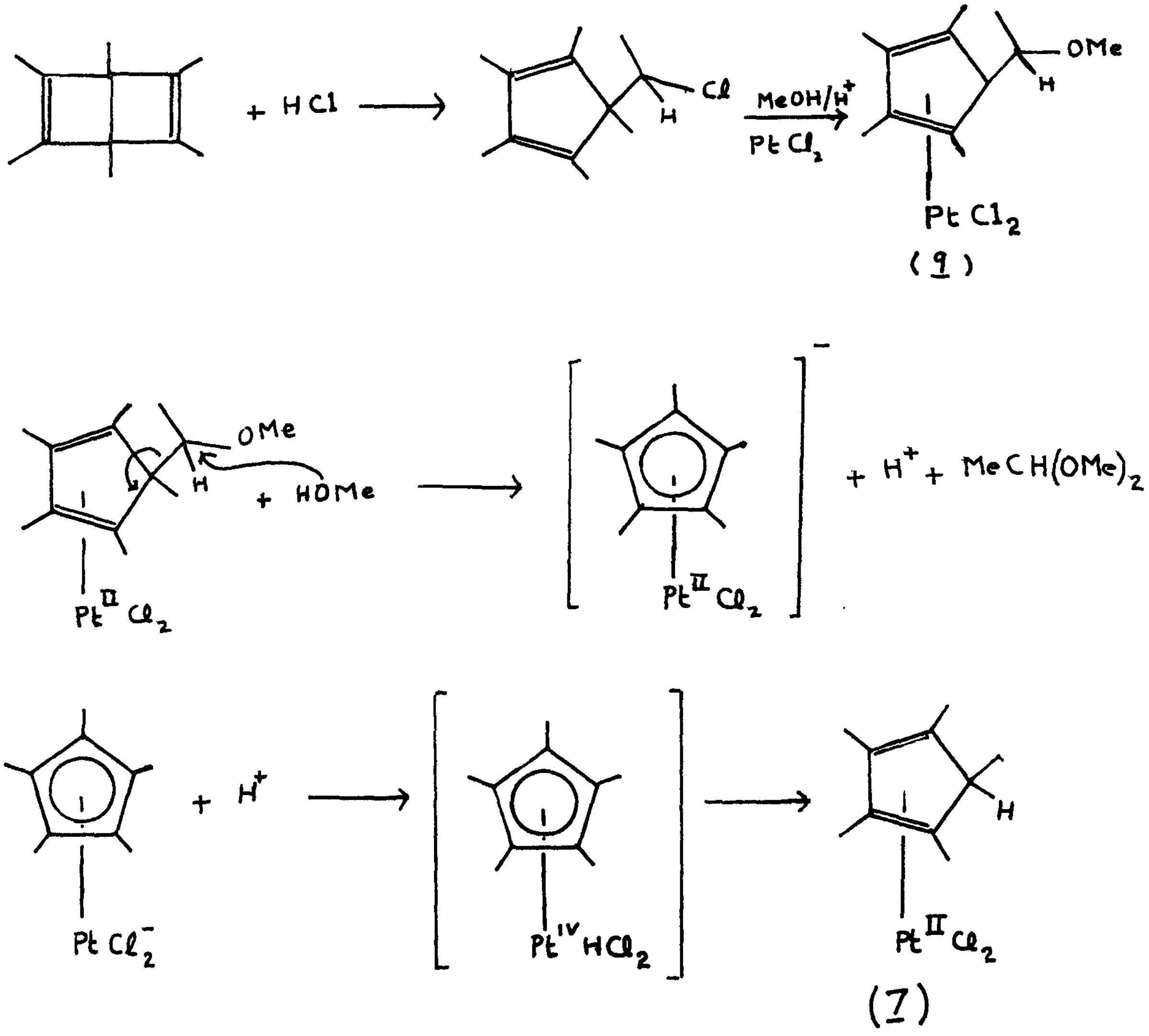
7 was also obtained, and in slightly higher yield (88%) from 8 (X=Cl) and, even, though in low yield (13%), from 8 (X=H). In fact, almost every 5-substituted pentamethylcyclopentadiene (including 5-acetylpentamethylcyclopentadiene) gave 7 from $K_2PtCl_4$ under the reaction conditions.

The overall reaction therefore closely parallels that of HMDB with rhodium and iridium trichlorides to give the dichloro-(pentamethylcyclopentadienyl)rhodium or -iridium dimer[150].



The first step in the reaction must be the formation of the diene complex, 9; attempts to prepare this and similar complexes from 8 and $\{Pt(C_2H_4)Cl_2\}_2$ failed, except when X=H and these are described later on. The overall mechanism for the reaction is proposed to be as depicted in the Scheme.

Scheme:



In the Rh and Ir reactions the cyclopentadienyl complex, corresponding to the proposed intermediate here, $[Pt(C_5Me_5)Cl_2]^-$, is stable with respect to transformation to the pentamethylcyclopentadiene. This does not appear to be the case with platinum and it is suggested that oxidative addition of $H^+$ to the Pt(II) intermediate occurs, giving a Pt(IV) hydride, which rapidly transfers the hydrogen onto the ring to give 7 with the bridgehead hydrogen endo-, as observed.

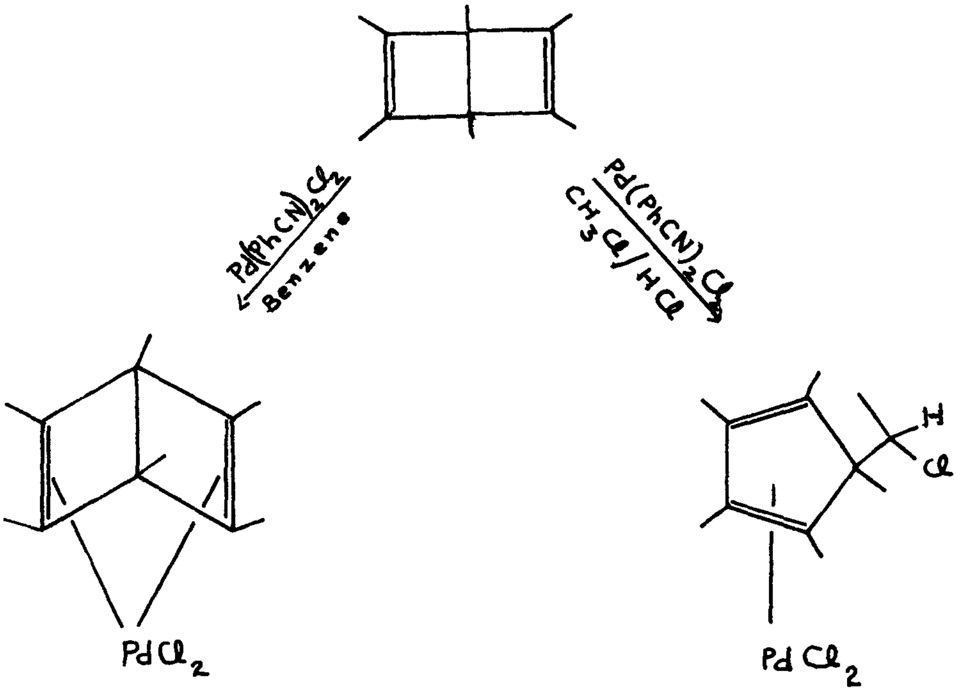
An alternative mechanism, in which the intermediate complex 9 is first protonated can be ruled out. Attempt to protonate 7 or to exchange hydrogen for deuterium (in $CF_3COOD$) there, were unsuccessful, and 7 was, in fact, quite stable in fluorosulphuric acid at ambient temperatures.

## II. Reaction of hexamethyl (Dewar benzene) with palladium chlorides:

Dichlorobis(benzonitrile)palladium reacted with HMDB to give dichloro(hexamethylbicyclo[2, 2, 0]hexadiene)palladium, 10 under neutral conditions[141]. The reaction of HMDB with $Pd(PhCN)_2Cl_2$ in chloroform in the presence of a stream of dry hydrogen chloride gave a yellow-orange complex, which analysed correctly for $Pd(C_5Me_5CHClMe)Cl_2$ and gave 5-(1-chloroethyl)pentamethylcyclopentadiene (8, X=Cl) quantitatively on treatment with triphenylphosphine[159]. The n.m.r. spectrum* is consistent with the formulation as dichloro{5-(1-chloroethyl)pentamethylcyclopentadiene}palladium, 11, for this complex:

---

* $\tau$ 6.15 (1H, q , J = 7Hz); 7.70(3H, s); 7.72(3H, s); 7.85(3H, s); 8.32(3H, s); 8.43(3H, s); 8.56(3H, d, J = 7Hz) in $CDCl_3$



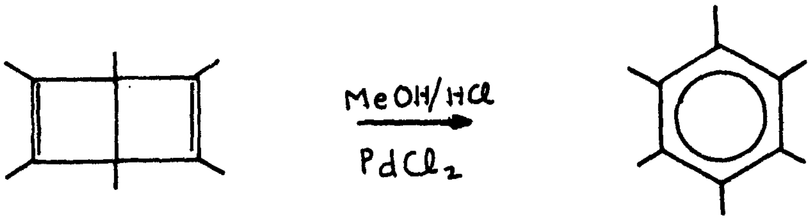
(10) (11)

On steric grounds the bridgehead methyl group is proposed to be endo- and the rather low field resonance at $\tau$ 7.85 is assigned to it.

The $\nu_{Pd-Cl}$ observed at 315 cm$^{-1}$ as a broad band in the far infrared (Table 3) is in the region for a terminal Pd-Cl stretch[154,155] and favours the monomeric structure. The osmometric molecular weight (807, in benzene; theory: 376 for monomer) apparently suggests a dimeric structure, but in view of the instability of the complex, particularly in solution (it was rapidly precipitated from solution as a yellow insoluble solid; slower decomposition occurred in solid), the measurement may not be reliable.

The formation of the complex 11 presumably occurred through the formation of 8 (X=Cl) in situ from HMDB.

Reaction of HMDB with palladium chloride in dilute methanolic hydrochloric acid afforded hexamethylbenzene quantitatively, and in sharp contrast to the analogous reaction with platinum chloride, no dichloro(pentamethylcyclopentadiene)palladium was obtained. Evidently, the rate of the palladium catalysed isomerisation of HMDB to HMB far exceeds that of any other reaction. Even the reaction of 8 (X=Cl) with $PdCl_2$ in methanol did not give any significant amount of $Pd(C_5Me_5H)Cl_2$. This complex was only obtained by reaction of pentamethylcyclopentadiene with $Pd(PhCN)_2Cl_2$.



It is very surprising that palladium(II) does not cause the conversion of HMDB or 8 into pentamethylcyclopentadiene as observed with platinum, rhodium[150] or iridium[150]. Palladium(II) normally undergoes similar reactions to platinum(II), but with greater ease owing to its higher kinetic lability. This is a rare example in which palladium is apparently more inert than platinum and the reason for this is not clear.

## III. Chemistry of dichloro(pentamethylcyclopentadiene)platinum, (7):

$Pt(C_5Me_5H)Cl_2$, (7), was transformed into the dibromo-complex by the nucleophilic displacement of the chloride by bromide on reaction with lithium bromide in acetone.

$$Pt(C_5Me_5H)Cl_2 \xrightarrow[\text{Acetone}]{\text{LiBr}} Pt(C_5Me_5H)Br_2$$

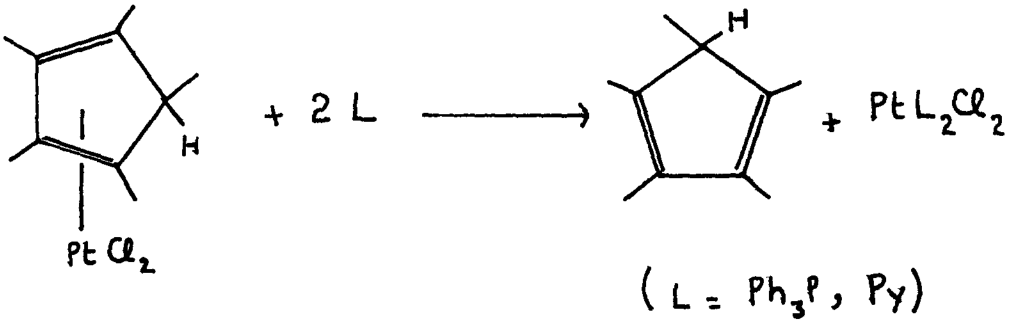
The n.m.r. (Table 4) and the i.r. spectra of the dibromo-complex are very similar to those of the dichloro- complex and hence the bridgehead hydrogen is endo- in this complex as well. The far i.r. spectrum (Table 2) shows only terminal $\nu_{Pt-Br}$ [154,155] and hence this complex is also monomeric in the solid. The molecular weight measured osmometrically in chloroform is a little high (530; theory: 491), but is in favour of a monomeric structure.

Reaction of 7 with alkali metal iodides did not lead only to displacement of the chloride by iodide but the olefinic ligand, pentamethylcyclopentadiene was displaced as well. However, the diiodo- complex was obtained on reaction with iodine in chloroform solution.

$$Pt(C_5Me_5H)Cl_2 \xrightarrow{I_2, CHCl_3} Pt(C_5Me_5H)I_2$$

The n.m.r. (Table 4) and the i.r. spectra suggest this complex also to be the endo- H pentamethylcyclopentadiene complex.

Triphenylphosphine and pyridine displaced pentamethylcyclopentadiene from 7, even at -50°. There was no n.m.r. evidence for an intermediate in which the cyclopentadiene acted as a monodentate ligand.



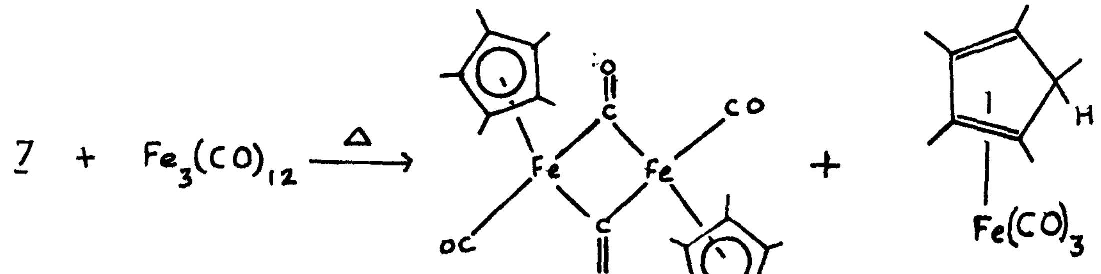
The reaction with pyridine shows that by comparison with 6 - the complex of HMDB, a 1,4-diene, the complex 7 was much more labile. Since the "bite" of a 1,3-diene is smaller than that of a 1,4-diene, the latter is a better shield towards nucleophilic attack by a nucleophile. However, the complex 7 did not exchange pentamethylcyclopentadiene with the dienes HMDB and 1,5-cyclooctadiene.

Bases like sodium carbonate (in methanol) or triethylamine (in chloroform) decomposed the complex and gave no characterisable product. This is in contrast with the behaviour of 1,5-diene complexes (e.g., dichloro-(1,5-cyclooctadiene)platinum)[89,90] or 1,4-diene complexes (e.g. dichloro(norbornadiene)platinum)[91,92] where nucleophilic attack on the ligand takes place and that of the 1,4-diene complex Pt(HMDB)$Cl_2$[143], where deprotonation of a methyl group takes place by the reaction of sodium carbonate in methanol.

The mechanism proposed for the formation of 7 from HMDB and 8 involves a step which implies that the driving force for the cleavage of the C-C bond was the tendency for the formation and/or the stability of a (pentamethylcyclopentadienyl)-platinum(II) species. It was, therefore, expected that in the presence of a suitable stabilising ligand such as acetylacetonate or allyl- the acetylacetonato- or the allyl(pentamethylcyclopentadienyl)platinum could be formed from 7. The reaction of 7 with acetylacetone in methanol both in the presence and the absence of a base as well as that with allylmagnesium chloride resulted in the displacement of pentamethylcyclopentadiene from the complex. This result is consistent with the assignment of *endo*- stereochemistry for the bridgehead hydrogen in complex 7, where it is probably more shielded from attack than an *exo*- hydrogen would be.

By analogy with the ligand-transfer reactions which were successfully carried out with cyclobutadiene complexes and metal carbonyls[160], it was reasonable to assume that such reactions would also be possible for 7. Reaction with di-μ-carbonyldicarbonylbis-

(cyclopentadienyl)diiron, $\{Fe(C_5H_5)(CO)_2\}_2$, gave a red paramagnetic oil which could not, however, be purified sufficiently for characterisation. Nickel tetracarbonyl displaced the ligand from 7, but did not give any complex with it. But dodecacarbonyltriiron in refluxing xylene gave two products, one, the known di-μ-carbonyldicarbonylbis(pentamethylcyclopentadienyl)diiron[161] (n.m.r., singlet at $\tau$8.37 in $CS_2$ solution; i.r., $\nu_{CO}$, 1748, 1923 $cm^{-1}$ in KBr disc); the other, a volatile yellow solid, was identified as tricarbonyl(pentamethylcyclopentadiene)-iron, (12).



(12)

The absence of a strong $\nu_{CH}$ band in the region below 2800 $cm^{-1}$ together with the high field position of the bridgehead methyl protons in the n.m.r. spectrum (Table 4) again suggested that in this complex the bridgehead hydrogen was endo- to the metal.

It is presumed that 12 is the intermediate in the formation of $\{Fe(C_5Me_5)(CO)_2\}_2$; with the hydrogen endo-, transfer to the metal to give $\left[Fe(C_5Me_5)(CO)_2H\right]$, a further probable intermediate, would be easy. A similar mechanism was proposed for the formation of $\{Fe(C_5H_5)(CO)_2\}_2$ in the reaction of cyclopentadiene and iron pentacarbonyl[108, 162].

