SYNTHETIC, STRUCTURAL AND HIGH FIELD NMR SPECTROSCOPIC

STUDIES OF ARENE-CHROMIUM COMPLEXES

by

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ABSTRACT

The reaction of chromium hexacarbonyl with arenes yields organometallic complexes of the type (arene)Cr(CO)$_3$. Complexation to naturally occurring chiral molecules gives diastereomers which can be differentiated by NMR spectroscopy. Typically, the α- and β-isomers of (methyl O-methylpodocarpate)Cr(CO)$_3$ have been assigned by using ^{1}H two-dimensional NMR techniques at 500 MHz.

Tricarbonylchromium complexes of 1,3,5-triphenylbenzene and of hexaphenylbenzene (HPB) have been characterized by NMR spectroscopy. The mono-, bis- and tris-Cr(CO)$_3$ complexes of C$_6$H$_3$Ph$_3$ exhibit rapid phenyl rotation but (hexaphenylbenzene)Cr(CO)$_3$ displayed restricted rotation. At -80°C, the chromium-bonded phenyl is effectively orthogonal to the central ring and ΔG$^\#$ for the fluxional process is ≈ 12.2 kcal mol^{-1} (≈ 51 kJ mol^{-1}), a value much lower than those of non-complexed hexa-aryl benzenes bearing *ortho* or *meta* substituents.

Sterically crowded chromium complexes of hexaethylbenzene (HEB), (HEB)Cr(CO)$_2$NO$^+$ and (HEB)Cr(CO)(CS)(NO)$^+$, exhibit restricted rotation about the arene-chromium bond below -100°C. In the variable-temperature ^{13}C NMR spectra of (HEB)Cr(CO)(CS)(NO)$^+$ each room temperature singlet observed for the methyl, methylene and arene ring carbons is split into six equally intense resonances at -105°C. This provides the first unequivocal demonstration of slowed tripodal rotation in a chromium complex. Two fluxional processes are observed; the lower energy one (ΔG$^\#$ ≈ 9.4 kcal mol^{-1} or 39 kJ mol^{-1}) involves interconversion **within** each *distal* and **within** each *proximal* set. The second process (ΔG$^\#$ ≈ 11.4 kcal mol^{-1} or 48 kJ mol^{-1}) requires exchange **between** *proximal* and *distal* environments.

The protonation of (HEB)M(CO)$_3$, M = Cr or W, yields species in which the proton directly bonded to the metal atom approaches along the three-fold axis of the molecule. In less sterically crowded systems the HM(CO)$_3$ fragment is fluxional and adopts a square-based pyramidal geometry.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

x

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 HISTORICAL BACKGROUND

Benzenetricarbonylchromium(0) was first prepared in 1957 by Fischer and Oefele[1] by treating dibenzenechromium with hexacarbonylchromium(0) in a sealed system at 220°C using benzene as a solvent. Later in 1959, Nicholls and Whiting[2] reported a simpler and more general method for the preparation of arenetricarbonylchromium(0) complexes. This involves heating hexacarbonylchromium(0) under reflux in an excess of the aromatic compound or with an equimolar quantity of arene in an inert solvent.

$$\text{arene} + Cr(CO)_6 \xrightarrow[\text{reflux}]{\text{solvent}} (\text{arene})Cr(CO)_3 + 3CO$$
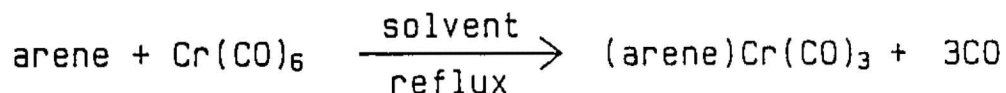
A range of solvents can be used as the reaction medium; the use of di-ethylene glycol dimethyl ether (diglyme), dibutylether, decalin and other high boiling solvents tends to improve the yields of these complexes. Addition of 10% (by volume) of a low boiling solvent such as tetrahydrofuran (THF) helps in washing down the sublimed hexacarbonylchromium(0) back into the reaction flask.[3] However, as high temperatures and long reaction times are required, this method is not suitable for compounds that undergo thermal rearrangement or thermal decomposition. Milder reaction conditions can

1

be maintained by first replacing three of the carbonyls in hexacarbonylchromium(0) with ammonia,[4] methylpyridine[5] or acetonitrile[6] and then treating the trisubstituted derivative with the desired arene. Compounds that are inaccessible by the direct hexacarbonyl-chromium(0) route such as $(C_6H_5Br)Cr(CO)_3$ and $(C_6H_5I)Cr(CO)_3$, have been prepared by this method.[4]

In 1972, Rausch[7] prepared benzenetricarbonylchromium in almost quantitative yield by treating hexacarbonylchromium(0) with benzene in the presence of 2-picoline. This reaction is thought to go *via* intermediates of the type (2-picoline)$_n$-$Cr(CO)_{6-n}$ (n = 1-3). A different route to $(C_6H_6)Cr(CO)_3$ has been observed in the reaction between the cation $[(\pi\text{-}C_7H_7)Cr(CO)_3]^+$ and sodium cyclopentadienide in which a contraction of the tropylium ring occurs giving the desired complex while the C_5H_5 ring expands to give free benzene.[8]

The mechanism of formation of arene chromium tricarbonyl complexes from an arene and hexacarbonylchromium(0) is still uncertain. Kinetic studies[9,10] on Mo and W show that $(arene)M(CO)_5$ is first formed in a reaction between arene and metal hexa-carbonyl followed by intramolecular displacement of carbonyl ligand to give (arene)-$M(CO)_3$. However, in their pioneering studies Nicholls and Whiting[2] had suggested that this pathway was very unlikely.

Even though many complexes containing more than one tricarbonylchromium moiety are known with non-fused multi-ring systems,[7,11-13] it has in general not proved possible to coordinate more than one tricarbonylchromium moiety to a fused ring system with a few exceptions.[7,14,15] In the fused arene complexes with three connected aromatic rings such as phenanthrene and anthracene, end rings are complexed in pref-erence to central rings.[16-20] As shown, there will be minimum disruption of aromaticity when chromium is complexed to the end ring (1) rather than the center ring (2). When the center ring is complexed the effect is very similar to having two diene units attached to

Cr
(CO)₃

1

Cr
(CO)₃

2
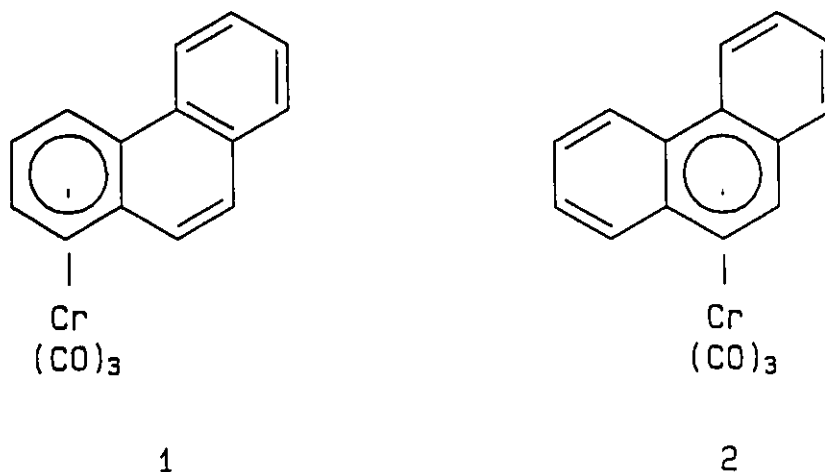
the complexed ring. In tricarbonylchromium(0) complexes of 1,3,5-triphenylbenzene [(C6H5)3C6H3][Cr(CO)3]n (where n = 1, 2 or 3), when n = 1 the Cr(CO)3 moiety is either bonded to the center ring or to the peripheral ring but when n = 2 or 3, the Cr(CO)3 moieties are bonded only to the peripheral rings.[22,23] 2,4,6-Triphenylpyridine also forms complexes of the type [(C6H5)3C5H2N][Cr(CO)3]n (where n = 1,2 or 3).[24]

1.2 STRUCTURE AND BONDING

In arene.ricarbonylchromium(0) complexes it has been found that the orientation of the tripod varies with the nature of the substituents. A considerable number of crystal structures of arenetricarbonylchromium(0) complexes have been determined. These could be divided into two groups:

(i)   those in which the tricarbonyl moiety adopts a staggered orientation (a) and

(ii)   those that adopt an eclipsed configuration (b) with respect to the carbon atoms of the arene ring.

(a)   (b)
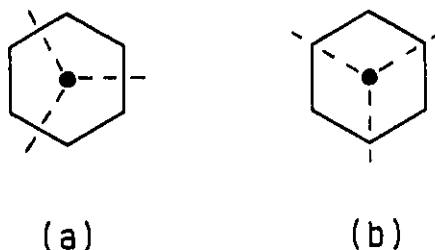
Taking the simplest of these arene-metal complexes, namely, (benzene)-Cr(CO)$_3$; this complex has been structurally analyzed at low temperatures both by X-ray and neutron diffraction studies.[25] The conformation was found to be staggered rather than eclipsed. The three ring C-C bonds that are eclipsed by the carbonyl ligands are significantly longer than the three non-eclipsed C-C bonds, 1.423(1) Å vs. 1.406(1) Å. The free benzene molecule possesses 6-fold symmetry with all C-C bond lengths being identical, 1.398(8) Å,[26] while in the chromium complex because of the alternation of the C-C bond lengths the symmetry of the benzene ligand has been reduced to 3-fold.

The orientation of the tripod, in many cases, is controlled by the nature of the substituents on the arene ring and the preferred conformations are attributed to both steric and electronic effects. A staggered orientation is adopted in the fully substituted arene complex [η^6-C$_6$(CH$_3$)$_6$]-Cr(CO)$_3$,[27] but when the substituent is changed from methyl to ethyl, the orientation of the carbonyl ligands change from staggered to eclipsed.[28]

(c)   (d)   (e)
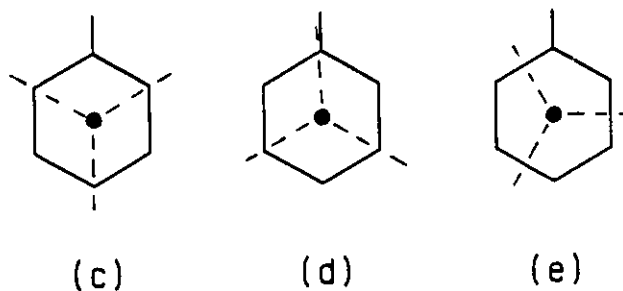
Monosubstituted arene ligands may possess one of three idealized conformations. In the first geometry (c), three alternating ring carbons and the three ligands are eclipsed and the substituent resides on one of the non-eclipsed ring carbon atoms. In conformation (d), the three ligands eclipse three of the ring carbons, but in this case one of the ring carbons is the one with the substituent. A staggered orientation (e), may also be found.
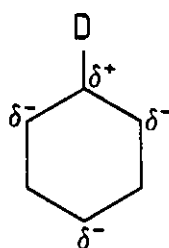
(f)

An electron donor substituent on the arene will produce a charge distribution on the ring as shown in (f).[29] This will give rise to conformation (d). $(\eta^6\text{-}C_6H_5CH_3)$-$Cr(CO)_3$[30] and $(\eta^6\text{-}C_6H_5OCH_3)Cr(CO)_3$[31] are examples of this conformation. An electron acceptor substituent will polarize electron density in an opposite manner with respect to (f). Consequently, orientation (c) is the electronically preferred one. $(\eta^6\text{-}C_6H_5COOCH_3)Cr(CO)_3$[32,33] is one such example. For weak donors and acceptors, crystal packing effects as well as steric factors can override these electronic effects. $(\eta^6\text{-}C_6H_5CH[C(CH_3)_3]_2)Cr(CO)_3$[34] is an example in which steric factors can be stereochemically dominant. Here the $Cr(CO)_3$ group is rotated by 44° because of contact between the very bulky alkyl group and carbonyl ligands giving conformation (e). Another example of conformation (e) is $[(OC)_3Cr(\eta^6\text{-}C_6H_5)]_2$.[35] Part of the reason for the concern about equilibrium conformations of arene-$Cr(CO)_3$ complexes has to do with nucleophilic and electrophilic attack on the coordinated arene ring. There is good

experimental and theoretical evidence[36] that the conformation of the $Cr(CO)_3$ group can determine the regioselectivity of attack on the arene ring.

A variety of orientations are possible for disubstituted arene complexes. Various possibilities exist in the case of arene ring substitution alone, namely *ortho*, *meta* or *para* disubstitution. Most compounds studied so far contain *ortho* substitution. Three orientations are possible in this group (g-i). Here (g) and (h) are the commonly observed orientations. $[\eta^6\text{-}o\text{-}C_6H_4(OCH_3)(COCH_3)]Cr(CO)_3$[37] possesses conformation (h).

(g)   (h)   (i)
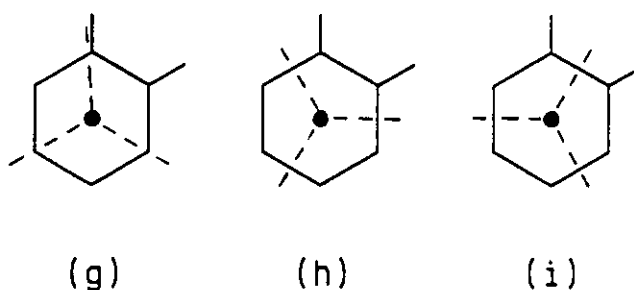
Condensed aromatic ligands are *ortho* disubstituted and they generally possess orientation (h). The exception is biphenylene-$Cr(CO)_3$[38] and compounds of its type in which conformation (i) is found.

1.3 REACTIONS OF ARENETRICARBONYLCHROMIUM(0) COMPLEXES

Arenetricarbonylchromium(0) complexes undergo a wide variety of reactions whereby the ligands around the metal center are either exchanged or modified. Even though aromatic rings are known to form stable complexes with every transition metal,[39] it is the arenetricarbonylchromium(0) complexes that have been carried furthest towards practical application. These complexes appear as the leading series for stoichiometric organic synthesis not only because the complexation and decomplexation steps are relatively simple and almost quantitative but also because the chemical properties of the arene are significantly altered on complexation.[40] The five general changes in arene reactivity that have been observed when $Cr(CO)_3$ is coordinated with the arene π-system are:

(1) enhanced acidity of arene ring hydrogens[41]

(2) addition of nucleophiles to the arene π-system leading

to nucleophilic aromatic substitution[42]

(3) stabilization of side chain cationic sites[43]

(4) stabilization of side chain anionic sites[44]

(5) steric effects of the metal ligand system.[45]

The hermaphroditic nature of tricarbonylchromium(0) moiety to stabilize both anions and cations expands the synthetic potential of these complexes in organic synthesis. The steric bulk of the $Cr(CO)_3$ group has also been exploited to promote and effect stereoselective reactions at centers adjacent to the ring.[46]

1.3.1 Arene Replacement Reactions:

The exchange of one arene ligand for another in arene metal tricarbonyl complexes has been of synthetic value. The kinetics of these exchange reactions have been studied by the use of ^{14}C-labelled arenes:[47-51]

$$(arene)M(CO)_3 + {^*arene} \longrightarrow ({^*arene})M(CO)_3 + arene$$
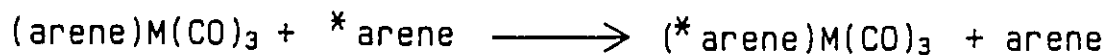
The rate of exchange for a given arene has been found to increase in the order Mo>W>Cr.[50]

The mechanism of this arene exchange was proposed to occur by two processes.[48,50,51] The first process involves the formation of a charge transfer complex which then fragments to release benzene and an active "Cr(CO)$_3$" group which reacts with the free arene. The second process involves direct replacement by the free arene in a bimolecular reaction.
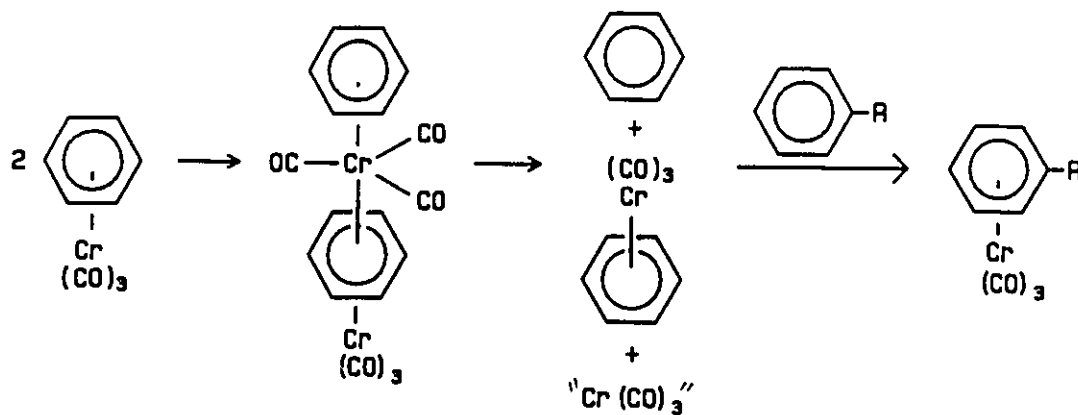
MECHANISM I
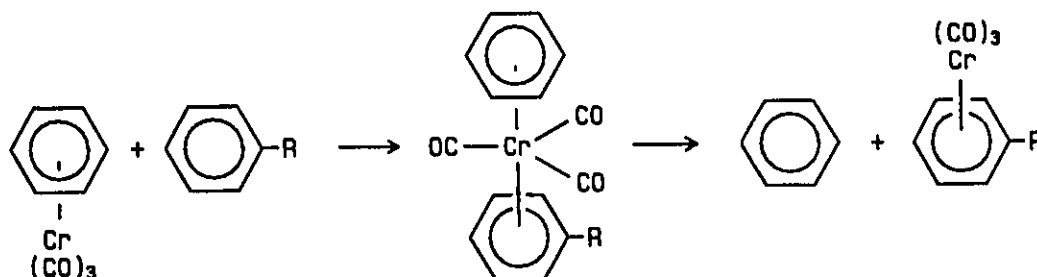
MECHANISM II

Phosphine and phosphite ligands react with arene tricarbonyl complexes of chromium, molybdenum and tungsten yielding complexes of the type fac-(PR₃)₃-M(CO)₃.[52-57] Kinetic studies revealed that the reaction proceeds by an S_N2 mechanism.[54-57] Here stepwise displacement of the arene *via* tetrahapto- and dihapto-coordinated arene intermediates is believed to be involved.[57]
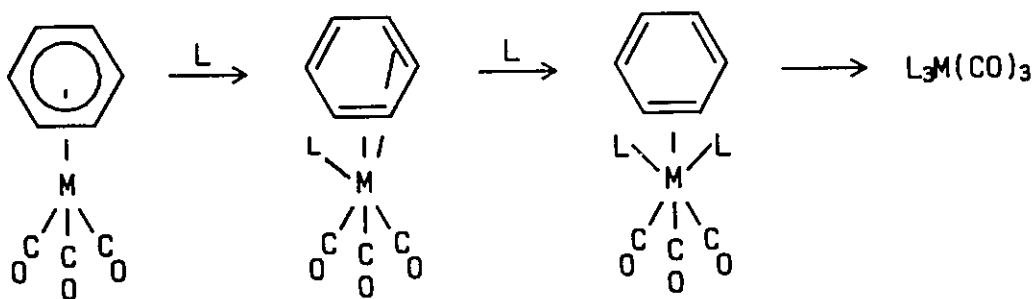
Recent studies on arene exchange reactions reveal this to be a simple stepwise displacement of arenes *via* reduction in coordination of the arene ligand in which there is essentially one mechanism involving a fluxional starting complex.[58]
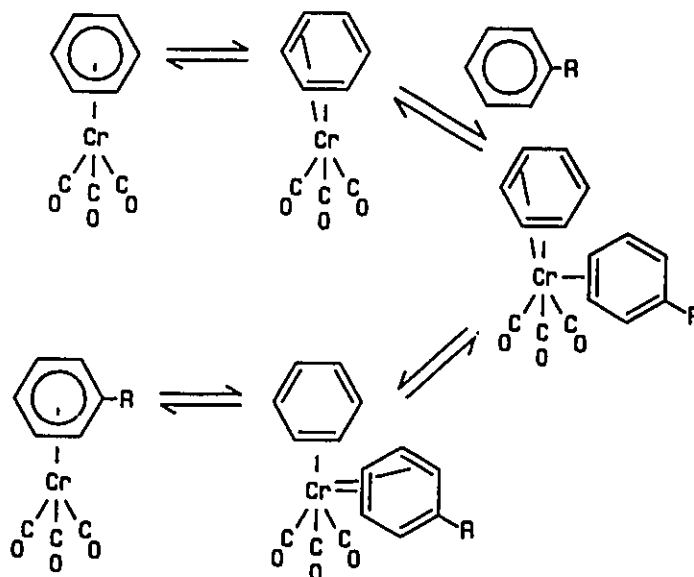
1.3.2 Carbonyl Replacement Reactions:

Replacement of one carbonyl ligand in arene chromium tricarbonyl complexes has been achieved with a variety of ligands. The reaction is usually carried out under UV irradiation:

$$(arene)Cr(CO)_3 + L \xrightarrow{UV} (arene)Cr(CO)_2L + CO$$
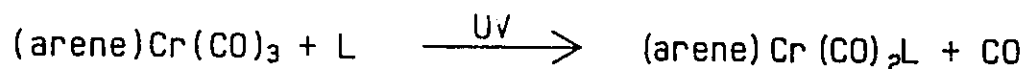
To improve yields, irradiation of the arenetricarbonylchromium(0) complex in donor solvents such as tetrahydrofuran (THF) or cyclooctene is performed.[59] Ligands

such as phosphines,[59,60] amines,[59] nitriles,[61] sulfides, sulfoxides,[62] olefins, acetylenes,[63] hydrazine and molecular nitrogen[64] have been employed. The reaction of $(C_6H_6)Cr(CO)_3$ with sodium cyanide yielded the anion $[(C_6H_6)Cr(CO)_2CN]^-$.[65] Similarly, treatment with the nitrosyl cation gives $[(C_6H_6)Cr(CO)_2NO]^+$.[66] A hydride complex $(C_6H_6)Cr(CO)_2(SiCl_3)H$ has also been prepared by UV irradiation of $(C_6H_6)Cr(CO)_3$ and $SiCl_3H$.[67]

1.3.3 Oxidation and Protonation Reactions:

Oxidation of $(Me_6C_6)W(CO)_3$ using iodine is known to give the cation $[(Me_6C_6)W(CO)_3I]^+$ for which the X-ray crystal structure is known.[68] Cations of the type $[(Me_6C_6)M(CO)_3Cl]^+$ have also been prepared by oxidation of the compounds $(Me_6C_6)M(CO)_3$ (M = Mo, W) with $SbCl_5$ in dichloromethane solution.[69,70]

Arenetricarbonylchromium(0) complexes can be protonated by strong acids such as $BF_3.H_2O$-CF_3COOH,[71,72] FSO_3H[73] and CF_3SO_3H in SO_2.[74] Protonation is enhanced by electron releasing groups on the arene ring and by substitution of one of the carbonyl ligands by PPh_3.[72,75] Isolation of the hydride ion has not been achieved; however, the observation of a high field resonance in the NMR spectra is consistent with the presence of a hydride cation of the type $[(arene)Cr(CO)_3H]^+$. Isolation of the closely related cation $[(arene)Mo(PR_3)_3H]^+$ (PR_3=tertiary phosphine) supports this formulation.[76]

1.3.4 Nucleophilic Reactions:

The most dramatic effect of coordination of $Cr(CO)_3$ to an arene is the powerful withdrawal of electron density from the aromatic ring. This effect has been equated to that of a nitro substituent in the sigma bond framework of an aromatic ring.[2] The possibility was first recognized when $(\eta^6$-chlorobenzene$)Cr(CO)_3$ was prepared and

shown to undergo nucleophilic substitution by methoxide anion at roughly the same rate as p-nitrochlorobenzene.[2,77] The intermediates in these reactions have been shown to be the η^5-cyclohexadienyl anionic complexes of the type 3.[78]
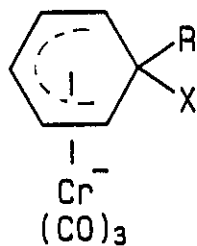
3

The electron withdrawing nature of the tricarbonyl chromium(0) moiety appears to be responsible for the significant enhancement of acidity of benzylic hydrogens in (η^6-alkylarene)Cr(CO)$_3$ complexes.[44] Earlier applications of this effect involved the generation of the enolate anion of methylphenylacetate via complexation of the phenyl group.[44] However, generation of significant concentrations of the simple benzyl anion attached to Cr(CO)$_3$ has since been observed.[41]
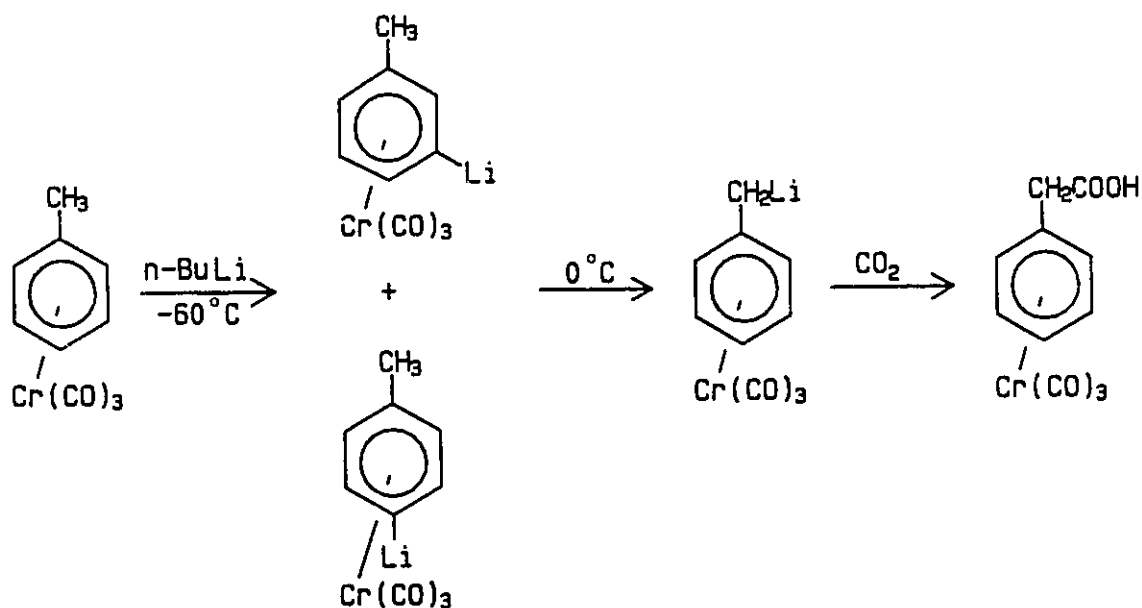
Reaction of n-butyllithium with (η^6-toluene)Cr(CO)$_3$ at low temperature gives proton abstraction predominantly from the ring position, but after equilibration at 0°C for a few hours the benzyl anion is observed. Quenching the reaction with CO_2 at this stage gives only (η^6-phenylacetic acid)-Cr(CO)$_3$.

Three general nucleophilic reactions are now well defined:

(i) Addition/Oxidation process:
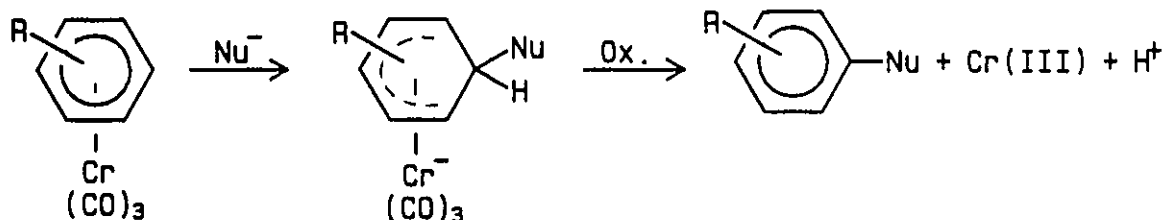
This process results in the formal replacement of hydride by a carbanion.[79] The overall process results in substitution for hydrogen and so in a simple arene several sites of substitution are possible. The approach of the nucleophile is considered to be *trans* to the Cr(CO)$_3$ group.[80] Molecular orbital calculations[36] on the regioselectivity of attack suggests that,

(a)   regioselectivity of attack on the arene should be controlled not only by the substituent on the arene but also by the conformation of the Cr(CO)$_3$ group.

(b)   the arene carbons which are eclipsed with a Cr-CO vector are preferentially attacked by nucleophiles.

However, it was later pointed out that, when either the size of the substituent or the size and reactivity of the nucleophile changes, the regioselectivity also changes.[81] *Meta* substitution is always preferred with strong resonance donors such as alkoxy and amino substituents.

0-10%   90-100%   0%

X=-OR, -NR₂
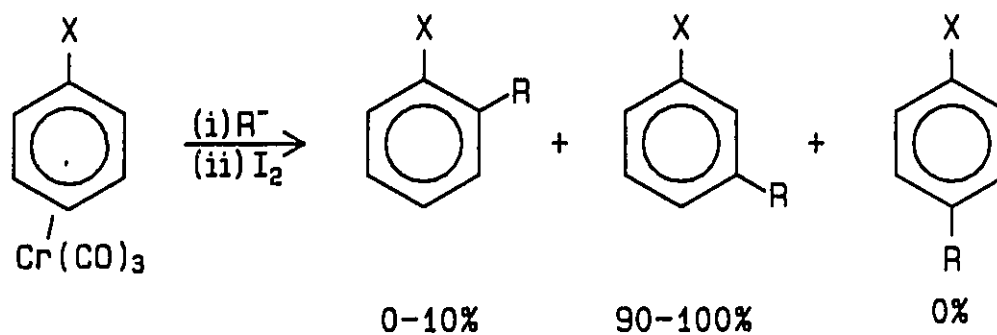
(ii) Addition/protonation reactions:

Generally, cyclohexadienyl anionic intermediates react with electrophiles by cleavage of the *exo* bond and transfer of the nucleophile to the new electrophile.[82-84]

E=RX, RCOX, R₂C=O
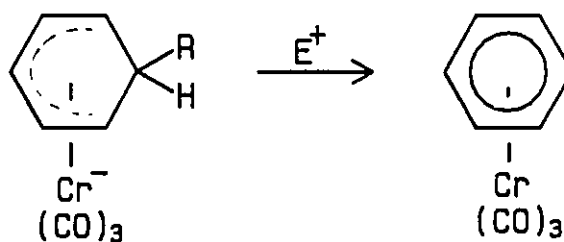
Addition of strong acids to the anionic intermediate leads to protonation of the ligand.[83,84]
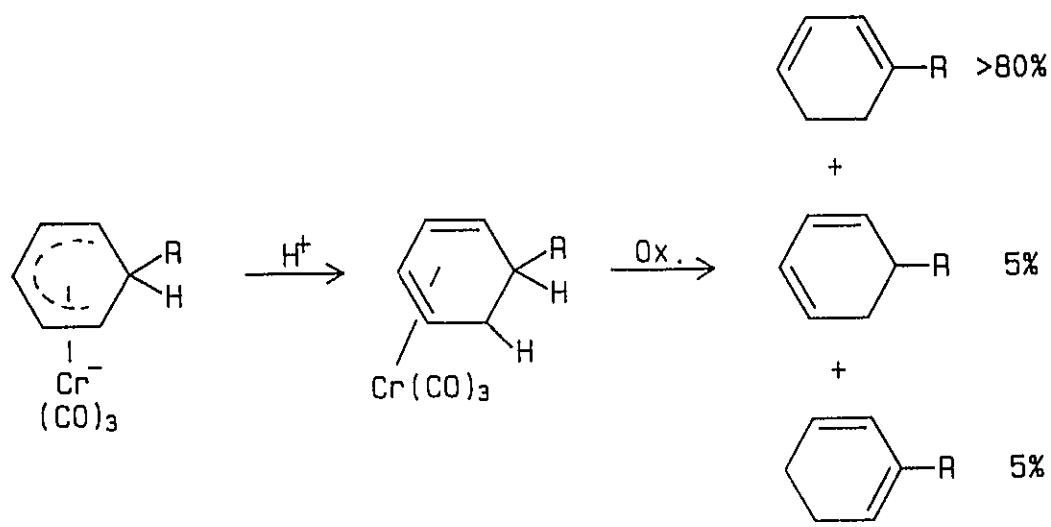
In (benzene)Cr(CO)$_3$ rapid hydrogen shifts occur in the intermediate diene-Cr(CO)$_3$ complex and the 1-substituted cyclohexa-1,3-diene predominates.