Reaction of dicobalt octacarbonyl with 7 in methylene chloride gave dicarbonyl(pentamethylcyclopentadienyl)cobalt, as seen from the n.m.r. spectrum of the red crystalline air sensitive product (singlet at $\tau$8.10, in $CS_2$ solution[161]).

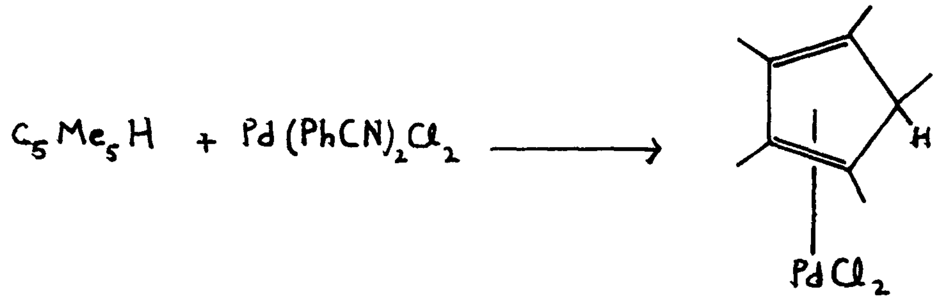
## IV. Attempted catalytic preparation of 1, 2, 3, 4, 5-pentamethylcyclopentadiene:

Pentamethylcyclopentadiene may be synthesised according to the method of deVries[163] using conventional organic reactions, but the method is rather involved and only gives poor yields. The transition metal catalysed conversion of HMDB to the pentamethylcyclopentadiene system seemed promising as a direct and convenient synthetic route to the pentamethylcyclopentadiene. And platinum(II) seemed to be the best catalyst since the reaction proceeded with great facility and led to the cyclopentadiene complex. However, when the reaction was tried with HMDB or 8 and catalytic amounts of $K_2PtCl_4$ under a variety of conditions, no pentamethylcyclopentadiene in quantities significantly greater than were produced from the acid catalysed cleavage of 8 in methanol[164] was observed, even though the Pt(II) was quantitatively converted to the complex 7. Even in the presence of iodide ion, which displaces pentamethylcyclopentadiene from 7, the reaction was not successful.

This failure is, perhaps, not surprising in view of the stability of the pentamethylcyclopentadiene-Pt(II) complexes, since, for the catalytic production of pentamethylcyclopentadiene from 8, a fairly labile system involving pentamethylcyclopentadiene and a metal from which the diene is easily displaced by, say, 8, might be expected to be required.

## V. Dichloro(pentamethylcyclopentadiene)palladium, (13):

The complex, 13, could not be obtained from HMDB or 8, but was formed on reaction of pentamethylcyclopentadiene with $Pd(PhCN)_2Cl_2$ in benzene. It was not readily purified since it decomposed in solution to an insoluble material. Analysis of the crude product from the reaction indicated the presence of ca. 1.1 $PdCl_2$ per diene; the ability of $PdCl_2$ to catenate with coordinated $PdCl_2$ in a number of complexes, particularly of olefins has been noted[165].

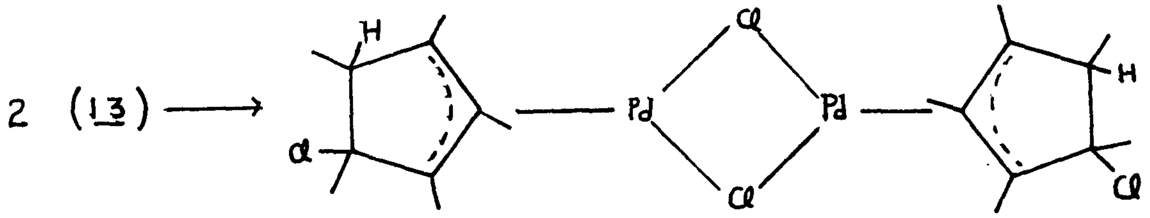


(13)

By n.m.r. (Table 5) it was shown that only one isomer of 13 was formed. The absence of a low frequency $\nu_{CH}$ in the i.r. spectrum, (characteristic of an *exo*- H), suggested that this complex had the hydrogen in the *endo*- position and the methyl in the *exo*- position on the $sp^3$ carbon of the five membered ring. The *exo*-methyl group appeared in the n.m.r. spectrum as a doublet at $\tau$ 8.95. The far infrared showed strong bands in the region for terminal Pd-Cl stretches[154-155] and some medium bands which may be ascribed to the excess catenated $PdCl_2$. Pentamethylcyclopentadiene was liberated on treatment of 13 with $PPh_3$.

$$Pd(C_5Me_5H)Cl_2 + 2\ PPh_3 \longrightarrow C_5Me_5H + Pd(PPh_3)_2Cl_2$$

The formation of insoluble material from solutions of 13 may be explained by the ready insertion of a double bond of a conjugated di-olefin into a Pd-Cl bond to give a dimeric $\pi$-allylic complex.



(14)

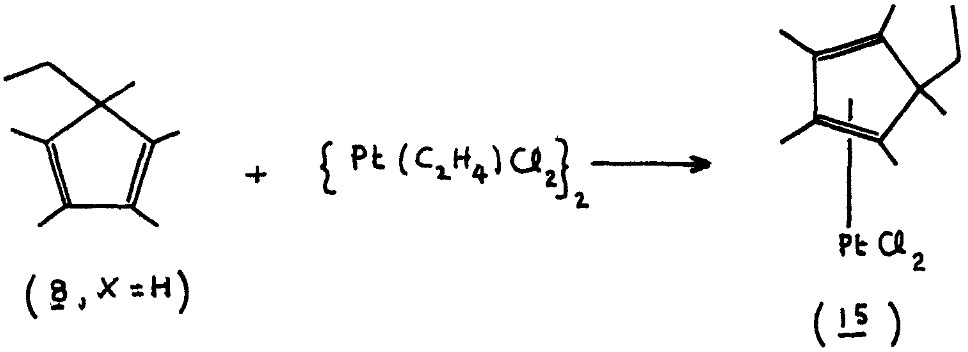
The complex 14 was synthesised by Dr. Hosokawa of this laboratory, who also observed that the insoluble compound obtained from solutions of 13 had an infrared spectrum essentially identical with that of 14 and showed a characteristic C-Cl stretch[166].

The reaction of cyclopentadiene ($C_5H_6$) with $PdCl_2$ was reported by Jira and Smidt to give $Pd(C_5H_5)X$ as a brown insoluble solid[119]. Attempts later by Robinson and Shaw to obtain this were unsuccessful[120]. They reported obtaining a yellow solid which soon darkened in colour. It seems likely that here also the cyclopentadiene complex was first formed and then underwent further reaction including an insertion into a Pd-Cl bond. The reaction is probably more complex since a very insoluble brown polymeric material is obtained.

## VI. 5-Ethylpentamethylcyclopentadiene complexes:

Since the reaction of pentamethylcyclopentadiene with both Pt(II) and Pd(II) gave only the isomer of the diene complexes 7 and 13 with the bridgehead hydrogen in the endo- position, presumably for steric reasons, it could be anticipated that with 5-substituted 1,2,3,4,5-pentamethylcyclopentadienes, the methyl group on the 5-carbon atom would take up the endo-position if the other 5-substituent (e.g., ethyl) is bulkier than methyl, to minimise non-bonded interactions.

5-Ethylpentamethylcyclopentadiene (8, X=H) reacted with $\{Pt(C_2H_4)Cl_2\}_2$ in ethanol-free chloroform to give the complex 15.

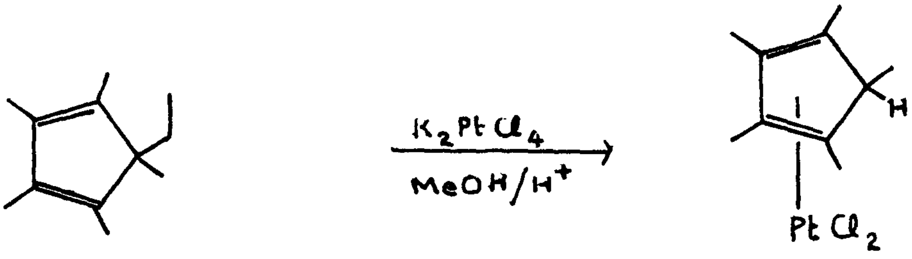


The far i.r. spectrum (Table 2) showed it to have only terminal Pt-Cl bonds. There was only a band at 1490 cm$^{-1}$ due to coordinated C=C in the i.r. and no band due to uncoordinated C=C (which is around 1650 cm$^{-1}$ in the free ligand), thus supporting the monomeric chelating 1,3-diene complex structure suggested by the symmetric nature of the n.m.r. spectrum (Figure 3). The n.m.r. resonance of the bridgehead methyl group appeared at rather lower field ($\tau$ 8.23; Table 4) compared to the exo- methyl group of 7 ($\tau$ 9.04).

The difference between the endo- and exo- methyl groups may be observed in the case of the exo- H and endo- H pentamethylcyclopentadienerhodium complexes, where the bridgehead methyl resonances appear at $\tau$ 8.69 and 9.67 respectively[126]. Other instances where endo- substituents resonated at lower fields compared to their positions when exo- have been noted[157]. It may thus be concluded that in pentamethylcyclopentadiene platinum complexes an endo- methyl group on the $sp^3$-carbon of the $C_5$-ring appears in the n.m.r. as a low field resonance around $\tau$ 8.2 compared to an exo- methyl group which appears at $\tau$ 9.0.

The endo- methyl group of the complex 15 showed coupling to $^{195}Pt$ ($J_{Me-Pt}$ = 5.5Hz).

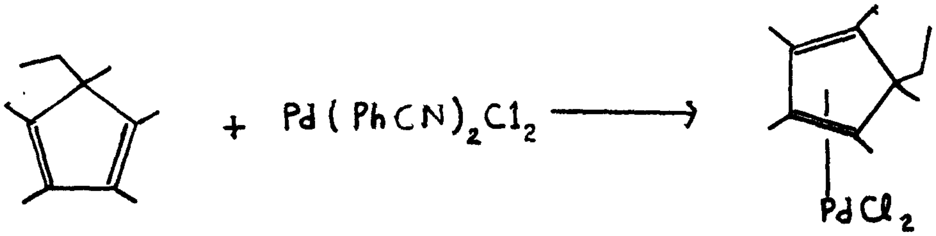
Reaction of 5-ethylpentamethylcyclopentadiene with potassium tetrachloroplatinate under acid conditions gave no 15, but only a low yield of 7



(7)

The low yield of 7 in this reaction is probably caused by the instability of the ligand, 8 (X=H), under the reaction conditions.

Reaction of 8 (X=H) with $Pd(PhCN)_2Cl_2$ in ethanol-free chloroform afforded the complex 16

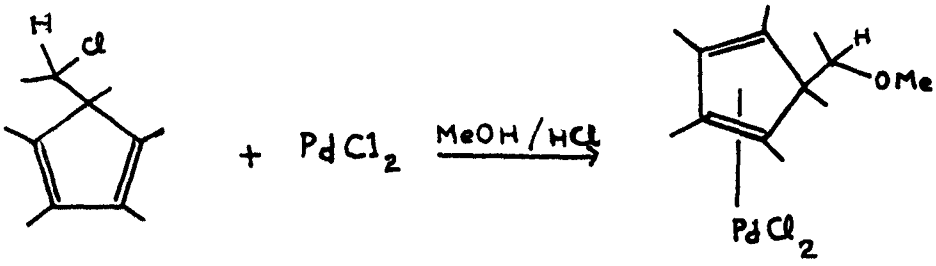


(16)

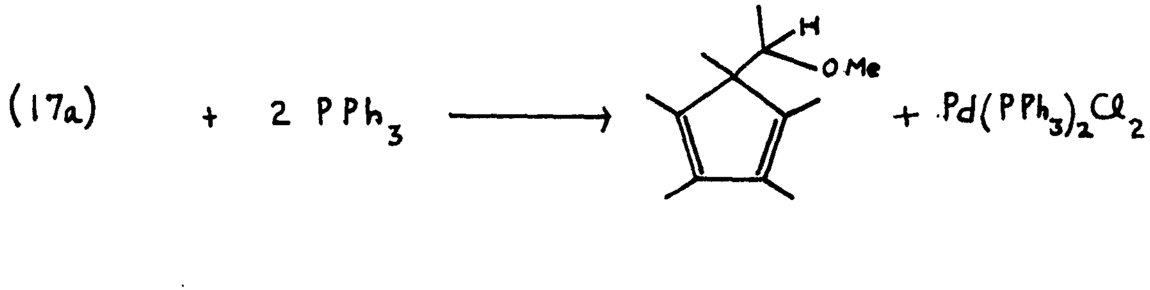
The i.r. and n.m.r. spectra were in agreement with the above structure for 16. The bridgehead endo- methyl group appeared in the n.m.r. (Figure 4) at $\tau$ 8.02 (Table 5), whereas, the exo-methyl in complex 13 resonated at $\tau$ 8.95.

### VII. {5-(1-Substituted-ethyl)pentamethylcyclopentadiene}palladium chloride complexes (17):

The reaction of 8 (X=Cl) with palladium chloride in dilute methanolic hydrochloric acid, unlike that with potassium tetrachloroplatinate, did not give the pentamethylcyclopentadiene complex, but, instead, gave a dark red complex, 17a, which analysed correctly for $Pd(C_5Me_5CH(OMe)Me)Cl_2$. The absence of a band due to an uncoordinated double bond in the infrared and the presence of only terminal Pd-Cl bonds[154,155], deduced from the far i.r. spectrum (Table 3), suggested a monomeric formula for the complex. The n.m.r. spectrum (Figure 5) can be interpreted in terms of the formulation for the complex 17a of dichloro{5-(1-methoxyethyl)pentamethylcyclopentadiene} palladium. The low field signal at $\tau$8.02 (Table 5) is assigned to the endo- methyl at $C_5$ in the cyclopentadiene ring.



(17a)

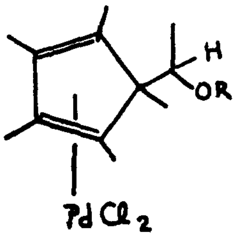


(8, X: OMe)

Treatment of the complex with triphenylphosphine liberated the ligand whose n.m.r. (Table 5) corresponded with that reported by Criegee and Grüner for 5-(1-methoxyethyl)pentamethylcyclopentadiene (8, X=OMe)[164].

Analogous reactions carried out in ethanol at 60° and isopropanol at 70° gave dark red complexes which were shown to be 5-(1-ethoxyethyl)- and 5-(1-isopropoxyethyl)pentamethylcyclopentadiene complexes 17b and 17c. The $C_5$-methyl appeared at τ 8.02 and 8.03 respectively (Table 5) and hence should be endo- in both cases.

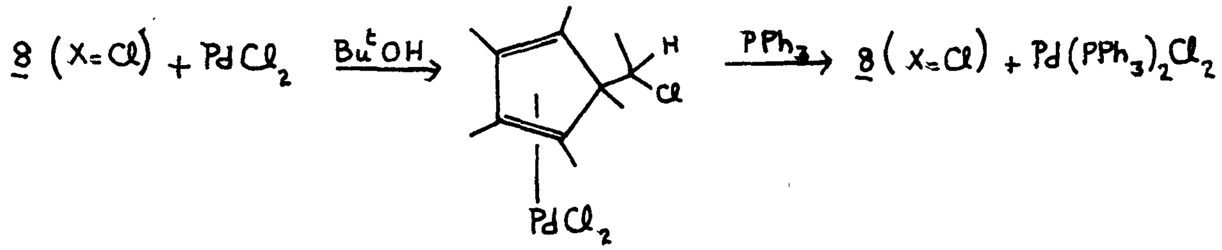
$$C_5Me_5CHClMe + PdCl_2 + ROH \xrightarrow{HCl}$$



17a, R = Me
17b, R = Et
17c, R = Pr$^i$

(17 a-c)

Reaction in t-butanol at 60° gave again a dark red complex, 17d, whose n.m.r. spectrum was identical with that of the yellow orange complex, 11, and also liberated 8 (X=Cl) on treatment with triphenylphosphine. It showed two bands, at 310 and and 322 cm$^{-1}$ (Table 3) in the far infrared, again in the region of terminal Pd-Cl bond stretching frequencies. But the dark red complex, 17d, was very stable in solution as well as in solid state unlike 11. The complexes 17d and 11 appear to be two different forms of a complex of the same structure, differing only in stability.



(17d)

When the reaction of PdCl$_2$ with 8 (X=Cl) was carried out at lower temperatures, a mixture of the appropriate alkoxy- complex (17a, b, or c) and the chloro- complex, 17d, was produced, the ratio of the alkoxy- to the chloro- complex depending on the temperature. The yield of the alkoxy- compound, compared to that of the chloro- compound decreased with decreasing temperature, as also the total yield. The results are given below.

Table 1. Nucleophilic substitution in $Pd(C_5Me_5CHClMe)Cl_2$

| Solvent | Ratio, $Pd(C_5Me_5CHORMe)Cl_2 : Pd(C_5Me_5CHClMe)Cl_2$ |
|---|---|
| Methanol (R=Me) | 0° - 1:1 |
| | 50° - 1:0 |
| Ethanol (R=Et) | 40° - 1:1 |
| | 50° - 3:2 |
| | 60° - 1:0 |
| Isopropanol ($R=Pr^i$) | 25° - 1:2 |
| | 50° - 1:1 |
| | 70° - 1:0 |

They are in accordance with the expected order of reactivity for nucleophilic substitution, i.e., $-OMe \gg -OEt > -OPr^i \gg -OBu^t$.

The conversion of 8 (X=Cl) to 8 (X=OR) seems to be catalysed by Pd(II), since in the absence of $PdCl_2$ the reaction did not proceed to the same extent under the same conditions.

The reaction in methanol at 0° and isopropanol at 25° gave, in addition to the soluble compounds 17, an insoluble yellow compound as the major product. This insoluble compound was identical with that obtained from the unstable yellow orange complex 11 and gave, on reaction with triphenylphosphine, 8 (X=Cl).

The complexes 17a and 17b were also obtained quantitatively from the reaction of 8 (X=OMe or OEt) with Pd(PhCN)$_2$Cl$_2$ in chloroform. Only the isomer with the bridgehead methyl endo- was again produced in this reaction. The methoxy- and the ethoxy- compounds, 8 (X=OMe, OEt) were prepared by a modification of the reaction described by Schäfer and Hellmann[134], who made 5-vinylpentamethylcyclopentadiene from HMDB and dimethylformamide hydrochloride in DMF. It was found that on heating HMDB with DMF-hydrochloride in DMF-alcohol (5:3) at 90° for 15 hrs, the alkoxy compounds (8, X=OMe, OEt) were obtained in 55% yield.

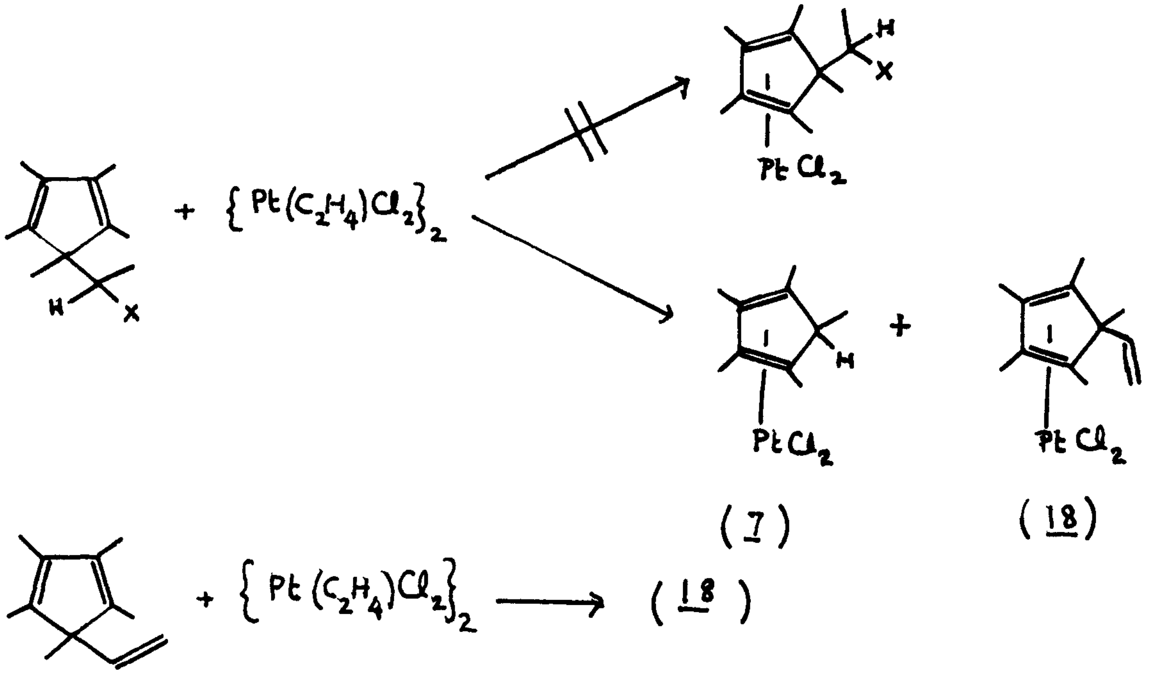
$$\text{HMDB+DMF.HCl+ROH} \xrightarrow{\text{DMF}} \text{C}_5\text{Me}_5\text{CH(OR)Me}$$

The chloroethylcyclopentadiene, 8 (X=Cl) on reaction with Pd(PhCN)$_2$Cl$_2$ in chloroform gave only the unstable yellow orange complex 11, instead of 17d.

In benzene, Pd(PhCN)$_2$Cl$_2$ and 8 (X=Cl, OMe or OEt) gave brownish yellow compounds insoluble in common organic solvents. The compound obtained with 8 (X=Cl) was very similar to the yellow insoluble compound obtained from 11. Palladium analysis showed it to contain one PdCl$_2$ unit per molecule of ligand. It seems probable that the reaction of the dienes 8 with Pd(PhCN)$_2$Cl$_2$ in benzene leads to the insertion of a double bond into a Pd-Cl bond giving π-allylic complexes analogous to 14.

### VIII. Dichloro(5-vinylpentamethylcyclopentadiene)platinum, 18:

Although dichloro{5-(1-methoxyethyl)pentamethylcyclopentadiene}platinum, (9), was proposed as an intermediate in the formation of 7 from HMDB and 8 (X=Cl), attempts to prepare this and other {5-(1-substituted ethyl)pentamethylcyclopentadiene}platinum complexes, analogous to the palladium complexes, 17, described above were unsuccessful. Even under mild conditions, the reaction of the cyclopentadienes 8 (X=Cl, OMe and OEt) with $\{Pt(C_2H_4)Cl_2\}_2$ in methylene chloride gave equal amounts of 7 and dichloro(5-vinylpentamethylcyclopentadiene)platinum, (18); the former was the only product from the reaction of 8 with $K_2PtCl_4$ in methanol.

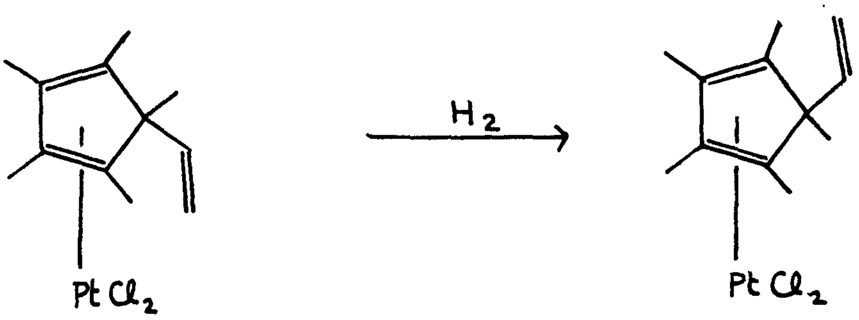


The pure complex 18 was synthesised by the reaction of 5-vinylpentamethylcyclopentadiene with $\{Pt(C_2H_4)Cl_2\}_2$ in methylene chloride. From the position of the bridgehead methyl protons in the n.m.r. spectrum (Figure 6, Table 4) and by comparison with other complexes, the methyl group is exo- and the vinyl endo- to the metal. The exo- methyl group in this complex showed coupling to $^{195}Pt$ (J = 5Hz) in the n.m.r. The geometry of the ligand, however, is such that the vinyl group cannot coordinate to the metal even in an apical position. This complex showed, in addition to the band at 1490 cm$^{-1}$ ($\nu_{C=C}$, coordinated), a medium band at 1636 cm$^{-1}$ arising from the uncomplexed vinylic double bond. In the free ligand it appeared as a strong band at 1627 cm$^{-1}$ [167]. The increase in this frequency on coordination of the ligand is perhaps due to the difference in the coupling of this vibration to others due to the change in symmetry.

The complex 18 underwent a most unusual isomerisation reaction when a slow stream of hydrogen was passed through a chloroform solution at 25°. The n.m.r. spectrum of the new species, 19, (Figure 6, Table 4) indicated it also to be a vinylpentamethylcyclopentadiene platinum complex, and reaction with triphenylphosphine liberated 5-vinylpentamethylcyclopentadiene as with 18. The n.m.r. spectrum showed only slight changes in chemical shift of the olefinic methyl groups, but the bridgehead methyl was shifted downfield ($\tau$8.23) and the vinylic protons upfield by comparison with 18. The $\nu_{C=C}$ (uncoordinated) in 19 was at 1629 $cm^{-1}$. These observations are most easily explained if 19 has the opposite stereochemistry to that of 18, with the vinyl group *exo*- to the metal and the methyl *endo*-. This is the stereochemistry observed for a variety of complexes, both for Pt(II) (for example, 15) and for Pd(II) (e.g. 17) and is presumably the thermodynamically most stable form. The formation of 18, particularly from 5-vinylpentamethylcyclopentadiene, is favoured probably for kinetic reasons, since the vinylic double bond would probably coordinate first to Pt(II) and lead it on to the diene system, thus resulting in the *endo*- disposition of the vinyl group.

The mechanism by which the isomerisation occurs is not clear, but it may involve the intermediate formation of a dihydrido-Pt(IV) complex, for example $\left[Pt(C_5Me_5CH{:}CH_2)H_2Cl_2\right]$, in which the diene ligand is labilised. The ligand may then either dissociate and recomplex to the same metal atom but on the opposite face, or altnernatively, it may be transferred to another metal atom in a bimolecular process.

The reaction with hydrogen usually proceeded up to ca. 90% completion after which slow decomposition to metal occurred.



(18) (19)

There was no evidence of hydrogenation nor were any intermediates detectable. Reagents such as $SnCl_2$, which might be expected to have a similar trans- labilising effect, did not cause this rearrangement.

IX. Infrared spectra and Molecular weights:

The substituted cyclopentadiene platinum and palladium complexes studied, showed a band at 1490 $cm^{-1}$ for the platinum(II) and 1500 $cm^{-1}$ for the palladium(II) complexes, owing to coordinated C=C stretching. No band arising from an uncoordinated double bond, which comes around 1650 $cm^{-1}$ in the free ligands, could be observed, except in the cases of the complexes 18 and 19 (which have uncoordinated double bonds due to the vinyl group) and therefore, both the olefinic bonds of the dienes must be complexed.

In the region 200-350 $cm^{-1}$, the complexes usually showed two (or occasionally three[+]) bands between 295 and 355 $cm^{-1}$ (Tables 2 and 3) for the chloro- complexes. This region is characteristic for vibrations arising from terminal M-Cl bonds (M=Pd, Pt)[154, 155]. In square planar complexes of the type cis-$[ML_2X_2]$, the $\nu_{M-Cl}$ fall in a rather wide range due to the high sensitivity of the metal-halogen bonds to the nature of the trans-ligands. In the case of cis-$[PtL_2Cl_2]$ a rough inverse correlation between the trans-effect of L and $\nu_{Pt-Cl}$ has been observed[168]. $[Pt(1,5\text{-cyclooctadiene})Cl_2]$ forms an exception in the series; the $\nu_{Pt-Cl}$ are high in spite of the high trans-effect of olefinic groups. This exception is explained as being due to the mesomeric mechanism by which olefins exert their trans-influence; this trans-influence will only be felt by a ligand which forms strong $\pi$-bond with the metal. Chloride does not form strong $\pi$-bonds with Pt(II) and $\nu_{Pt-Cl}$ is, therefore, not greatly affected by cyclooctadiene. A very similar situation seems to exist in the case of the cyclopentadiene Pt(II) and Pd(II) complexes. The $\nu_{Pt-Cl}$ for the cyclopentadiene platinum complexes and $Pt(HMDB)Cl_2$ (Table 2) are very similar to those of $[Pt(1,5\text{-cyclooctadiene})Cl_2]$ and hence contain only

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[+] The third band may arise from a crystal splitting effect in the solid state; cis-dichlorides are expected to have two bands.

## Table 2

Far i.r. spectra of the diene-platinum complexes

| | $\nu_{\text{Pt-X}}$ (cm $^{-1}$) |
|---|---|
| Pt (HMDB)Cl$_2$ (6) | 298(m), 318(vs), 338(vs) |
| Pt (C$_5$Me$_5$H)Cl$_2$ (7) | 312(vs), 330(s) |
| Pt (C$_5$Me$_5$H)Br$_2$ | 222(s), 227(sh) |
| Pt (C$_5$Me$_5$Et)Cl$_2$ (15) | 317(sh), 335(vs) |
| Pt (C$_5$Me$_5$CH:CH$_2$)Cl$_2$ (18) | 300(sh), 315(s), 337(vs) |
| Pt (COD[+])Cl$_2$ (Ref. 154) | 316, 338 |
| Pt (COD[+])Br$_2$ (Ref. 154) | 215, 229 |

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[+] COD = 1,5-cyclooctadiene

## Table 3

Far i.r. spectra of the diene-palladium complexes

| | $\nu_{\text{Pd-X}}$(cm $^{-1}$) |
|---|---|
| Pd (C$_5$Me$_5$CHClMe)Cl$_2$ (11) | 315 (broad) |
| Pd (C$_5$Me$_5$CHClMe)Cl$_2$ (17d) | 310(vs), 322(vs) |
| Pd (C$_5$Me$_5$CH(OMe)Me)Cl$_2$ (17a) | 315(vs, b) |
| Pd (C$_5$Me$_5$CH(OEt) Me)Cl$_2$ (17b) | 300(sh), 315(vs) |
| Pd (C$_5$Me$_5$CH(OPr$^i$) Me)Cl$_2$ (17c) | 300(vs), 320(vs) |
| Pd (C$_5$Me$_5$Et)Cl$_2$ (16) | 302(sh), 311(vs) |
| Pd (C$_5$Me$_5$H)Cl$_2$ (13) | 290(s), 315(s), 335(vs), 340[*](sh) |
| Pd (COD[+])Cl$_2$ (Ref. 154) | 296, 325, 335 |
| Pd (HMDB)Cl$_2$ (Ref. 146) | 313, 329 |

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[*] Sample contains excess PdCl$_2$ to which some of the bands may be ascribed.

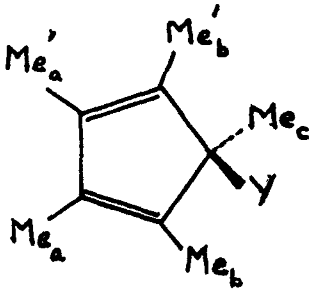
terminal Pt-Cl bonds. The palladium complexes (Table 3) also show $\nu_{Pd-Cl}$ similar to those observed in the complexes $[Pd(1,5\text{-cyclooctadiene})Cl_2]$[154] and $[Pd(HMDB)Cl_2]$[146] and so they also contain only terminal Pd-Cl bonds. The bridging M-Cl bonds trans to olefinic groups are observed at lower frequencies (220-280 cm$^{-1}$ for Pd(II) and 250-300 cm$^{-1}$ for Pt(II)).

The dibromo-complex, $[Pt(C_5Me_5H)Br_2]$, showed $\nu_{Pt-Br}$ in the region of terminal Pt-Br bonds, as observed for $[Pt(1,5\text{-cyclooctadiene})Br_2]$ (Table 2).

Thus, on the basis of infrared evidence all these complexes are monomeric in the solid since any dimerisation would be expected to occur via halogen bridges, which are not detected. But, osmometric molecular weight measurements in chloroform gave rather high values especially for the palladium(II) complexes. The molecular weight of the palladium complexes were 20-50% too high for monomeric species and suggested that some degree of association was occurring. However, the n.m.r. spectra in this solvent showed no noticeable dependence on temperature or concentration and are best interpreted in terms of the presence of only one species. If the molecular weight results are correct, and not simply due to the choice of an inappropriate calibrant, there is a contradiction between them and the other properties of the complexes. This conflict could only be resolved if there were an equilibrium (in solution) between monomer and halogen-bridged dimer and if the n.m.r. chemical shifts of the two species were identical in all cases.

## X. N.m.r. Spectra:

The $^1$H nuclear magnetic resonance data are shown in Tables 4 and 5 for the 5-substituted-1,2,3,4,5-pentamethylcyclopentadienes both as free ligands and in complexes with platinum(II) and palladium(II).



(20)

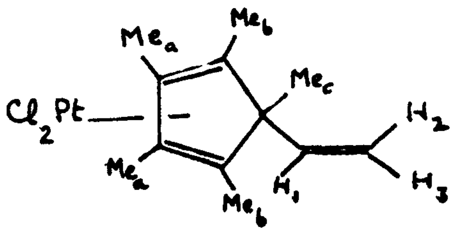
The olefinic methyl protons ($Me_a$, $Me_b$) in the free ligands, 20, show two different types of spectra, depending on the nature of the substituent Y. When Y contains an asymmetric centre (-CHXMe), $Me_a$ and $Me'_a$, and $Me_b$ and $Me'_b$, are no longer equivalent and should appear as four separate resonances. This effect is often complicated by accidental overlapping and homoallylic coupling between the methyl groups, particularly in $CDCl_3$, even at 100 MHz. However, in benzene, when Y = -CHClMe or -CH(OR)Me, four resonances are resolved. Pentamethylcyclopentadiene, 5-ethyl(pentamethylcyclopentadiene, and 5-vinylpentamethylcyclopentadiene[167] where there is no asymmetric centre at Y, show two resonances and $\tau(\mathrm{Me}_a) = \tau(\mathrm{Me}'_a)$, $\tau(\mathrm{Me}_b) = \tau(\mathrm{Me}'_b)$.

The spectra of the complexes are less complicated, even in $CDCl_3$. Except for the complexes 11 and 17(a-d), which show three or four resonances due to the olefinic methyls, all the others show two resonances - singlets in the case of Pd(II) complexes and with the satellites arising from coupling to $^{195}$Pt (34% abundant) in the case of Pt(II) complexes. The Pd(II) complexes show a characteristic pattern in that the lowest field signals due to two of the four olefinic methyl groups, are always around $\tau$7.72 and within 0.02 ppm of each other, while the higher field resonances are in the region, $\tau$8.25-8.45 and slightly more different in chemical shift (0.05-0.10 ppm). In the case of the platinum complexes, the corresponding signals are around $\tau$ 7.77 and $\tau$8.5-8.7 respectively. The lower field olefinic methyl protons are usually ascribed to $\mathrm{Me}_a(\mathrm{Me}'_a)$ and the present results confirm this assignment for the complexes, since the effect of the substituent Y and its asymmetry should be felt more by $\mathrm{Me}_b$ and $\mathrm{Me}'_b$ than by $\mathrm{Me}_a$ and $\mathrm{Me}'_a$. In two cases, 17a and 17b, $\mathrm{Me}_a$ and $\mathrm{Me}'_a$ are indeed coincident, in spite of the asymmetry of the -Y group.