(iii) Direct substitution for halogen:

Direct nucleophilic *ipso* addition followed by elimination of halide parallels the classical nucleophilic aromatic substitution. These reactions seem to be more
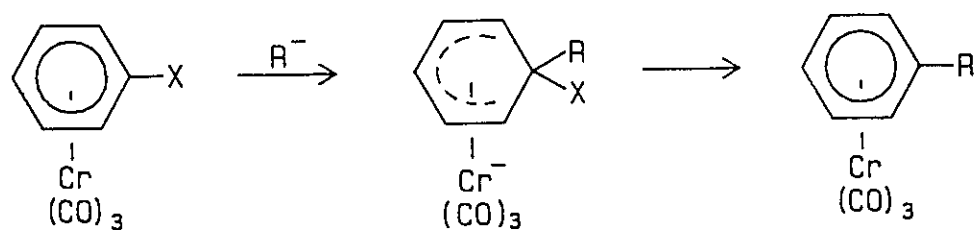
complicated than the overall conversion suggests. The reaction of 2-lithio-2-methyl-propionitrile with (η^6-chlorobenzene)Cr(CO)$_3$ at -78°C gives mainly substitution for hydrogen at the *meta* position. However, at 25°C the intermediate isomerizes to give the substitution product.[85]
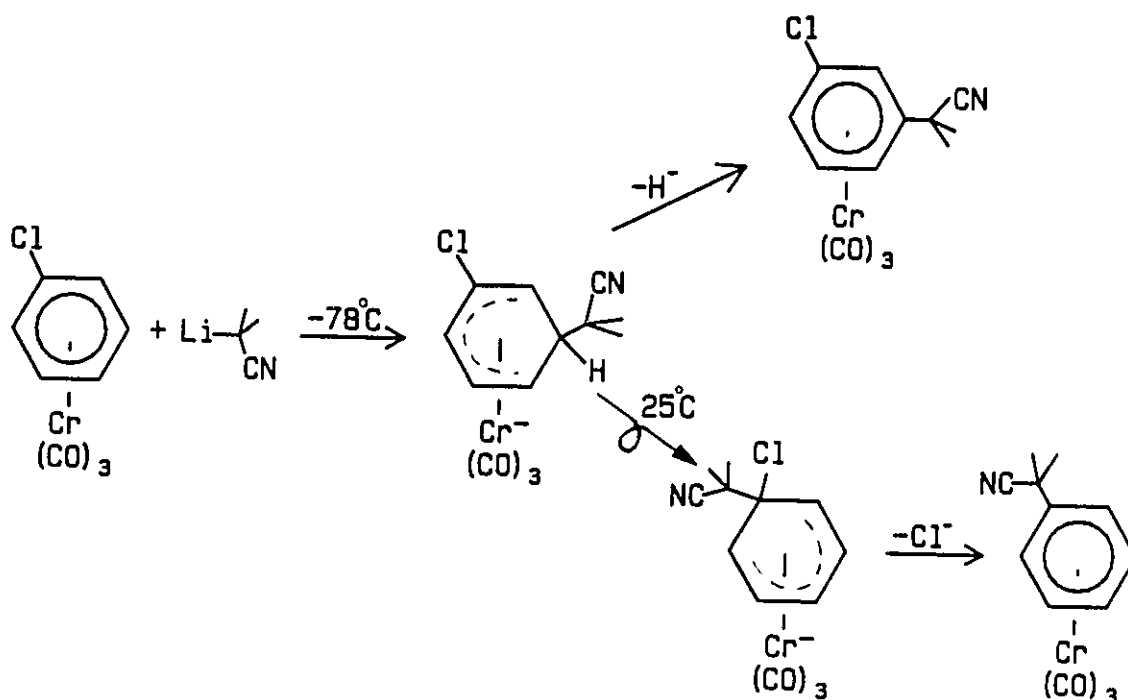
1.3.5 Electrophilic Reactions

Even though Nicholls and Whiting[2] initially believed benzenetricarbonyl-chromium(0) to be inert towards electrophilic substitution, Reimschneider *et al.*[86] succeeded in acetylating this complex. The only electrophilic substitution of arenetricarbonylchromium(0) complexes so far achieved is Friedel-Crafts acetylation. Benzene and substituted (benzene)Cr(CO)$_3$ complexes undergo this reaction under mild conditions giving the corresponding acetyl-substituted complex.[87-90]
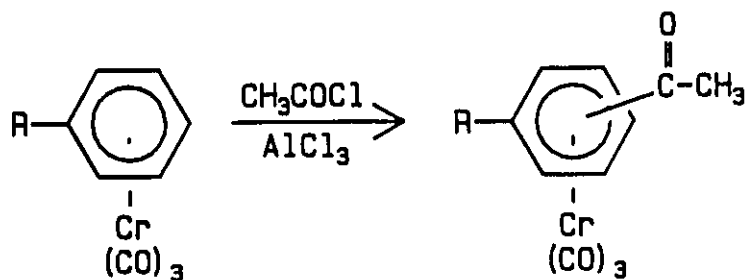
Toluene-Cr(CO)$_3$ on acetylation gives a mixture of *ortho* : *meta* : *para*-acetylated complexes in the ratio of 39:15:46 while the non-complexed toluene gives 9:2:89.[90] It has been reported that alkylbenzene-Cr(CO)$_3$ complexes upon acetylation react much more slowly than the free ligand.[88] This is attributed to the presence and orientation of the Cr(CO)$_3$ group.

Substituent[88] and conformational[91] effects play an important rôle in directing the position of acetylation in arenetricarbonylchromium(0) complexes. Inversion of regioselectivity from a methyl to a *t*-butyl group is a typical example. This suggests that the attack of the electrophile occurs at the staggered arene-ring carbons as predicted from molecular orbital calculations.[80]
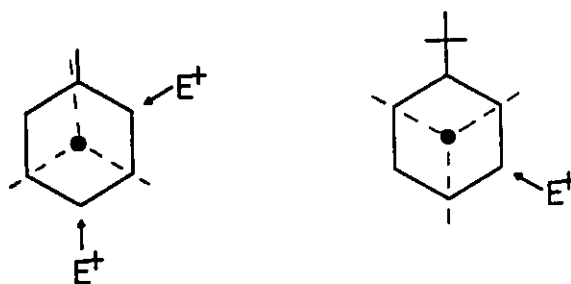
One of the many applications of (η^6-arene)Cr(CO)$_3$ reagents to synthetic problems include the regiocontrolled spirocyclization reactions. In (methylanisole)-

(i)allyl-MgBr
(ii)CF$_3$COOH, Et$_3$SiH

(i)HBr
(ii)KCN

Cr(CO)$_6$

(i)L1
CN

(ii) I$_2$
(iii)H$^+$
(iv)OH$^-$

(i)LDA
(ii)CF$_3$SO$_3$H
(iii)NH$_4$OH
(iv)H$^+$/H$_2$O

CH$_2$OH
|
CH$_2$OH

(i)LDA
(ii)O$_2$
(iii)Me$_2$S
(iv)OH$^-$

PPh$_3$=CH$_2$
H$^+$

(Ph$_3$P)$_3$RhCl
H$_2$

ACORENONE B

MeO
CN
Cr(CO)$_3$
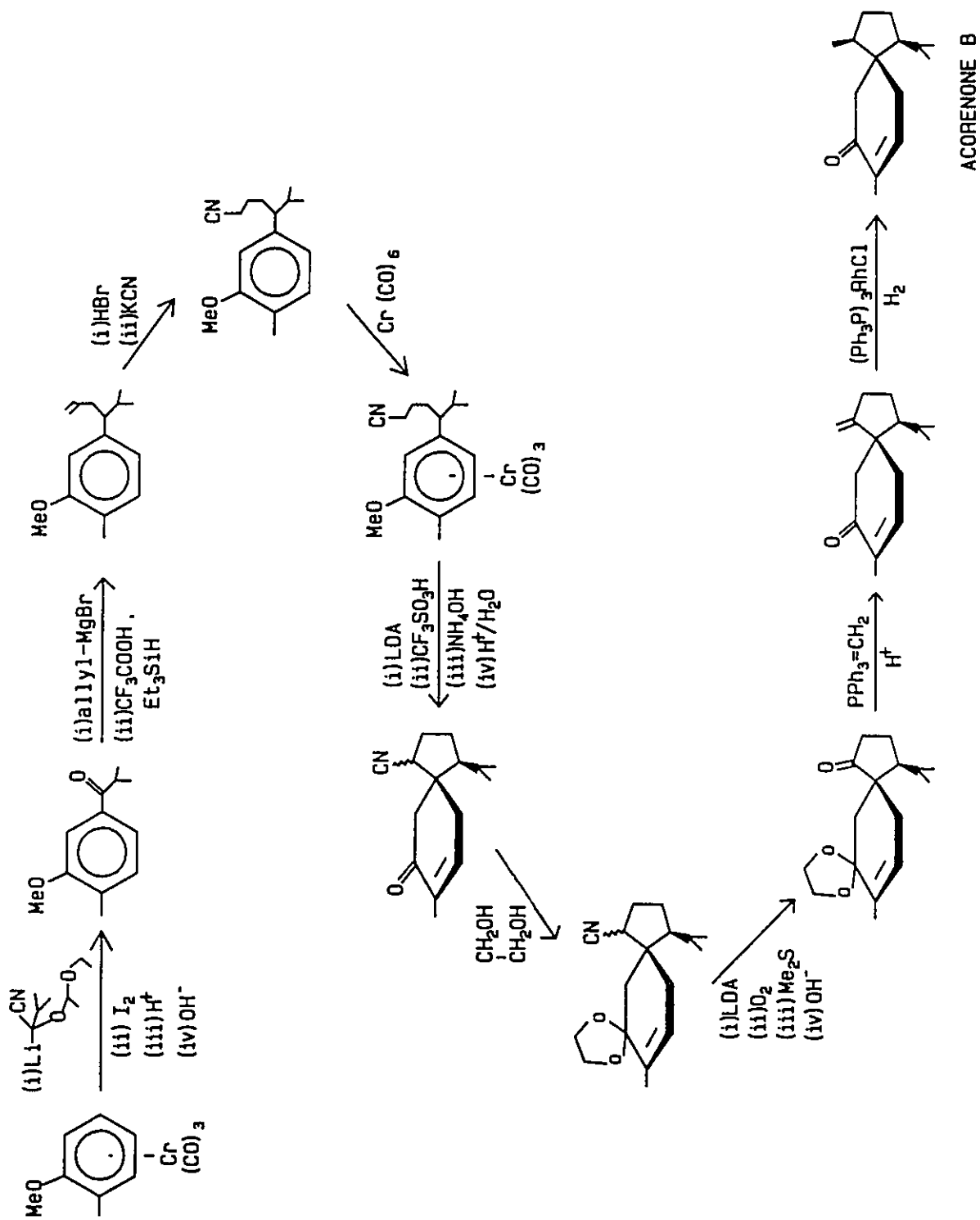
Cr(CO)$_3$ it has been shown that two *meta* positions are activated by methoxy group and reaction takes place with good selectivity at the less hindered *meta* position specially with tertiary carbanions. In 1980, Semmelhack *et al.* took advantage of the selectivity exhibited by donor substituents in (arene)Cr(CO)$_3$ complexes in formulating strategies for synthesis of a number of aromatic natural products. Acorenone is a member of spiro-cyclic natural products that belong to the class of sesquiterpenes. The synthesis of acorenone is a good example of generation of a quaternary carbon in a spirocyclic ring system with good control over stereochemistry. Their strategy relies on the activating and *meta*-directing effects of the tricarbonylchromium(0) group to introduce the spiro-cyclopentane unit by nucleophilic addition to an anisole derivative.[92]

Recent studies have also demonstrated the potential utility of π-arene chromium complexes as substrates for enantiospecific organic synthesis.[93]

CHAPTER 2

DIFFERENTIATION OF α- AND β-Cr(CO)₃ COMPLEXES OF METHYL

O-METHYLPODOCARPATE BY THE USE OF NMR SPECTROSCOPY

2.1 INTRODUCTION

The incorporation of organometallic moieties into naturally occurring chiral molecules is an area of considerable importance both synthetically[94-98] and medically.[99] In the past, organometallic moieties have been used very successfully for stereospecific functionalization of steroids. For instance, complexation of ring B diene unit in ergosterol by tricarbonyliron(0) enables hydrogenation of the exocyclic double bond at C_{22};[95] modifications of steroidal side chains have been accomplished by allyl palladium intermediates;[96] and double bond migration in ergosterol was achieved *via* a rhodium chloride intermediate.[97] Activation of benzylic positions brought about by complexation

$R = -CO_2CH_3$

$R = Si(t-Bu)Me_2$
$R' = Me$
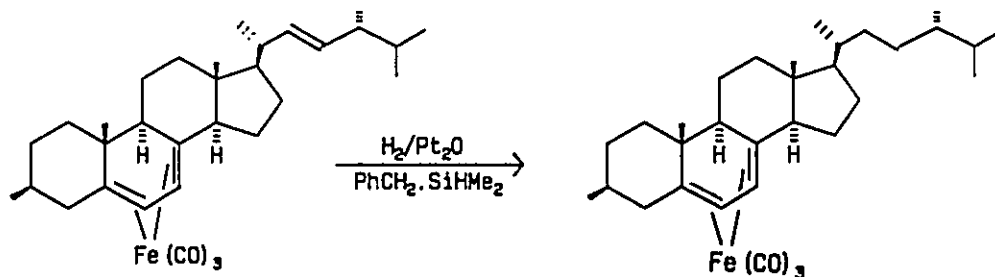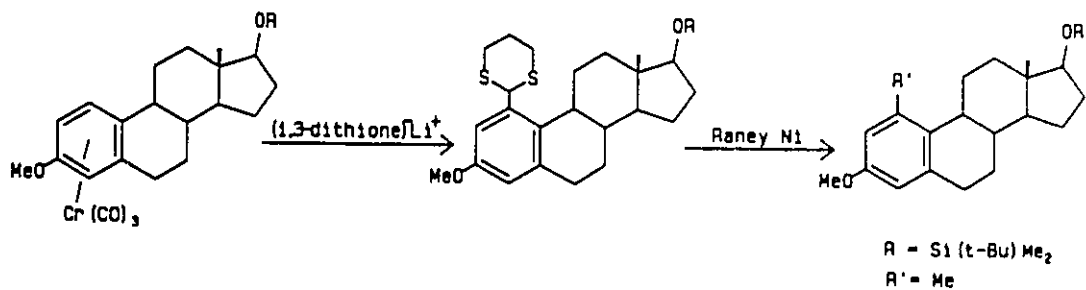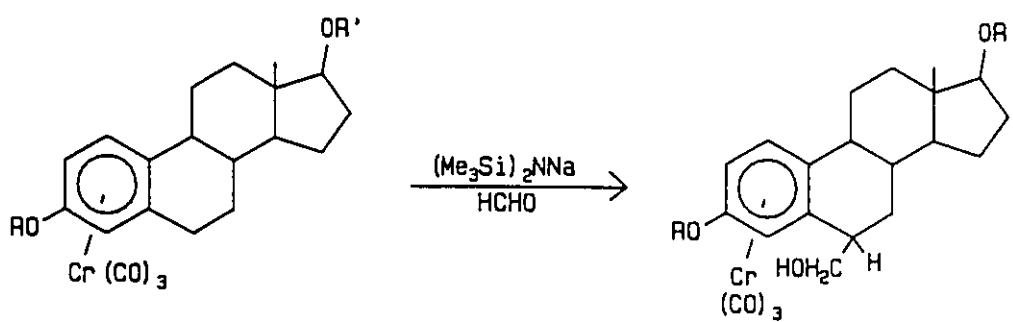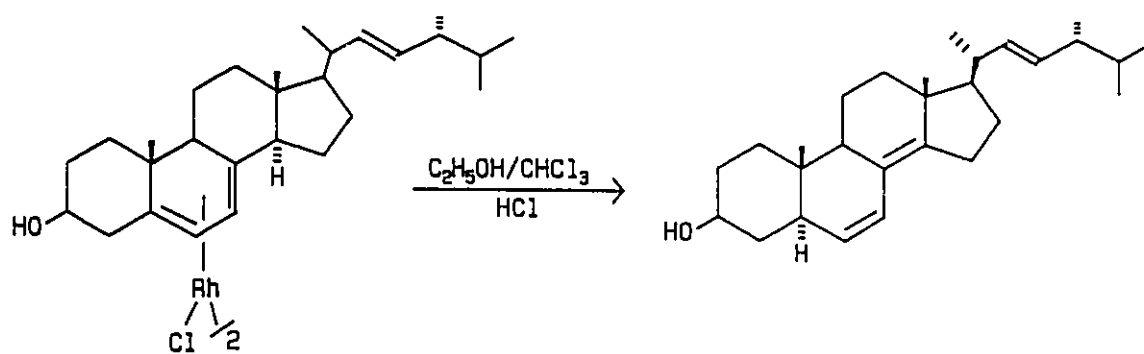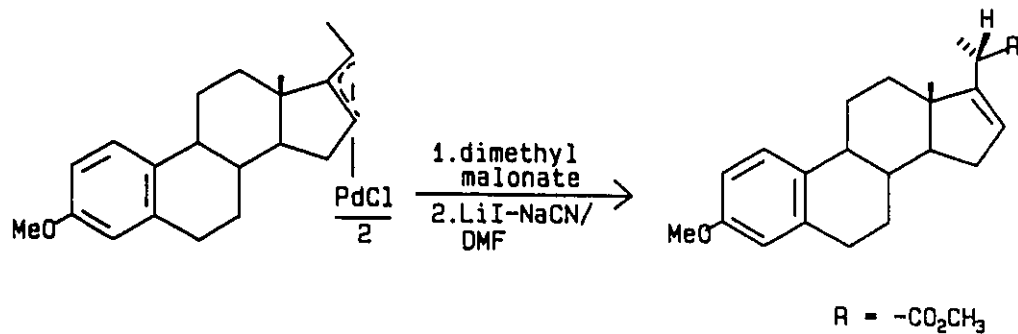
of a $Cr(CO)_3$ unit to the aromatic A ring has been exploited by Jaouen and his colleagues.[98] Recently, Künzer was successful in obtaining a C_1 substituted steroid *via* an arene-$Cr(CO)_3$ intermediate.[99]

Since some types of breast cancers are hormone-dependent and the effectiveness of chemotheraputic treatment is related to the hormone receptor count, Jaouen and his colleagues have used steroidal hormones labelled with metal carbonyls to assay these receptor sites.[100] Metal carbonyls show intense infrared absorption in the range 1850-2000 cm^{-1} but the proteins do not absorb in this frequency range. They have taken advantage of this characteristic to study the receptor binding affinity of steroids. As Fourier Transform Infrared Spectroscopy (FTIR) can be used to detect femtomolar quantities, their technique once it has been well developed may provide a tool for monitoring the hormone dependence of breast cancer.

A tricarbonylchromium(0) unit can bind to the aromatic A ring of estrogens either on the α- or the β-face of the molecule as shown in 4a or 4b, respectively.[101] The site of attachment and the stereochemistry is usually not very easy to establish without resorting to a technique such as X-ray crystallography.
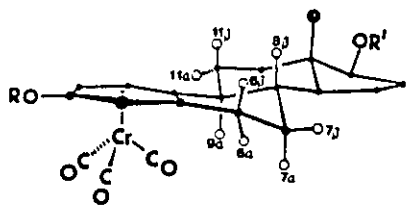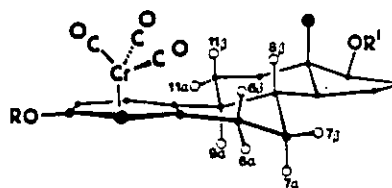
4a   **4b**

In 1986, an NMR method of distinguishing between such diastereomeric pairs was proposed by McGlinchey et al.[102] This approach relies on the observation that protons positioned *proximal* to the metal carbonyl ligands will be deshielded relative to those that are *distal*. The diamagnetic anisotropy of a metal carbonyl ligand is similar to that of an alkyne, a nitrile or any other multiply-bonded cylindrical fragment. Protons positioned along the C_∞ axis are shielded while those on either side of the carbonyl ligand are deshielded.
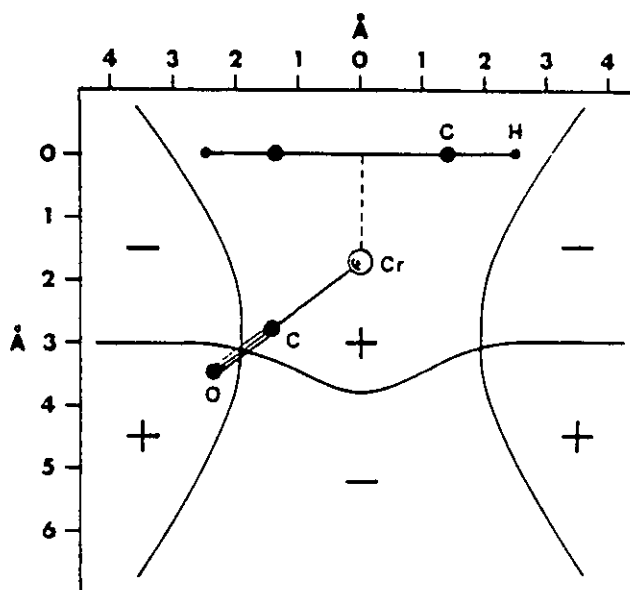
Podocarpic acid is a naturally occurring diterpene. It is readily available from the New Zealand rimu tree otherwise known as *Dacrydium cupressinum*.[103,104] Podocarpic acid has been considered a potential precursor for steroid synthesis. Hoehn and Bible carried out a synthesis to prepare steroids by modifying the A ring of podocarpic acid.[105] Bell et al. have extensively investigated this acid as a precursor to the labdane group of diterpenoids.[106,107] Cambie and his colleagues have focussed their efforts on the synthesis of ring-C aromatic steroids by cyclopenta-annulation of ring C *via* a penta-carbonylcarbenechromium intermediate.[108] They have also prepared the chromium

complexes of podocarpate[109,110] and studied the effect of some nucleophiles.[110]

The reaction of hexacarbonylchromium(0) with chiral arenes gives rise to diastereomers if the tricarbonylchromium moiety can bind to either face of the aromatic ring. Clark *et al.* synthesized the diastereomeric chromium complexes of methyl *O*-methylpodocarpate and characterized them by X-ray crystallography.[109] Our goal was to be able to differentiate the diastereomeric chromium complexes by the use of NMR spectroscopy.

2.2 RESULTS AND DISCUSSION

The naturally occurring diterpene podocarpic acid, 5, was first converted to methyl *O*-methylpodocarpate, 7, by the following route.[111]

PODOCARPIC ACID
5

1. 2M NaOH/
   (CH₃O)₂SO₂
2. reflux 3hrs
3. dil. HCl

O-METHYLPODOCARPIC ACID
6

Et₂O/
Diazomethane

METHYL O-METHYLPODOCARPATE
7
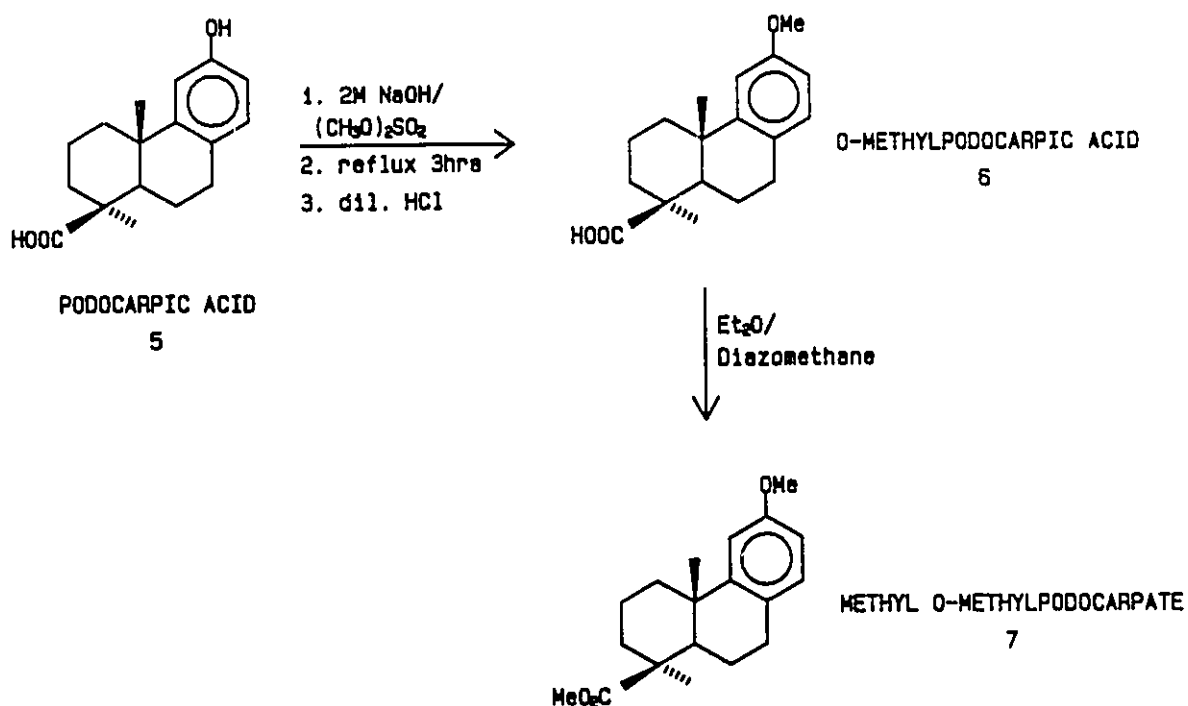
Methyl O-methylpodocarpate, **7**, when treated with Cr(CO)₆ yields the diastereomers **8a** and **8b**, respectively.
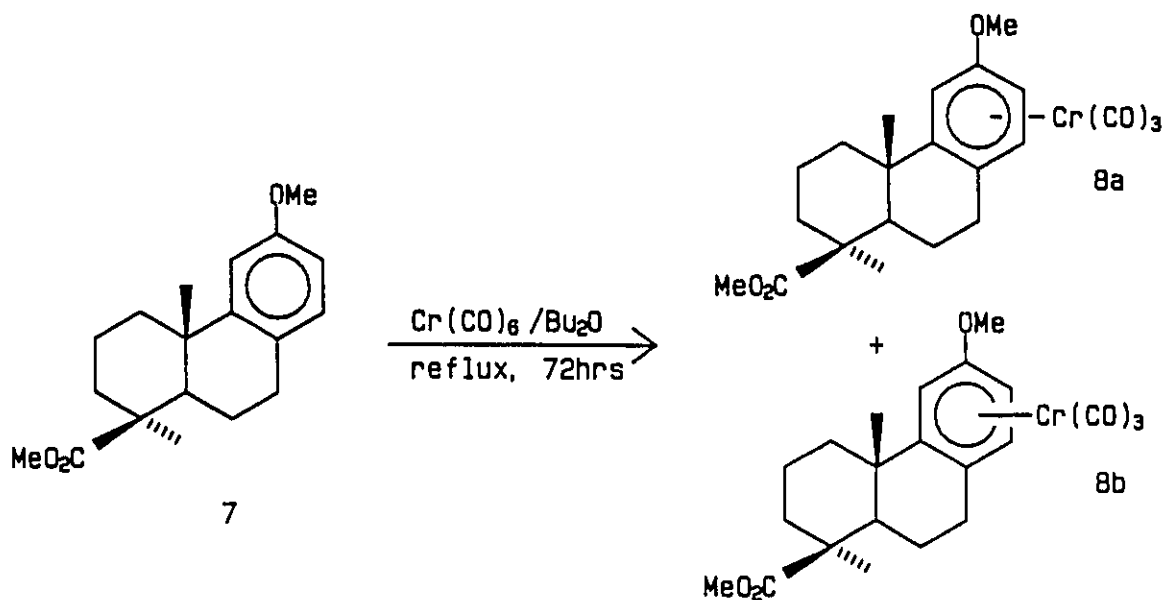
In order to do some chemistry on one of them, the diastereomers needed to be separated and identified. Therefore it was necessary to have a quick and reliable method of distinguishing between such diastereomers. In an attempt to achieve this some high field NMR spectroscopic studies were performed on this system.