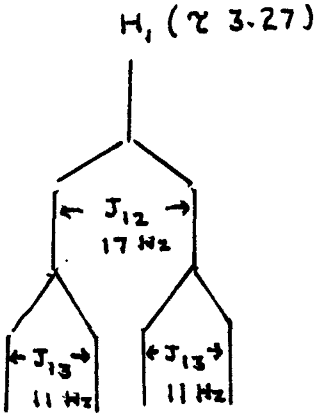
The assignment of the olefinic methyl resonances in the free ligands 8 (X = Cl, OR) is less straightforward and the pattern usually observed (at 100 MHz, benzene) is that the two central peaks are sharp multiplets with a splitting of ca. 1 Hz, while the highest and lowest field methyl resonances appear as somewhat broader resonances with no splitting resolvable (Figure 7). These shapes arise from homo-allylic coupling and one possible interpretation is that the highest and lowest resonances are due to $Me_a$ and $Me'_a$, which can couple to each other as well as to $Me_b$ (or $Me'_b$), while the latter, which can only couple with $Me_a$ (or $Me'_a$) are seen as sharper resonances, probably quartets.

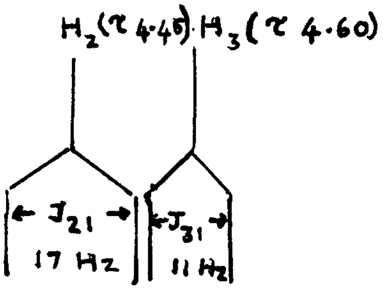
The position of the bridgehead methyl, $Me_c$, in the spectrum is also of interest. In the free ligands it is usually at ca. $\tau$ 9.0 and is in the same position in the pentamethylcyclopentadiene complexes 7 (and its bromo- and iodo-analogues), and 13 and in 18. In all other complexes it has shifted to lower field by approximately 1 ppm, implying that considerable deshielding has occurred, possibly through its interaction with the metal. These results are consistent with $Me_c$ being *endo*- to the metal in the complexes 11, 15, 16, 17(a-d) and 19 and *exo*- in the rest.

The deshielding of an endo- substituent on the $C_5$-carbon of the cyclopentadiene ring as well as the shielding of the substituent in the exo- position is clearly seen from the n.m.r. spectra of 5-vinylpentamethylcyclopentadieneplatinum complexes and the free ligand. The vinyl protons of the free ligand appear as an unresolved, closely spaced multiplet at τ 4.96 (in $CDCl_3$)[167], which is at rather high field for such protons. In the complex 18, which has an endo-vinyl group, the proton $H_1$ comes at the low field value of 3.27 and



shows coupling to $^{195}Pt$ ($J_{H\,Pt}$ = 7Hz); the protons $H_2$ and $H_3$ also appear at lower fields and the spectrum is of the AA'X type, usually observed with vinyl groups.





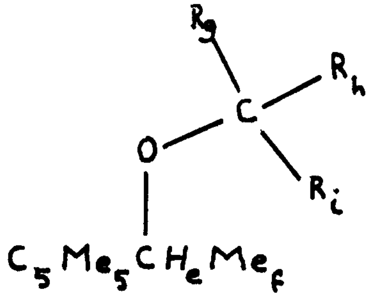
In complex 19, with the vinyl group in the exo- position these protons come higher field while still showing the characteristics of an AA'X spectrum. In this case the vinyl protons, especially $H_1$, are shielded by the $\pi$-electrons of the cyclopentadiene. The geometry of the cyclopentadiene ring in the complex, probably, is such that the proton $H_1$ is not as close to the $C_5$-ring as in the case of the free ligand where the chemical shifts of $H_1$, $H_2$ and $H_3$ are so similar that the spectrum becomes more complex than AA'X. A bending up of the tetrahedral carbon from the plane of the four olefinic carbons of the cyclopentadiene ring, would explain the difference in shielding of the vinyl group in the free ligand and the complex 19.

Comparison of the resonances due to the Y group in complexes and the free ligands gives information regarding the conformation and geometry of the coordinated cyclopentadienes. For example, the methyl group $Me_f$ of Y (Y = $CHXMe_f$; X = H, Cl or OR) is shifted downfield by 0.13 - 0.41 ppm in the complexes. The proton $H_e$ of the $-CH_eXMe$ (X = Cl, OR) group in the palladium complexes 17a-d resonate 0.14-0.28 ppm to higher field compared to the free ligands 8 (X = Cl or OR). Thus the preferred conformation for the -CHXMe group in the complexes $[M(C_5Me_5CHXMe)Cl_2]$ (M = Pt, X = H; M = Pd, X = H, Cl, OR) seems to be that in which the methyl group $Me_f$ is turned away from, rather than over the $C_5Me_5$ ring.

In the n.m.r. spectrum of 8 (X = OEt), the proton $H_e$ and the methylene protons $H_g$ and $H_h$ of the ethoxy- group appear as a complex multiplet consisting of 20 lines between $\tau$6.26 and 6.90 (Figure 2). However, this has been resolved into an $ABX_3$ pattern due to $H_g$ and $H_h$, which are inequivalent and further split by the methyl $Me_i$, and an $AX_3$ pattern due to the proton $H_e$ split by $Me_f$. The protons $H_g$ and $H_h$ differ in chemical shift by 0.27 ppm. This assignment has been verified by spin decoupling experiments.

In the complex 17b also, a similar pattern is observed. Analysis of the spectrum yields for the difference in chemical shifts for $H_g$ and $H_h$ a value of 0.39 ppm, with the diamagnetic shift for $H_h$ (0.17 ppm) compared to the free ligand being higher than that for $H_g$ (0.05 ppm). The coupling constant $J_{(H_g-H_h)}$ is the same (9 Hz) in the free ligand and the complex.

An exactly similar effect is observed for the magnetically inequivalent isopropoxy methyls ($Me_g$, $Me_h$) in 17c.



($R_g = R_h = H$ ; $R_i = Me$)

($R_g = R_h = Me$ ; $R_i = H$)

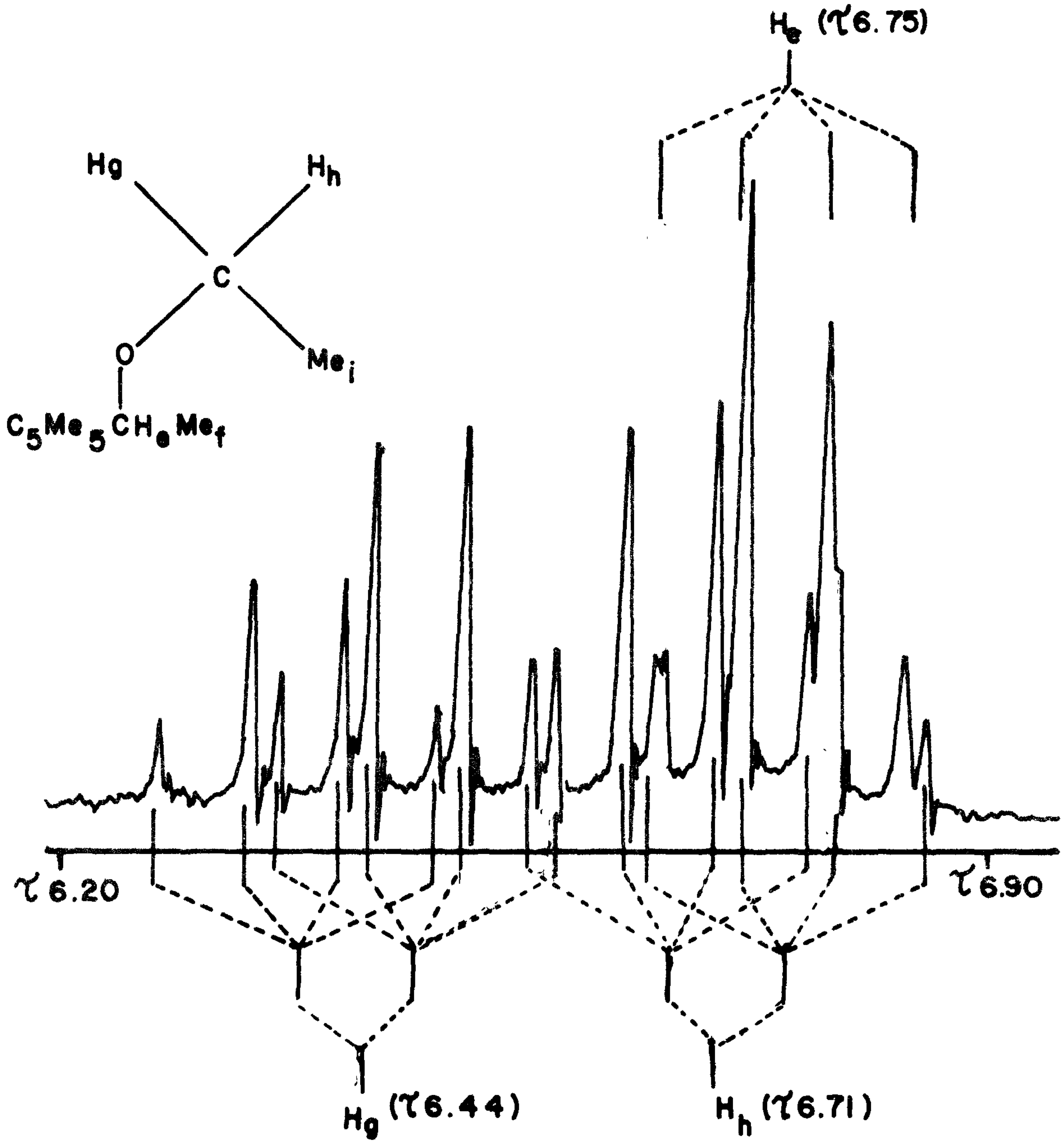
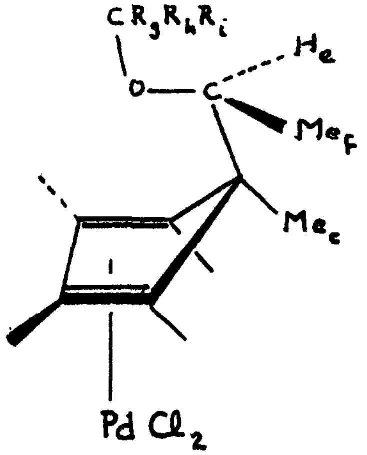


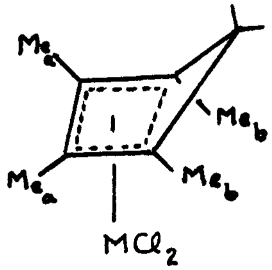
Figure 2: N.m.r. spectrum of 5-(1-ethoxyethyl)pentamethylcyclopentadiene (100 M Hz, CDCl$_3$) from τ6.20 - 6.90.

The greater inequivalences of $R_g$ and $R_h$, the diamagnetic shift of their resonances, and the deshielding of $Me_f$ on complexation can be understood if the preferred conformer in the complex is 21, or its enantiomer, rather than the conformer where $Me_f$ is over the $C_5Me_5$ ring. It is also likely that the bridgehead carbon is bent away from the plane of the other four carbons in the ring. This geometry is common in many cyclopentadiene complexes[57].



( 21 )

Apart from the chemical shift data which suggest the bending away of the $sp^3$ carbon of the cyclopentadiene ring from the plane of the four $sp^2$ carbons, some other features in the n.m.r. spectra also support the nonplanarity of the $C_5Me_5$ ring. No homoallylic coupling, which is significant in the free ligands, can be observed between any of the olefinic methyl protons in the complexes. In the complexes the olefinic methyl groups $Me_a$ and $Me_b$ must have changed their relative orientations, thus reducing the coupling between them[169]. In the platinum complexes the coupling of $^{195}Pt$ to $Me_a$ is much larger (30-40 Hz) than to $Me_b$ (10-14 Hz). Johnson, et al.[31], have suggested on the basis of some studies of olefin-Pt(II) complexes, that J(Pt-C-C-H) decreases with a decrease in the distance between the metal atom and the methyl proton. They also concluded that $^{195}Pt$-H coupling constants of olefin ligand are more complex in origin than would be expected from consideration of only the Fermi contact term and that they are not a reliable indication of the s-character of the metal-olefin bond. If the same situation applies to the present system, i.e., the $^{195}Pt$-H coupling constants are determined more by the proximity in space of the methyl protons to the platinum than by the $\sigma$-character of the Pt-olefin bond, it would suggest that the methyls, $Me_b$, were bent towards the metal in the complexes. This would be expected if the structures of the complexes tended towards that of a 'homo-cyclobutadiene' complex (22).



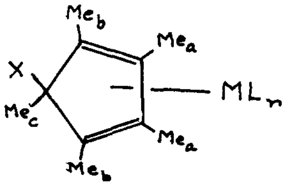
(22)

A tendency towards a 'homo-cyclobutadiene' structure would lead to an increase in non-bonded interactions between the $C_5Me_5$ ring and the $-OCR_gR_hR_i$ group and to an increase in the non-equivalence of $R_g$ and $R_h$ as observed in the palladium complexes where complexing even affects the chemical shifts of the magnetically inequivalent $H_g$ and $H_h$ (in 17b) or $Me_g$ and $Me_h$ (in 17c).

Since a large number of cyclobutadiene complexes of the general form $\{M(C_4R_4)X_2\}_2$ (M = Ni, Pd, Pt; X = halogen) are known and are relatively stable[66], this would also rationalise the stability of the cyclopentadiene complexes on electronic grounds. However, in contrast to the cyclobutadienepalladium and platinum halides, which are dimeric with a 5-coordinate metal[65, 66], the cyclopentadiene complexes are monomeric.

With the exception of the cyclobutadiene complexes, 1, 3-diene complexes of palladium and platinum in which both diene linkages are bonded to one metal atom were hitherto unknown. The ability of the 5-substituted pentamethylcyclopentadienes to complex symmetrically as a diene can be ascribed largely to the diene being constrained in the cisoid manner which ensures that if one double bond is complexed, the other must also be.

Table 4. 'H n.m.r. spectra of pentamethylcyclopentadiene platinum complexes and tricarbonyl(pentamethylcyclopentadiene)iron



Chemical shifts($\tau$), coupling constants (Hz) to platinum given in parentheses.

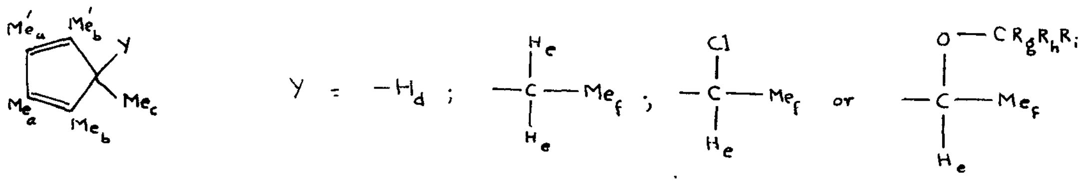
| | $Me_a$ | $Me_b$ | $Me_c$ | X |
|---|---|---|---|---|
| $Pt(C_5Me_5H)Cl_2$ (7) | 7.77(38) | 8.54(10) | 9.04d<br>($J_{HMe}$ 6.5) | 6 65q<br>(1H, $J_{HMe}$ 6.5) |
| $Pt(C_5Me_5H)Br_2$ | 7.82(39) | 8.50(12.5) | 9.03d<br>($J_{HMe}$ 6.5) | a |
| $Pt(C_5Me_5H)I_2$ | 7.88(33) | 8.45(14) | 9.03d<br>($J_{HMe}$ 6.5) | a |
| $Fe(C_5Me_5H)(CO)_3$ (12) | 7.87 | 8.49 | 9 31d<br>($J_{HMe}$ 6 5) | 7.31q<br>(1H, $J_{HMe}$ 6.5) |
| $Pt(C_5Me_5CH{:}CH_2)Cl_2$ (18) | 7.73(37) | 8.71(12.5) | 8.97(5) | 3.27m(1H, $J^{cis}_{HH}$ 11; $J^{trans}_{HH}$ 17; $J_{HPt}$ 7).<br>4.45d (1H; $J^{cis}_{HH}$ 11; $J^{gem}_{HH}$ ~0). 4.60d (1H, $J^{trans}_{HH}$ 17) |
| $Pt(C_5Me_5CH{:}CH_2)Cl_2$ (19) | 7.77(36) | 8.57(12) | 8.23(5) | 4.73m(1H)<br>4.98d(1H, $J^{cis}_{HH}$ 11)<br>5.13d(1H, $J^{trans}_{HH}$ 17) |
| $Pt(C_5Me_5Et)Cl_2$ (15) | 7.78(37) | 8.73(11) | 8.27(5.5) | 8.73q (2H)<br>9.53t<br>(3H, $J_{HH}$ 7) |

[a] The bridgehead hydrogen was not observed here.

Table 5

$^1$H N.m r. spectra (τ) of some pentamethylcyclopentadienes and their palladium chloride complexes in $CDCl_3$ at 100 MHz.

Coupling Constants are given in Hz



| Compound | $Me_a$, $Me_a'$, $Me_b$, $Me_b'$ | $Me_c$ | $H_d$ | $H_e$ | $Me_f$ | $R_g$ | $R_h$ | $R_i$ |
|---|---|---|---|---|---|---|---|---|
| $C_5Me_5CHClMe$ (8, X=Cl) | 8.12(3H,b), 8.26(6H,m),<br>8.31(3H,b)[a] | 8.90 | | 5.87q<br>($J_{e-f}$ 6.5) | 8.97d<br>($J_{f-e}$ 6.5) | | | |
| $Pd(C_5Me_5CHClMe)Cl_2$ (17d) | 7.70, 7.72, 8.32, 8.43 | 7.85 | | 6.15q<br>($J_{e-f}$ 7) | 8.56d<br>($J_{f-e}$ 7) | | | |
| $C_5Me_5CH(OMe)Me$ (8, X=OMe) | 8.1 - 8.4 (12H, m,b)[b] | 8.98 | | 6.83q<br>($J_{e-f}$ 6.5) | 9.38d<br>($J_{f-e}$ 6.5) | $R_g = R_h = R_i$ = H. 6.70(s) | | |
| $Pd(C_5Me_5CH(OMe)Me)Cl_2$ (17a) | 7.73(6H,s), 8.36, 8.42 | 8.00 | | 7.03q<br>($J_{e-f}$ 6.5) | 9.03d<br>($J_{f-e}$ 6.5) | $R_g = R_h = R_i$ = H. 6.78(s) | | |
| $C_5Me_5CH(OEt)Me$ (8, X=OEt) | 8.1 - 8.4 (12H, m,b)[c] | 8.97 | | 6.75q<br>($J_{e-f}$ 6) | 9.39d<br>($J_{f-e}$ 6) | $H_g$ 6.44dq<br>($J_{g-h}$ 9<br>$J_{g-i}$ 7) | $H_h$. 6.71dq<br>($J_{h-g}$ 9<br>$J_{h-i}$ 7) | $Me_i$ 8.84t<br>($J_{i-g}$ =<br>$J_{i-h}$ = 7) |

Table 5 (continued)

| Compound | $Me_a$, $Me_{a'}$, $Me_b$, $Me_{b'}$ | $Me_c$ | $H_d$ | $H_e$ | $Me_f$ | $R_g$ | $R_h$ | $R_i$ |
|---|---|---|---|---|---|---|---|---|
| $Pd(C_5Me_5CH(OEt)Me)Cl_2$ (<u>17b</u>) | 7.74(6H, s), 8.37, 8.42 | 8.02 | | 6.95q<br>($J_{e-f}$ 6.5) | 9.01d<br>($J_{f-e}$ 6.5) | $H_g$, 6.49 dq<br>($J_{g-h}$ 9,<br>$J_{g-i}$ 7) | $H_h$, 6.88 dq<br>($J_{h-g}$ 9<br>$J_{h-i}$ 7) | $Me_i$ 8.91t<br>($J_{i-g}$ =<br>$J_{i-h}$ = 7) |
| $C_5Me_5CH(OPr^i)Me$ (<u>8</u>, $X$-$OPr^i$) | 8.20(3H, s, b), 8.26(3H, m),<br>8.29(3H, m), 8.37(3H, s, b) | 9.02 | | 6.74q<br>($J_{e-f}$ 6) | 9.43d<br>$J_{f-e}$ 6) | $Me_g$ 8.88d<br>($J_{g-i}$ 6) | $Me_h$ 8.90d<br>($J_{h-i}$ 6) | $H_i$, 6.53<br>(Septet,<br>$J_{i-g}$=$J_{i-h}$ 6) |
| $Pd(C_5Me_5CH(OPr^i)Me)Cl_2$ (<u>17c</u>) | 7.76, 7.78, 8.39, 8.45 | 8.03 | | 6.88q<br>($J_{e-f}$ 6.5) | 9.03d<br>($J_{f-e}$ 6.5) | $Me_g$, 8.94d<br>($J_{g-i}$ 6) | $Me_h$ 9.03d<br>($J_{h-i}$ 6) | $H_i$, 6.60m |
| $C_5Me_5Et$ (<u>8</u>, X=H) | 8.23(6H, s), 8.34(6H, s)[d] | 9.13 | | 8.61q<br>($J_{e-f}$ 7) | 9.75t<br>($J_{f-e}$ 7) | | | |
| $Pd(C_5Me_5Et)Cl_2$ (<u>16</u>) | 7.72(6H, s), 8.42(6H, s) | 8.02 | | 8.55q<br>($J_{e-f}$ 7) | 9.62t<br>($J_{f-e}$ 7) | | | |
| $C_5Me_5H$ | 8.18(12H, m)[e] | 9.00d<br>($J_{c-d}$ 7.5) | 7.52m | | | | | |
| $Pd(C_5Me_5H)Cl_2$ (<u>13</u>) | 7.72(6H, s), 8.25(6H, s) | 8.95d<br>($J_{c-d}$ 7.5) | | | | | | |

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[a] In benzene, 8.08(3H, s, b), 8.40(3H, m), 8.45(3H, m), 8.59(3H, s, b)

[b] In benzene, 7.92(3H, s, b), 8.20(3H, m), 8.23(3H, m), 8.30(3H, s, b)

[c] In benzene, 7.73(3H, s, b), 8.00(3H, m), 8.03(3H, m), 8.05(3H, s, b)

[d] In benzene 8.13(6H, s), 8.22(6H, s)

[e] In benzene, 7.88(6H, s), 7.93(6H, s)

## XI. Summary and Conclusions:

A number of 1, 3-diene complexes of palladium(II) and platinum(II) were prepared with 5-substituted-1, 2, 3, 4, 5-pentamethylcyclopentadienes, $C_5Me_5Y$, by reaction with hexamethylbicyclo$[2, 2, 0]$-hexadiene,HMDB, or with ligands derived from HMDB.

Reaction of HMDB with $\{Pt(C_2H_4)Cl_2\}_2$ gave $[Pt(HMDB)Cl_2]$ and with $K_2PtCl_4$ under acid conditions, it gave $[Pt(C_5Me_5H)Cl_2]$, (7). The latter complex was also obtained from the reaction of $K_2PtCl_4$ with $C_5Me_5CHXMe$ (X = H, Cl, OMe, OEt) or $C_5Me_5COMe$ in acidic methanol. A mechanism was proposed for these reactions.

A mixture of 7 and dichloro(5-vinylpentamethylcyclopentadiene)-platinum, (18), was obtained on reaction of $C_5Me_5CHXMe$ with $\{Pt(C_2H_4)Cl_2\}_2$ in aprotic solvents. Complex 18 was the sole product from a similar reaction with 5-vinylpentamethylcyclopentadiene and an analogous complex was obtained from 5-ethylpentamethylcyclopentadiene. The stereochemistries of these complexes have been determined. The vinylpentamethylcyclopentadiene complex (18, vinyl endo-) underwent an unusual hydrogen-catalysed reaction to give the isomeric complex (19, vinyl exo- to the metal).

Reaction of 7 with $Fe_3(CO)_{12}$ gave $\{Fe(C_5Me_5)(CO)_2\}_2$ and endo-H-$[Fe(C_5Me_5H)(CO)_3]$. Reaction with $Co_2(CO)_8$ gave $[Co(C_5Me_5)(CO)_2]$.

Reaction of 5-substituted-pentamethylcyclopentadienes with palladium chloride gave the appropriate cyclopentadienepalladium chloride complexes, $Pd(C_5Me_5Y)Cl_2$. Reaction with HMDB or $C_5Me_5CHClMe$, (8, X = Cl) under acid conditions did not give any $Pd(C_5Me_5H)Cl_2$, (13), which was prepared from $C_5Me_5H$ and $Pd(PhCN)_2Cl_2$. Reaction of 8 with $PdCl_2$ in acidic alcohol gave the corresponding dichloro{5-(1-alkoxyethyl)pentamethylcyclopentadiene}-palladium, (17a-c), except in t-butanol where dichloro{5-(1-chloroethyl)pentamethylcyclopentadiene}palladium, (17d), was produced. N.m.r. spectra showed all these Pd(II) complexes, except $Pd(C_5Me_5H)Cl_2$, to have the bridgehead methyl endo- . In $Pd(C_5Me_5H)Cl_2$, the H- was endo- to the metal.

On the basis of differences in the proton magnetic resonance spectra of the free ligands and the complexes, it is concluded that a deformation of the ligand, probably towards a 'homo-cyclobutadiene' structure, occurs on complexation. The stability of these complexes can be understood on the basis of this type of structure.

# EXPERIMENTAL

# EXPERIMENTAL

Melting Points:

These were determined using a Thomas Hoover Capillary melting point apparatus and are uncorrected. The melting point capillaries were, in general, sealed under vacuum ( $<0.1$ mm Hg).

Infrared Spectra:

These were run on samples made up as potassium bromide discs. Spectra were recorded on a Beckmann IR5 or Perkin Elmer 337 spectrophotometer. Far infrared spectra were recorded on a Beckmann IR12 spectrophotometer with samples made into Nujol mull and held between polyethylene plates.

Nuclear Magnetic Resonance Spectra:

Proton Magnetic Resonance spectra were obtained on a Varian A60, Varian T60 and a Varian HA100 spectrometer. Tetramethylsilane (TMS) was used as an internal reference. All decoupling experiments were carried out on the HA100 instrument.

## Microanalyses:

Elemental analyses and determination of osmometric molecular weights were performed by Chemalytics, Inc., Tempe, Arizona, Galbraith Laboratories Inc., Knoxville, Tenn. and A. B. Gygli, Toronto.

## Reagents:

Reagent grade solvents were used. The petroleum ether used was the fraction boiling between 30-60°. Palladium Chloride and potassium tetrachloroplatinate were obtained from Johnson, Mathey and Mallory. Hexamethyl (Dewar benzene) was obtained as a gift from Dr. W. Schäfer.

## Experimental Techniques:

All reactions were carried out under nitrogen atmosphere. Solutions were stirred magnetically using Teflon-coated micro-stirring bars. Solvents were removed under vacuum on a rotary evaporator.

## Potassium trichloroethyleneplatinate - Zeise's salt:

Zeise's salt was prepared following the method developed by Cramer, *et al.*[153,170]. Potassium tetrachloroplatinate (2.75g, 6.63 mmoles) was dissolved in water (12 ml) containing hydrochloric acid (2 ml conc.). The solution was flushed with ethylene, stannous chloride (0.05g, 0.23 mmole) added and ethylene bubbled for about

15 hours. The solution was chilled to $0^{o}$ and yellow crystals, which formed, separated by filtration, washed with a minimum amount of cold methanol and dried in air (1.7g, 69%).

Di-μ-chlorodichlorobis(ethylene)diplatinum - Zeise's dimer

This was prepared according to the method described by Chatt and Searle[171]. Zeise's salt (1.61g, 4.37 mmoles) was taken up in ethanol (~40 ml) containing 4% hydrochloric acid. The potassium chloride precipitated was filtered off and the filtrate evaporated under reduced pressure to yield an orange oil, which solidified on warming up to $60^{o}$. The orange solid obtained (1.23g, 96%) was purified by recrystallisation from boiling benzene.

Dichlorobis(benzonitrile)palladium, $\left[Pd(PhCN)_2Cl_2\right]$:

The method of Kharasch, *et al.*[172], was used for the preparation of the above complex. Palladium chloride (8g, 46 mmoles) was dissolved in benzonitrile (200 ml) by stirring with heating to $115-120^{o}$ for 2 hrs. The hot solution was filtered and poured into light petroleum (2 litres). The yellow precipitate (17g, 98%) was filtered, washed with petroleum ether and air-dried.

5-(1-Chloroethyl)pentamethylcyclopentadiene, (8, X = Cl):

This was prepared adapting the method described by Paquette and Krow[158]. Hexamethyl(Dewar benzene), HMDB, (Hexamethylbicyclo-$[2,2,0]$hexadiene), (4) (20g, 123 mmoles) was dissolved in methylene chloride (100 ml) and dry hydrogen chloride gas bubbled through it, until it turned dark violet in colour (~2 hrs.). Then it was left stirring overnight. The solvent was then evaporated off and the brown oil remaining was distilled under vacuum (0.02 mm Hg). The pure product distilling at 52° was collected (16g, 65%). The identity of the product was established by its n.m.r. spectrum (Figure 7, Table 5), which does not agree with that reported by Paquette and Krow.

5-(1-Alkoxyethyl)pentamethylcyclopentadiene, (8, X = OR):

Hexamethyl (Dewar benzene) (8g, 50 mmoles) and dimethylformamide hydrochloride (8.2g, 75 mmoles) were heated together in dimethylformamide (25 ml) containing methanol (15 ml) (for the methoxy-compound, 8 (X = OMe)) or ethanol (15 ml) (for preparing the ethoxy-compound, 8 (X = OEt)) at 90° for 15 hours. The mixture was then poured into excess water and extracted with petroleum ether. Evaporation of the petrol afforded a brown oil, the n.m.r. spectrum of which showed it to be a mixture containing hexamethylbenzene, HMB (10%), 5-vinylpentamethylcyclopentadiene (13%), the required alkoxy-compound, 8 (X = OMe or OEt) and an unidentified alkoxy-compound (22%). The mixture was chromatographed over alumina in petrol ether and the alkoxy compound, 8, separated from the impurities. Final purification was done by vacuum distillation. The methoxy-compound

8 (X = OMe), distilled at ~50°/0.02 mm and the ethoxy-compound, 8 (X = OEt), at 55°/0.02 mm. The identity of these compounds was, again, checked by n.m.r. spectra (Table 5). The n.m.r. spectrum of the methoxy-compound agrees well with that reported by Criegee and Grüner[166], but not with that by Paquette and Krow[158]. The ethoxy-compound was also identified by elemental analysis. Anal. calcd. for $C_{14}H_{24}O$: C,80.7; H,11.6; Found: C, 81.7; H, 11.0.

5-Vinylpentamethylcyclopentadiene:

This was prepared as described by Schäfer and Hellmann[132]. Hexamethyl (Dewar benzene) (4.05g, 25 mmoles) was heated in dimethylformamide (20 ml), containing dimethylformamide hydrochloride (8.2g, 75 mmoles) at 115° for 15 hrs. The product was extracted with light petrol. The petrol extract was evaporated to yield a mixture of the desired product (75%) and hexamethylbenzene (25%). Vacuum distillation afforded pure 5-vinylpentamethylcyclopentadiene (B.P. 33°/0.4 mm) (3g, 75%). The n.m.r. spectrum in $CDCl_3$ was identical with that described by Maitlis, et al.[167], and was as follows:

$\tau$ 4.96 (3H,m), 8.21 (6H), 8.33 (6H) and 8.99 (3H,s).

The 'Dietl Complex', $\{Cl(Me_2C_2)_3PdCl\}_2$

The 'Dietl Complex' was prepared from dichlorobis(benzonitrile)palladium and 2-butyne as described by Maitlis, et al.[173]. Benzene (400 ml) was saturated with nitrogen and hydrogen chloride gas bubbled through it in a slow stream for 1 min. 2-Butyne (13.5 ml, 170 mmoles) was then added and the solution cooled to 5°C. $\left[Pd(PhCN)_2Cl_2\right]$ (10g, 26.8 mmoles) was then added in small quantities, with stirring, such that the temperature of the reaction mixture did not rise above 15°. The mixture was then filtered and after allowing it to warm up to room temperature, the benzene was removed under reduced pressure. The residual brown oil was shaken with light petroleum ether (150 ml) containing 2-butyne (5 ml) and filtered to remove some pale yellow solid. The filtrate was then saturated with nitrogen and left to stand at -10 to -15° with occasional shaking for 5 hrs. The bright yellow microcrystalline solid thus obtained (4.0g, 45%) was collected on a filter and dried.

5-Ethylpentamethylcyclopentadiene[167], 8(X = H):

$\left\{Cl(Me_2C_2)_3PdCl\right\}_2$ (2.55g, 3.8 mmoles) was added to a stirred suspension of 1.10g (30 mmoles) of lithium aluminum hydride in dry ether (30 ml) at -40°. Black metallic palladium separated immediately. After 10 min. the solution was allowed to warm up to 20° and filtered. The solvent was then removed to obtain a pale yellow oil, which was distilled under vacuum. The product thus obtained (0.6g, 50%) was used without further purification. Its n.m.r. spectrum indicated it to be at least 95% pure. The spectrum is given in Table 5.

5-Acetylpentamethylcyclopentadiene:

a) From 'Dietl Complex'[167]:

The 'Dietl Complex' (1g, 1.47 mmole) was stirred overnight in methanol (50 ml) in the presence of a small amount (0.02g) of sodium carbonate. The metallic palladium formed was filtered off and the filtrate treated with a drop of concentrated sulphuric acid and let stand for 2 hrs. It was then evaporated and the residual oil extracted with chloroform. The extract was washed with water and dried over anhydrous sodium sulphate. The chloroform was then evaporated off, the oil left behind dissolved in petrol and passed through an alumina chromatographic column. The pure product was eluted from the column with benzene and further purified by sublimation at $\sim 50^\circ/0.2$ mm to yield a pure white crystalline compound (0.4g, 77%), m.p. 55°. N.m.r. spectrum in $CDCl_3$: $\tau$ 8.13 (6H), 8.39 (6H), 8.41 (3H, s) and 8.91 (3H, s). This is the same as that reported by Junker, et al.[174]. Anal. calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18; mol. wt., 178. Found: C, 80.58; H, 10.13; mol. wt., 178 (mass spectroscopic).

b) From 2-butyne:

Palladium chloride (0.5g, 2.82 mmoles) was dissolved in methanol (100 ml) saturated with hydrogen chloride and a solution of 2-butyne (5 ml, 69 mmoles) dissolved in 30 ml methanol was added dropwise, while oxygen was bubbled through. The addition was completed in 2 hrs. The solution was stirred and oxygen bubbled through it overnight. The solvent was then removed under reduced pressure and the oil remaining extracted with petrol. The petrol extract was washed with water, dried over anhydrous magnesium sulphate and evaporated. The brown oil left behind was then absorbed on an alumina column and washed with petrol. The acetyl-compound was eluted from the column with a 3:1 mixture of petrol and benzene. Evaporation of the solvent gave pale yellow needle-like crystals of the product (0.35g, 1.97 mmole, 70% based on $PdCl_2$), which was further purified by vacuum sublimation.