The 500 MHz ^{1}H NMR spectra of methyl O-methylpodocarpate, **7**, and its α- and β-Cr(CO)₃ complexes, **8a** and **8b**, respectively, appear as Figure 2.1. All of the ^{1}H and ^{13}C assignments were obtained by the use of homonuclear ^{1}H-^{1}H correlated spectroscopy (COSY) and heteronuclear ^{1}H-^{13}C shift-correlated two-dimensional NMR experiments. These data are collected in Tables 2.1 and 2.2. A typical COSY spectrum of **7** is shown in Figure 2.2 and this reveals the coupling between protons. Here the 1-D spectrum lies along the diagonal and the off-diagonal peaks reveal the resonances that are related by scalar coupling. Figure 2.3 shows the two-dimensional ^{1}H-^{13}C shift-
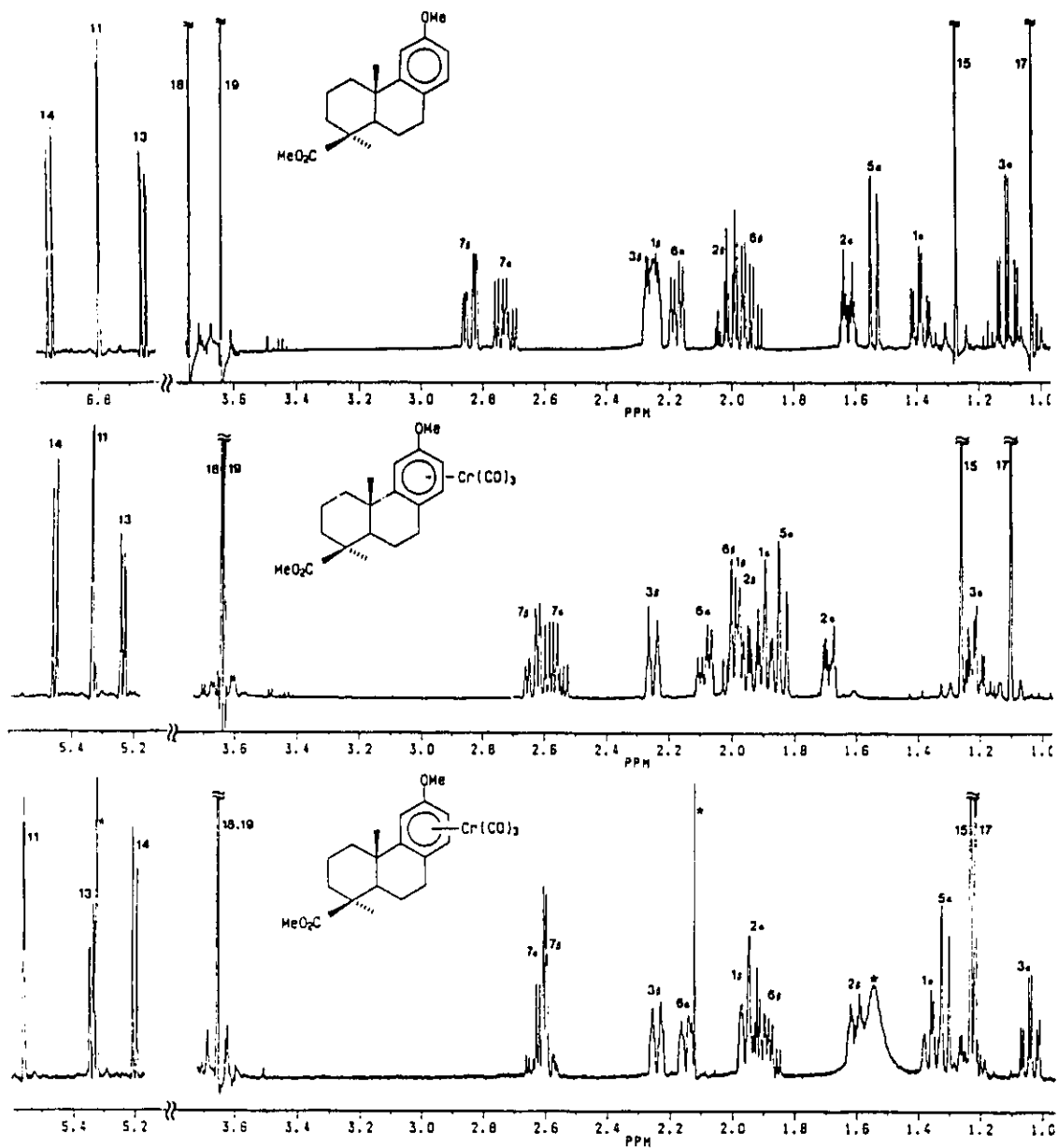
Figure 2.1 : 500 MHz ^{1}H NMR spectra of **7, 8a** and **8b** recorded in CD_2Cl_2. Peaks marked with an asterisk are solvent peaks.
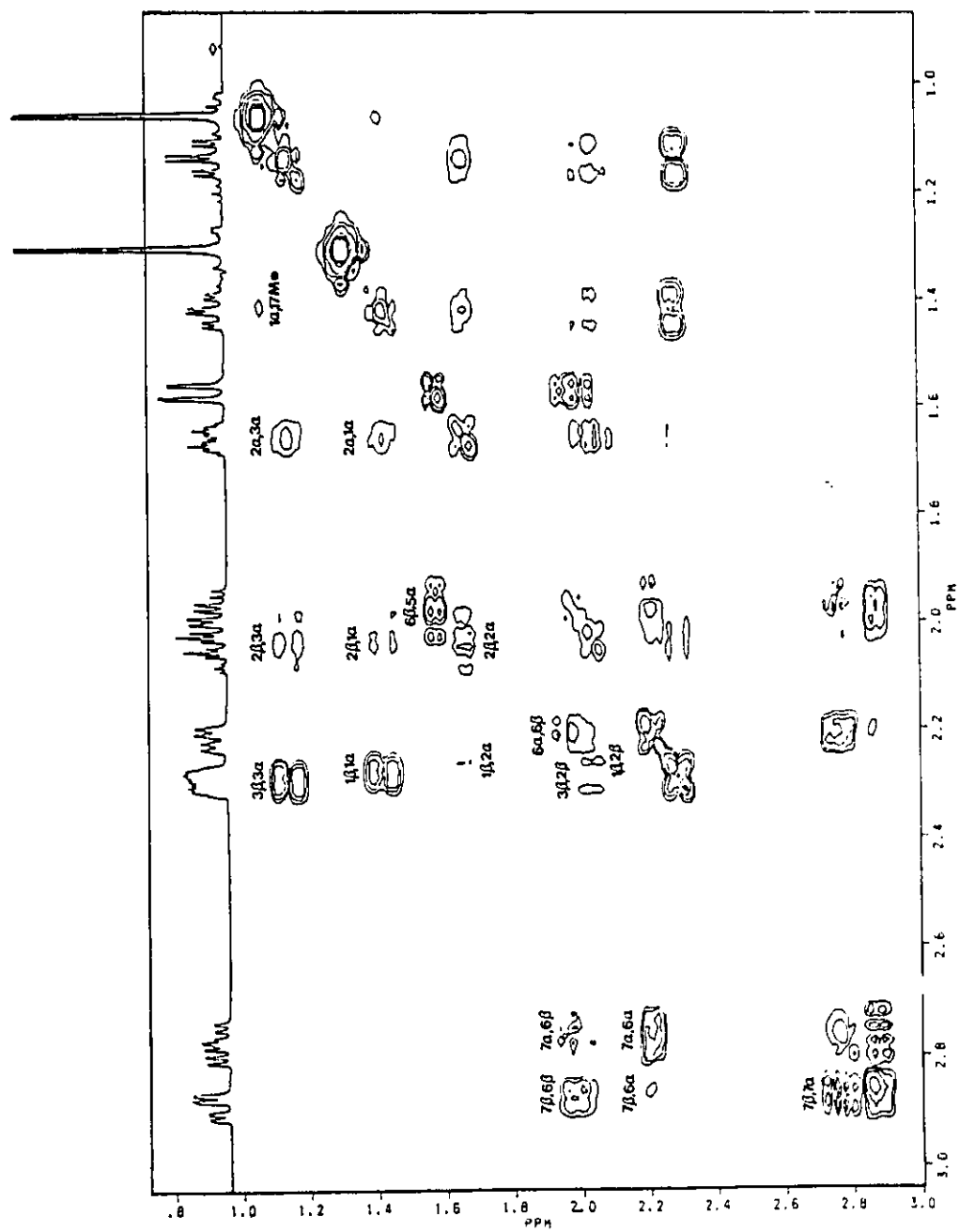
Figure 2.2 : 500 MHz two-dimensional ^{1}H-^{1}H NMR spectrum of 7 in CD_2Cl_2. Expanded contour plot of a portion of the matrix of a COSY experiment.
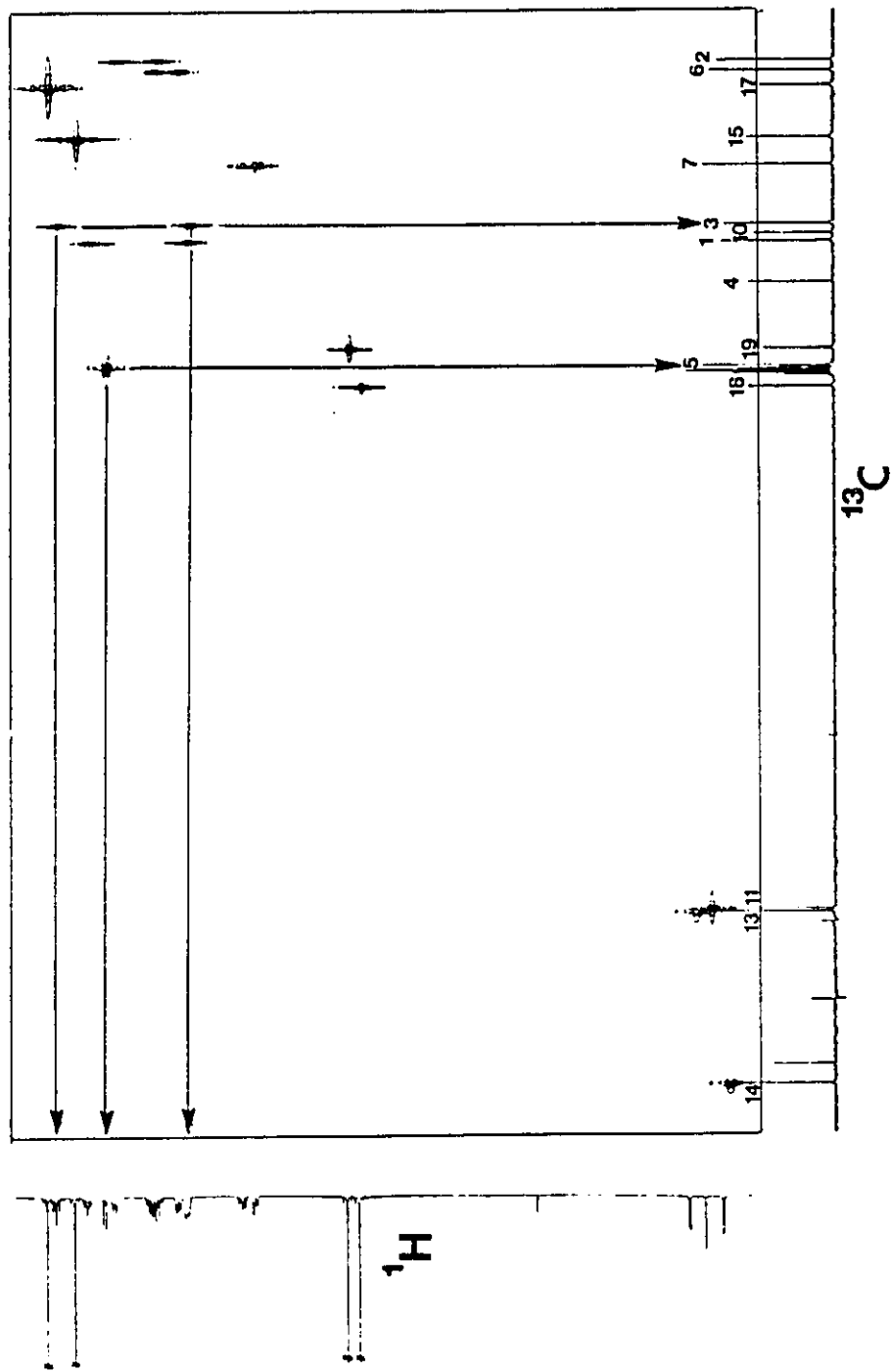
Figure 2.3 : Two-dimensional ^{1}H-^{13}C shift-correlated NMR spectrum of 7. A ^{1}H NMR spectrum is projected onto the vertical axis and a ^{13}C NMR spectrum on the horizontal axis. ^{1}H Correlations of two ^{13}C resonances (C-3 and C-5) are indicated.

TABLE 2.1

500 MHz ^{1}H NMR data for methyl O-methylpodocarpate (MOM), 7, and α- and β-tricarbonylchromium complexes, 8a and 8b, in CD_2Cl_2.

H	α-MOMCr(CO)$_3$ 8a	β-MOMCr(CO)$_3$ 8b	MOM 7	Estradiol[a]
1α	1.88	1.35	1.41	1.70 [11β]
1β	1.96	1.96	2.26	2.41 [11α]
2α	1.67	1.61	1.65	
2β	1.90	1.91	2.03	
3α	1.22	1.05	1.13	
3β	2.25	2.24	2.29	
5α	1.85	1.31	1.57	1.57 [8β]
6α	2.08	2.14	2.20	1.96 [7β]
6β	1.96	1.88	1.98	1.44 [7α]
7α	2.55	2.64	2.76	2.99 [6β]
7β	2.63	2.61	2.86	2.96 [6α]
11	5.32	5.56	6.83	7.04 [4]
13	5.23	5.34	6.70	7.11 [2]
14	5.45	5.25	6.95	7.44 [1]
15	1.25	1.23	1.30	
17	1.08	1.23	1.05	
18	3.63	3.65	3.78	
19	3.63	3.65	3.60	

[a]These data are for a 3,17-alkylated estradiol from Ref. 101.

TABLE 2.2

125MHz ^{13}C NMR data for methyl O-methylpodocarpate (MOM), 7, and its tricarbonyl-chromium complexes, 8a and 8b, in C_6D_6.

C	α-MOMCr(CO)$_3$ 8a	β-MOMCr(CO)$_3$ 8b	MOM 7
1	37.64	41.81	40.25
2	20.00	21.33	21.02
3	37.47	37.93	38.54
4	44.00	44.30	44.70
5	49.58	54.05	53.56
6	20.40	21.02	22.24
7	28.57	32.68	32.18
8	102.12	107.60	128.19
9	126.00	125.60	150.16
10	39.98	38.50	39.52
11	79.38	83.29	112.08
12	140.70	139.00	159.26
13	77.34	82.46	112.37
14	93.55	89.30	130.80
15	28.40	28.65	29.08
16	176.80	177.00	177.83
17	24.86	24.88	23.76
18	55.26	56.50	55.39
19	50.82	51.54	51.35
Cr(CO)$_3$	234.87	235.48	

correlated spectrum of 7. This technique readily identifies the protons that are directly attached to a given carbon atom.

At this point it is essential to explain the numbering scheme used for steroids and our target molecule. During the discussion of the coupling patterns of some protons the similarity between our system and 3,17β-estradiol is explained. The general framework of podocarpic acid resembles a reoriented steroid as depicted below except there is no five-membered ring in podocarpic acid.

β-estradiol   Estradiol reoriented

Methyl O-methylpodocarpate
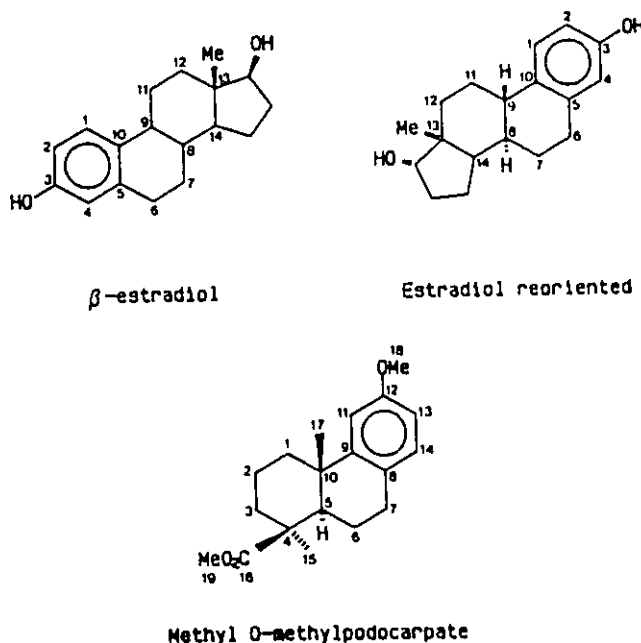
The unambiguous identification of each proton of a methylene unit as either the α- or the β-proton is less trivial to establish. As podocarpate very closely resembles a steroid the assignments for 7 was compared with those previously reported for 3,17β-estradiol (Figure 2.4).[101] Re-oriented estradiol and methyl O-methylpodocarpate have several proton environments that are analogous in the two systems. For instance, the 1α, 1β, 5α, 6α, 6β, 7α and 7β protons in 7 correspond to 11β, 11α, 8β, 7β, 7α, 6β and 6α protons, respectively in estradiol. As seen in Figure 2.5, the benzylic protons at C7 in 7 show almost identical coupling patterns to those of the C6 protons in the estradiol system.
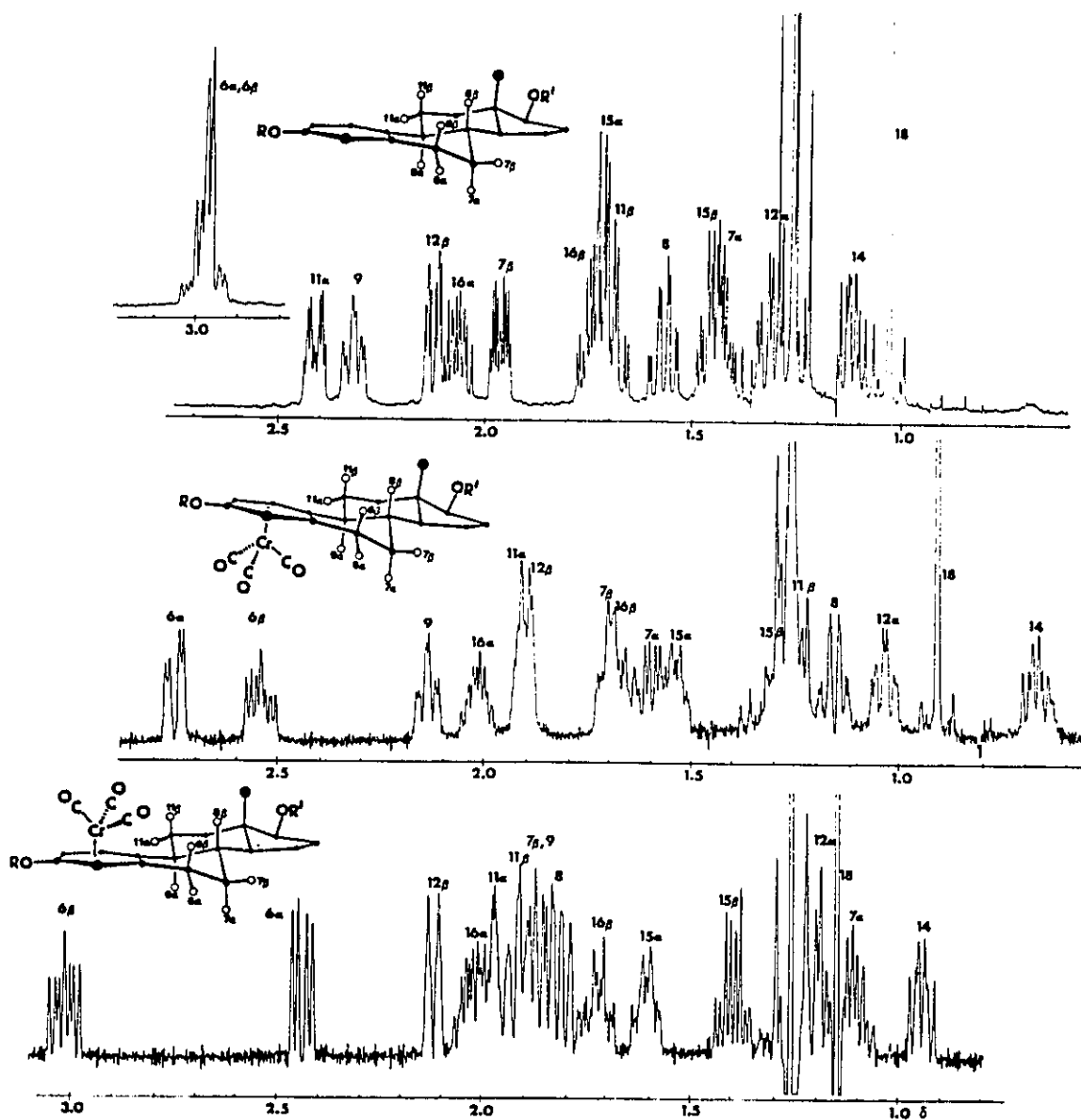
Figure 2.4 : Sections of the 500 MHz ^{1}H NMR spectra of an estradiol derivative and its α- and β-Cr(CO)$_3$ complexes 4a and 4b obtained from reference 101.
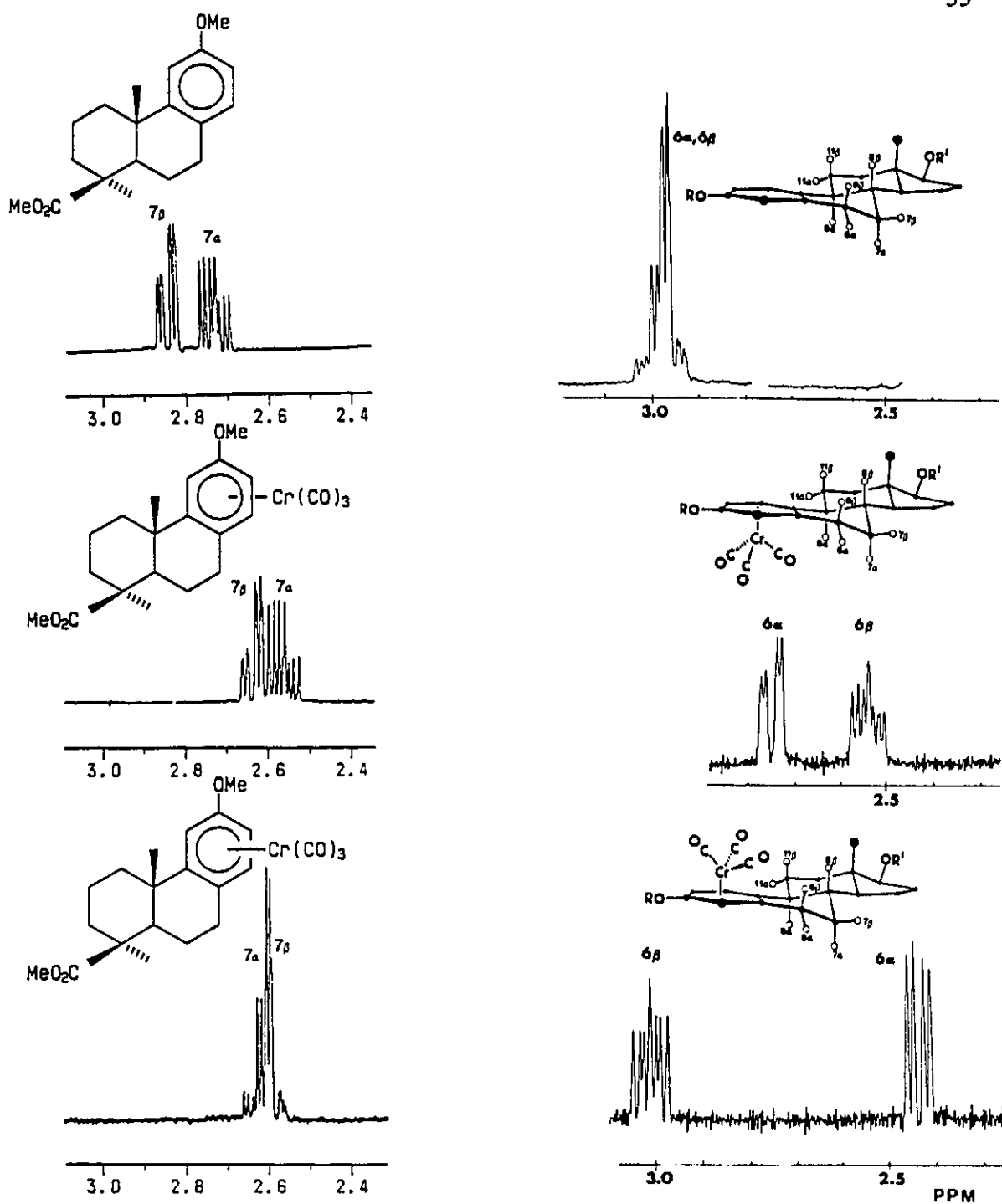
Figure 2.5 : Similarities observed in the coupling patterns for the C_7 benzylic protons of methyl O-methylpodocarpate and the C_6 protons of 3,17β-estradiol and their α- and β-Cr(CO)₃ complexes.

The differentiation of the 6α and 6β protons in estradiol was established *via* nuclear Overhauser enhancement measurements[101] and so, by analogy, the unambiguous identification of the 7β and 7α protons in methyl O-methylpodocarpate was evident. From work done previously on steroidal systems it is clear that protons positioned anti-periplanar to angular methyl groups usually exhibit a correlation in the COSY spectrum because of long range coupling. Using this criterion, it was easy to assign the 1α proton in podocarpate *via* its correlation to the C_{10} methyl protons. As a final confirmation of the correctness of these assignments, a complete simulation of the spectrum of 7 was obtained and is presented as Figure 2.6.

Application of the Karplus relationship between $^3J_{HH}$, the vicinal coupling constant, and the appropriate dihedral angles is very valuable in conformational analysis.[112] The 5α, 6α, 6β, 7α and 7β protons in methyl O-methylpodocarpate give rise to six vicinal couplings. A knowledge of these coupling constants together with the use of the Karplus relationship proposed by Bothner-By:[112(d)]

$$J = 7 - \cos \Theta + 5 \cos 2\Theta$$

allows one to estimate the dihedral angles between the vicinally disposed C-H bonds. The structure of methyl O-methylpodocarpate has not been determined X-ray crystallo-graphically. Allinger's MM2 program[113] was used to calculate the energy-minimized conformation of methyl O-methylpodocarpate. As presented in Table 2.3, the dihedral angles obtained from this conformation agrees reasonably well with the values derived from the Karplus analysis. However, it is well known that the angles predicted by the Karplus equation are less reliable when the methylene protons are situated near strongly electron-withdrawing substituents.[114] · Nevertheless, as shown in Figure 2.7, the agreement is quite good for most of the data points. The chromium complexes of methyl
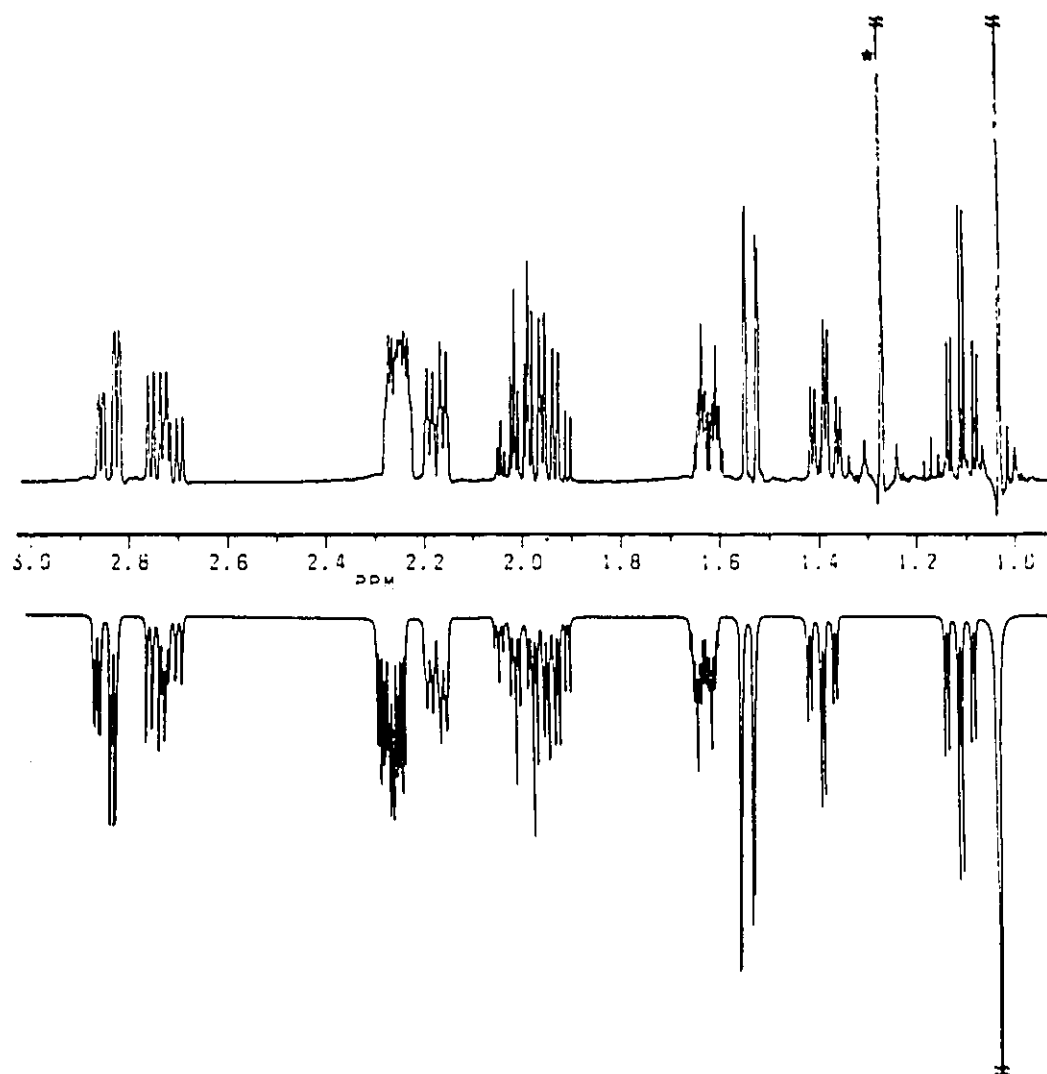
Figure 2.6 : Experimental (upper trace) and simulated (lower trace) ^{1}H spectra of 7. The singlet marked with an asterisk assigned to the methyl group at C(15) was not included in the simulation.

TABLE 2.3

Dihedral angles calculated from NMR coupling constants for methyl O-methyl-podocarpate *versus* dihedral angles from a molecular mechanics energy-minimized structure.

	J_{exptl} (Hz)	Dihedral Angle (Karplus equation)	Dihedral Angle (MM2)
1α-2α	4.2	59	-55.6
1α-2β	13.6	≈180	-171.5
1β-2α	2.9	69	59.2
1β-2β	3.9	61	-56.6
2α-3α	4.2	58	55.0
2α-3β	2.9	69	-59.7
2β-3α	13.8	≈180	170.8
2β-3β	3.9	61	56.1
5α-6α	1.8	≈85	-73.0
5α-6β	12.3	165	167.8
6α-7α	6.2	46	51.0
6α-7β	1.9	≈85	-66.4
6β-7α	13.1	≈180	166.4
6β-7β	5.5	50	49.0

Figure 2.7 : Karplus type curve relating the vicinal ^{3}J(HH) coupling constants in 7 with dihedral angles obtained from an MM2 calculation. The line is derived from the Karplus equation.[112(d)]

O-methylpodocarpate, **8a** and **8b**, were also completely assigned using 2-D NMR techniques. The ^1H and ^{13}C NMR data are collected in Tables 2.1 and 2.2.

As mentioned earlier, protons situated *proximal* to the tricarbonylchromium(0) moiety experience a deshielding effect relative to those that are *distal* to the metal. It is apparent from Figure 2.1 and Table 2.1 that the major differences in proton chemical shifts observed for the diastereomers **8a** and **8b** occur for the 1α, 5α and C_{17}-methyl protons. In one isomer the 1α and 5α protons are markedly deshielded. Therefore, we can assume that the tricarbonylchromium(0) moiety in this molecule is on the α face of the molecule. Again, looking at the ^1H chemical shifts of the C_{17} methyl groups in the two isomers, the methyl shift in the free ligand and the α isomer are almost identical whereas complexation of $Cr(CO)_3$ on the same face as the methyl substituent, i.e., β-face, leads to marked deshielding. The downfield shift of the methyl protons cannot be entirely due to the anisotropic effect of the tripodal fragment as other factors such as steric effects must be taken into consideration. This can be very clearly seen in Figure 2.8, which shows the superposition of the free ligand, the α- and the β-complexes. Here the structures of the $Cr(CO)_3$ complexes are taken from the X-ray data while the free ligand geometry was derived from our MM2 calculations. Comparing the diastereomers assigned by our NMR approach with those of Cambie *et al.*, the X-ray results and the NMR assignments are in complete accord.

Several years ago, Emmanuel and Randall proposed that the preferred orientation of a $Cr(CO)_3$ moiety relative to an aromatic ring could be inferred *via* the shifts of the arene ring protons.[115] Figure 2.9 shows the relevant molecular fragments from Cambie's published X-ray data.[109] This provides an ideal opportunity to examine their proposal. If the chemical shift of an arene ring-proton is influenced by the anisotropy of the metal carbonyl ligands, then one would predict that the H_{14} nucleus in the α isomer should be deshielded relative to that found for the β-isomer. In contrast, the
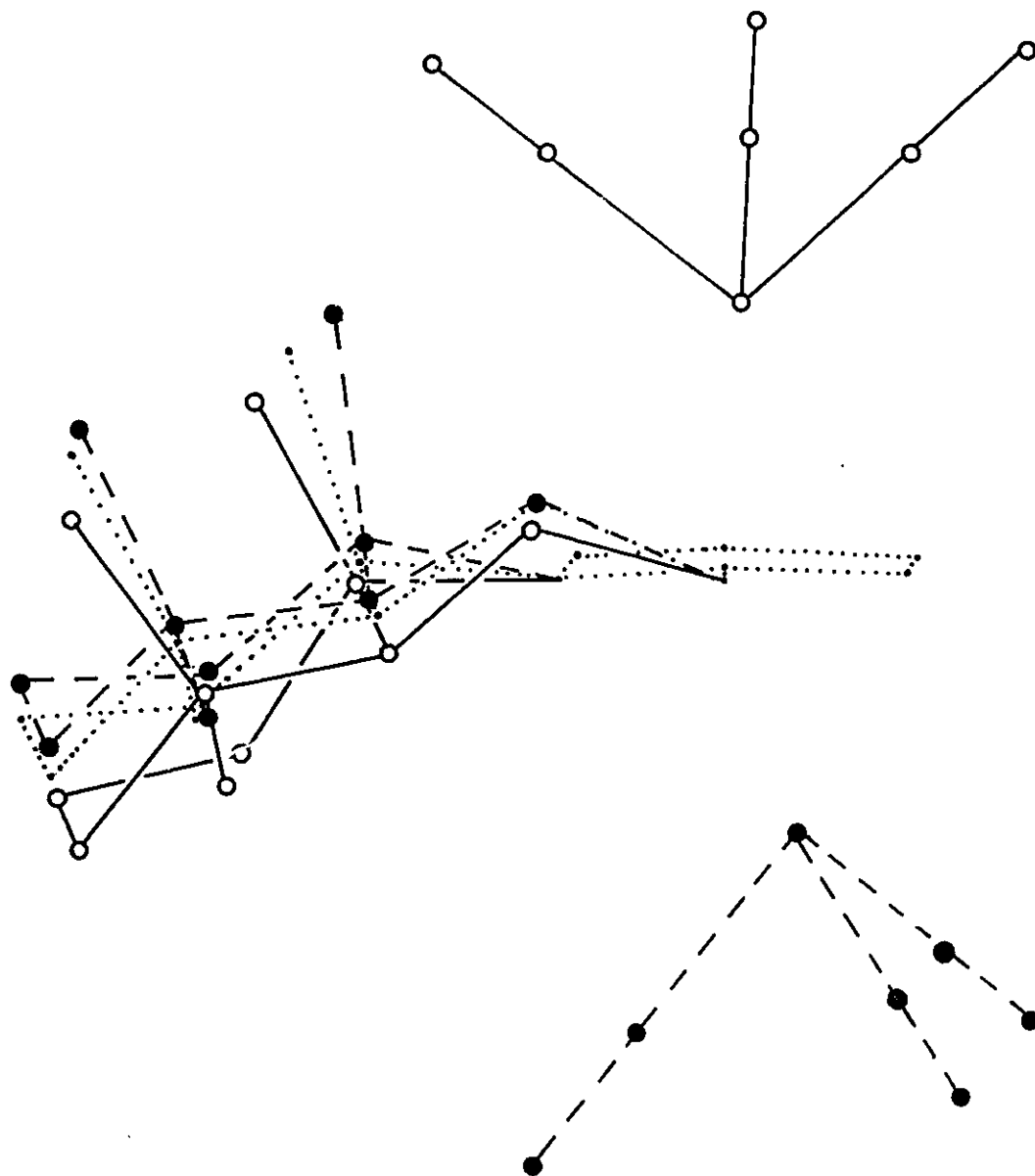
Figure 2.8 : Molecular conformation of **7** (dotted line), **8a** (dashed line) and **8b** (solid line) drawn such that their aromatic rings overlap.
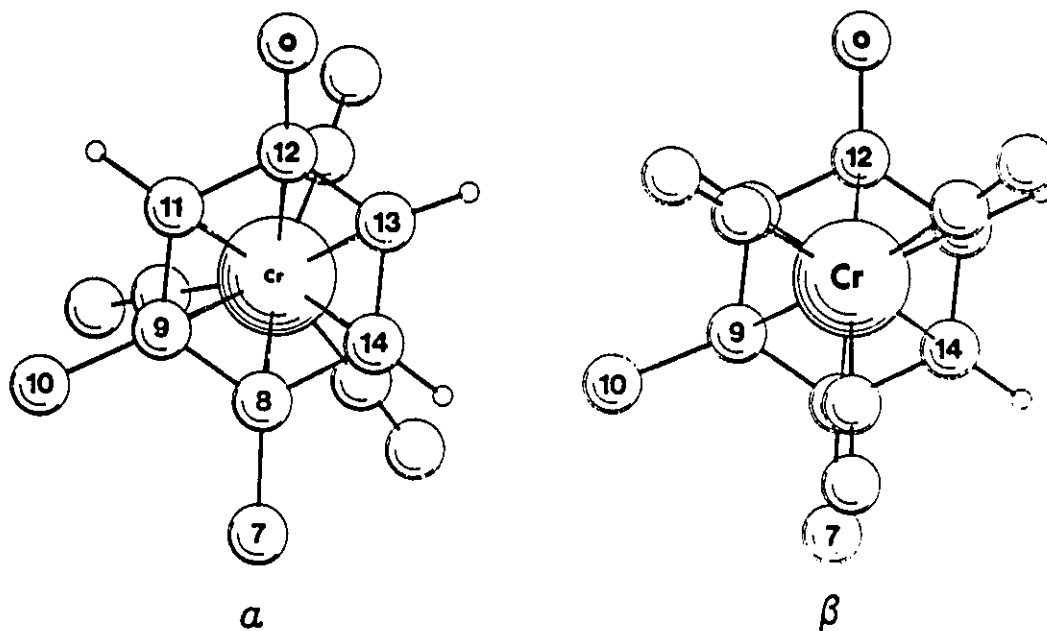
Figure 2.9 : The orientation of the $Cr(CO)_3$ moieties relative to the aromatic ring in **8a** and **8b**.

H_{11} and H_{13} protons should be shielded in the α-isomer. In fact, this is indeed the case from our NMR data.

In conclusion, it has been demonstrated that high resolution two-dimensional NMR spectroscopy is a valuable tool for detecting subtle changes in molecular geometry. The ^1H chemical shifts and coupling constants readily allow the unambiguous identification of diastereomers that differ only in the site of attachment of a metal carbonyl fragment. Although, the ^{13}C NMR spectra are not as diagnostic, the shielding of the C_8, C_{11} and C_{13} in the α-complex relative to its β-counterpart is obvious. This is readily attributable to the different orientations of the tricarbonylchromium moiety in the two diastereomers.

One can take advantage of the highly anisotropic nature of organometallic fragments to identify which face of an asymmetric molecule bears a metal. This has been successfully extended to the α- and β-isomers of [(Cp)Ru-estradiol]+ which were first differentiated by NMR spectroscopy; these assignments were subsequently confirmed by X-ray crystallography.[116] Clearly, this is a general method which should have wide applicability.

CHAPTER 3

CHROMIUM COMPLEXES OF POLYPHENYL ARENES:

THE BARRIER TO PHENYL ROTATION

3.1 INTRODUCTION

Molecules are in constant motion and the different conformations which are interconverted by bond rotations and other molecular gymnastics often have different NMR spectra. N,N-dimethylacetamide is a simple example which illustrates the special case in which the exchange produces indistinguishable molecules.[117]

$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - N \overset{\nearrow Me_A}{\searrow Me_B} \quad \rightleftharpoons \quad H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - N \overset{\nearrow Me_B}{\searrow Me_A}$$
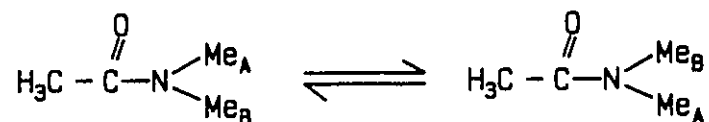
At lower temperatures, restricted rotation around the C-N bond produces different shielding zones for the methyl groups, so two methyl resonances arise in the spectrum. As the sample temperature is raised, rotation becomes more rapid, and in consequence the life-time of each methyl group in each separate shielding zone is reduced. This gives rise to broad signals. Ultimately when the rotation is very rapid the life-times become so short that only one resonance is detected, mid-way between the separate signals.

The ^{13}C NMR spectrum of N-methylaniline shows four signals for the arene ring carbons down to -120°C due to the effect of free rotation of the Ph-N bond. Near -135°C the rotation "freezes" and this produces six separate resonance positions for the ring carbons.[118]

For a molecule interconverting between two states A and B the rate of interconversion is determined by the free energy of activation ($\Delta G^\#$), where

$$k = (RT/Nh) \exp (-\Delta G^\#/RT)$$

At coalescence, the life-time of either nucleus A or nucleus B is given by

$$\tau = \sqrt{2} / \pi \Delta \nu$$

and the rate constant, k, for the interconversion from A to B is given by

$$k = 1 / \tau$$

Therefore, the free energy of activation $\Delta G^\#$ from the coalescence point and temperature T_c is

$$\Delta G^\#/RT_c = \ln (\sqrt{2}R / \pi Nh) + \ln (T_c/\Delta \nu)$$

$$= 22.96 + \ln (T_c/\Delta \nu)$$

This equation is only valid for a mutually exchanging, equally populated system where there is no coupling involved.[119]

In the case of a multiple site exchange, involving coupled nuclei, one must take advantage of a program such as DNMR3[120] which allows the simulation of exchange broadened spectra. Thus, comparison of experimental spectra (at known temperatures) with simulated spectra (with known rate constants) allows one to evaluate E_a *via* an Arrhenius plot of ln k *vs.* 1/T. Furthermore, $\Delta H^{\#}$ and $\Delta S^{\#}$ can be determined from an Eyring plot of ln(k/T) *vs.* 1/T.

NMR spectroscopy has also been employed to investigate hindered rotation around the arene-R bond in a variety of substituted π-bonded arene complexes. For example, the barrier to rotation around the bond between the formyl group and the complexed ring in *para*-dimethylaminobenzaldehyde-Cr(CO)$_3$ has been estimated as 8.6 kcal mol^{-1} from variable-temperature ^{13}C NMR spectroscopy and line shape analysis.[121] The decrease in rotational barrier compared to the free arene ($\Delta G^{\#}$ =10.2 kcal mol^{-1}) was attributed to either electron-withdrawal by the Cr(CO)$_3$ group and/or to a stabilizing interaction in the transition state between the negative oxygen of the formyl group and the Cr(CO)$_3$ moiety. In a related study of the bulkier arene (t-Bu)$_2$CHC$_6$H$_5$, a
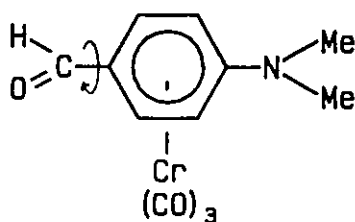
similar decrease of the rotational barrier about the alkyl-arene ring bond upon complexation to Cr(CO)$_3$ ($\Delta G^{\#}$ decreases from 22 to 17 kcal mol^{-1}) was ascribed to additional steric strain between the alkyl and Cr(CO)$_3$ groups in the complex.[122]
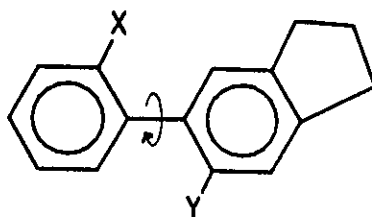
The dynamics of internal rotation of aryl rings in organic and organometallic polyaryl compounds have attracted considerable attention for several years.[123] Sternhell and others[124] studied the internal rotations in a series of biphenyl derivatives.

In 1973, Gust and Mislow developed a general and systematic approach to the topological analysis of isomerism and isomerization for compounds belonging to the triaryl systems such as Ar_3CH, Ar_3N, Ar_3P, Ar_3B and Ar_3CH^+.[125] In a paper published in 1976 by Mislow, he noted that the motions of these aryl rings are coupled in such a way that none of the rings move independently of the others, and he called it a *correlated rotation*.[126] They have also looked at these systems with substituted aryls.

In 1,3,5-triphenylbenzene the peripheral phenyl rings rotate freely showing the barrier to rotation is quite low. The work of Gust on molecular crowding, on derivatives of pentaphenylbenzene and hexaphenylbenzene is very interesting.[127,128] In terms of molecular crowding, of all the systems studied so far, hexaphenylbenzene derivatives are the most hindered. The parent molecule, hexaphenylbenzene, has been crystallographically characterized and it has been shown that the peripheral phenyl substituents are oriented so as to make dihedral angles of approximately 67° with the center ring.[129] In an attempt to evaluate the barriers to peripheral ring rotation Gust labelled one or more phenyls with *ortho*- or *meta*-substituents. This technique allows one to generate a number of stereoisomers. The rates of interconversion of these stereoisomers may be followed by dynamic NMR (DNMR) spectroscopy.

The following conclusions were drawn from Gust's studies: (i) inter-conversions occur *via* mechanisms involving uncorrelated rotation of aryl rings (ii) the incorporation of an *ortho* methyl or methoxy group brings about an activation energy barrier of about 33 kcal mol^{-1} while in the corresponding *meta* substituted systems the barrier is about 17 kcal mol^{-1}.[128] In their study they labelled the peripheral rings by effectively "painting the edges different colors" whereas our approach was to "paint the faces differently".

In order to study the dynamics of these potentially sterically demanding ligands tricarbonylchromium(0) complexes of 1,3,5-triphenylbenzene was prepared. Although it is clear that the potential steric hindrance in 1,3,5-triphenylbenzene is unlikely to be as severe as that encountered in hexaphenylbenzene, the incorporation of rather bulky Cr(CO)$_3$ groups as π-bonded substituents will certainly exacerbate the situation. Subsequently, an even more crowded system, namely, hexaphenylbenzene-Cr(CO)$_3$ was studied.

3.2 RESULTS AND DISCUSSION

3.2.1 *(1,3,5-triphenylbenzene)[Cr(CO)$_3$]$_n$, n = 1, 2 or 3*

The reaction of 1,3,5-triphenylbenzene (TPB) with chromium hexacarbonyl is reported to give a number of Cr(CO)$_3$ complexes 9, 11 and 12 containing one, two and three metal fragments, respectively. In (TPB)Cr(CO)$_3$, 9, the metal atom is π-bonded to the central ring of the ligand. This reaction was repeated under the experimental conditions described by Nöth and the products purified using reverse phase low pressure liquid chromatography.[23] Tiny quantities of 9 were obtained but the major product was a yellow microcrystalline material readily assignable as the isomeric (TPB)Cr(CO)$_3$ complex, 10. The identity of the product was easily established by the mass spectrum and

9

10

11

12
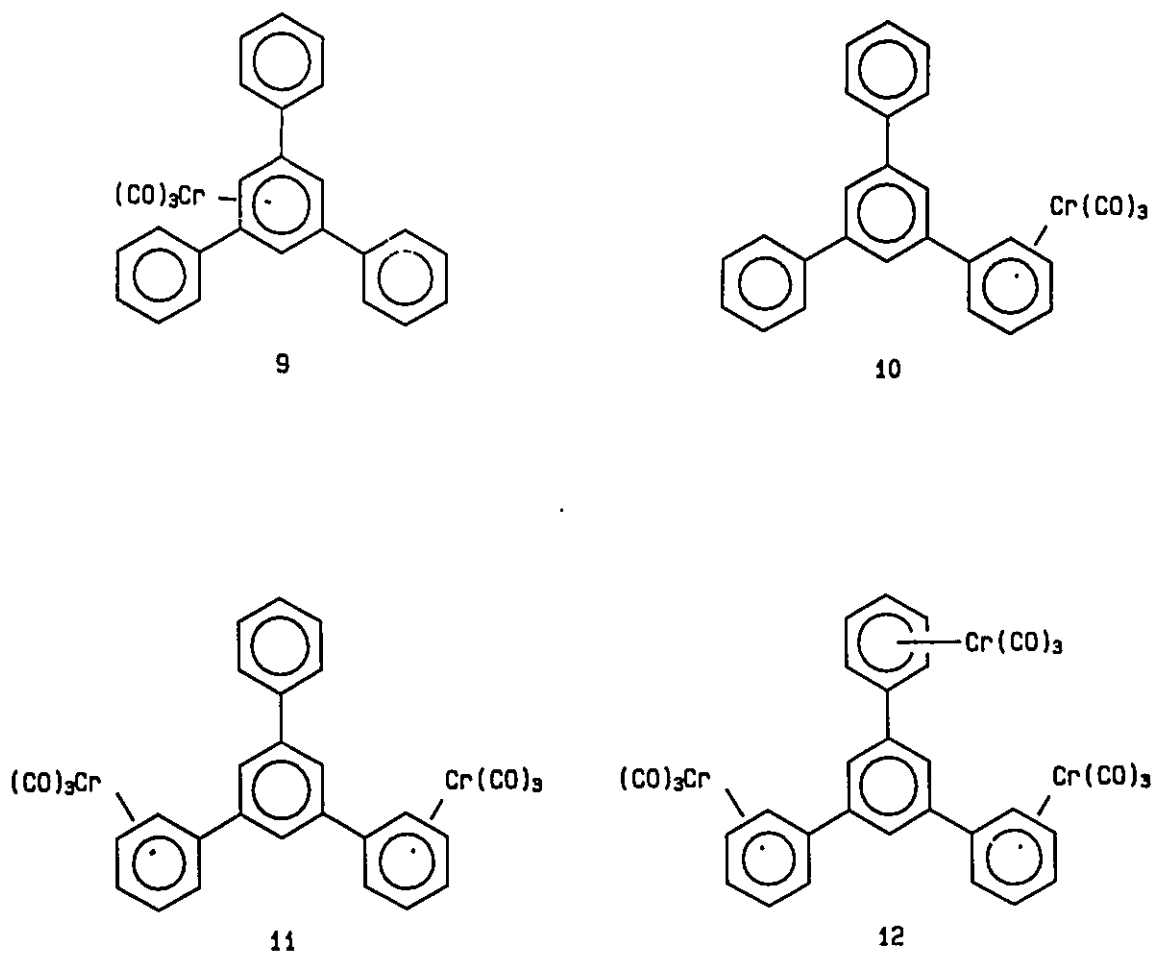
by the NMR spectra. Figure 3.1(b) shows the 500 MHz ^{1}H NMR spectrum of 10, and all the assignments are collected in Table 3.1. In the whole series of organo-chromium complexes described here the aromatic protons of π-complexed rings are in their expected resonance positions in the range δ 5.6 - δ 6.3 while the non-complexed ring protons lie in the region δ 7.3 - δ 8.0. At this very high field, the *ortho*, *meta* and *para* protons are clearly resolved and the peak intensities unequivocally demonstrate that one peripheral phenyl ring bears a Cr(CO)$_3$ unit. The three protons of the central arene ring in 10 are now split
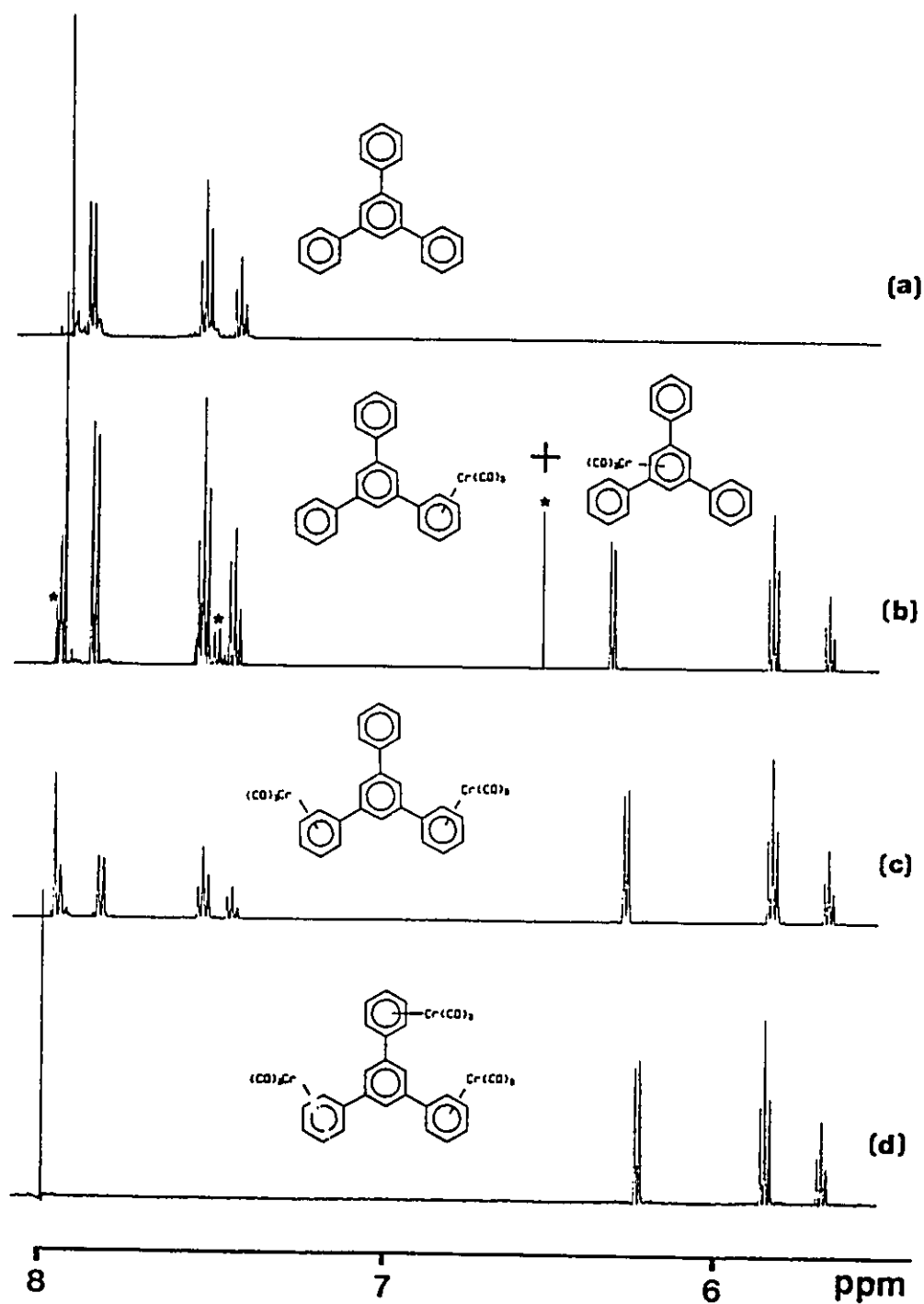
Figure 3.1 : 500 MHz ¹H NMR spectra of 1,3,5-triphenylbenzene and of (1,3,5-triphenylbenzene)[Cr(CO)₃]ₙ, where n = 1, 2, 3. Peaks marked with an asterisk are attributable to the centrally-bonded isomer 1.

TABLE 3.1

500 MHz ^{1}H NMR data for 1,3,5-triphenylbenzene-Cr(CO)$_3$ complexes.

COMPOUND	CENTRAL RING	PERIPHERAL RINGS		
		COMPLEXED		NON-COMPLEXED
TPB	7.90(s)[3H]	---	*ortho-*	7.84(d.d)[6H]
			meta -	7.52(d.d)[6H]
			para -	7.41(t.t)[3H]
TPB.Cr(CO)$_3$ 9	6.52(s)[3H]	---	*ortho-*	7.93(t)[6H]
			meta -	7.51(t)[6H]
			para -	7.45(d)[3H]
TPB.Cr(CO)$_3$ 10	7.91(d)[2H] 7.92(t)[1H]	6.32(d)[2H] 5.86(t)[2H] 5.69(t)[1H]	*-ortho-* *-meta* - *-para* -	7.82(d)[4H] 7.50(t)[4H] 7.41(t)[2H]
TPB.2Cr(CO)$_3$ 11	7.93(d)[2H] 7.92(t)[1H]	6.27(d)[4H] 5.86(t)[4H] 5.69(t)[2H]	*-ortho-* *-meta* - *-para* -	7.80(d)[2H] 7.50(t)[2H] 7.42(t)[1H]
TPB.3Cr(CO)$_3$ 12	7.96(s)[3H]	6.24(d)[6H] 5.87(t)[6H] 5.71(t)[3H]	*-ortho* *-meta* *-para*	---

into a 1.7 Hz doublet (2H) and a 1.7 Hz triplet (1H) in accordance with the lowered symmetry. The NMR spectrum also reveals the presence of the minor isomer, 9, in which the metal atom is now attached to the central ring and consequently gives rise to a singlet at δ 6.52 as well as the peaks attributable to the non-complexed peripheral rings.

As previously reported by Nöth and Deberitz, TPB and excess $Cr(CO)_6$ gave the *bis-* and *tris-* $Cr(CO)_3$ complexes. The ^1H NMR spectra of complexes 11 and 12 are presented in as Figures 3.1(c) and (d). The ^{13}C NMR spectral data for molecules 9 through 12 are collected in Table 3.1 and are completely consistent with the above assignments. The ^1H-^{13}C shift-correlated two-dimensional NMR spectrum of 11 appears in Figure 3.2 and allows the unambiguous assignment of the carbon shifts. The ^1H and ^{13}C spectra of these molecules were also recorded at -90°C and found that they were essentially unchanged from their +30°C counterparts. Clearly, despite the possibility of hindered rotations of the phenyl rings, the aryl rotational barriers must be so small as to preclude the slowing of any fluxional processes on the NMR time scale — at least using line-broadening techniques. This contrasts with the situation in the $Cr(CO)_3$ complexes of the diphenylmethyl anion and related species, such as 13 in which rotation of the phenyl rings can be stopped on the NMR time scale at low temperature.[130]
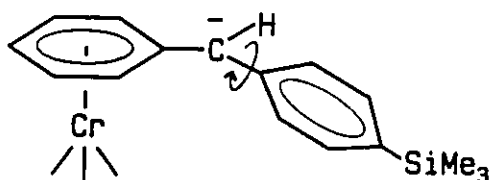
13
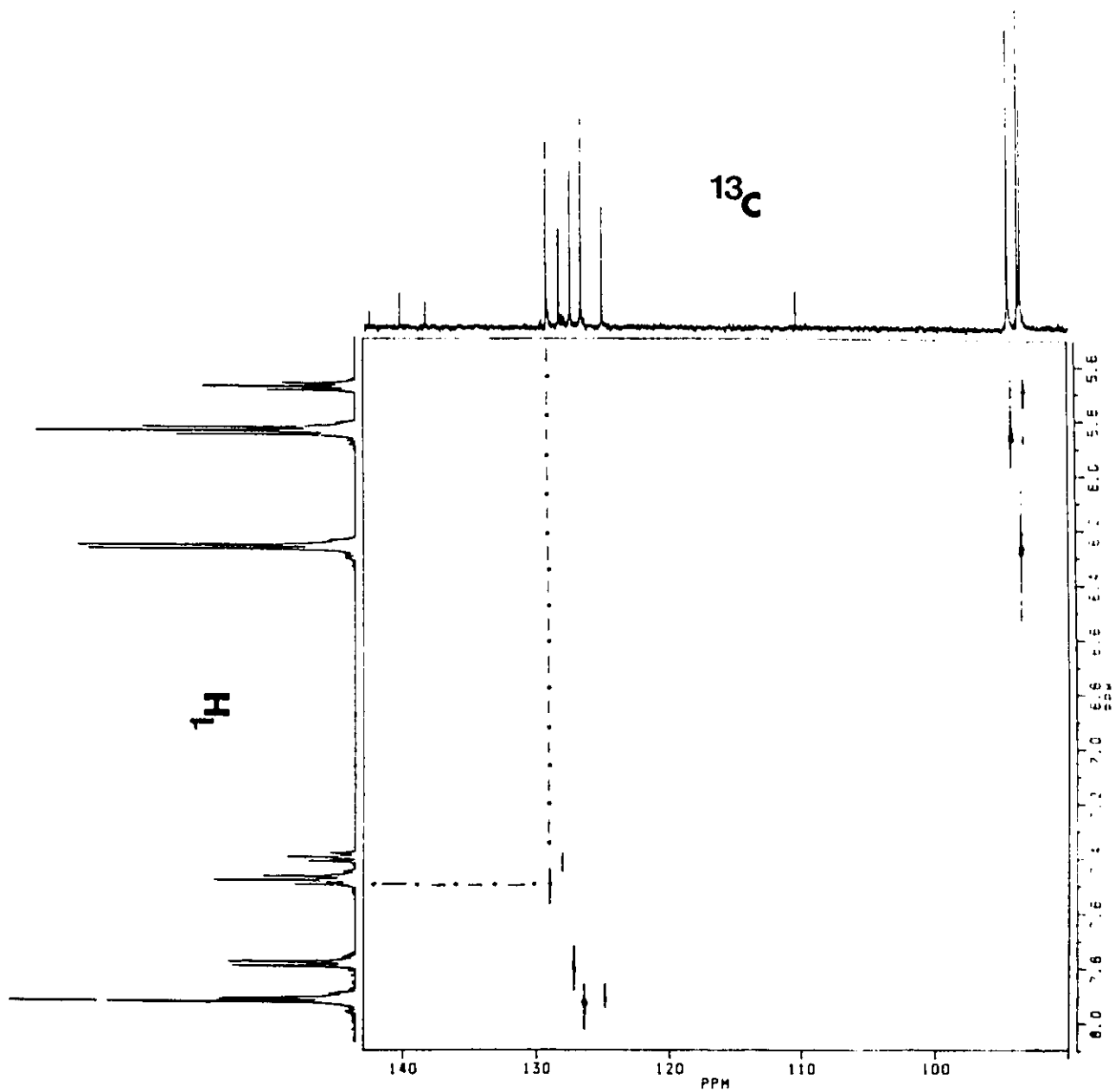
Figure 3.2 : 500 MHz ^{1}H-^{13}C Shift-correlated NMR spectrum of (1,3,5-triphenyl-benzene)[Cr(CO)$_3$]$_2$, 11.

The steric interactions between peripheral phenyl rings is evident not only in 1,3,5-triphenylbenzene itself but also in the organometallic derivatives of related molecules. Thus, the X-ray crystal structure of TPB itself reveals that the peripheral phenyls are not aligned coplanar with the central ring but instead are rotated through torsional angles of +34°, -27° and +24° ; that is, the phenyls are not arranged as in a propeller but rather the pitch of one ring is in the opposite sense to that of the other two.[132] In contrast, the phenyls in (1,3,5-triphenylphosphabenzene)Cr(CO)₃, 14, in
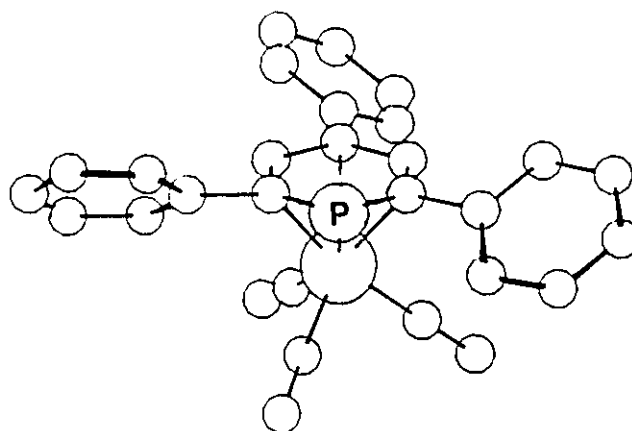
14

which the chromium is attached to the central ring, are all twisted in the same sense (i.e., like a propeller) and the torsional angles are 43°, 28° and 34°.[133] However, in the analogous pentacarbonylchromium complex, 15, in which the metal carbonyl fragment is σ-bonded to the phosphorus atom, the peripheral phenyls are not all rotated in the same sense. The phenyls positioned *ortho* to the Cr(CO)₅ unit are oriented so as to avoid the large organometallic substituent and adopt relatively large torsion angles of +61° and -74°. The *para* phenyl ring is, of course, too far away to be affected by the metal carbonyl

15
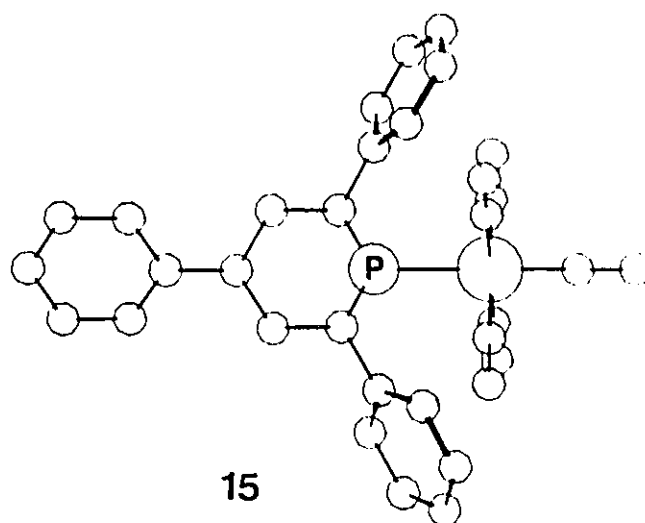
unit and adopts its "normal" torsional angle of +31°. It would seem that torsional angles in the range 30° to 40° are the best compromise so as to minimize steric interactions between the *ortho* hydrogens yet not lose the benefits of conjugation of the rings which is, of course, maximized when the rings are coplanar. Interestingly, an energy minimization using Allinger's Molecular Mechanics calculation[113] on 1,3,5-triphenylbenzene itself yields torsion angles of approximately 38°.