Dichlorohexamethyl(Dewar benzene)platinum, (6):

To hexamethyl(Dewar benzene). (4) (1.30g, 8.02 mmoles) in dry benzene (50 ml) was added Zeise's dimer (1.17g, 2.00 mmoles) and stirred. Some gas (presumably ethylene) was evolved during the first 10 min. and white flaky crystals began to separate. The reaction was stopped when signs of reduction to metallic platinum started appearing. The reaction mixture was filtered, the precipitate washed with benzene and then dissolved in chloroform and filtered to free it from metallic platinum. The chloroform solution was evaporated to a low volume and the pure complex isolated from the solution, by adding benzene, as white flaky crystals (1.41g, 83%), m.p. 75°(dec.). Anal. calcd. for $C_{12}H_{18}Cl_2Pt$: C, 33.65; H, 4.24; Cl, 16.55, Mol.

Wt., 428. Found: C, 33.78; H, 4.28; Cl, 16.50; Mol. Wt., 500, 506 (osmometric, in chloroform).

The benzene filtrate from the above reaction was analysed by n.m.r. and was found to contain, apart from unreacted excess HMDB, hexamethylbenzene (HMB) (1.60 mmole, $\sim\frac{1}{2}$ mole per mole of <u>6</u> formed).

## Reactions of the Complex 6:

### Stability in solution:

$Pt(HMDB)Cl_2$ — complex 6 (0.043g, 0.1 mmole) was dissolved in 1 ml $CDCl_3$ in a n.m.r. sample tube and its n.m.r. spectrum run at various intervals. At the end of 8 days at 25°, it was observed that the solution also contained hexamethylbenzene (50%).

A similar solution heated at 70° for 2 hrs showed the presence of HMB corresponding to 5% conversion of the initial complex 6.

### Reaction with dichlorobis(benzonitrile)palladium:

To complex 6 (0.043g, 0.1 mmole) dissolved in 1 ml $CDCl_3$ was added $Pd(PhCN)_2Cl_2$ (0.039g, 0.1 mmole) and the mixture kept in a n.m.r. tube at 25° for 8 days. The n.m.r. spectrum at the end of this period showed that about 50% of the complex 6 was converted to HMB.

Reaction with acid:

A solution of the complex 6, in $CDCl_3$ as in the above reactions, was saturated with gaseous hydrogen chloride and kept at 25° for 3 days, in a n.m.r. tube. The n.m.r. spectrum after this period showed conversion of 11% of the complex 6 to HMB, which corresponds closely to the spontaneous non acid-catalysed conversion.

However, when complex 6 (0.065g, 0.15 mmole) was stirred in methanol (4.5 ml) containing HCl (0.5 ml, concentrated) for 1 hr., evaporated, and the n.m.r. of the residue run in $CDCl_3$, 66% of it was observed to be decomposed to produce HMB.

Reaction with Iodine:

To a solution of complex 6 (0.043g, 0.1 mmole) in 1 ml $CDCl_3$ in a n.m.r. tube was added iodine (0.051g, 0.2 mmole) and the mixture kept at 25° for 2 days. The n.m.r. remained unchanged during this period, i.e., there was no reaction.

Reaction with pyridine:

No reaction occurred between complex 6 (0.043 g, 0.1 mmole) and pyridine (0.016g, 0.2 mmole) in $CDCl_3$ (1 ml) at 25° during 2 days, according to the n.m.r. spectrum of the reaction mixture.

Reaction with triphenylphosphine:

Triphenylphosphine (0.026g, 0.1 mmole) was added to the complex 6 (0.043g, 0.1 mmole) in 1 ml $CDCl_3$. The n.m.r. spectrum taken immediately showed a 1:1 mixture of complex 6 and HMDB. A white precipitate also was observed (presumably, dichlorobis(triphenylphosphine)platinum).

Action of ultraviolet light:

A solution of complex 6 (0.052g, 0.12 mmole) in $CDCl_3$ (1 ml) was exposed to ultraviolet light (a Hanovia, high pressure, 450 watt lamp was used) for 12 min. at the end of which its n.m.r. spectrum was run; 35% of the complex 6 was converted to hexamethylbenzene.

Thermal decomposition:

The complex 6 (0.050g, 0.11 mmole) was sealed in a glass tube under vacuum (0.1 mm Hg) and heated at 100° for 10 min. A white sublimate (0.13g, 73%) appeared at the top of the tube, which was collected, and its n.m.r. spectrum run in $CDCl_3$. The n.m.r. spectrum was identical with that of HMB.

Reaction with base:

$Pt(HMDB)Cl_2$ (0.052g, 0.12 mmole) and anhydrous sodium carbonate (0.021g, 0.020 mmole) were stirred together in methanol

(5 ml) at room temperature for 3 hrs. The yellow precipitate formed was filtered off and recrystallised from methylene chloride/methanol to yield a bright yellow crystalline material (0.030g, 65%). The n.m.r. spectrum of this material was found to contain only five resonances due to methyl groups. This complex was simultaneously prepared by Shaw and a crystal structure determination was carried out by Mason[143]. In view of this, no further work was carried out on the complex.

Dichloro(pentamethylcyclopentadiene)platinum (7)

a) From hexamethyl (Dewar benzene) and potassium chloroplatinate:

Potassium tetrachloroplatinate (0.422g, 1.02 mmole) and stannous chloride (0.034g, 0.16 mmole) were dissolved in methanol (25 ml) containing aqueous hydrochloric acid (4 ml, 6 N). Hexamethyl (Dewar benzene) (0.444g, 2.73 mmole) was added and the mixture heated at 65° with stirring for 3 hrs. The methanol was distilled off and the residue extracted with chloroform. The chloroform extract was washed with water and dried over anhydrous $Na_2SO_4$. The chloroform was then removed under reduced pressure and the residue washed with petrol. The yellow solid thus obtained was dissolved in the minimum amount of methylene chloride and precipitated with ether. This procedure was repeated until the precipitate was bright yellow and crystalline, and the supernatant liquid almost colourless. The product obtained (0.311g, 78%) was collected on a filter and dried. An analytical sample was prepared by repeated recrystallisation of the above product from methylene chloride/methanol. m.p. 218 - 220° (dec.) Anal. calcd. for $C_{10}H_{16}Cl_2Pt$: C, 29.86; H, 4.01; Cl, 17.63; Mol. Wt., 402; Found: C, 29.62; H, 4.24; Cl, 17.69; Mol. Wt., 410 (osmometric in chloroform).

The methanol distilled off from the reaction mixture was analysed by vapour phase chromatography and was found to contain 1,1-dimethoxyethane (1 mole for each mole of complex 7 formed).

A variation of the above method, which also gave a good yield of the complex 7 is as follows: HMDB (2.03g, 12.5 mmoles) in methylene chloride (20 ml) was treated with hydrogen chloride for about 1 hr (until it turned violet) and then stirred overnight. The methylene chloride was then evaporated off to leave a brown oil. To this was added potassium chloroplatinate (2.01g, 4.82 mmoles), stannous chloride (0.044g, 0.20 mmole) aqueous hydrochloric acid (4 ml, 6N) and methanol ( 20 ml). The mixture was heated at 65° for 5 hrs after which it was worked up as above to yield 1.45g of the complex 7 (75%).

b) From 5-(1-chloroethyl)pentamethylcyclopentadiene(8, X = Cl) and potassium chloroplatinate:

To potassium tetrachloroplatinate (0.416g, 1.00 mmole) in methanol (30 ml) containing aqueous hydrochloric acid (3 ml, 3N) was added the compound, 8 (X = Cl) (0.40g, 2.00 mmole) and stannous chloride (0.023g, 0.10 mmole) and the mixture heated at 65°, with stirring, for 6 hrs. Work up as above yielded 0.353g (88%) of the pure complex 7.

c) From 5-acetylpentamethylcyclopentadiene and potassium tetrachloroplatinate:

Potassium tetrachloroplatinate (0.104g, 0.25 mmole) and the acetyl- compound (0.09g, 0.50 mmole) were reacted together in methanol (10 ml) containing hydrochloric acid (0.2 ml, 12N) and stannous chloride (0.017g, 0.08 mmole), at 65° for 2 hrs. The reaction mixture was worked up as in the preceding case and 0.08g (80%) of the complex 7 was isolated. The reaction mixture also contained unreacted excess of the acetyl- compound and some hexamethylbenzene in the ratio 10:1, as estimated by n.m.r.

d) From 5-ethylpentamethylcyclopentadiene (8, X = H) and potassium chloroplatinate:

Potassium tetrachloroplatinate (0.10g, 0.25 mmole) and the compound 8 (X = H) (0.098g, 0.60 mmole) were heated together in methanol (15 ml) containing aqueous hydrochloric acid (3 ml, 3N) in the presence of stannous chloride (0.02g, 0.09 mmole), at 65° for 4 hrs. The complex 7 (0.025g, 13%) was isolated from the reaction mixture.

Dibromo(pentamethylcyclopentadiene)platinum:

Complex 7 (0.105g, 0.26 mmole) and lithium bromide (0.131g, 1.5 mmoles) were reacted together in acetone (15 ml) solution at 56° for 3 hrs. The solvent was removed under reduced pressure. The yellow residue was extracted with methylene chloride and the solution filtered. The filtrate was evaporated to a low volume and ether added to it to precipitate the pure dibromo- complex. The yellow crystalline product (0.057g, 47%) was collected on a filter and dried in air. m.p. 205° (dec.). Anal. calcd. for $C_{10}H_{16}Br_2Pt$: C, 24.45; H, 3.28; Br, 32.53; Mol. Wt., 491; Found: C, 24.73; H, 3.30; Br, 32.76; Mol. Wt., 530 (osmometric, in chloroform).

Diiodo(pentamethylcyclopentadiene)platinum:

Complex 7 (0.050g, 0.124 mmole) and iodine (0.140g, 0.55 mmole) were stirred together in refluxing chloroform (5 ml) for 2 hrs. The solid residue left after evaporation of the chloroform from the reaction mixture was washed repeatedly with petrol to remove excess iodine. It was then dissolved in the minimum amount of methylene chloride and precipitated by the addition of hexane. After two such reprecipitations, the diiodo- complex was obtained in pure state as brown crystalline material (0.040g, 55%). Anal. calcd. for $C_{10}H_{16}I_2Pt$: C, 20.52; H, 2.76; I, 43.37; Mol. Wt., 585; Found: C, 20.45; H, 2.96; I, 43.81; Mol. Wt., 658 (osmometric, in chloroform).

Reaction of 7 with alkali metal iodides in refluxing acetone led only to decomposition giving pentamethylcyclopentadiene and an insoluble iodoplatinum compound.

### Reactions of $Pt(C_5Me_5H)Cl_2$ (complex 7)

### Reaction with triphenylphosphine - Preparation of 1,2,3,4,5-pentamethylcyclopentadiene:

a) To complex 7 (0.020g, 0.05 mmole) in deuteriochloroform (1 ml) in a n.m.r. tube, was added triphenylphosphine (0.026g, 0.10 mmole) and the n.m.r. spectrum run immediately. The spectrum showed a multiplet centred at $\tau$ 7.52 (1 H), another multiplet centred at $\tau$ 8.18 (12 H) and a doublet at $\tau$ 9.00 (J = 7.5 Hz, 3H). This spectrum closely agrees with that of 1,2,3,4,5-pentamethylcyclopentadiene reported by Criegee and Grüner[166].

A white precipitate, presumably dichlorobis(triphenylphosphine)platinum, was observed in the n.m.r. tube.

b) Complex 7 (0.193g, 0.48 mmole) was heated at 70° with triphenylphosphine (0.472g, 1.8 mmole) in vacuo. A clear colourless liquid that distilled off from the mixture was collected in a receiver cooled in an acetone-dry ice bath (-78°) (0.057g, 87%). This distillate was identified as pentamethylcyclopentadiene by n.m.r. and mass spectra (molecular weight 136)[126].

Reaction with bases:

a) Pyridine: Complex 7 (0.020g, 0.05 mmole) dissolved in $CDCl_3$ was taken in a n.m.r. tube. Pyridine (10 μl, 0.012 mmole) was added to it and the n.m.r. spectrum run at intervals. The spectrum indicated the formation of pentamethylcyclopentadiene which was complete in 30 min. The initial rate of disappearance of the complex was 5% per min.

b) Sodium Carbonate: A methanolic solution of $Pt(C_5Me_5H)Cl_2$ (0.101g, 0.25 mmole) was stirred with anhydrous sodium carbonate (0.027g, 0.25 mmole) for 2 hrs. The solution turned brown. It was filtered and evaporated to dryness. The brownish solid residue was washed with ether and dried. The n.m.r. spectrum of the solid was run in $CDCl_3$. It showed several broad peaks at $\tau$ 8.25 - 9.20.

However, no characterisable products could be isolated from this decomposition product of complex 7.

c) Triethylamine: The reaction described above was repeated with triethylamine (6 μl, 0.04 mmole) and the complex 7 (0.016g, 0.04 mmole) in $CDCl_3$ in a n.m.r. sample tube. The reaction again proceeded to give the same decomposition product as with sodium carbonate, together with triethylamine hydrochloride, and was complete in 1 hr. There was *no* indication of the presence of $C_5Me_5H$ in the system at any time. The reaction was not reversed with HCl.

Reaction with acetylacetone:

a) In the presence of sodium carbonate: Complex 7 (0.10g, 0.25 mmole), acetylacetone (0.05g, 0.50 mmole) and anhydrous sodium carbonate (0.054g, 0.50 mmole) were stirred together in methanol at 25° for 15 hrs. The solution was filtered, the solvent removed and the residue washed with hexane. The yellow solid (0.07g) did not show in its n.m.r. spectrum any methyl resonance due to the pentamethylcyclopentadiene ligand, but showed a resonance due to the acetylacetone ligand. Presumably, the acetylacetone displaced the pentamethylcyclopentadiene from 7.

b) In the absence of sodium carbonate: The above reaction was repeated, but without any sodium carbonate. It led to the same results, i.e. to decomposition of the complex 7. Pentamethylcyclopentadiene could be detected in this reaction as one of the products.

Reaction with allyl magnesium chloride:

The Grignard reagent was prepared from 3-chloropropene (0.15g, 2.20 mmoles) and magnesium (0.05g, 2.10 mmole) in dry ether (20 ml) at 0°C. The solution was then cooled down to -78° and a suspension of complex 7 (0.195g, 0.49 mmole) in anhydrous ether added to it with stirring in small portions. The reaction mixture was stirred for 6 hrs. at -78°. During the reaction black metallic platinum was produced. Work up of the mixture gave free pentamethylcyclopentadiene (identified by its n.m.r. spectrum) as one of the decomposition products.

Reaction with dienes:

Complex 7 (0.02g, 0.05 mmole) in deuteriochloroform (1 ml) in a n.m.r. sample tube, was mixed with 1,5 cyclooctadiene (0.022g, 0.20 mmole) and the spectrum run at intervals. The spectrum was unchanged even after 24 hrs. at 25°, indicating that there was no reaction.

A similar reaction was carried out with hexamethyl (Dewar benzene). Here again there was no reaction.

Reaction with metal carbonyls:

a) Dodecacarbonyltriiron: Dichloro(pentamethylcyclopentadiene) platinum, 7, (0.43g, 1.1 mmole) and dodecacarbonyltriiron (1.18g, 2.3 mmoles) were heated together in xylene (40 ml) at 120° for 2 hr. The solution turned black, owing to the formation of metal, and this was removed by filtration to give a red solution. The solvent was removed in vacuo in a distillation apparatus, leaving a dark red crystalline solid, which was recrystallised from dichloromethane-hexane to give the pure di-μ-carbonyldicarbonylbis(pentamethylcyclopentadienyl)diiron[161] (0.06g, 24%), m.p. 280° (dec). Anal. Calcd. for $C_{24}H_{30}O_4Fe_2$: C, 58.32; H, 6.12; Mol. Wt., 494; Found: C, 56.99; H, 6.04; Mol. Wt., 494 (mass spectroscopic). N.m.r.: $CS_2$ solution, singlet at $\tau$ 8.37[161]. Infrared: $\nu_{CO}$ 1748 and 1923 $cm^{-1}$ [161].

A yellow crystalline solid sublimed in the condenser during the distillation of the xylene. This was collected and resublimed (20°/ 0.1 mm) and was shown to be tricarbonyl(endo-H-pentamethylcyclopentadiene)iron, 12 (0.06g, 20%), m.p., 96°. Anal. Calcd. for $C_{13}H_{16}O_3Fe$: C, 56.54; H, 5.84; Found: C, 57.23; H, 5.93. Infrared: $\nu_{CO}$ 1946(s), 1953(sh), 2024(s) $cm^{-1}$.

b) Di-μ-carbonyldicarbonylbis(cyclopentadienyl)diiron: $Pt(C_5Me_5H)Cl_2$ (0.113g, 0.28 mmole) and di-μ-carbonyldicarbonylbis(cyclopentadienyl)diiron (0.094g, 0.27 mmole) were stirred together in benzene (25 ml) at 25° for 3 hrs. The black insoluble precipitate formed was filtered off and the red filtrate evaporated to yield a red oily residue, which was washed with petroleum ether and dried. The n.m.r. spectrum, in $CDCl_3$, of the oil showed protons due to both the cyclopentadienyl ligand and the pentamethylcyclopentadiene, but the resonances were very broad due to the presence of some paramagnetic impurities. The oil could not be crystallised or purified.

The reaction was repeated in benzene at 5°, refluxing benzene, and tetrahydrofuran at -78° and its boiling point (66°). The results were the same as above.

c) Dicobalt octacarbonyl: To a solution of dichloro(pentamethylcyclopentadiene)platinum (0.20g, 0.50 mmole) in dichloromethane (30 ml) was added dicobalt octacarbonyl (0.89g, 2.00 mmoles) and the solution refluxed for 3 hrs. under nitrogen. The reaction mixture was evaporated under vacuo to remove the solvent. The residue was extracted with hexane and filtered to remove the black insoluble material. The red-brown solution was evaporated to afford a red crystalline material (0.06g, 50%), which was very air sensitive and turned blue slowly in the solid state. The n.m.r. spectrum in $CS_2$ corresponded to that of dicarbonyl(pentamethylcyclopentadienyl)cobalt[161] (singlet at $\tau$ 8.10) except that the resonance was very broad due to paramagnetic impurities.

d) Nickel tetracarbonyl: Nickel tetracarbonyl (1.5 ml, 1.18 mmole) and complex 7 (0.103g, 0.25 mmole) were stirred together in benzene at 25° for 2 hrs. The reaction mixture was filtered to remove the black insoluble precipitate. The filtrate was evaporated under reduced pressure to remove the solvent. A small amount of a liquid was left behind. The n.m.r. spectrum of the liquid corresponded with that of free pentamethylcyclopentadiene.

### Reaction of pentamethylcyclopentadiene with di-μ-chlorodichlorobis-(ethylene)diplatinum:

Pentamethylcyclopentadiene (0.04g, 0.3 mmole) and $\{Pt(C_2H_4)Cl_2\}_2$ (0.06g, 0.1 mmole) were stirred in benzene (15 ml) at 20° for 3 hrs. The benzene was removed and the residue was recrystallised from dichloromethane-hexane to give dichloro(pentamethylcyclopentadiene)platinum (0.04g, 43%).

### Attempted catalytic preparation of pentamethylcyclopentadiene:

5-(1-Chloroethyl)pentamethylcyclopentadiene, 8 (X = Cl) (0.5g, 2.5 mmoles), potassium tetrachloroplatinate (0.20g, 0.50 mmole) and stannous chloride (0.02g, 0.09 mmole) were heated together with stirring in methanol (20 ml) containing aqueous hydrochloric acid

(3 ml, 3M) at 65° for 4 hrs. The mother liquor after separation of the complex 7, from the reaction mixture was evaporated and the residual oil analysed by n.m.r. It was found to contain 5(1-chloroethyl)- and 5(1-methoxyethyl)pentamethylcyclopentadiene, 8 (X = Cl and OMe) and hexamethylbenzene in the ratio 4:20:1 and no free pentamethylcyclopentadiene.

The reaction above was repeated with a smaller quantity of chloroplatinate (0.029g, 0.07 mmole) and at Pt:Sn ratio of 1:5 (0.083g $SnCl_2$, 0.35 mmole) which was heated for 15 hrs. Work up yielded pentamethylcyclopentadiene, but not more than was expected from the acid catalysed cleavage of the 5-substituted pentamethylcyclopentadiene, 8 (X = Cl)[166].

The reaction was carried out with different ratios of Pt:Sn from 0 to 5 and in no case was pentamethylcyclopentadiene produced in any appreciable quantity in excess of that to be expected from the acid catalysed reaction in the absence of metal.

Dichloro(5-ethylpentamethylcyclopentadiene)platinum, 15:

Di-μ-chlorodichlorobis(ethylene)diplatinum (0.11g, 0.2 mmole) and ethylpentamethylcyclopentadiene (0.09g, 0.55 mmole) were stirred together in ethanol-free chloroform (10 ml) at 20° for 10 mins. The solution turned violet, and was decolourised by filtering through a layer of activated charcoal. The solvent was then removed in vacuo, and the residue washed with ether to leave the yellow crystalline dichloro(5-ethylpentamethylcyclopentadiene)platinum, m.p. 150° (dec.). (0.09g, 54%). Anal. calcd. for $C_{12}H_{20}Cl_2Pt$: C, 33.49; H, 4.69; Found: C, 33.48; H, 4.51.

Reaction of hexamethyl (Dewar benzene) with palladium chloride:

Hexamethyl (Dewar benzene) (0.48g, 3 mmoles) was added to palladium chloride (0.18g, 1 mmole) in methanol (30 ml) containing aqueous hydrochloric acid (2 ml, 12N) and heated at 65° for 2 hrs. Work up of the reaction mixture did not yield any palladium complex, but gave hexamethylbenzene quantitatively.

Reaction of 5-(1-chloroethyl)pentamethylcyclopentadiene with palladium chloride in methanol - Preparation of dichloro {5-(1-methoxyethyl)pentamethylcyclopentadiene}-palladium, 17a:

Palladium chloride (0.197g, 1.10 mmole) and 5-(1-chloroethyl)pentamethylcyclopentadiene (0.5g, 2.5 mmoles) were heated together in methanol (20 ml) containing hydrochloric acid (2 ml, 12N) for 2 hrs. at 50°. The solution turned clear red. It was filtered to remove the small amount of metallic palladium formed and the solvent was removed under reduced pressure. The residue was extracted with chloroform. The chloroform solution was washed with water and dried over anhydrous sodium sulphate. Evaporation of the chloroform followed by stirring the oily residue with ether afforded a red microcrystalline palladium complex (0.20g, 49%), m.p. 143° (dec.). Anal. calcd. for $C_{13}H_{22}Cl_2OPd$: C, 42.01; H, 5.97; Cl, 19.08; Mol. Wt., 371; Found: C, 41.90; H, 6.02; Cl, 19.15; Mol. Wt., 450, 458 (osmometric in chloroform).

Addition of triphenylphosphine to the complex in deuteriochloroform liberated the free ligand, the n.m.r. spectrum of which was identical with that of 8 (X = OMe).

Dichloro{5-(1-chloroethyl)pentamethylcyclopentadiene} palladium, 17d:

Palladium chloride (0.59g, 3.00 mmoles) and 5-(1-chloroethyl)pentamethylcyclopentadiene (1.05g, 5.28 mmoles) were heated together in t-butanol (30 ml) containing aqueous hydrochloric acid (3 ml., 12N) at 60° for 4 hrs. The reaction mixture was worked up as above to yield a dark red crystalline palladium complex (0.32g, 26%), m.p. 178° (dec.). Anal. calcd. for $C_{12}H_{19}Cl_3Pd$: C, 38.33; H, 5.09; Cl, 28.29; Mol. Wt., 376; Found: C, 39.25; H, 5.05; Cl, 27.7; Mol. Wt., 480 (osmometric, chloroform).

Addition of triphenylphosphine liberated the free ligand, which was identified by its n.m.r. spectrum to be 5-(1-chloroethyl)-pentamethylcyclopentadiene, 8 (X=Cl).

Dichloro{5-(1-ethoxyethyl)pentamethylcyclopentadiene} palladium, 17b:

This was prepared from the reaction of palladium chloride (1.00g, 5.64 mmoles) and 5-(1-chloroethyl)pentamethylcyclopentadiene (2g, 10 mmoles) in ethanol (30 ml) containing aqueous hydrochloric acid (3 ml, 12N) at 60-65° for 4 hrs. and worked up as usual to yield complex 17b (0.75g, 35%) as a dark red crystalline solid, m.p. 137° (dec.). Anal. calcd. for $C_{14}H_{24}Cl_2OPd$: C, 43.61; H, 6.27; Cl, 18.39; Mol. Wt., 385; Found: C, 44.21; H, 5.79; Cl, 18.20; Mol. Wt., 500 (osmometric, in chloroform).

Dichloro{5-(1-isopropoxyethyl)pentamethylcyclopentadiene} palladium, 17c:

The complex 17c was prepared from palladium chloride (0.50g, 2.82 mmoles) and 5-(1-chloroethyl)pentamethylcyclopentadiene (0.75g, 3.75 mmoles) in a manner similar to the preparation of the above alkoxy-complexes. The reaction was done in isopropanol (30 ml) in presence of hydrochloric acid (3 ml, 12N), at 70° for 5 hrs. The complex was obtained as a red crystalline solid (0.25g, 22%), m.p. 105° (dec.). Anal. calcd. for $C_{15}H_{26}Cl_2OPd$: C, 45.07; H, 6.56; Cl, 17.73; Mol. Wt., 400; Found: C, 45.18; H, 6.18; Cl, 18.12; Mol. Wt., 592 (osmometric, in chloroform).

Reaction of 5-(1-alkoxyethyl)pentamethylcyclopentadienes, 8 (X=OR) with dichlorobis(benzonitrile)palladium:

a) In chloroform: To 8 (X=OMe or OEt) (0.04g, 0.2 mmole) in $CDCl_3$ (1 ml) in a n.m.r. tube was added $Pd(PhCN)_2Cl_2$ (0.02g, 0.05 mmole) and the spectrum recorded. The n.m.r. spectra showed the formation of the palladium chloride complexes, 17a or 17b. The complexes could be isolated pure, in quantitative yields, by removing the solvent and washing with ether-hexane.

b) In benzene: To 8 (X=OMe or OEt) (0.4g, 2 mmoles) in dry benzene was added $Ph(PhCN)_2Cl_2$ (0.19g, 0.50 mmole) and the solution stirred for 1 hr. A brown precipitate formed, which was collected on a filter (0.19g, nearly quantitative), washed with ether and dried. These complexes were insoluble in common organic solvents such as alcohols, chloroform, dichloromethane, benzene, etc.

Treatment of the insoluble complexes with pyridine or triphenylphosphine, liberated the free ligands 8 (X=OMe or OEt) also producing $L_2PdCl_2$ (L=pyridine, triphenylphosphine).

Dichloro(pentamethylcyclopentadiene)palladium, 13:

To pentamethylcyclopentadiene (0.034g, 0.25 mmole) in benzene, was added dichlorobis(benzonitrile)palladium (0.079g, 0.21 mmole) in small quantities with stirring. A yellow brown precipitate was formed immediately. The reaction mixture was stirred for

3 hrs. at 20°. The precipitated complex was then filtered off, washed with hexane and recrystallised from methylene chloride-hexane to afford the yellowish complex (0.04g, 60%). Anal. calcd. for $C_{10}H_{16}Cl_2Pd$: C, 38.32; H, 5.14; Cl, 22.61; Found: C, 36.12; H, 4.73; Cl, 23.67; Calcd. for $C_{10}H_{16}Cl_{2.2}Pd_{1.1}$: C, 36.27; H, 4.87; Cl, 23.55.

### Dichloro(5-ethylpentamethylcyclopentadiene)palladium, 16:

Dichlorobis(benzonitrile)palladium (0.16g, 0.41 mmole) was added to a solution of 5-ethylpentamethylcyclopentadiene (0.08g, 0.49 mmole) in ethanol-free chloroform (10 ml) and stirred for 10 min. The solvent was then removed under reduced pressure from the reaction mixture and the residue was washed with light petroleum ether-ether mixture. Recrystallisation of the solid thus obtained, from methylene chloride/ether, afforded 16 (0.09g, 63%) as a red microcrystalline solid, m.p. 95° (dec.). Anal. calcd. for $C_{12}H_{20}Cl_2Pd$: C, 42.2; H, 5.9; Found: C, 42.8; H, 5.9.

### Reaction of $\{Pt(C_2H_4)Cl_2\}_2$ with 5-(1-substituted ethyl)pentamethylcyclopentadienes, 8 (X=Cl, OR):

The Zeise's dimer (0.20g, 0.33 mmole) was added to a solution of 5-(1-chloroethyl)pentamethylcyclopentadiene, 8 (X=Cl) (0.20g, 1.00 mmole) in methylene chloride (15 ml) and stirred for 10 min. at 20°. The solution turned violet and was decolourised by filtering through a layer of activated charcoal. The clear yellow filtrate was evaporated and the residue washed with hexane-ether to afford a crystalline yellow solid (0.2g, ~60%).

The n.m.r. spectrum of the product in $CDCl_3$ showed it to be a mixture of platinum complexes, one being dichloro(pentamethylcyclopentadiene)platinum (7). The elemental analysis corresponded to the composition $C_{11}H_{17}Cl_2Pt$.

The above reaction repeated using the alkoxy- compounds 8 (X=OMe, OEt) gave the identical product, as seen from the n.m.r. spectrum and elemental analysis.

Melting this product with a stoichiometric amount of triphenylphosphine ($2PPh_3$:1 Pt) under vacuum (70°/~0.1 mm) afforded a liquid in the cooled (-78°) part of the apparatus, the n.m.r. spectrum of which showed it to be a 1:1 mixture of pentamethylcyclopentadiene and 5-vinylpentamethylcyclopentadiene. This was confirmed by mass spectrographic analysis of the liquid. The mass spectrum contained two mass peaks at 162 and 136 in about 1:1 ratio, corresponding to the molecular ions of 5-vinylpentamethylcyclopentadiene and pentamethylcyclopentadiene.

Dichloro(5-vinylpentamethylcyclopentadiene)platinum (18, vinyl, endo-):

Zeise's dimer (0.10g, 0.17 mmole) and 5-vinylpentamethylcyclopentadiene (0.17g, 1.05 mmole) were reacted together in dichloromethane (20 ml) at 20° for 10 min. and worked up as described before to give 18 as a yellow crystalline solid (0.14g, 93%), m.p. 195° (dec.). It was further purified by recrystallisation from boiling benzene. Anal. calcd. for $C_{12}H_{18}Cl_2Pt$: C, 33.65; H, 4.24; Cl, 16.55; Found: C, 33.21; H, 4.15; Cl, 16.30.

Reaction of 18 with hydrogen:

Hydrogen gas was bubbled through a solution of 18 (0.02g, 0.05 mmole) in deuteriochloroform (1 ml) in a n.m.r. sample tube, and the n.m.r. spectrum recorded at intervals. The spectrum showed that 18 (vinyl, endo-) isomerised to dichloro(5-vinylpentamethylcyclopentadiene)platinum, 19 (vinyl, exo-), to the extent of ~90% after $1\frac{1}{2}$ hr., after which slow decomposition to metal occurred.

Treatment of 19 with triphenylphosphine liberated 5-vinylpentamethylcyclopentadiene, as seen from the n.m.r. spectrum of the reaction mixture.