In order to clarify the situation, the X-ray crystal structure of (TPB)-[Cr(CO)₃]₃, 12, was determined and a view of the molecule is shown in Figure 3.3. The crystallographic data and important bond lengths and angles are collected in the Appendix as Tables A1 and A2. The first and most obvious result was that the metal atoms were indeed coordinated to the peripheral phenyls as had already been deduced from the NMR data. The orientation of the phenyls with respect to the plane of the central arene ring is shown clearly in Figure 3.3. The torsional angles are remarkably similar to those in the free ligand itself. In fact, two of them are almost identical (+35° versus +34°; -26° versus -27°) while the third differs only by 10° (+14° versus +24° for TBP). It is also noteworthy
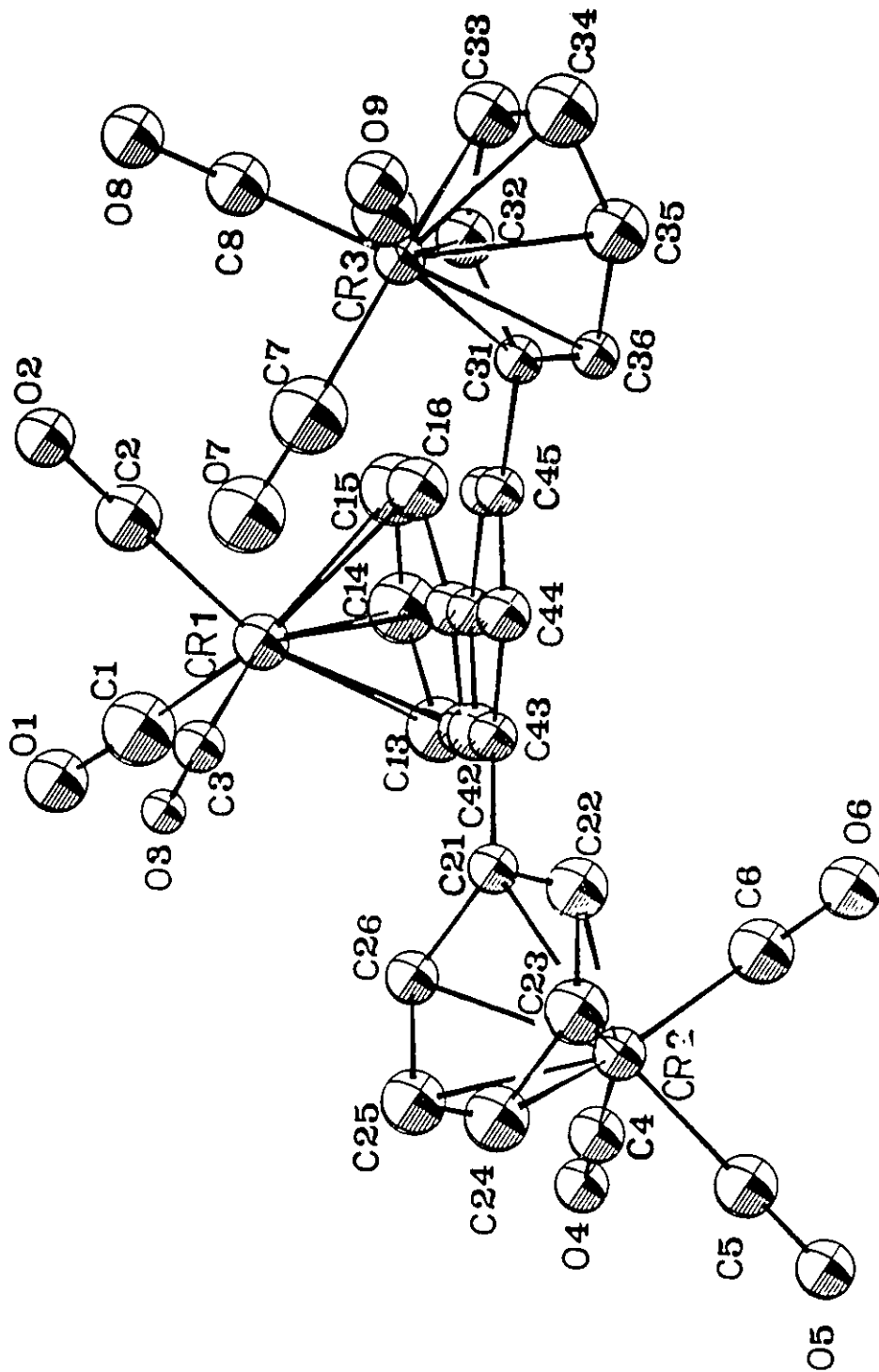
Figure 3.3 : SNOOPI plot of (1,3,5-triphenylbenzene)-[Cr(CO)₃]₃, **12**.

that the phenyl rings in 12 which have torsional angles of +35° and -26° (and which are thus facing towards each other) bear Cr(CO)₃ groups which are oriented in a distal fashion and hence minimize steric interactions. Likewise, the third chromium tricarbonyl moiety is positioned so as to avoid the other two.

In each case the disposition of the tripodal fragment is such as to place the carbonyls within a few degrees of being perfectly staggered with respect to the aryl carbon atoms. For exact staggering, the dihedral angles made by the carbonyl vectors with the bonds which join the peripheral and central rings should be +30°, +150° and -90°. As shown in Figure 3.4, these criteria are well satisfied and the largest deviation from
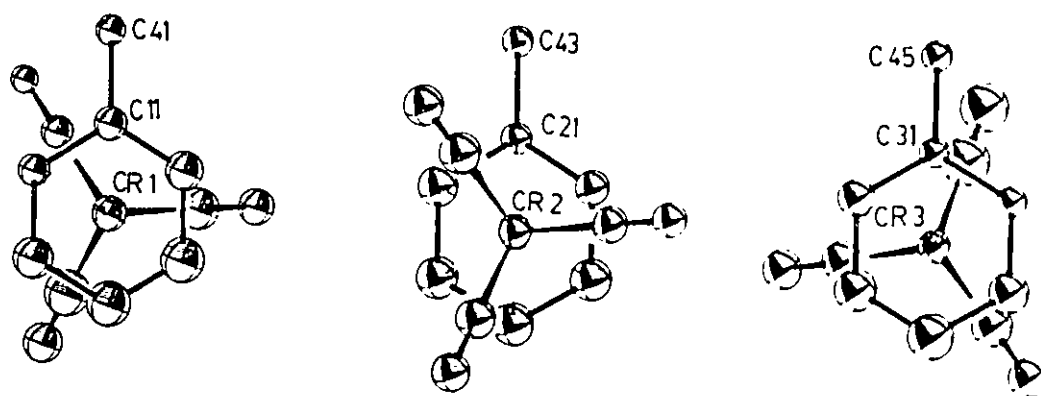
Figure 3.4 : The almost perfectly staggered orientations of the Cr(CO)₃ groups attached to the phenyl rings in 12.

ideality is 11°. In (biphenyl)[Cr(CO)$_3$]$_2$, 16, the tripodal units are oriented in exactly this same fashion and the Cr(CO)$_3$ groups are disposed on opposite faces of the planar biphenyl system.[35]
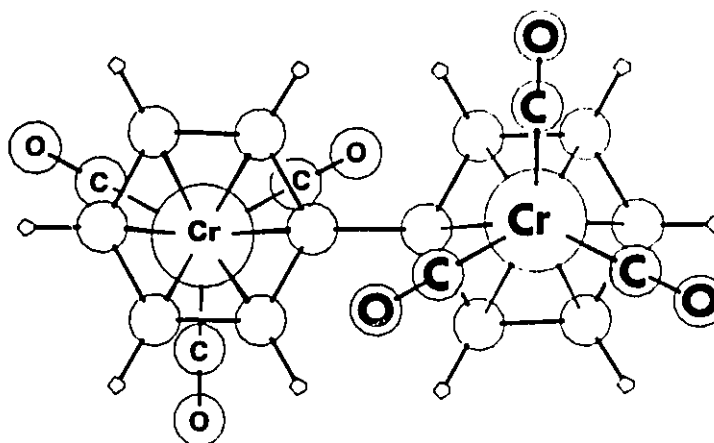
16

It is now clear that although molecule 12 has C$_1$ symmetry in the solid state and is chiral, the NMR spectra in solution are consistent with much higher effective symmetry. The magnetic equivalence of all the *ortho* and *meta* protons and carbon-13 nuclei of the peripheral rings militate for the presence of a molecular mirror plane; this, together with the single resonance for the three central arene protons (and carbons), suggests overall C$_{3h}$ symmetry. The most probable time-averaged conformation is the one in which the complexed phenyl rings are perpendicular to the plane of the central ring and all three chromium atoms are oriented in the same sense, as in 17. Indeed, conformations in which two tricarbonylchromium moieties are coplanar and point toward each other possess unacceptably short non-bonded interactions. This situation has been simulated using the program CHEM-X[133] by commencing with the crystallographic data and rotating the peripheral phenyls as in 18. To render equivalent the *ortho* or the *meta* carbons or protons it is not necessary to allow complete rotation of the complexed phenyl
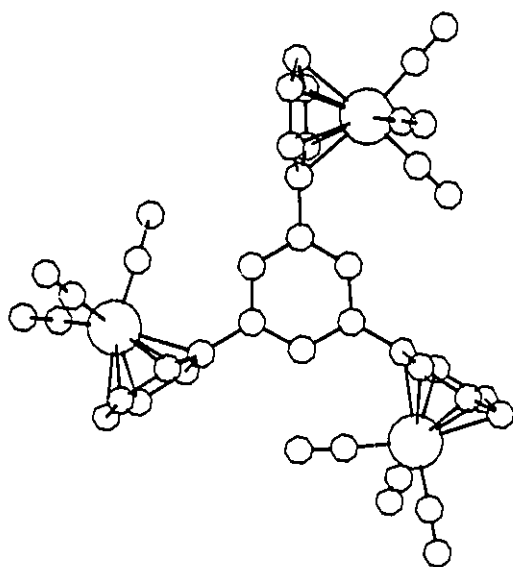
17

18
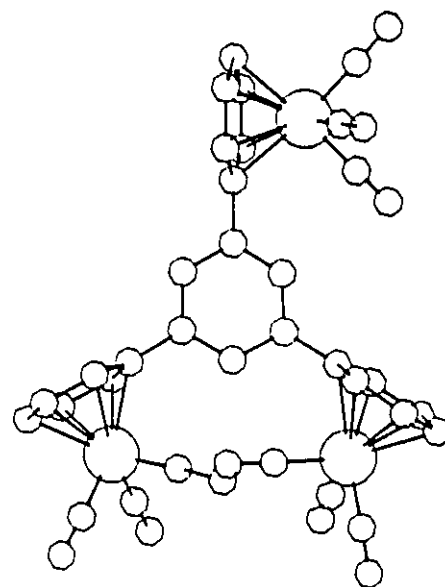
rings through 2π radians, one needs merely an oscillation above and below the plane of the central ring.

However, the situation is slightly different for the *mono-* and *bis*-Cr(CO)$_3$ complexes **10** and **11** which each exhibit effective C$_{2v}$ symmetry. For the latter, one can envisage two rotamers **11a** and **11b** which do not place the Cr(CO)$_3$ substituents uncomfortably close to each other while a third, **11c**, would appear to be unacceptable.
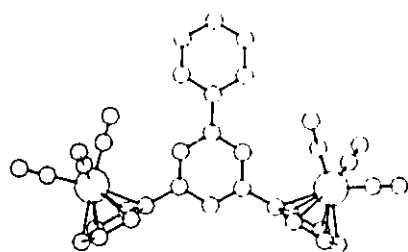
11a
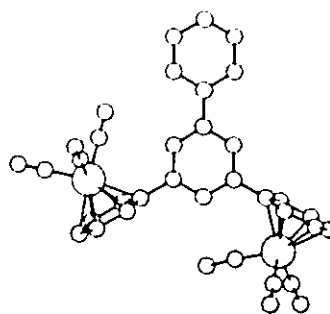
11b
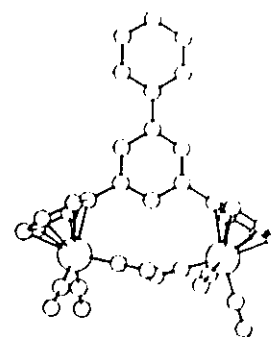
11c

Nevertheless, the NMR evidence tells us that the rotational energy barriers are below the levels detectable by line-broadening techniques.

Since it is not possible to split the degeneracies of the *ortho* and *meta* protons and carbon nuclei, one has no real information on the conformations of these TPB complexes. This is reminiscent of the problem of the structure of hexaphenylbenzene which in the solid state has been shown by X-ray diffraction to adopt a propeller conformation in which the peripheral rings make torsional angles of $\approx$ 67° with respect to the plane of the central ring.[129] An electron diffraction study[131] in the gas phase showed the peripheral rings to be approximately perpendicular to the center ring, with oscillations of $\pm$ 10°. In a number of studies, Gust has shown that hexaarylbenzenes exist in conformations in which the peripheral rings are perpendicular to the central ring on the NMR time scale.[127] By preparing molecules in which the aryl rings possessed substituents at the *ortho* and/or *meta* positions, he showed that the interconversions of the multitude of stereoisomers could be accounted for by a mechanism in which only one peripheral ring at a time rotated by $\approx$ π radians.[128]

3.2.2 Hexaphenylbenzenetricarbonylchromium(0)

The reaction of hexaphenylbenzene with $Cr(CO)_6$ gives a mixture of chromium complexes in low yields. Separation of the mixture using high pressure liquid chromatography and identification by mass spectrometry indicated the presence of *mono-* and *bis*-chromium complexes. However, the yields were such that sufficient material for variable-temperature ^{13}C NMR studies was available only for the *mono*-chromium complex. The 500 MHz ^{1}H NMR spectrum of (HPB)$Cr(CO)_3$, 19, indicates very clearly that the $Cr(CO)_3$ moiety is bonded to a peripheral phenyl ring. The aromatic ring protons of the complexed ring lie in the range δ 4.7 - 5.4 while the non-complexed ring protons are positioned between δ 6.8 - 7.1. Measurement of peak intensities in the proton
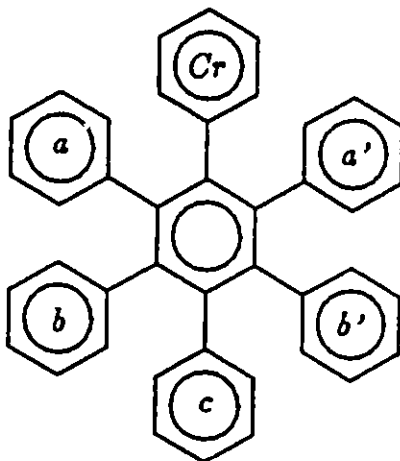
19

spectrum gave a ratio of 1:5 for the complexed versus non-complexed ring protons.

The ^{13}C spectrum of (HPB)Cr(CO)$_3$, 19, at 30°C exhibits for the *ortho*, *meta* and *para* carbons of the five non-complexed rings two sets of 4:4:2 peak patterns corresponding to the a,a' and b,b' rings and a 2:2:1 peak pattern for the C ring. Likewise, the complexed ring shows a 2:2:1 pattern in the δ 85 - 105 region typical of π-complexed arenes as depicted in Figure 3.5. Hence, at room temperature the molecule has effective C$_{2v}$ symmetry.

However, as shown in Figure 3.6, on cooling the sample to -80°C the various *ortho*, *meta* and *para* carbons gave doublets indicating slowed phenyl rotation on the NMR time scale. The ^{13}C NMR data are collected in Table 3.2. Figure 3.7 shows two viable structures, 19a and 19b, for (HPB)Cr(CO)$_3$ at this low temperature. In 19a, the five non-complexed rings are orthogonal to the center ring but the complexed ring is coplanar with the central ring whereas in 19b both the complexed and the non-complexed rings are orthogonal to the center ring. In assigning either of these structures to the low
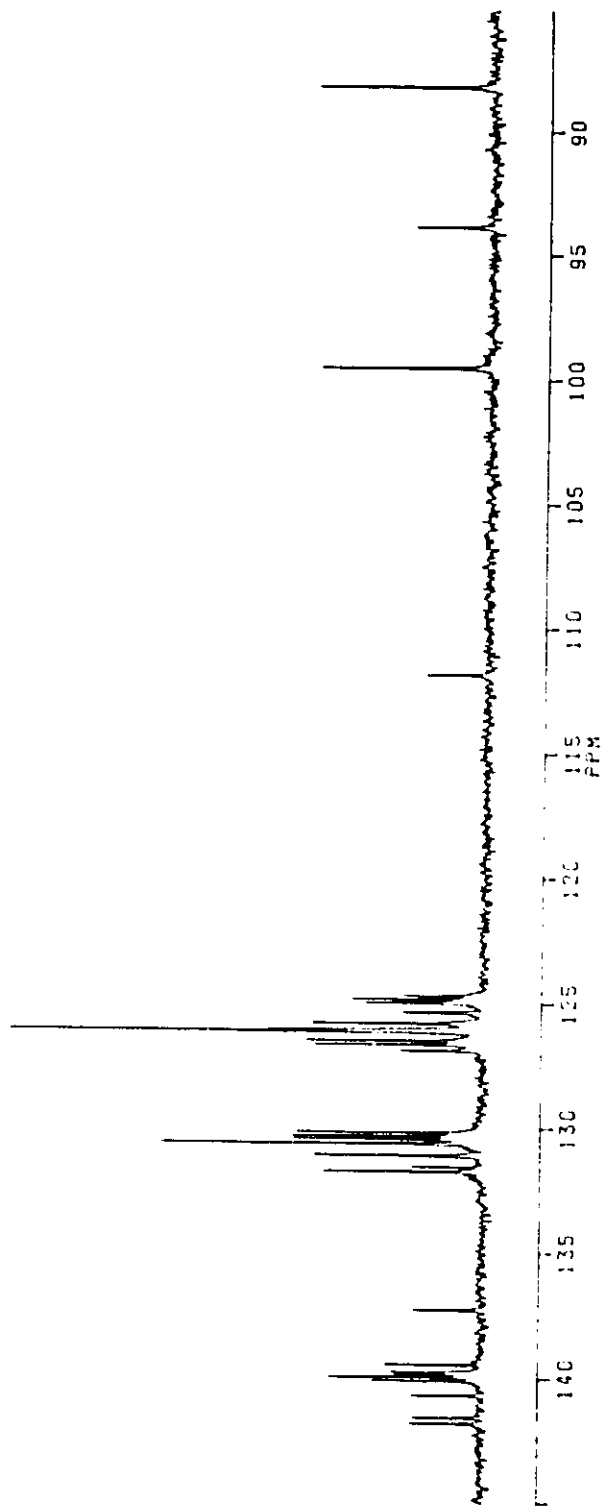
Figure 3.5 : 125 MHz ^{13}C NMR spectrum of **19** at -80°C showing the complexed ring carbon region.
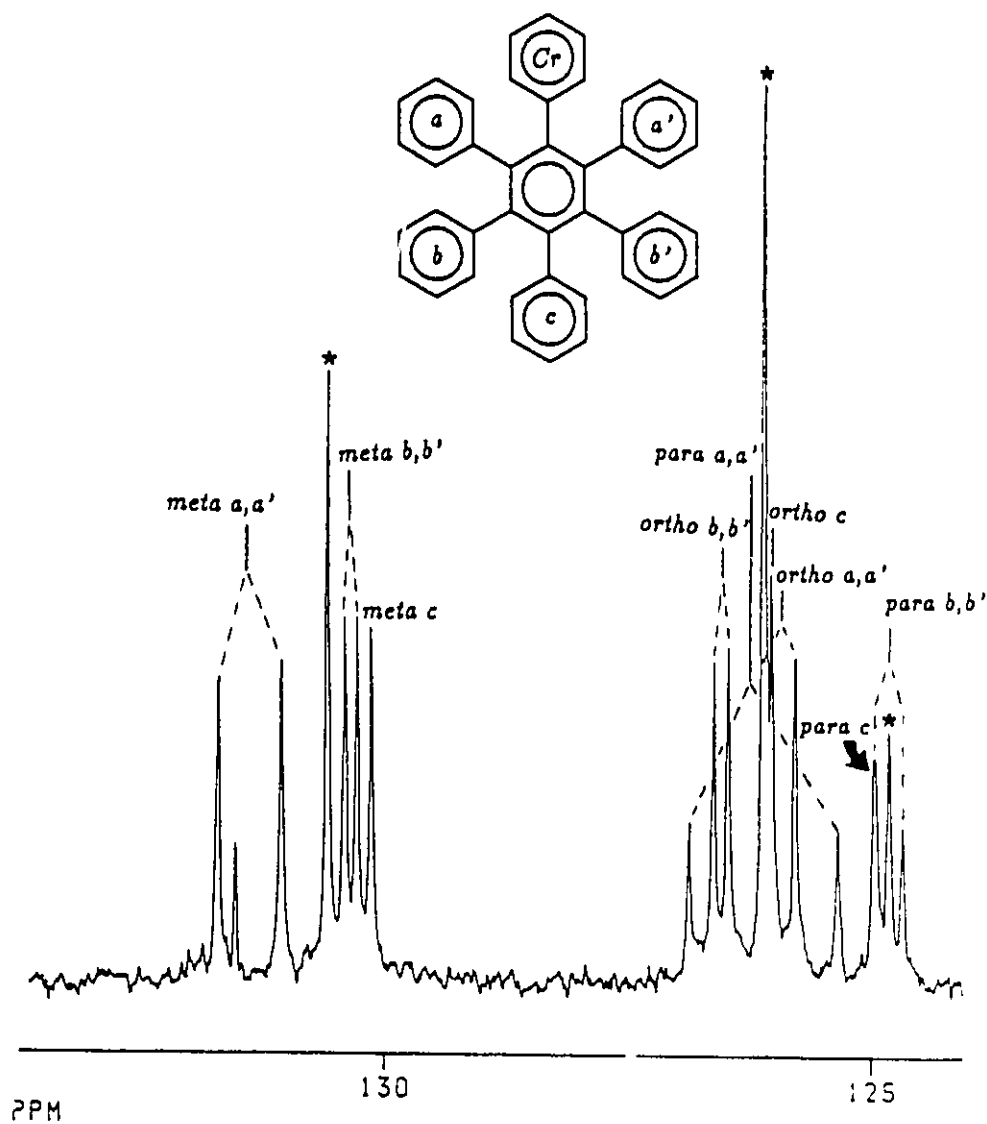
Figure 3.6 : 125 MHz ^{13}C NMR spectrum of HPBCr(CO)$_3$ at -80°C showing the splittings of the *ortho*, *meta* and *para* carbons of the non-complexed peripheral phenyl rings. The peaks marked with an asterisk(*) are from HPB.

TABLE 3.2

^{13}C NMR data for HPBCr(CO)$_3$, 19, at -80°C in CD$_2$Cl$_2$.

Molecule	*ortho*	*meta*	*para*
HPB	126.09	130.57	124.80
HPBCr(CO)$_3$			
Cr Ring	88.14	99.50	93.81
Rings a,a'	126.09 125.76	131.69 131.05	126.86 125.32
Rings b,b'	126.61 126.46	130.40 130.27	124.93 124.66
Ring c	126.09	130.12	124.93
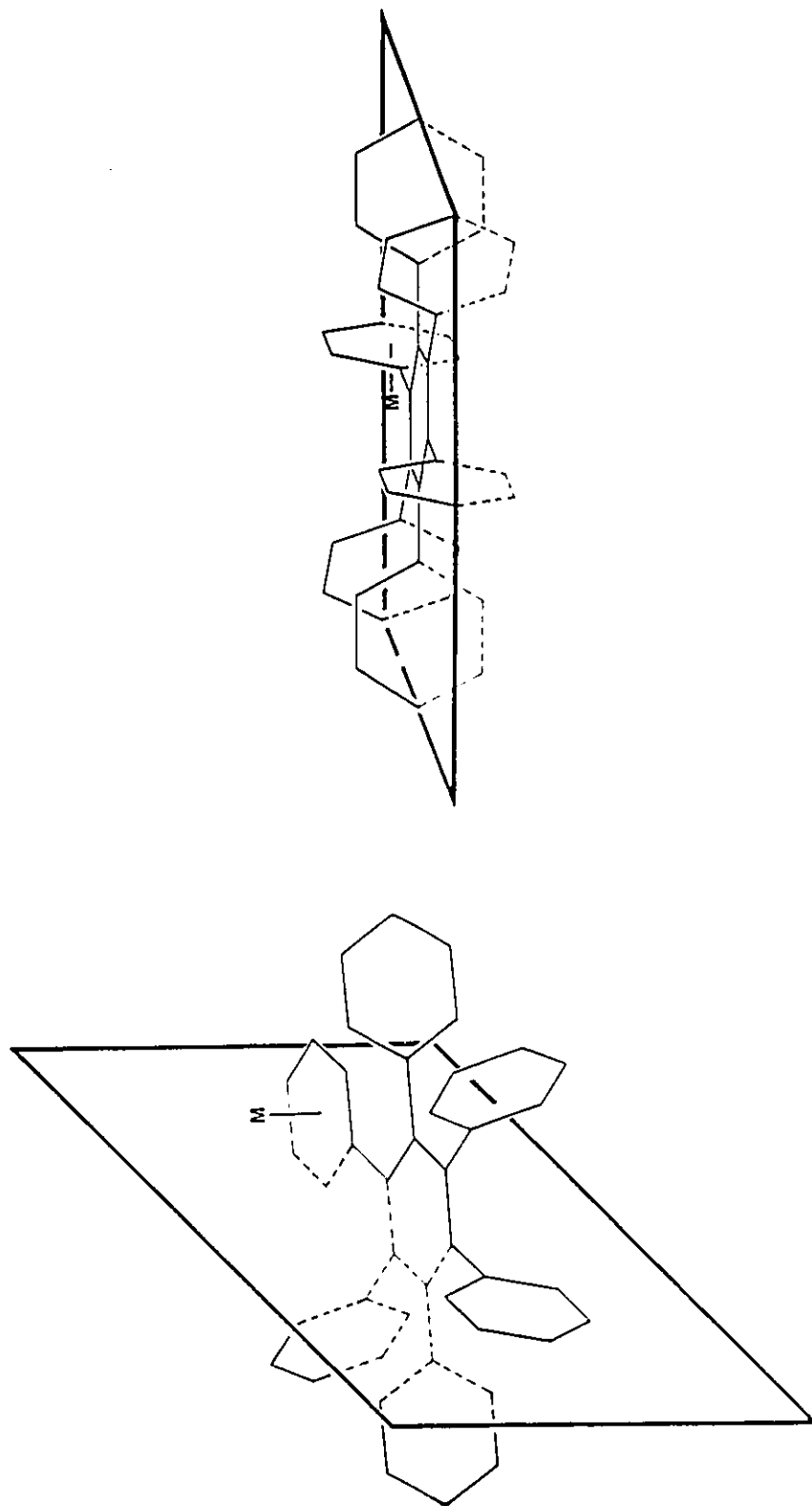
19(a)

19(b)

Figure 3.7 : Idealized conformations 19a and 19b of HPBCr(CO)₃ possessing C_s symmetry at low temperature.

temperature spectrum the peak patterns of the various *ortho*, *meta* and *para* carbons should be taken into consideration. Of the three types, the *para* carbons are the simplest to consider. In the case of 19a a 2:2:1 pattern is expected while a 1:1:1:1:1:1 peak pattern is anticipated for structure 19b. The experimentally observed spectrum (Figure 3.6) shows the latter peak pattern which confirms that the molecule adopts conformation 19b at -80°C. Figure 3.8 depicts the beautiful coalescence pattern observed in this system on warming the sample. The activation energy for the interconversion of the various environments average out to be 12.2 ± 0.2 kcal mol^{-1}.

These results can be rationalized in terms of a conformation whereby all the peripheral phenyl rings are orthogonal to the center ring and the molecule possesses a single mirror plane which contains all six atoms of the central ring, giving the molecule C_s symmetry at low temperature. This renders the two *ortho* carbons of a phenyl ring equivalent. For instance, the two *ortho* carbons of ring a are equivalent but the *ortho* carbons of rings a and a' are not equivalent.

Ideally, one would prefer to make the ^{13}C assignments for the a, b and c rings on the basis of unequivocal 2-D correlations between the protons and their attached carbons. Such experiments were not viable in this instance because of the limited quantities of sample available. Each regular 1-D ^{13}C NMR spectrum required 3-4 hours even on the AM 500. In Table 3.2, the *ortho*, *meta* and *para* resonances for ring c are readily assigned not only on the basis of intensities but also these environments are not split at low temperature. The *ortho*, *meta* and *para* resonances of rings a/a' and b/b' have been differentiated on the basis of the magnitude of their chemical shift separations at low temperature. We made the reasonable assumption that the proximity of the a/a' rings to the Cr(CO)$_3$ fragment will lead to a greater chemical shift discrimination.

However, at room temperature, the molecule has effective C_{2v} symmetry. This equilibrates the *ortho*, *meta* and *para* carbon pairs that are symmetrically disposed on
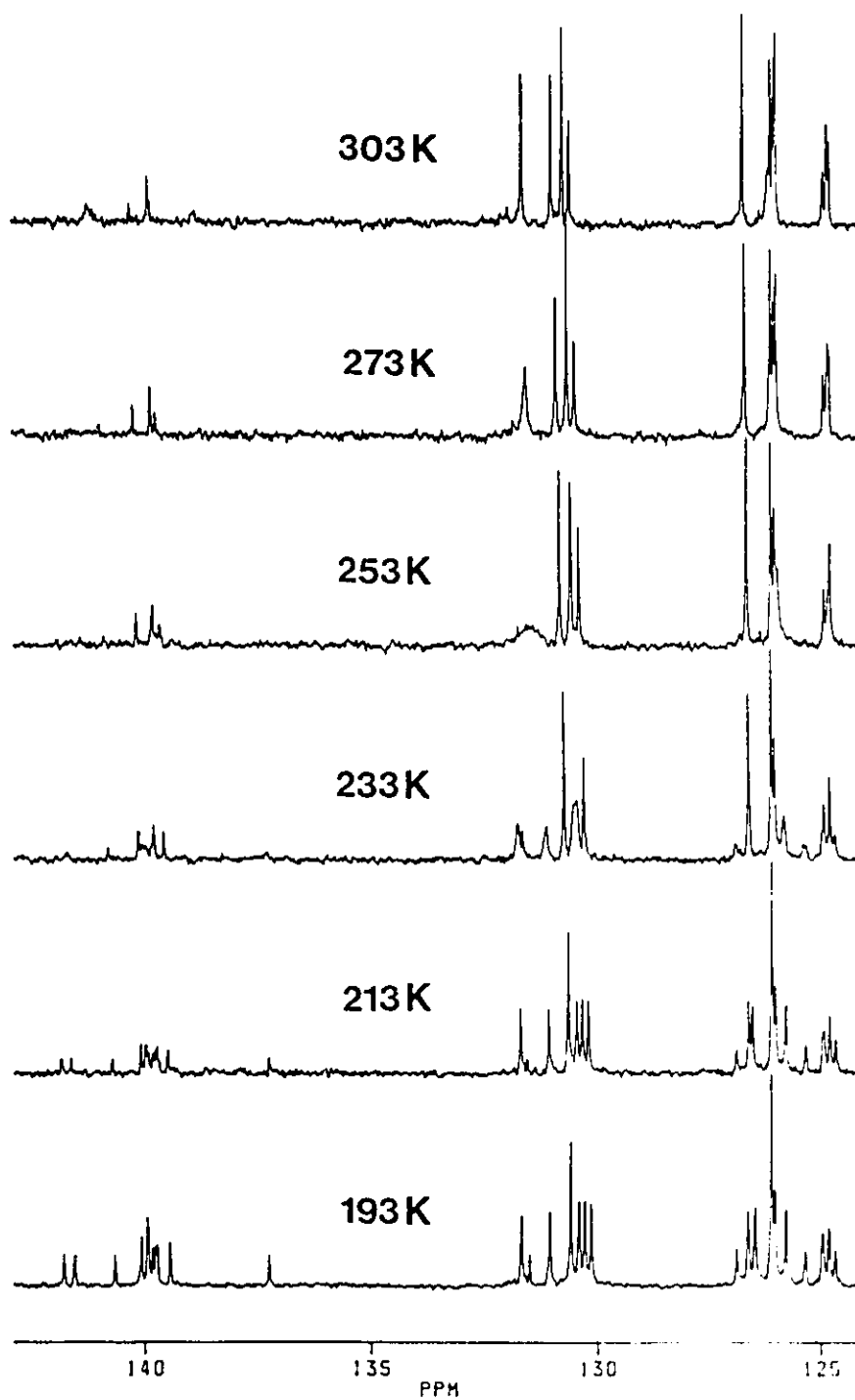
Figure 3.8 : 125 MHz variable-temperature ^{13}C NMR spectra of (hexaphenylbenzene)-Cr(CO)₃, 19, over the range -80°C to +30°C showing six sets of peak coalescences.

Figure 3.8 : 125 MHz variable-temperature ^{13}C NMR spectra of (hexaphenylbenzene)-Cr(CO)$_3$, 19, over the range -80°C to +30°C showing six sets of peak coalescences.

either side of the complexed ring, e.g., *ortho* a and *ortho* a' carbons coalesce to give a singlet. Hence, (hexaphenylbenzene)$Cr(CO)_3$ displays restricted rotation about the single bond joining the central ring and the complexed peripheral ring. We cannot say whether or not the non-complexed peripheral rings are undergoing rapid rotation since, for example *ortho* carbons of any given ring are magnetically equivalent for either situation. However, it is probably a safe assumption that these rings are free to spin. The reason for the slowed rotation of the π-complexed ring is presumably the presence of a bulky tripodal metal carbonyl fragment. This is evident from the work of Gust on substituted hexaarylbenzenes which exhibited a range of free energies of activation; 33 kcal mol^{-1} for rotations of rings bearing an *ortho* methoxy group to about 17 kcal mol^{-1} for rotations of rings bearing *meta* methyl substituents. In our case the barrier to rotation is even less, about 12 kcal mol^{-1} for a ring bearing a π-bonded addendum.

In conclusion, it is now apparent that slowed rotation of a π-$(C_6H_5$-$Cr(CO)_3)$ group is not observed in the triphenylbenzene case, even when all three peripheral rings are complexed. In contrast, a single $Cr(CO)_3$ group is sufficient to bring about this effect in hexaphenylbenzene. However, the incorporation of a π-bonded bulky substituent (in this case $Cr(CO)_3$) apparently causes less steric problem ($\Delta G^{\#} = 12$ kcal mol^{-1}) than does *meta* methyl substitution ($\Delta G^{\#} = 17$ kcal mol^{-1}).

One could suggest extensions of this concept whereby π-complexed addenda are incorporated into polyaryl ring systems. For example, instead of the relatively small $Cr(CO)_3$ group one could use a Cp-metal or indenyl-metal fragment which might bring about much more severe steric problems and perhaps freeze out the entire molecule.

CHAPTER 4

COMPLEXES OF HEXAETHYLBENZENE-Cr(CO)₃:

EVIDENCE FOR SLOWED TRIPODAL ROTATION

4.1 INTRODUCTION

For over two decades the question of the possibility of stopping tripodal rotation in arenetricarbonylchromium(0) complexes has been a somewhat controversial issue.[135-138] The first of such articles appeared in 1966 when Gracey et al.[135] reported that (isopropylbenzene)tricarbonylchromium, 20, displayed temperature-dependent NMR spectra. In this molecule the aromatic ring protons appear as a singlet at +30°C but broaden into a multiplet below -15°C. They also looked at (t-butylbenzene)tricarbonyl-chromium, 21, where the aromatic protons appear as a multiplet and remain unchanged

20   21
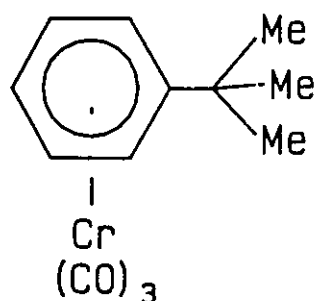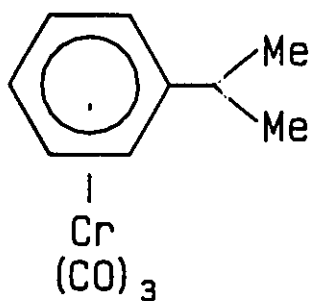
over the temperature range +50°C to -40°C. They explained their findings in terms of

severe restriction of rotation of the arene-chromium bond in (t-butylbenzene)tricarbonyl-

chromium and less severe restriction in (isopropylbenzene)tricarbonylchromium. This

was later disproved independently by Seyferth[136] and Taddei.[137]

The only kno vn example of slowed tripodal rotation in a chromium complex

up to the year 1988 is that reported by Nambu and Siegel.[139] They were able to show

that the carbonyls in the *bent*-terphenylenetricarbonylchromium, 22, complex gave a sharp

2:1 doublet at 170 K.
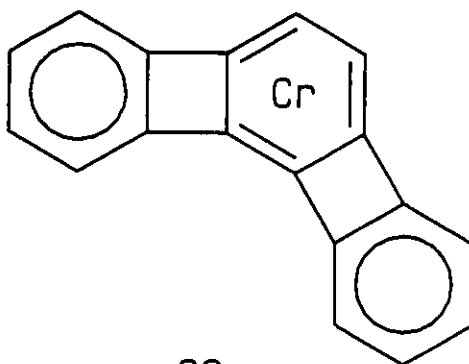
22

4.1.1 Early work on chromium complexes of hexaethylbenzene

Controversy over slowed tripodal rotation in hexaethylbenzenechromium

complexes exists.[140,143] McGlinchey and co-workers believe they have stopped

tripodal rotation in (HEB)Cr(CO)₃, 23, and (HEB)Cr(CO)₂CS, 24, at low temperature on

the NMR time scale. However, Mislow and his colleagues disagree with McGlinchey's

interpretation.

The X-ray crystal structure[28,144] of non-complexed hexaethylbenzene (HEB) indicates that the ethyl groups project alternately above and below the plane of the arene ring giving the molecule point group D_{3d}. In (HEB)Cr(CO)$_3$, 23, the arene adopts the same conformation. Hence, methyl carbons positioned *proximal* and *distal* to the Cr(CO)$_3$ group are rendered magnetically non-equivalent. Similarly, the methylene and arene ring carbons would be split in accordance with the overall C_{3v} symmetry of the complex. The low-temperature ^{13}C NMR spectrum of (HEB)Cr(CO)$_3$ in solution shows the methyl, methylene and arene ring carbons to each split into two equally intense resonances. In the solid[28] state (HEB)Cr(CO)$_3$ adopts the alternating *proximal-distal* arrangement of ethyl groups and the organometallic tripod is oriented such that the metal carbonyl ligands lie directly beneath the *distal* ethyls and so minimize any steric interactions with the *proximal* alkyl chains. The overall molecular symmetry can be idealized to C_{3v} and thus explains the doubling of the C, CH$_2$ and CH$_3$ resonances. However, this result does not provide unequivocal evidence concerning rotation of the Cr(CO)$_3$ tripod. Although the metal carbonyl ligands would have considerable difficulty maneuvering their way past the *proximal* ethyls, it is not possible in this case to differentiate between a rotating or a non-rotating Cr(CO)$_3$ group, since the effective point group is C_{3v} in either case. Nevertheless, Mislow assumed that the tripodal unit continues to rotate and estimated the barrier from variable-temperature T_1 measurements to be ≈ 3 kcal mol^{-1}.[28,140] However, as it was not possible to separate the contributions from overall molecular tumbling and internal rotation about the arene-metal bond, it was not possible to provide a reliable measure of the barrier but they proposed that it was unlikely to exceed ≈ 5 kcal mol^{-1}.

Mislow also performed some energy calculations on the numerous conformers of HEB and showed the 1,3,5-*distal*-2,4,6-*proximal* isomer (I) to be favored over the structures which place adjacent ethyls on the same face of the arene. The highest

(I)

(II)

(III)

(IV)
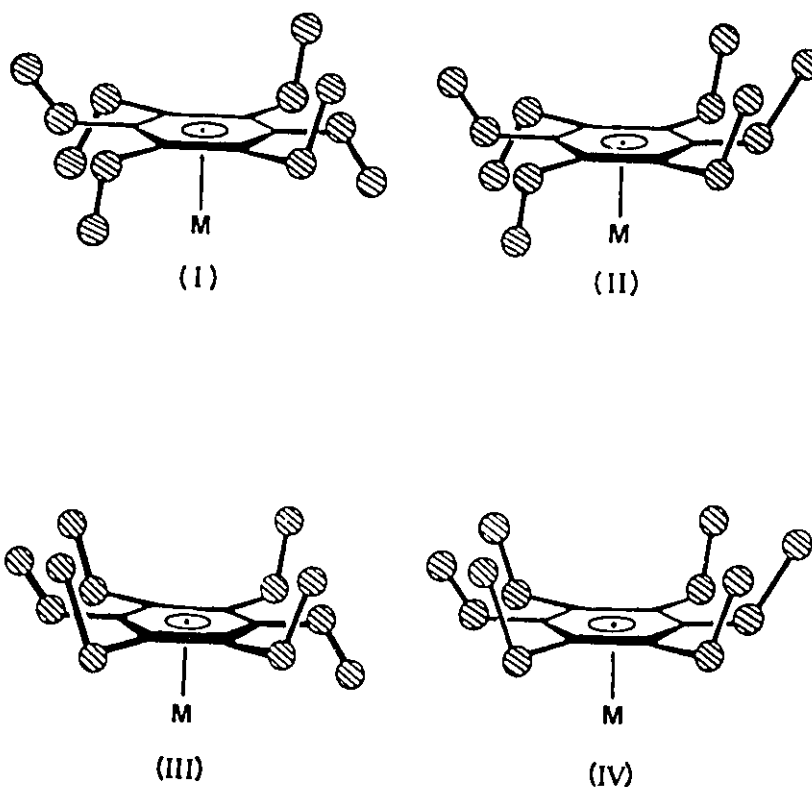
energy conformation (IV) is that in which all six ethyls are oriented the same way and the molecule has C_{6v} symmetry.[28] In a metal π-complex of type (IV) all six ethyls must be *distal* with respect to the metal.

When 23 was allowed to react with triphenylphosphine, the resulting complex $(HEB)Cr(CO)_2PPh_3$, 25, exhibited a ^{13}C NMR spectrum which was essentially temperature-independent.[140] The room temperature singlets for the methyl, methylene and arene ring carbons remained unsplit at low temperature. The X-ray crystal structure of 25 yielded a straightforward explanation in that the bulk of the triphenylphosphine ligand apparently hinders the ethyl groups from occupying *proximal* positions; hence, the HEB ligand itself maintains essentially C_{6v} symmetry, as in (IV).[140]

In (HEB)Cr(CO)$_2$CS, 24,[141] the HEB ligand adopts an almost identical conformation to that in 23. The variable-temperature ^{13}C NMR spectra of 24 exhibit decoalescence behavior leading ultimately to a 2:1:2:1 pattern for each of the ring carbon, methylene and methyl environments. The X-ray crystal structure of 24 shows conformation I and the CPMAS ^{13}C NMR spectrum of 24 is remarkably similar to that observed in solution at low temperature. It is clear that the overall molecular symmetry has been reduced to C$_s$, i.e., a single mirror plane. On the basis of these data McGlinchey et al. claimed that tripodal rotation had been stopped on the NMR time scale and interpreted the limiting spectrum in solution in terms of a 1,3,5-*distal*-2,4,6-*proximal* conformation as found for 23 and 24 in the solid state. However, Mislow[142] argued that if conformer II is present in solution then the arene itself will adopt C$_s$ symmetry and such a molecule could indeed give rise to the observed set of 2:1:2:1 patterns in the NMR spectrum and would not require the cessation of tripodal rotation.

Until that time, no HEB complexes of type (II) had been characterized crystallographically, but since then two such examples have appeared in the literature. They are [(HEB)Fe(C$_5$H$_5$)]$^+$ PF$_6^-$, 26,[145] and (HEB)Cr(CO)$_2$PMe$_3$, 27;[146] both of which crystallized in the 1,2,3,5-*distal*-4,6-*proximal* arrangement. In neither case was it possible to observe a limiting ^{13}C NMR spectrum for the methyl and methylene regions which was compatible with the presence in solution of a single conformer of type (II). However, the observation of multiple cyclopentadienyl resonances for 26, and several ^{31}P peaks for 27, led to the suggestion of the co-existence of several HEB-metal conformers in solution at low temperature.[146] A corresponding ruthenium sandwich complex of 26, [(HEB)Ru(C$_5$H$_5$)]$^+$, 28, has been reported by Green and is thought to adopt the energetically most favored 1,3,5-*distal*-2,4,6-*proximal* structure.[147] It was suggested that the increased size of the ruthenium atom relative to iron diminishes the steric hindrance between the six-membered and five-membered rings.

If (HEB)Cr(CO)$_2$CS, 24, could be unequivocally shown to adopt conformation (I) in solution then the assertion of restricted tripodal rotation would be on firm ground; it is only by freezing out the Cr(CO)$_2$CS rotation that one can generate a molecule possessing a single mirror plane. On the other hand, if it could be shown that the predominant isomer(s) of 24 present in solution were (II) and/or (III) then the cessation of tripodal rotation would remain an open question; the arene conformation itself would impose C$_s$ symmetry on the molecule and there would be no necessity to invoke slowed rotation of the tripod.

In order to demonstrate the slowed tripodal rotation in these hexaethylbenzene-chromium complexes an experiment was devised for which the results would be unequivocal. To achieve this goal the metal was made chiral by having three different ligands on the tripod that are all linear and stereochemically non-demanding. As the molecule is chiral it renders the methyl, methylene and arene ring-carbons magnetically non-equivalent.

4.2 RESULTS AND DISCUSSION

4.2.1 [(HEB)Cr(CO)$_2$NO]$^+$ BF$_4^-$, 29

It has been shown that treatment of polyalkylated (arene)Cr(CO)$_3$ complexes with a source of the nitrosonium ion yields the corresponding [(arene)Cr(CO)$_2$NO]$^+$ salt.[148] To this end, (HEB)Cr(CO)$_3$, 23, was allowed to react with NO$^+$ BF$_4^-$ and yielded crystals of [(HEB)Cr(CO)$_2$NO]$^+$ BF$_4^-$, 29.

The variable-temperature ^{13}C NMR spectra of 29 (see Figure 4.1) reveal that the methyl, methylene and ring carbon sites undergo decoalescence such that each room temperature singlet exhibits a 2:1:2:1 pattern at 153 K. In assigning the various ^{1}H and
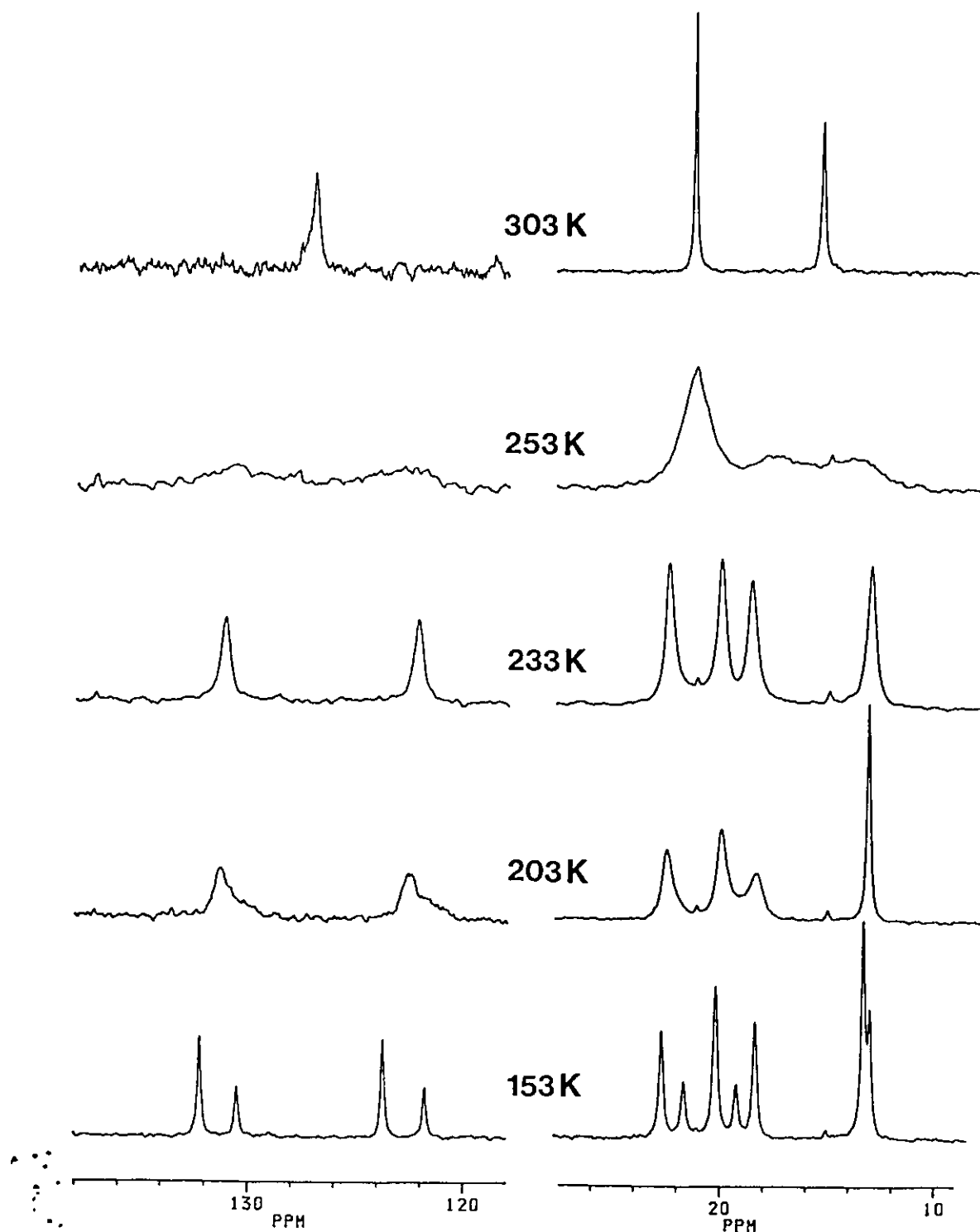
Figure 4.1 : Variable-temperature ^{13}C NMR spectra of $[(HEB)Cr(CO)_2NO]^+$ BF_4^-, 29, in CD_2Cl_2.

[13]C chemical shifts in the nitrosyl complex the assignment of the methyl and methylene carbon environments in (HEB)Cr(CO)$_2$PPh$_3$, 25, was taken into consideration. As demonstrated by Mislow, all the ethyl groups in 25 are *distal* with respect to the organometallic moiety and so the ^{13}C resonance positions for the CH$_3$ (δ 15.9) and CH$_2$ (δ 22.4) units of a *distal* ethyl group are evident. It is gratifying that the methyls in 25 (which should be affected only slightly by the distant chromium atom) resonate close to the observed chemical shift of the methyls in non-complexed HEB (δ 15.5), despite the fact that the ethyls in 25 are presumably in a more crowded environment than in HEB itself. Similarly, the complexes (HEB)M(CO)$_3$, where M = Cr, 23, Mo, 30, W, 31, exhibit methyl resonances at δ 14.2, 14.4 and 14.6, respectively, at low temperature;[28,140,143] we assign these relatively constant shifts to the *distal* methyl groups. In contrast, the *proximal* methyls fall in quite a different region (Cr, δ 20.1; Mo, δ 23.4; W, δ 24.6) and are to some extent affected by the identity of the nearby M(CO)$_3$ moiety. Analogously, the chemical shift ranges appropriate for methylene carbons in *proximal* and *distal* environments are readily assigned, as shown in Table 4.1.

It has long been assumed that arene ring carbons which can be considered directly bonded to an octahedrally coordinated metal are shielded relative to their ring partners.[149] However, this assumption was only verified very recently when Pomeroy observed scalar coupling between the more shielded ring carbon and a *trans*-carbonyl ligand in [1,4-bis(*tert*-butyl)benzene]Ru(CO)(SiCl$_3$)$_2$, 32 — a molecule in which tripodal rotation has certainly stopped on the NMR time-scale.[150] This trend was followed in assigning the directly-bonded ring carbons, *i.e.*, those attached to the *proximal* ethyl groups, to the lower frequency (higher field) resonances.

The low temperature ^{1}H NMR spectra of the complexes (HEB)M(CO)$_3$, where M = Cr, 23, Mo, 30, W, 31, likewise show methyl and methylene resonances characteristic of the *proximal* and *distal* environments. It is, of course, obvious that *proximal*

75 of 146

TABLE 4.1

^{13}C NMR Data for Hexaethylbenzene-Metal Complexes.[a]

	Distal Ethyl Groups			Proximal Ethyl Groups			Ref.
	CH$_3$	CH$_2$	C$_{Ar}$	CH$_3$	CH$_2$	C$_{Ar}$	
(HEB)	15.5[6]	14.6[6]	137.2[6]	---	---	---	28
(HEB)Cr(CO)$_3$	14.2[3]	22.8[3]	117.2[3]	20.1[3]	19.4[3]	108.8[3]	28
(HEB)Mo(CO)$_3$	14.4[3]	22.8[3]	121.6[3]	23.4[3]	19.5[3]	114.7[3]	28
(HEB)W(CO)$_3$	14.6[3]	22.6[3]	117.5[3]	24.6[3]	19.6[3]	111.4[3]	143
(HEB)Cr(CO)$_2$PPh$_3$	15.9[6]	22.4[6]	108.0[6]	---	---	---	28
(HEB)Cr(CO)$_2$CS	13.6[2] 13.2[1]	21.7[3]	121.7[2] 119.9[1]	17.8[2] 18.5[1]	19.2[2] 20.7[1]	113.4[2] 112.8[1]	141
(HEB)Cr(CO)$_2$NO$^+$	13.4[2] 13.1[1]	22.9[2] 21.8[1]	130.9[2] 129.1[1]	18.4[2] 20.3[1]	20.3[2] 19.4[1]	122.4[2] 120.4[1]	
(HEB)Cr(CO)(CS)(NO)$^+$	12.8[1] 13.2[1] 13.4[1]	21.7[1] 22.5[1] 23.2[1]	130.6[1] 131.5[1] 131.7[1]	17.0[1] 18.2[1] 19.0[1]	20.1[2] 21.1[1]	122.2[1] 124.0[1] 124.1[1]	

[a]Numbers in brackets give peak intensity.

(*distal*) methyl protons will show scalar couplings to the neighboring methylene protons in the same *proximal* (*distal*) ethyl group and such connectivities are trivial to ascertain *via* double resonance experiments and such experiments have been carried out for molecule 29. Furthermore, the corresponding carbon-proton connectivities are also unambiguously obtainable (as shown for (HEB)W(CO)$_3$, 31, in Figure 4.2), and the resulting assignments are collected in Table 4.2.

In light of the chemical shift data presented above, the spectrum of (HEB)Cr(CO)$_2$NO$^+$, 29, can now be assigned to a single stereoisomer in which the ethyl groups are arranged in the 1,3,5-*distal*-2,4,6-*proximal* manner. As with all the other (HEB)M(CO)$_2$L systems in which L is a cylindrical ligand with minimal steric requirement, the spectra are readily rationalized in terms of a 1,3,5-*distal*-2,4,6-*proximal* conformation for the arene. Again, we see resonances at δ 13.4 and 13.1 clearly attributable to three methyls in *distal* positions and at δ 20.3 and 18.4 which can be assigned to the three *proximal* methyl groups. As shown in Tables 4.1 and 4.2, there is always a clear distinction such that the ring carbons attached to *proximal* ethyl substituents are shielded by 6 - 8 ppm relative to those bearing *distal* ethyls. Thus the orientation of the alkyl substituents relative to the organometallic tripod can be unambiguously determined from the solution ^{13}C NMR spectrum at low temperature. These results are reinforced by the solid state CPMAS ^{13}C NMR spectrum of (HEB)Cr(CO)$_2$NO$^+$, 29, which exhibits methyl resonances at δ 18.6 and 22.9, methylene peaks at 24.9 and 28.5, ring carbons at 125.5 and 134.8 and Cr-C≡O at δ 232. These solid state absorptions are deshielded by ≈ 5 ppm relative to their shifts in dichloromethane solution. The peaks are in an approximate 3:3 intensity ratio and further splitting into a 2:1:2:1 pattern is not evident, presumably because the CPMAS spectra were measured at only 25 MHz as opposed to the high resolution data in solution in CD$_2$Cl$_2$ which were obtained at five times the field.

Recrystallization of 29 yielded crystals suitable for structure determination by
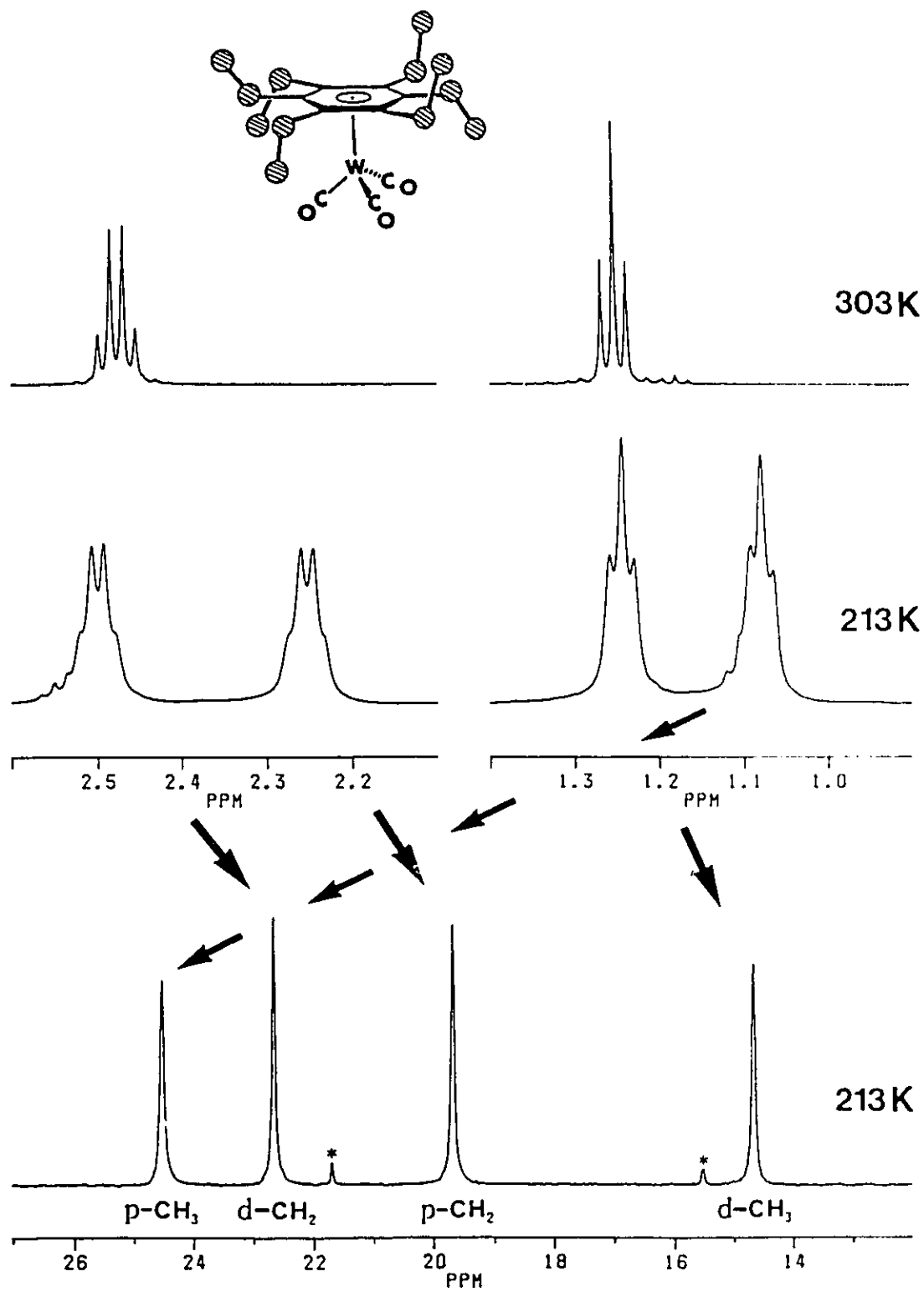
Figure 4.2 : Proton-carbon connectivities in (HEB)W(CO)₃, 31.

TABLE 4.2

^{1}H NMR Data for Hexaethylbenzene-Metal Complexes.[a]

	Distal Ethyl Groups		Proximal Ethyl Groups		Ref.
	CH$_3$	CH$_2$	CH$_3$	CH$_2$	
(HEB)Cr(CO)$_3$	1.16 [9]	2.49 [6]	1.12 [9]	2.24 [6]	141
(HEB)Mo(CO)$_3$	1.21 [9]	2.47 [6]	1.07 [9]	2.25 [6]	141
(HEB)W(CO)$_3$	1.23 [9]	2.49 [6]	1.06 [9]	2.24 [6]	141
(HEB)Cr(CO)$_2$CS	1.23 [9]	2.47 [6]	1.07 [9]	2.29 [6]	141
(HEB)Cr(CO)$_2$NO$^+$	1.28 [9]	2.58 [6]	1.13 [9]	2.44 [6]	

[a]Numbers in brackets give peak intensity.

using X-ray diffraction techniques. A view of the $[(C_6(C_2H_5)_6)Cr(CO)_2NO]^+$ cation with an atom numbering scheme appears as Figure 4.3. The stereochemistry of the co-ordinated hexaethylbenzene moiety is very similar to that found for the complexes $(HEB)Cr(CO)_3$, 23,[28] $(HEB)Mo(CO)_3$, 30,[28] and $(HEB)Cr(CO)_2CS$, 24,[141] with the ethyl groups adopting the 1,3,5-*distal*-2,4,6-*proximal* conformation, i.e., stereoisomer (I). The $Cr(CO)_2NO$ tripod adopts an eclipsed orientation with respect to hexaethylbenzene such that the carbonyl and nitrosyl ligands are located almost directly below the *distal* ethyl groups; the torsional angles for C(2)-CTRD-Cr-X(1), C(4)-CTRD-Cr-X(2) and C(6)-CTRD-Cr-X(3), are $2.0°$, $1.2°$ and $0.4°$, respectively, where X is either C or N, and CTRD is defined as the centroid of the ring given by averaging the coordinates of atoms C(1) through C(6). Other structural features of 29 also mimic those found in the afore-mentioned HEB complexes 23, 24 and 30. The C_{ar}-CH_2-CH_3 bond angles of the *proximal* (non-eclipsed) ethyl groups have increased relative to those found in free hexaethylbenzene.[28] The mean values are C_{ar}-CH_2-CH_3 *distal* $110.3°$ and C_{ar}-CH_2-CH_3 *proximal* $114.7°$; concomitantly, the terminal methyl carbons of the *proximal* ethyls are approximately 0.25 Å closer to the plane of the arene ring than are the corresponding carbon atoms of the *distal* ethyl groups. The ring centroid - chromium distance in 29 is 1.795 Å, slightly longer than the value of 1.729 Å found in 23; this lengthening may be rationalized in terms of enhanced back-donation from the chromium to the tripodal ligands in 29. The stronger π-accepting ability of NO^+ relative to CO presumably weakens the metal-arene interaction thus leading to a slight lengthening of the Cr– ring-carbon bonds. The differences in the mean dihedral angles made between the least-squares plane of the arene ring and the *distal* and *proximal* C_{ar}-CH_2-CH_3 groups are $89.9°$ and $90.3°$, respectively. The crystallographic data (Tables A3 and A4) and important bond lengths and angles (Table A5) are collected in the Appendix.
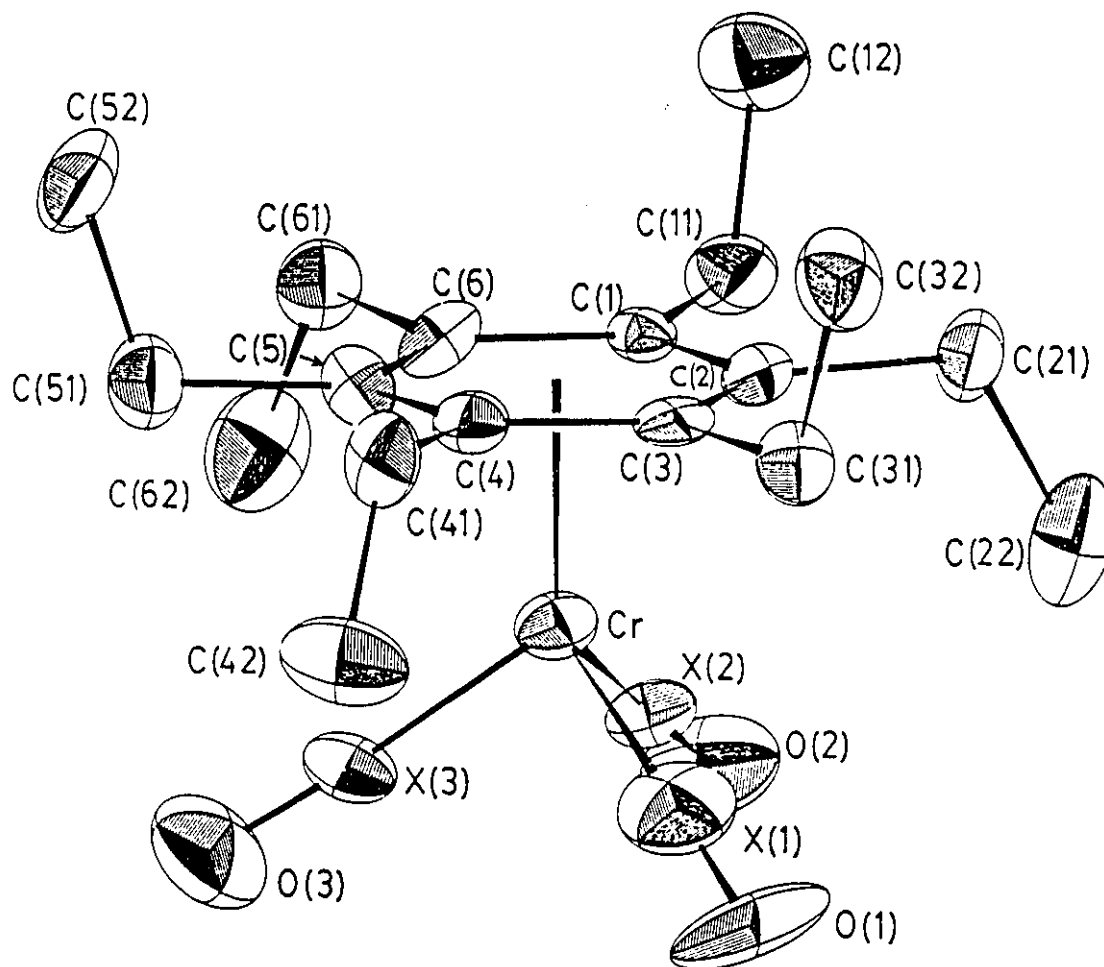
Figure 4.3: X-ray crystal structure of (HEB)Cr(CO)$_2$NO$^+$ BF$_4^-$, **29**.