# APPENDIX

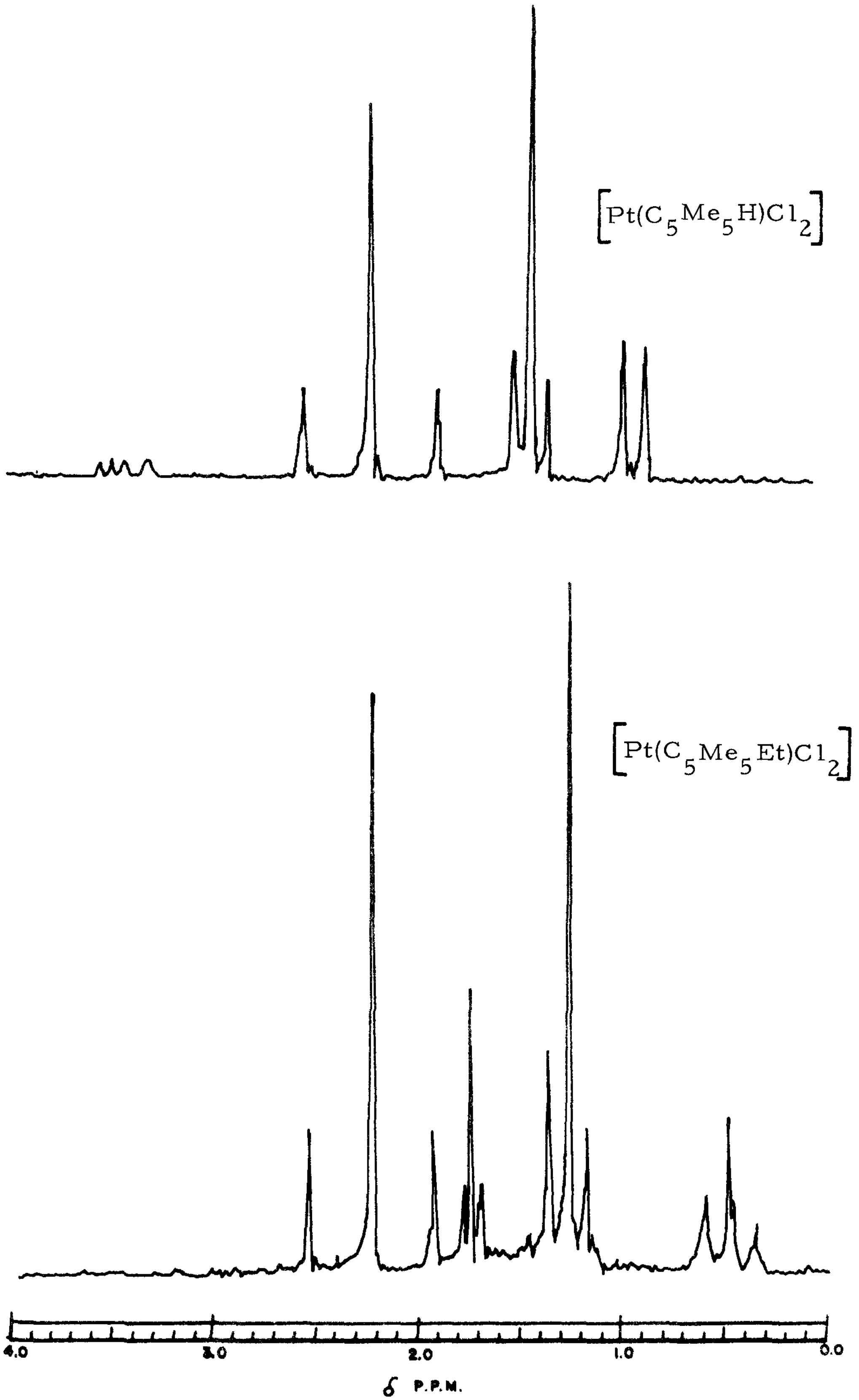


Figure 3: $^1$H n.m.r. spectra of Pt($C_5Me_5H$)$Cl_2$ and Pt($C_5Me_5Et$)$Cl_2$

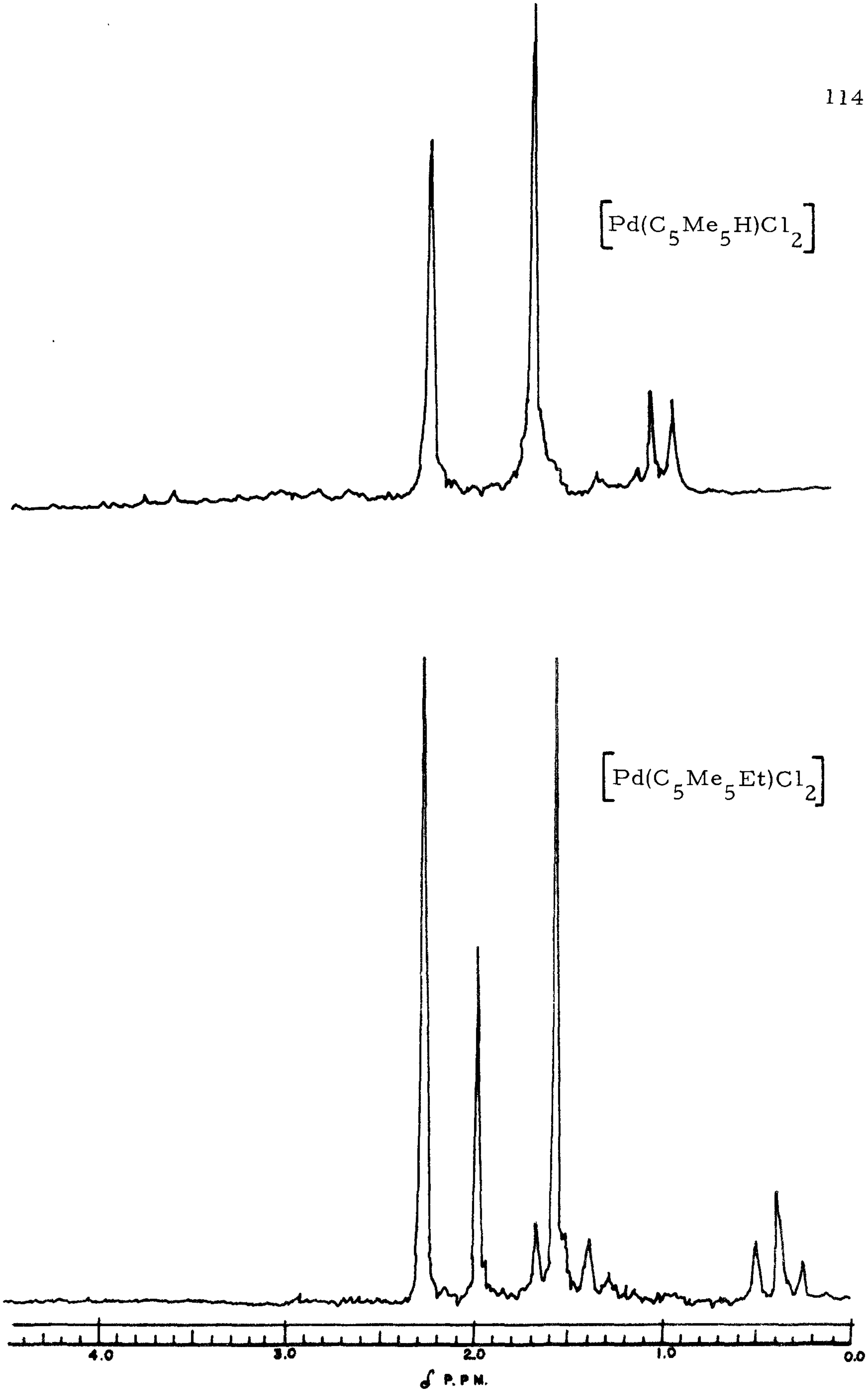


Figure 4: ¹H n.m.r. spectra of $Pd(C_5Me_5H)Cl_2$ and $Pd(C_5Me_5Et)Cl_2$

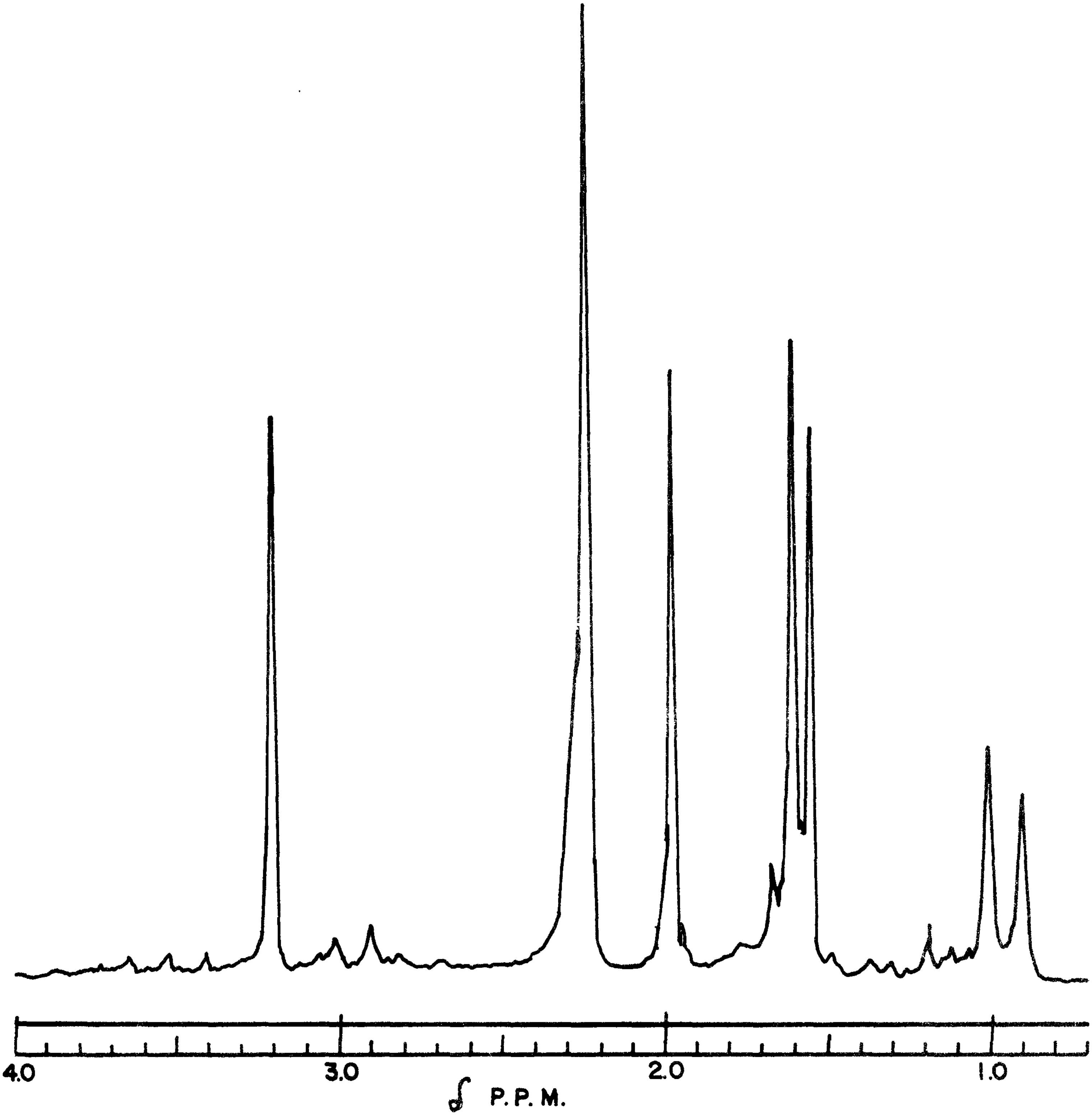
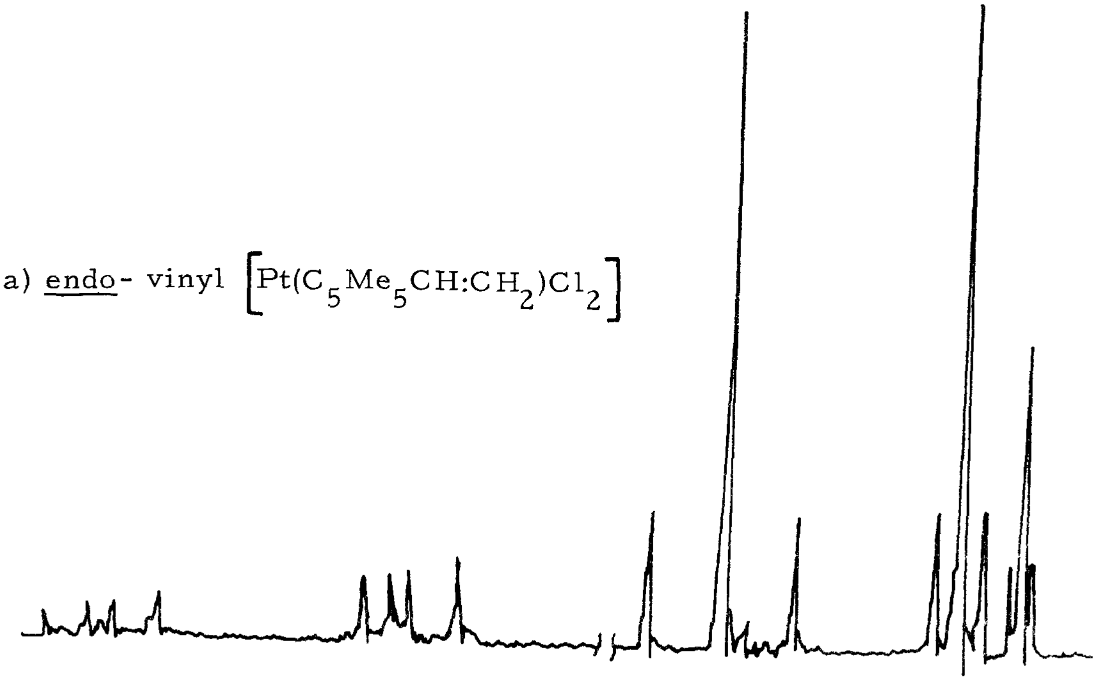
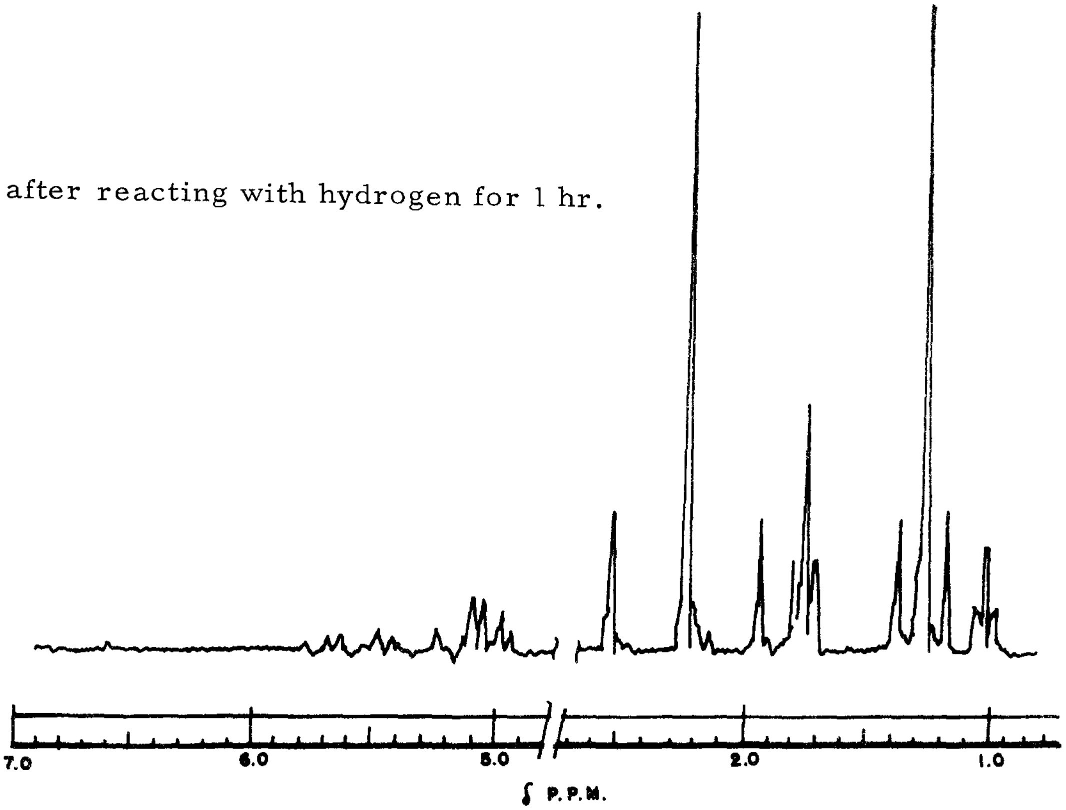


Figure 5: 'H n.m.r. spectrum of Pd$\{C_5Me_5CH(OMe)Me\}Cl_2$



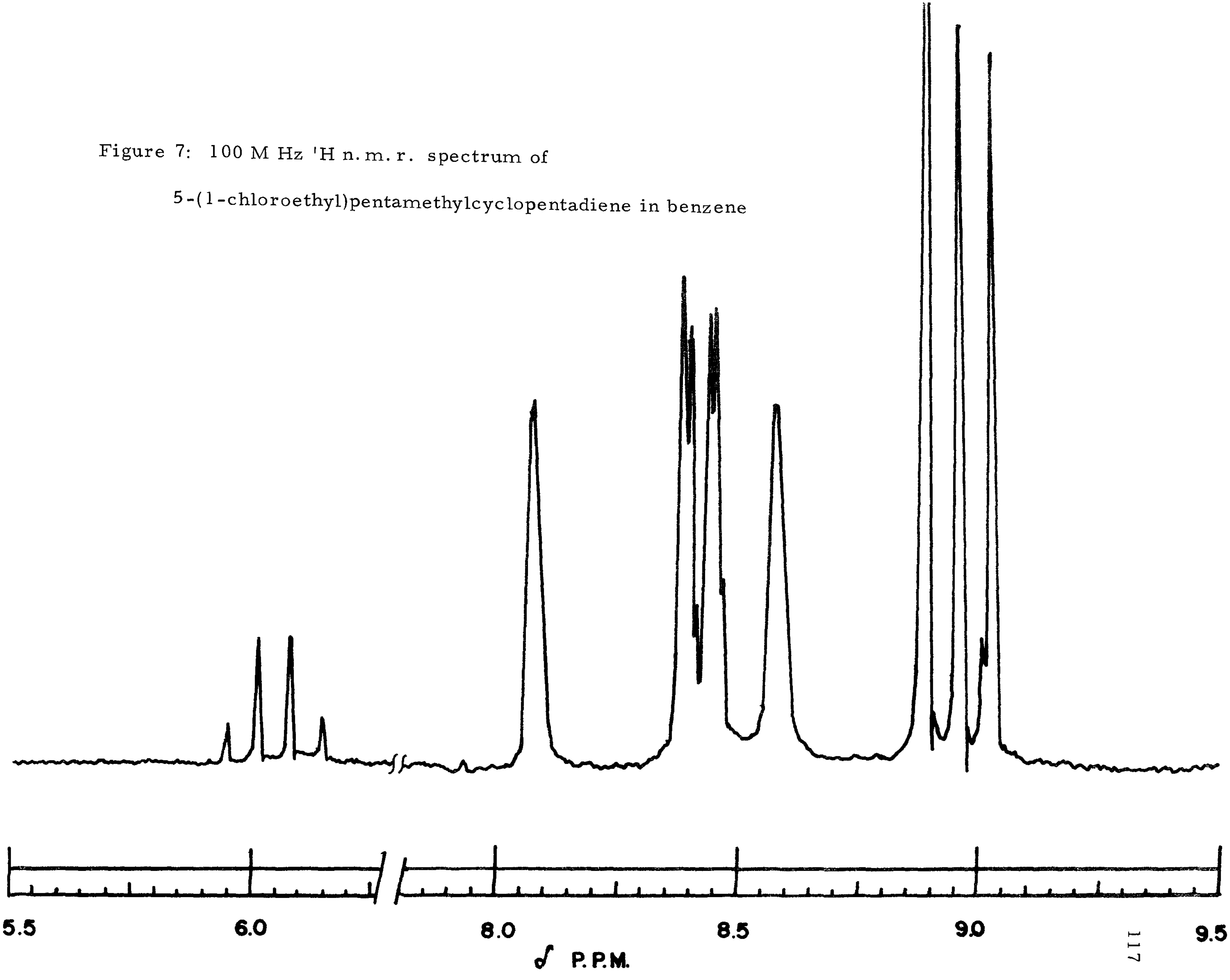
a) <u>endo</u>- vinyl $\left[Pt(C_5Me_5CH{:}CH_2)Cl_2\right]$



b) after reacting with hydrogen for 1 hr.

Figure 6: Isomerisation of <u>endo</u>- vinyl $\left[Pt(C_5Me_5CH{:}CH_2)Cl_2\right]$ by hydrogen

Figure 7: 100 M Hz 'H n.m.r. spectrum of 5-(1-chloroethyl)pentamethylcyclopentadiene in benzene



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