Other $Cr(CO)_2NO$ complexes which have been crystallographically characterized include $(\eta^5-C_5H_5)Cr(CO)_2NO$, 33, and $(\eta^5-C_{13}H_9)Cr(CO)_2NO$, 34.[151] The bond lengths and angles within the $Cr(CO)_2NO$ tripod of 29 are comparable to those found in the $(\eta^5-C_5H_5)$ complex where, as mentioned previously,[151] disorder within the tripod exists.

The overall picture emerging from the X-ray structure determination of 29 is one in which a single carbonyl ligand in $(HEB)Cr(CO)_3$, 23, has been replaced by an iso-electronic NO^+ fragment with essentially no change in the molecular geometry; indeed, one cannot with certainty differentiate crystallographically between the CO and NO sites in 29.

4.2.2 [(HEB)Cr(CO)(CS)(NO)]⁺ BF₄⁻, 35

Photolysis of $(HEB)Cr(CO)_3$, 23, in cis-cyclooctene and subsequent treatment with CS_2 and PPh_3 gives $(HEB)Cr(CO)_2CS$, 24. Treatment of 24 with $NO^+BF_4^-$ yields $(HEB)Cr(CO)(CS)(NO)^+$ BF_4^-, 35, as a maroon solid.

The variable-temperature ^{13}C NMR spectra of 35 reveal very clearly that each of the singlets corresponding to the methyl, methylene and ring carbons observed at room temperature yields a spectacular 1:1:1:1:1:1 pattern at 168 K as depicted in Figure 4.4. In the aromatic ring carbon region, three of the signals are shielded relative to the other three by about 6 ppm and of the three resonances in a specified region one resonance is situated upfield relative to the other two by about 1-2 ppm. This pattern is less obvious in the methyl and methylene regions. In assigning the ^{1}H and ^{13}C chemical shifts the same arguments used for the nitrosyl complex 29 were also used here. This interpretation places the three *distal* methyls at δ 12.8, 13.2 and 13.4 and the *proximal* methyls at δ 17.0, 18.2 and 19.0. The resonance positions for the CH_2 shifts are δ 21.7, 22.5 and 23.2 for the *distal* methylenes and δ 20.1, 20.1 and 21.1 for the *proximal*
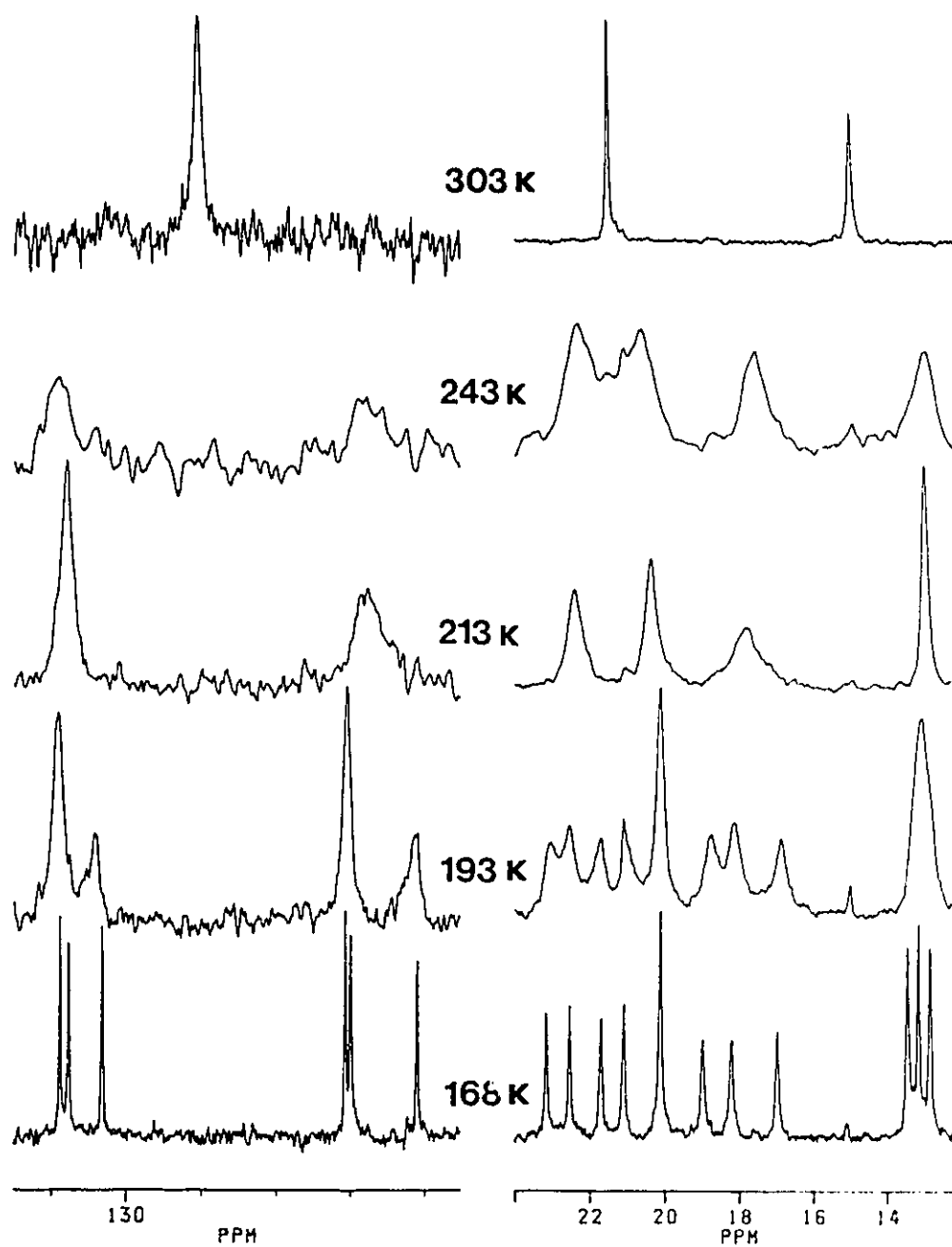
Figure 4.4 : Variable-temperature ^{13}C NMR spectra of [(HEB)Cr(CO)(CS)(NO)]$^+$ BF$_4^-$, 35, in CD$_2$Cl$_2$.

methylenes. The arene ring-carbons resonate at δ 130.6, 131.5 and 131.7 for those that are bonded to the *distal* ethyl groups and at δ 122.2, 124.0 and 124.1 for those bonded to the *proximal* ethyl groups. These assignments are collected in Table 4.1. From the information obtained thus far, it is difficult to say with certainty which arene carbons are *trans* to NO+, CS and CO, but based on π-acceptor ability one can tentatively assign the carbons at δ 122.18, 123.96 and 124.11 as being *trans* to NO+, CS and CO, respectively.

Nevertheless, these NMR spectra demonstrate beyond any doubt that tripodal rotation has been stopped on the NMR time-scale at 168 K in 1,3,5-*distal*-2,4,6-*proximal* hexaethylbenzene chromium complexes. Making the metal center chiral renders all six arene, methylene and methyl carbons magnetically non-equivalent provided there is slowed tripodal rotation. If the tripod and the ethyls are rapidly spinning, all six arene environments will be equivalent and this is observed at room temperature (see Figure 4.4). But as the sample is cooled the ethyl and tripodal rotations become slower; at 168 K (-105°C) six signals are observed in each region showing that the tripod has stopped spinning. The variable-temperature NMR spectra indicate that there are two kinds of processes: (i) ethyl rotation and (ii) tripodal rotation. The barrier to ethyl rotation is much higher than the barrier to tripodal rotation. Rough estimates using the Gutowsky-Holm approximation indicate these barriers to be 11 kcal mol^{-1} and 9 kcal mol^{-1}. Simulation of the spectra of (HEB)Cr(CO)$_2$NO+, 29, and (HEB)Cr(CO)(CS)(NO)+, 35, using the program EXCHANGE (kindly provided by Prof. R. E. D. McClung of the University of Alberta) allows the simulation of 10 exchange sites. The spectra could only be simulated by invoking two separate processes with quite different activation barriers. The first involves only interconversion within each *proximal* set and within each *distal* set of resonances. The second, and higher energy process, requires exchange between *proximal* and *distal* environments. A comparison of the solution spectra and the simulated spectra for [(HEB)Cr(CO)(CS)(NO)]+ BF$_4$-, 35, appear as Figures 4.5. The ΔG$^{\#}$ values obtained
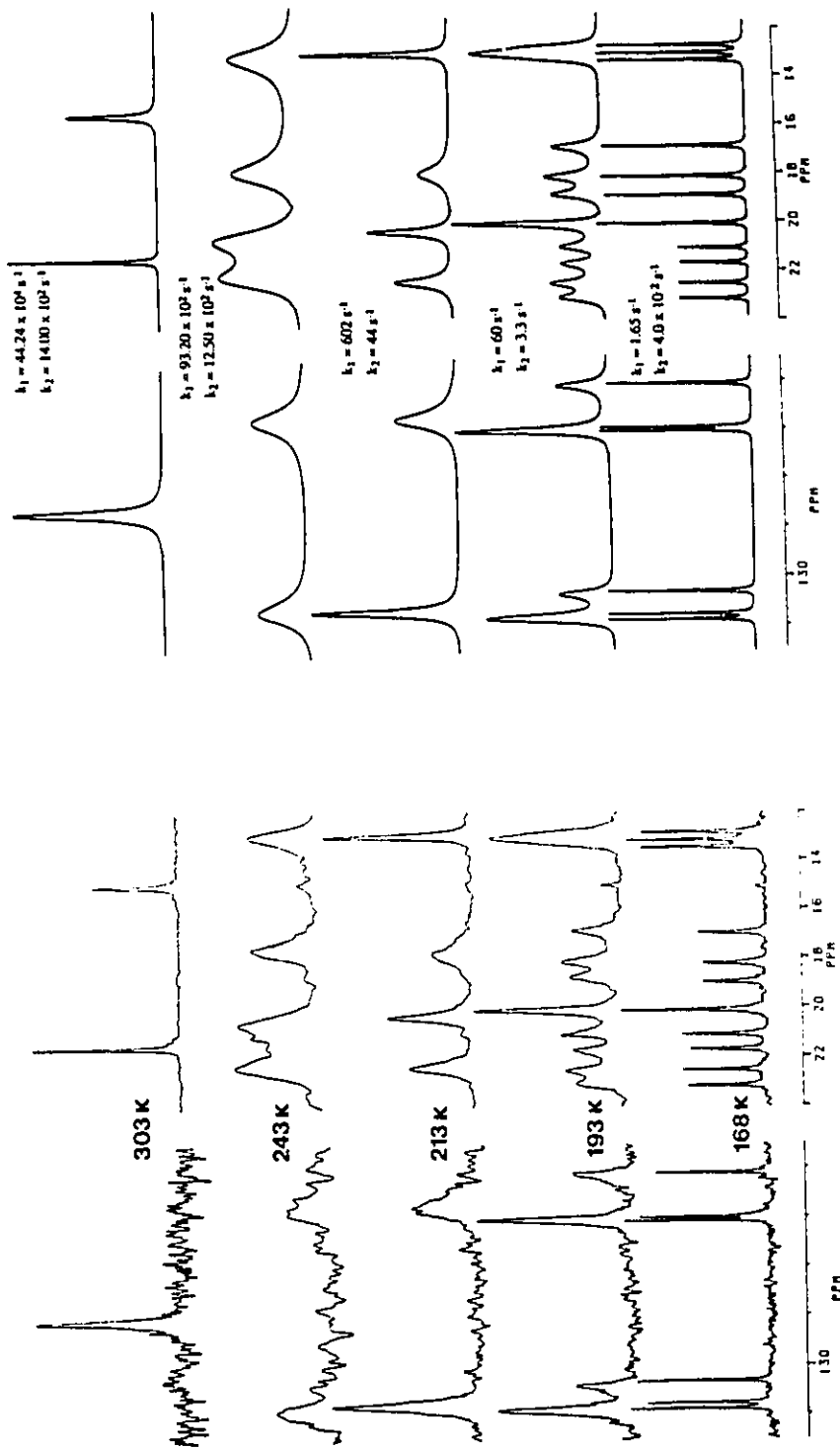
Figure 4.5 : Variable-temperature ^{13}C NMR solution spectra (left) and the corresponding simulated spectra (right) of [(HEB)Cr(CO)(CS)(NO)]$^+$ BF$_4^-$, 35.

are 9.4 kcal mol⁻¹ for the tripodal rotation and 11.4 kcal mol⁻¹ for the proximal-distal ethyl interconversion. The latter value is typical of several estimates of the barrier to ethyl rotation. Mislow reports a $\Delta G^\#$ value of 9.4 kcal mol⁻¹ for the (HEB)Cr(CO)$_2$(CS) case but attributes it to the interconversion of various conformers in which tripodal rotation is still rapid on the NMR time-scale.[153]

In conclusion, it has been demonstrated unequivocally that it is possible to observe restricted rotation about the arene-metal bond in molecules of the type [1,3,5-*distal*-2,4,6-*proximal*-hexaethylbenzene]CrL$_1$L$_2$L$_3$, where L$_1$, L$_2$ and L$_3$ are stereo-chemically non-demanding, linear ligands. If restricted rotation is observed in molecules 24, 29 and 35 then by implication the same process should be observed in 23. This provides an excellent opportunity to examine not only the rotational behavior of the ethyl groups attached to the arene but also the electronic effects brought about at the arene by different ligands bonded to the metal. Normally, such localized effects are only detectable by using techniques such as vibrational spectroscopy or X-ray crystallography for which the time-scale of the interaction is very fast. However, in systems such as 24, 29 and 35 the ligands are essentially locked in place and so the time-scale moves into the NMR regime. In complexes for which tripodal rotation is rapid, one sees only the average shift brought about at the ring carbons by all the groups attached to the metal rather than the specific contributions of each individual ligand. Of course, it is now apparent that π-complexes of hexaethylbenzene can exhibit great conformational variability and that the orientations of the ethyl groups are a reflection of the steric requirements of the ligands attached to the metal.[152] Two different fluxional processes can be detected in these systems, *viz.*, the higher energy ethyl rotation and the lower energy tripodal rotation. The factor influencing the slowed tripodal rotation is the presence of the three *proximal* ethyl groups which more or less locks the tripod in its position.

Now that it is clearly established that the low temperature ^{13}C NMR spectra of the complexes 23, 24, 29, 30, 31 and 35 are of the molecules in which tripodal rotation of the ML_3 moiety can become slow on the NMR time-scale, one can directly evaluate the influence of a given ligand, CO, CS or NO on the ring carbon *trans* to it. A particularly noteworthy observation is that incorporation of a thiocarbonyl or nitrosyl ligand in place of a carbonyl group in (arene)Cr(CO)$_3$ complexes leads to a marked deshielding of the ring carbon nuclei.[152] The logical deduction might well have been that in a normal system, in which tripodal rotation is unhindered, the carbon atoms *trans* to the CS or NO ligands experience relatively large shifts to high frequency resulting in an overall deshielding effect on the time-averaged ring carbon shift. We can now see that such a deduction would have been erroneous. In (HEB)Cr(CO)$_2$CS, 24, and [(HEB)-Cr(CO)$_2$NO]$^+$, 29, the carbons situated *trans* to the CS or NO ligands are clearly the more shielded. In each case the spectra exhibit 2:1 patterns such that the unique ring carbon (which must be one associated with the non-carbonyl ligand) resonates at lower frequency than its doubly intense partners. Thus, although the overall effect of substituting a CO by a CS or NO ligand in an (arene)Cr(CO)$_3$ complex is to deshield the ring carbons, the isolated effect of a thiocarbonyl or nitrosyl ligand is to shield the carbon *trans* to it relative to the situation when the *trans* ligand is CO. The strong π-accepting ability of a CS or NO$^+$ ligand relative to that of CO results in decreased π back-donation from the metal to the remaining carbonyl ligands and is reflected in increased ν_{CO} frequencies in the infrared spectra, and also in the shielding of the [13]CO NMR resonances.[148,152] The

ν_{CO} frequencies of (HEB)Cr(CO)$_3$, 23, are 1852 cm^{-1} and 1940 cm^{-1}; (HEB)Cr-(CO)$_2$CS, 24, are 1900 cm^{-1} and 1957 cm^{-1} and (HEB)Cr(CO)$_2$NO$^+$, 29, are 2015 cm^{-1} and 2062 cm^{-1} and their [13]CO NMR resonances are δ 235.4, 234.7 and 226.2, respectively. This enhanced π-acidity of the CS or NO$^+$ ligand relative to that of the CO groups must have the secondary effect of deshielding the ring carbons *trans* to the

remaining carbonyl ligands, and so the global effect of replacing a CO by CS or NO^+ is to increase the mean resonance frequency of the ring carbons. In 29 and 35 the presence of a formal positive charge seems to have little effect on the absolute chemical shifts of the ethyl carbons, but the shifts of the ring carbons and of the ethyl protons do reflect the lowered electron density in the cation.

The conclusions from these experiments must be placed in context with some very recent reports concerning other metal π-complexes of sterically demanding arenes. In particular, Herrmann reported the preparation of $[(HEB)Mo(CO)_3Cl]^+ MoCl_6^-$, 36, in which the chlorine and the three carbonyl ligands occupy the vertices of a square-based pyramid capped by the molybdenum atom.[154] Interestingly, in this complex, the hexaethylbenzene exists as yet another stereoisomer, the 1,2,4,5-*distal*-3,6-*proximal* conformer which presumably minimizes the interactions between the ethyl substituents and the ligands on the metal without having to resort to the high-energy all-*distal* arrangement. No variable-temperature NMR data have yet been reported on this fascinating molecule. Another relevant study is that carried out by Pomeroy who examined the complex (1,4-di-*tert*-butylbenzene)Ru(CO)(SiCl_3)_2, 32.[150] In this and related molecules the tripod RuL_3 fragment exhibits slowed rotation in the NMR at low temperature.

As an extension of this project, one can suggest approaching the problem in a different fashion. Previous attempts to provide unequivocal evidence of slowed rotation of the organometallic fragment in complexes of the type $(HEB)CrL_1L_2L_3$ were based on the idea of breaking the three-fold degeneracy of the tripod and then detecting this lowered symmetry *via* the NMR behavior of the HEB ligand. An alternate approach would be to synthesize an arene which itself has only mirror symmetry but which can present a conformation closely analogous to the 1,3,5-*distal*-2,4,6-*proximal* arrangement found in 23, 24, 29 and 35. In principle, the cessation of tripodal rotation would then be

reflected in a splitting of the three-fold symmetry of the Cr(CO)$_3$ moiety. This has been successfully accomplished by preparing the tricarbonylchromium complex of pentaethyl-acetophenone, **37**.[155] The X-ray crystal structure of this molecule indicates that the acetyl and ethyl groups adopt the 1-*proximal*-acetyl-3,5-*proximal*-2,4,6-*distal*-pentaethyl
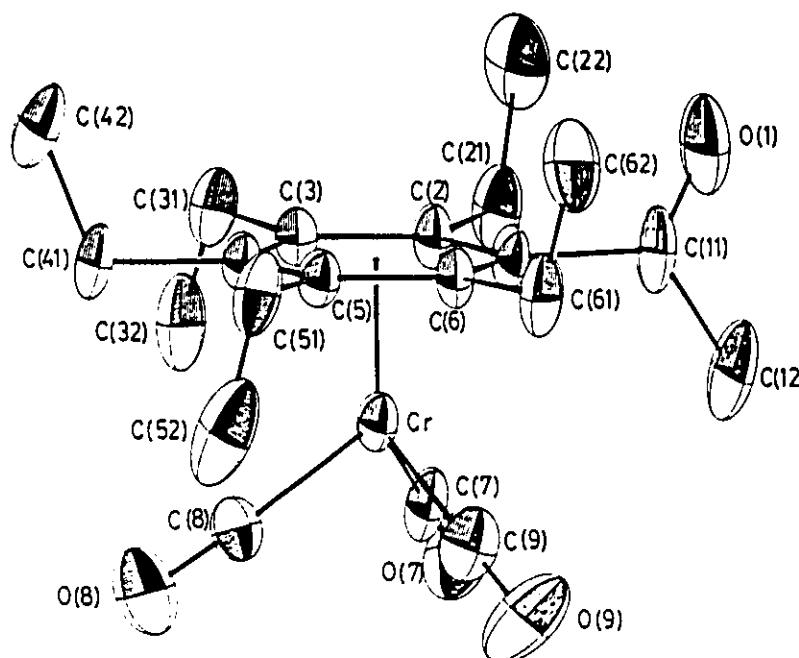
conformation. In this case, the tricarbonylchromium(0) fragment would be attached to an arene possessing C$_s$ rather than C$_{3v}$ symmetry and so the differentiation between a rotating or non-rotating tripod is easily made. The variable-temperature ^{13}C NMR data on this molecule exhibits a [13]CO signal at δ 234 attributable to the chromium carbonyl moiety which is clearly split into a 2:1 pattern at -100°C, thus showing that the Cr(CO)$_3$ moiety now has mirror symmetry and that the original three-fold degeneracy has been broken.

CHAPTER 5

PROTONATION OF (HEXAETHYLBENZENE)M(CO)₃, M = Cr, W

5.1 INTRODUCTION

Protonated arenetricarbonylchromium complexes were first reported by Wilkinson et al. in 1962.[71] The metal hydride signals in these complexes were observed at δ -3.5 to -4.0. Even though both metal-protonated, 38, and ring-protonated, 39, structures have been proposed[73] for these systems, the work by Kursanov et al.[72,75] on (arene)Cr(CO)₂PPh₃, complexes was consistent only with structure 38 as they observed a

38   39
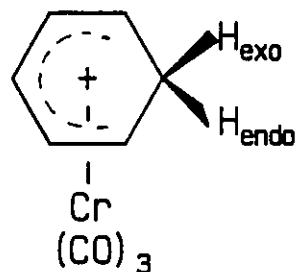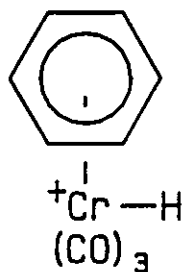
splitting of the hydrido hydrogen signal into a doublet due to a coupling with the ^{31}P nucleus. They also studied the effect of substituents on the π-bonded benzene ring of (arene)Cr(CO)₃, and (arene)Cr(CO)₂PPh₃, upon the ability of these complexes to protonate at the metal atom and suggested that electron-releasing groups enhance

protonation while electron-withdrawing groups hinder the protonation of these complexes. The basicity of the complex increases when a carbonyl ligand in (arene)Cr(CO)$_3$ is replaced by triphenylphosphine thus enhancing the ease of protonation in an acidic medium.

The studies by Flood and his colleagues[156] on the protonation of a series of (arene)M(CO)$_2$PPh$_2$Me complexes established not only the square-based pyramidal nature of the organometallic fragment attached to the arene but also the intramolecular character of the fluxional processes. The study of Flood et $al.$ together with the previous work of Faller and Anderson[5] on analogous CpM(CO)$_2$LH systems suggest an intermediate, 40, possessing pseudo three-fold symmetry as shown below.
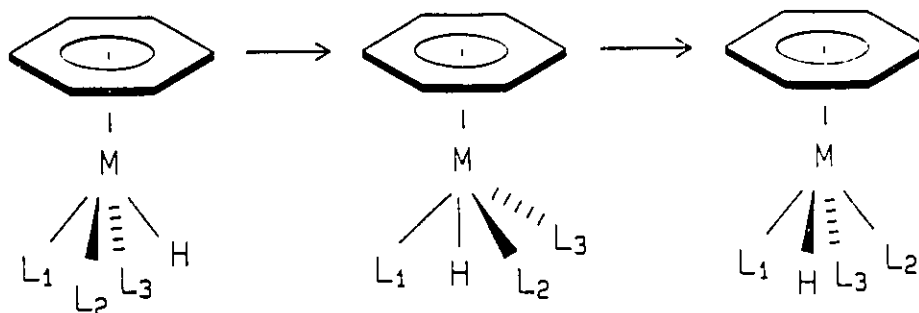
40

In protonated (anisole)tricarbonylchromium(0), Olah noted that the ^{13}C NMR spectrum recorded at -70°C exhibited a 2:1 pattern for the metal carbonyl resonances.[158] This result was rationalized in terms of a C$_s$ geometry for the M(CO)$_3$H moiety. From the examples presented in the previous chapter it is evident that hexaethylbenzene can exhibit remarkable conformational variability when complexed to organometallic

moieties. The various conformations adopted by the organic ligand depends on the bulkiness of the attached fragment. Recently, Herrmann reported the crystal structure of $[(HEB)Mo(CO)_3Cl]^+$ $[MoCl_6]^-$, **36**, and showed that the ethyl groups adopt the previously unknown 1,2,4,5-*distal*-3,6-*proximal* conformation(V).[154] In **36**, the $Mo(CO)_3Cl$ fragment forms an approximate square-based pyramid which is oriented such that the basal ligands eclipse two bonds of the hexaethylbenzene ring, as in **41a**; in the closely analogous cation $[(C_6Me_6)W(CO)_3I]^+$, **42**, the structure of which had been described earlier,[68] the $W(CO)_3I$ moiety eclipses two ring carbons and two bonds, as in **41b**.

(V)

41(a)

41(b)

41(c)
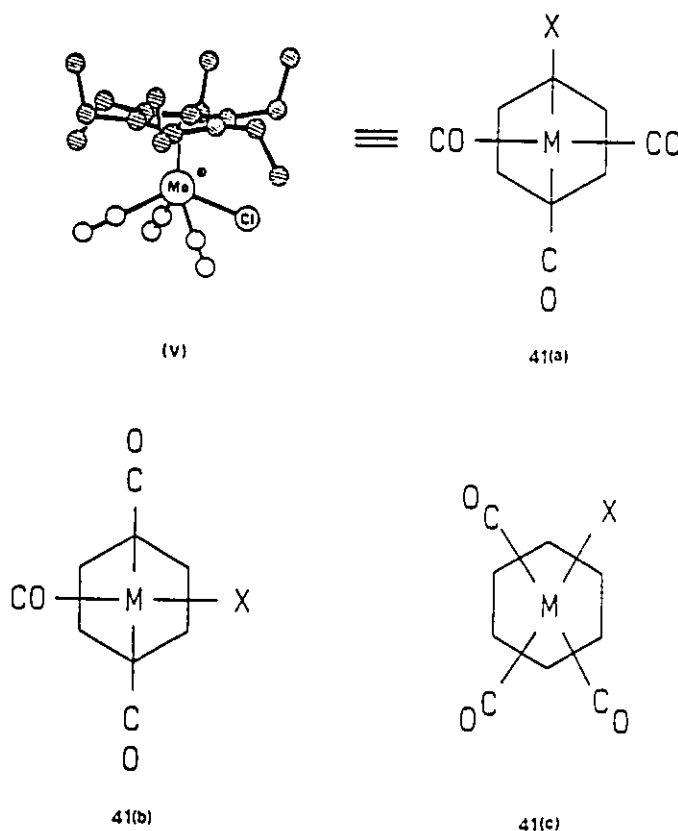
The conformation adopted by the ethyl substituents of molecule **36** in solution remains an open question. So far, no variable-temperature NMR spectra have been reported and indeed the presence of the paramagnetic hexachloromolybdate(V) anion

would perhaps preclude such studies. In an attempt to prepare another hexaethylbenzene complex of type (V) which might be more amenable to an NMR investigation, (HEB)Cr(CO)$_3$, 23, and (HEB)W(CO)$_3$, 31, were protonated.

5.2 RESULTS AND DISCUSSION

5.2.1 ^{13}C NMR Spectroscopic Studies

Treatment of an SO$_2$ solution of (HEB)Cr(CO)$_3$, 23, with CF$_3$SO$_3$H (or a CD$_2$Cl$_2$ solution with CF$_3$CO$_2$H) at -80°C causes an almost immediate color change from yellow to deep red. As anticipated from the previous reports, the proton spectrum exhibited a singlet at δ -5.2. The ^{13}C resonances for the hexaethylbenzene ligand were also clearly resolved showing that the methyl and ring carbon peaks had separated into pairs of equal intensity. At -100°C the methylene carbons broadened but did not separate. However, unlike Olah's example of (C$_6$H$_5$OMe)Cr(CO)$_3$ in which the ^{13}CO's split into a 2:1 pattern (at -70°C at 25 MHz), the metal carbonyl resonance in 23 remains unsplit even at -100°C at 125 MHz. A comparison of the ^{13}C chemical shift data for 23 and protonated (HEB)Cr(CO)$_3$, 43, appears in Table 5.1.

The analogous reaction with (HEB)W(CO)$_3$, 31, likewise yields a ^1H resonance at δ -6.4 typical of a metal hydride environment; the attachment of the proton to the tungsten atom is clearly indicated by the observation of tungsten satellites with J(^{183}W-^1H) = 26.4 Hz. The ^{13}C spectra of 31 and of protonated (HEB)W(CO)$_3$, 44, are shown in Figure 5.1 and the striking similarities lead to the conclusion that the HEB ligand has maintained its 1,3,5-distal-2,4,6-proximal conformation in the protonated species. As with the chromium analogue 43 the carbonyl resonance in 44 maintains its singlet character even at low temperature.

TABLE 5.1

^{13}C NMR Data for (HEB)M(CO)$_3$ and for the Corresponding Protonated Systems.[a]

	Distal Ethyl Groups			Proximal Ethyl Groups			
	CH$_3$	CH$_2$	C$_{Ar}$	CH$_3$	CH$_2$	C$_{Ar}$	CO's
(HEB)Cr(CO)$_3$	14.2	22.8	117.2	20.1	19.4	108.8	235.4
(HEB)CrH(CO)$_3$$^+$	13.5	20.5	126.1	23.1	20.5	124.8	225.2
(HEB)W(CO)$_3$	14.6	22.6	117.5	24.6	19.6	111.4	214.8
(HEB)WH(CO)$_3$$^+$	13.9	23.5	130.4	24.0	21.1	126.2	201.0

[a]Data for the neutral complexes were obtained in CD$_2$Cl$_2$ and those for the protonated systems in SO$_2$ solution.
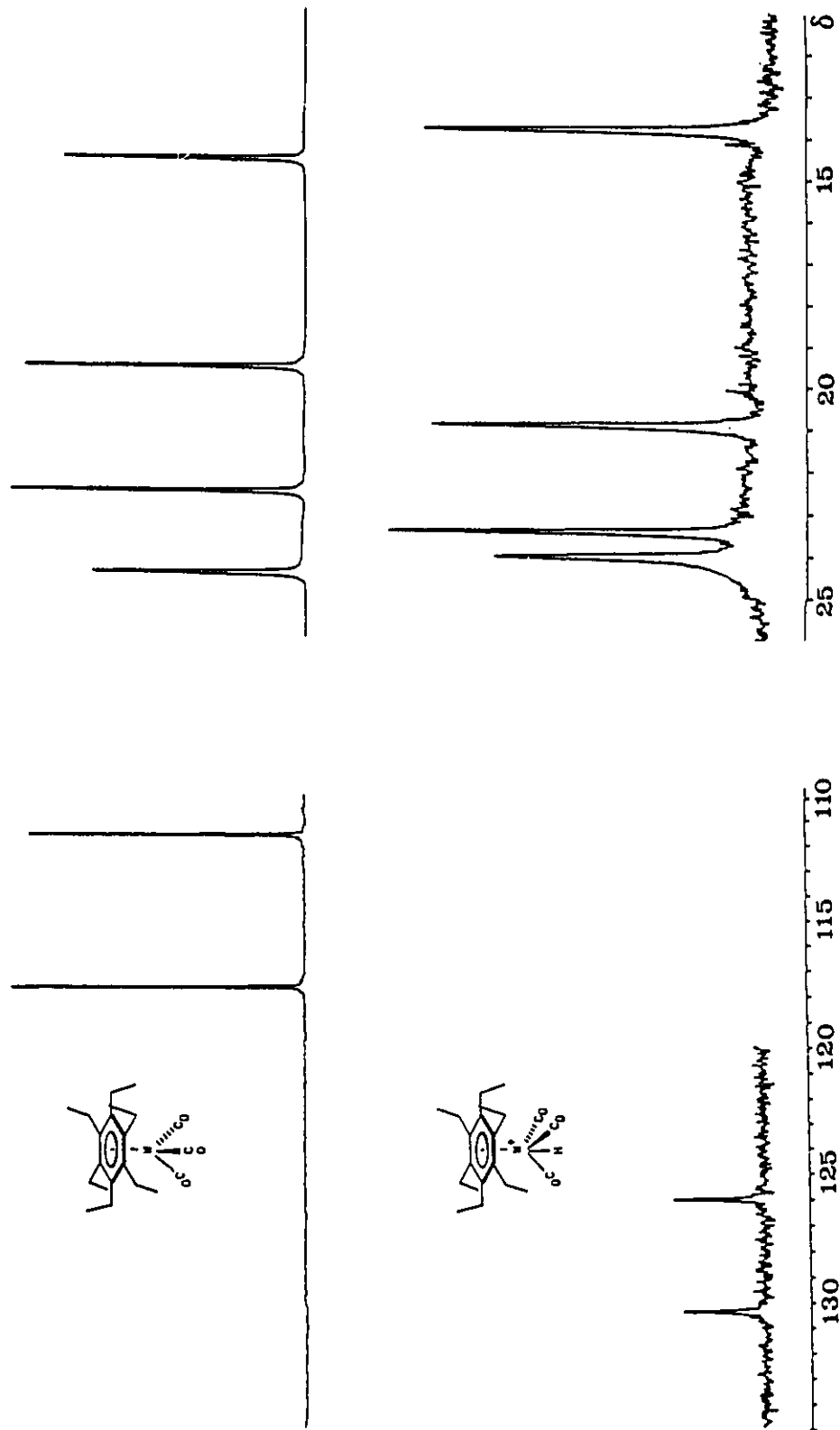
Figure 5.1 : 125.7 MHz ^{13}C NMR spectra of (HEB)W(CO)$_3$ and of its protonated analogue; spectra were recorded at -70°C.

These observations can be rationalized either in terms of a ground state C_{3v} geometry or by postulating interconversion of the C_s isomers in a process which is still rapid on the NMR time scale, even at low temperature. The former view is in favor for the following reasons: Olah's protonation of $(C_6H_5OMe)Cr(CO)_3$ revealed a limiting 2:1 pattern for the ^{13}CO resonances at -70°C at a field of 2.35 Tesla. The use of Gutowsky-Holm approximation puts the minimum activation energy for carbonyl exchange of this system in the range 10 - 11 kcal mol^{-1}. Studies on $[(arene)CrH(CO)_2PPh_2Me]^+$ systems reported by Flood yield similar barriers of 12 - 13 kcal mol^{-1}. If a similar chemical shift separation is assumed for the ^{13}CO resonances of the supposed square-pyramidal isomer of 43 then one should certainly detect a 2:1 pattern for 43 at low temperature on the 11.74 Tesla instrument. However, no evidence for splitting of the carbonyl resonance was observed even at -100°C. This would need a $C_s \rightleftharpoons C_{3v}$ interconversion barrier of $\approx$ 6 - 7 kcal mol^{-1} which would be a reduction in $\Delta G^{\#}$ of approximately 5 kcal mol^{-1} relative to those values already reported in comparable molecules.

The fluxional behavior of the neutral (HEB)M(CO)$_3$ molecules, 23, 30 and 31, where M = Cr, Mo and W, respectively, has been described in the previous chapter. At low temperature, the original singlets for the methyl, methylene and arene ring carbons are each split into two equally intense resonances. This phenomenon is readily explicable in terms of the interconversion of *proximal* and *distal* ethyl substituents,[71,73] and the barrier to ethyl rotation in these molecules is generally $\approx$ 11 kcal mole^{-1}. In the protonated system 43 the analogous rotation barrier can be obtained from the coalescence behavior of the methyls and yields a value of $\Delta G^{\#}_{224}$ = 9.8 $\pm$ 0.4 kcal mole^{-1}. It is presumably the presence of the ethyl groups which stabilizes the C_{3v} structure of the cations 43 and 44 with respect to the normally favored C_s geometry. In order for the M(CO)$_3$H fragment to adopt its preferred square-based pyramidal structure, it is necessary to overcome the barrier to ethyl rotation ($\approx$ 10 - 11 kcal mole^{-1}) and generate a

conformer of type (V) as observed in the solid state for 36. Thus, the C_{3v} structure can become competitive with the square-based pyramidal geometry when the arene imposes severe steric constrains. In order to gain an understanding of the electronic factors involved extended Hückel molecular orbital (EHMO) calculations were performed on $[(C_6H_6)Mo(CO)_3E]^+$, where E = H or Cl.

5.2.2 Extended Hückel Molecular Orbital Calculations

Molecules of the type (arene)M(CO)$_3$ have been extensively studied by using the EHMO approach and the general electronic features have been elucidated.[29] Figure 5.2 shows the effect on the total energy of the system of varying the angle made by the carbon monoxide ligands with the three-fold axis of the molecule. It is clear that placing the three CO's coplanar with the metal atom ($\Theta = 90°$) is strongly disfavored. Not surprisingly, attempts to push the tripodal ligands too close together raises the energy of the system. The minimum energy geometry is found when $\Theta \approx 125°$ and this can be readily rationalized on the basis of the alignment of the nodal planes of the π^* orbitals of the carbonyl ligands with that of the d_{z^2} orbital on molybdenum. It is apparent that this optimum overlap will occur for $\Theta = 125.3°$ since the nodal plane of the d_{z^2} orbital lies at 54.7° to the C_3 axis. In fact, the M(CO)$_3$ moiety effectively retains its octahedral parentage and the back-donation from the metal to the CO's occurs *via* the remnants of the original t_{2g} set.[159] Clearly, as the carbonyls are bent back towards the metal, this back-donation from metal d_{z^2} into π^* on the carbonyls is greatly diminished; indeed, when $\Theta = 90°$ the overlap should be rigorously zero by symmetry. However, concomitant with the decrease in Θ we observe that the HOMO which was initially an almost pure d_{z^2} orbital steadily mixes with s and p_z resulting in a hybrid which "squeezes" the electron density away from the arene ring and along the C_3 axis, as depicted in Figure 5.3. In essence, the electrons which were previously delocalized onto the CO ligands are now concentrated on
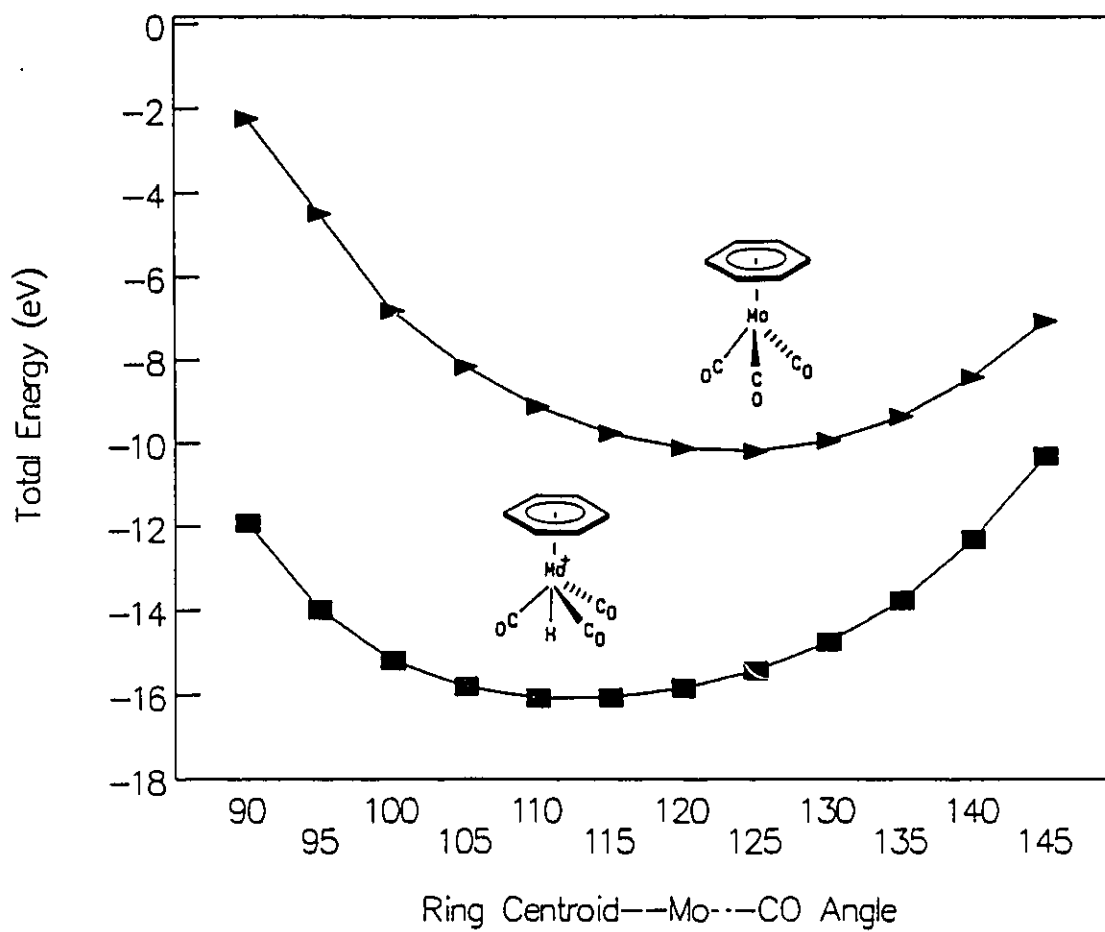
Figure 5.2 : Plots of total energy (EHMO) versus ring centroid - Mo - CO angle showing the minimum energy conformations.
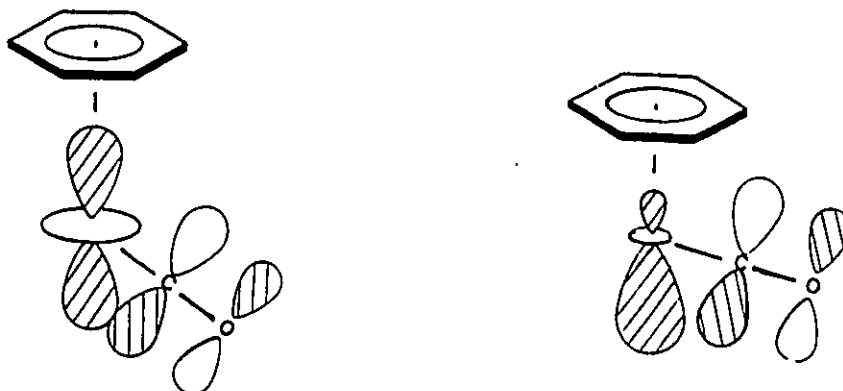
Figure 5.3 : Frontier orbitals of a metal carbonyl fragment of $(C_6H_6)Mo(CO)_3$ showing how the pure d_{z^2} (at $\Theta = 125°$) is distorted along the three-fold axis at $\Theta = 105°$.

on the metal. The net result is the raising of the energy of the HOMO and a decreased positive charge on molybdenum. The resulting structure could be described as a trigonal bipyramid with an axial lone pair—a situation which would appear to be ideal for the approach of a proton along the three-fold axis. As shown in Figures 5.2 and 5.3, a compromise is reached between the development of a hybrid orbital suitable for attachment to the proton and the need to delocalize electron density via back-donation from the metal to the carbonyls. For the protonated system the situation is optimal when $\Theta \approx 110°$ but the energy surface is rather flat suggesting that considerable conformational mobility is possible.

It is known from the experiments of Flood[156] and of Faller[157] that in molecules containing arenes which impose no steric problems the favored structure has the square-based pyramidal geometry and the C_{3v} isomer is merely a way-point during the fluxional process. Figure 5.4 depicts the energy changes along a somewhat arbitrary
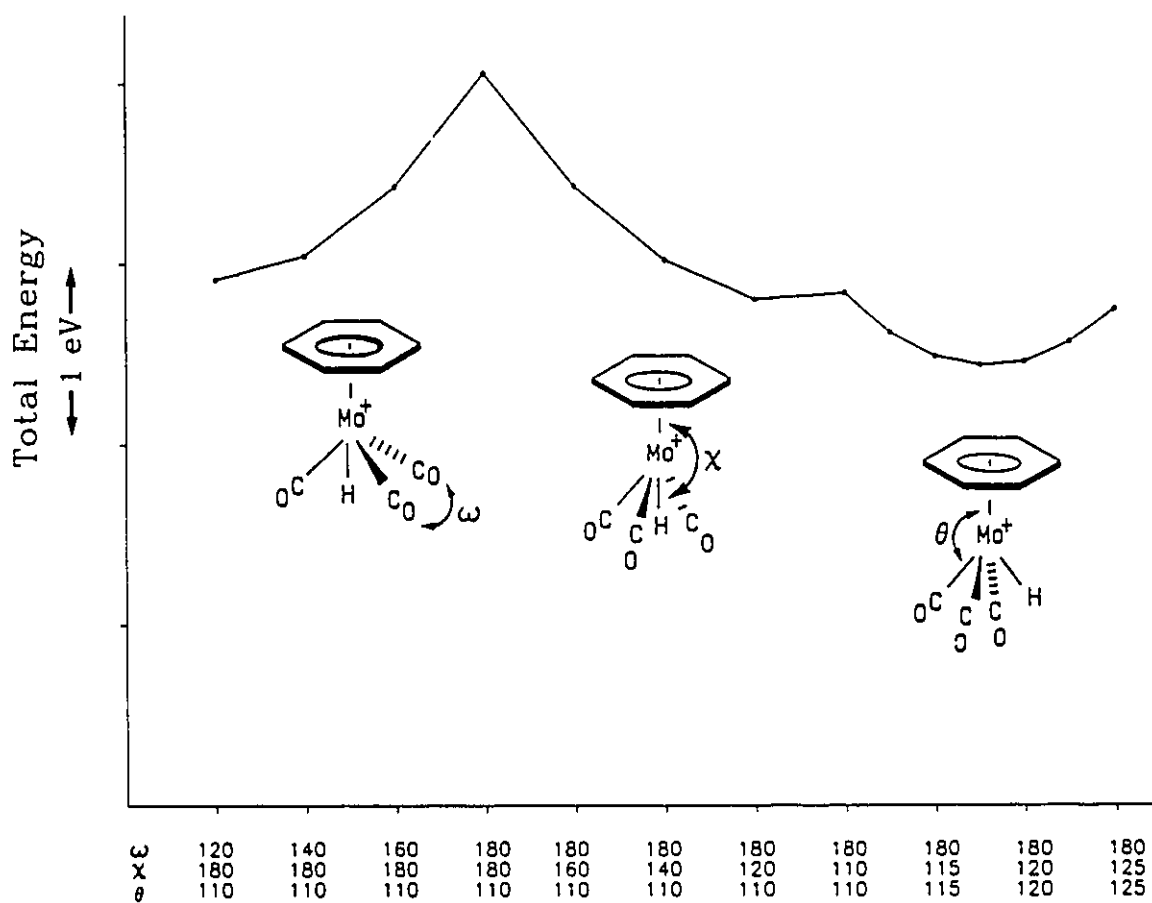
Figure 5.4 : Energy profile of an idealized reaction path which interconverts the C_{3v} and square-pyramidal isomers of $[(C_6H_6)MoH(CO)_3]^+$.

reaction path which opens up one OC-Mo-CO bond angle, ω, from 120° to 180° and allows the hydride ligand to move into its preferred location by reducing the centroid-Mo-H angle, X, from 180° to 110°. Finally, when the square-based pyramidal structure is allowed to minimize, the centroid-Mo-CO angle, Θ, is found to be ≈ 117°.

41(a)   41(b)   41(c)
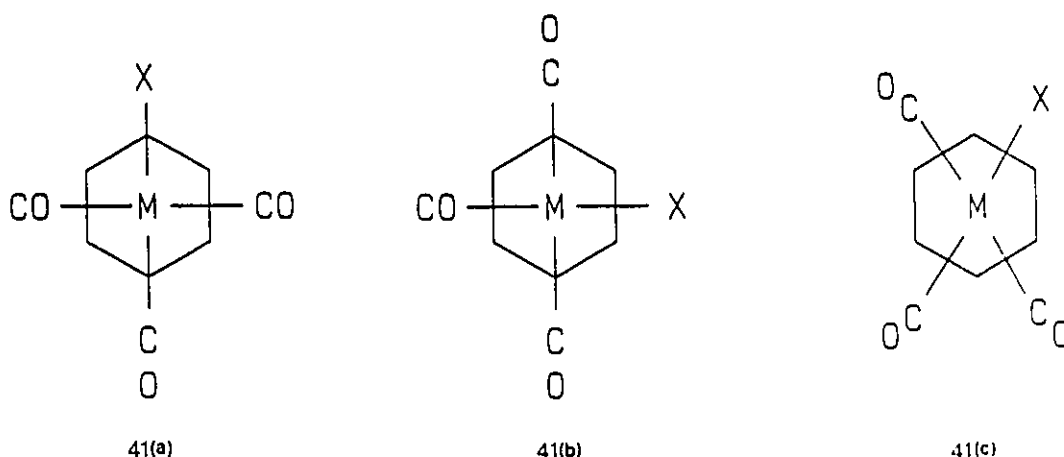
As described above, the orientation of the M(CO)₃X fragment with respect to the arene ring is different in [(C₆Et₆)Mo(CO)₃Cl]⁺, 36, and in [(C₆Me₆)W(CO)₃I]⁺, 42; in the former case the molecule is found to have structure 41a while the latter adopts 41b.[68,154] In order to see whether there is any electronic preference, EHMO calculations were carried out on the model system [(C₆H₆)Mo(CO)₃Cl]⁺ in the orientations 41a, 41b and 41c. The result is that 41b is favored over 41a while 41c is the least favored of all; however, the differences are so small (≈ 0.1 eV) that the rotational

barrier would not be detectable by NMR line-broadening techniques. Presumably, the HEB complex adopts structure 41a to minimize the interactions with the ethyl substituents. One can also profitably use the EHMO approach to compare molecules with structures as in 41 to an isomer in which the chlorine is bonded to molybdenum along the three-fold axis. Not surprisingly, the relatively large chlorine atom raises the energy markedly (by $\approx$ 0.4 eV) and indeed the minimized centroid-Mo-CO angle is now $\approx$ 105°. Apparently the disadvantages of placing a chlorine along the three-fold axis of (HEB)Mo(CO)$_3$ are more severe than those encountered by rotating an ethyl group out of the way and allowing the Mo(CO)$_3$Cl unit to adopt its preferred square-pyramidal geometry.

In 1971, Green reported the treatment of (C$_6$H$_6$)Mo(PPh$_3$)$_3$ with CF$_3$CO$_2$H and observed that the high field proton exhibited equivalent coupling constants to all three phosphorus nuclei, even at -96°C. At that time he interpreted this result in terms of a square-based pyramidal structure in which the phosphorus nuclei positioned *cis* and *trans* to the metal-bonded hydrogen were undergoing rapid exchange.[160] However, in light of the present results and considering the bulky nature of the three phosphine ligands, one might prefer to assign a C$_{3v}$ structure to the molecule analogous to the situation encountered for (HEB)M(CO)$_3$ complexes described herein.

In summary, therefore, it has been shown that the protonation of (HEB)M(CO)$_3$, 23, yields a cation in which the added hydrogen atom is directly bonded to the metal atom and is positioned along the three-fold axis of the molecule. In effect, one has trapped the transition state (or intermediate) proposed by Flood[156] for the fluxional process which interconverts the *cis* and *trans* carbonyl ligands in [(arene)M(CO)$_3$H]$^+$ systems where the metal resides in a square-based pyramidal environment. EHMO calculations suggest that this situation will only arise when the attacking electrophile has minimal steric requirements.

These protonations are currently being extended to systems such as aceto-phenonetricarbonylchromium(0) and pentaethylacetophenonetricarbonylchromium(0). An interesting feature to look for in these types of systems is the site of protonation.

CHAPTER 6

EXPERIMENTAL

6.1 GENERAL SPECTROSCOPIC TECHNIQUES

NMR spectra were recorded on a Bruker AM500 spectrometer. The 500 MHz ^{1}H and 125.7 MHz ^{13}C spectra were acquired using a 5 mm dual frequency ^{1}H/^{13}C probe. All spectra were measured in benzene-d_6, methylene chloride-d_2 or acetone-d_6 and chemical shifts are reported relative to tetramethylsilane. Proton spectra were acquired in 16 scans over a 3000 Hz spectral width in 32K data points, processed using Gaussian multiplication for line enhancement and zero filled to 64K before Fourier transformation.

Homonuclear shift correlation spectroscopy (COSY-45) experiments were carried out by using the pulse sequence: delay - (π/2,^{1}H) - t_1 - (π/4,^{1}H) - acquisition. Pulses were phase cycled according to the method of Bax and Morris.[161] A 2 s relaxation delay was used; the π/2 pulse was 18 μs. The spectra were acquired in 8 scans for each of 256 FID's which contained 1024 data points in f_2. The data were zero filled once in the t_2 domain and yielded a 512 x 512 matrix after transformation. The transformed matrix was symmetrized.

Heteronuclear shift correlation spectroscopy was obtained by using the pulse sequence: delay - (π/2,^{1}H) - (t_1/2) - (π,^{13}C) - (t_1/2) - Δ_1 - (π/2,^{1}H; π/2,^{13}C) - Δ_2 - acquisition with decoupling. A 2 s relaxation delay was used and the delay times Δ_1 = 1/2J and Δ_2 = 1/4J were calculated from a compromise value of ^{1}J(C,H) = 125 Hz. The π/2 ^{1}H pulse was 18 μs and π/2 ^{13}C pulse was 7.3 μs. The spectral width in the

103

t_2 (carbon) domain was 17857 Hz (140 ppm) and in the t_1 (proton) domain was 3000 Hz. The spectra were acquired containing 4K data points in f_2 for each of 256 FID's. Zero filling twice in f_2, followed by 2-D transformation created a 2K x 512 data matrix. Gaussian enhancement of the data was applied.

Spectral simulation was undertaken by using the commercially available Bruker PANIC program.

NH_3 chemical ionization (CI, positive) was performed on a VG 7070-F mass spectrometer. Fast Atom Bombardment (FAB) mass spectrometry was performed on a VG analytical micromass ZAB-SE reversed-geometry double-focusing mass spectrometer with an accelerating potential of 8 kV and a resolving power of 10,000 and a VG11/250 data system. 3-Nitrobenzyl alcohol was used as the sample matrix and Xe as the bombarding gas. Infrared data were obtained on a Perkin-Elmer 283 spectrometer using either NaCl solution cells or KBr pellets.

6.2 GENERAL PROCEDURES

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[162] Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

6.3 EXPERIMENTAL PROCEDURES

Preparation of O-methylpodocarpic acid, 6

Podocarpic acid was purified by recrystallization from methanol. Following the procedure of Bennett and Cambie[104] the phenolic hydroxyl group was methylated in

the following manner.

Podocarpic acid (5.0 g, 18 mmol) was dissolved in 2M sodium hydroxide (20 ml) and then treated dropwise with dimethyl sulphate (7 ml) at room temperature. The off-white precipitate formed was filtered using suction, dried and then heated under reflux with petroleum ether (250 ml) for 3 hours. The solid was washed with warm ether and suspended in water acidified with 10% HCl. The product obtained was washed with distilled water until the filtrate was neutral and air dried. Recrystallization from methanol gave 2.2 g (41% yield) of pure material. m.p. 157-158°C (lit. m.p. 158°C).[104]

Preparation of methyl O-methylpodocarpate, 7

O-Methylpodocarpic acid (8.0 g, 7 mmol) suspended in diethyl ether (50 ml) was treated with an excess of ethereal diazomethane solution and stirred overnight at room temperature. The solvent was removed and the crude product recystallized from diethyl ether to give white flakes, m.p. 128-128.5°C, (lit. m.p. 127-128°C).[104] IR ν_{max} (CCl$_4$) 2940, 2830, 1720, 1605, 1485, 1373 cm^{-1}.

Preparation of tricarbonylchromium(0) complexes of methyl O-methylpodocarpate, 8a and 8b

The procedure employed was a modification of the method of Clark et al.[109] Methyl O-methylpodocarpate (3.02 g, 10 mmol) and Cr(CO)$_6$ (2.45 g, 11 mmol) in freshly distilled di-n-butyl ether (90 ml) and THF (10 ml) were heated under reflux for 22 h under an atmosphere of dry nitrogen. The reaction mixture was filtered under nitrogen while still hot and the solvent removed under vacuum. Reverse phase high pressure liquid chromatography was used to separate the diastereomers using a mobile phase of methanol/water 75/25 at a flow rate of 4 ml/min on a Whatman M9 ODS-2 column. The β-isomer elutes with a k' value of 3.7 whereas k' for the α-isomer was 4.7.

Two fractions were collected, concentrated using a rotary evaporator and then analyzed on a reverse phase analytical column (Partisil ODS-2); the purities of the isomers exceeded 99% in each case. Recrystallization of the two fractions from hexane/ethyl acetate afforded sharp melting orange crystals. The ratio of α- to β-isomers in the crude product in this experiment was 0.64:1. Subsequently, the reaction was repeated but the time of reflux was increased to 72 h; the ratio of α- to β-isomers changed to 5.2:1.

α-*isomer*, 8a: m.p. 125-126°C. IR (CCl₄) exhibits ν_{co} 1960 and 1882 cm⁻¹.

Mass spectrum, m/z 439 [M]⁺, 354 [M-3CO]⁺, 302 [M-Cr(CO)₃]⁺.

β-*isomer*, 8b: m.p. 173-174°C. IR (CCl₄) exhibits ν_{co} 1960 and 1882 cm⁻¹.

Mass spectrum, m/z 439 [M]⁺, 302 [M-Cr(CO)₃]⁺.

Preparation of tricarbonylchromium(0) complexes of (1,3,5-triphenylbenzene), 9, 10, 11 and 12

Following a minor modification of the method of Deberitz and Nöth,[22] 1,3,5-triphenylbenzene (2.00 g, 6.5 mmol) and Cr(CO)₆ (0.88 g, 4.0 mmol) in freshly distilled di-n-butyl ether (50 ml) and THF (10 ml) were heated under reflux for 24 h under an atmosphere of dry nitrogen. The reaction mixture was allowed to cool to room temperature, filtered under nitrogen and the solvent removed under vacuum. Reverse phase low pressure liquid chromatography (Merck Lobar RP-8 column) was used to separate the mono-chromium products (isolated yield ≈ 13%) from the starting material using a mobile phase of methanol/water 80/20 at a flow rate of 4 ml/min on the Merck Size B column. The yellow microcrystalline product was shown by ¹H NMR spectroscopy to be the previously unreported isomer 10 (m.p. 160°) but small quantities of isomer 9 were also detectable. The ¹³C NMR spectrum of 10, in CDCl₃, exhibits peaks at δ 233.1 (CrCO), 142.1 (central ring, 2C), 140.6 (phenyls, 2C), 137.3 (central ring, 1C),

128.9 (phenyls, 4 meta CH), 127.8 (phenyls, 2 para CH), 127.5 (central ring, 1CH), 127.2 (phenyls, 4 ortho CH), 125.2 (central ring, 2CH), 109.9 (Cr-phenyl, 1C), 93.5 (Cr-phenyl, 2 meta CH), 92.0 (Cr-phenyl, 2 ortho CH), 91.5 (Cr-phenyl, 1 para CH). The mass spectrum of 10 showed major peaks at m/z (%) 442 (5) $C_{27}H_{18}CrO_3$; 386 (7) $C_{25}H_{18}CrO$; 358 (26) $C_{24}H_{18}Cr$; 306 (100) $C_{24}H_{18}$.

The reaction was repeated using a six-fold excess of $Cr(CO)_6$ and heating under reflux for 24 h. The product mixture was separated *via* reverse phase low pressure liquid chromatography as described above using an 80/20 methanol/water mobile phase. The products eluted in the order of decreasing molecular weight. The fractions collected were concentrated using a rotary evaporator and the fraction containing 12 was recrystallized from THF/pentane by the vapor diffusion technique to give orange parallelepipeds which were subsequently used for the crystal structure determination. The products 10, 11 and 12 were obtained pure in isolated yields of 6 %, 14 % and 5 %, respectively. No attempt was made to optimize these yields. ^{13}C NMR data: 11: (in acetone-d_6) δ 227.0 (CrCO), 143.0 (phenyl, 1C), 140.7 (central ring, 2C), 138.8 (central ring, 1C), 129.8 (phenyl, 2 meta CH), 128.9 (phenyl, 1 para CH), 128.1 (phenyl, 2 ortho CH), 127.3 (central ring, 2CH), 125.7 (central ring, 1CH), 111.1 (Cr-phenyl, 2C), 95.1 (Cr-phenyl, 4 meta CH), 94.4 (Cr-phenyl, 4 ortho CH), 94.1 (Cr-phenyl, 2 para CH). 12: (in acetone-d_6) δ 226.8 (CrCO), 138.5 (central ring, 3C), 128 (central ring, 3CH), 110.0 (Cr-phenyls, 3C), 94 (overlapping Cr-phenyl CH's).

X-Ray crystallography of 12

A crystal of 12 was selected and sealed in a Lindemann glass capillary tube. Precession photographs showed the crystal to be monoclinic and unit cell parameters were obtained from a least-squares fit of X, Ø and 2Θ for 15 well-centered reflections in the range 20°< 2Θ< 28°. Data were collected on a Nicolet P3 diffractometer using

MoKα radiation (λ = 0.71069 Å) at 22°C. Crystal data and other parameters related to

data collection are summarized in Table A1 (see Appendix). Corrections were made for

Lorentz and polarization effects but not for absorption. The density was determined by

flotation in aqueous zinc chloride solution.

Solution of the structure

Systematic absences were consistent with the space group $P2_1/n$ (a non-

standard setting of $P2_1/c$, No. 14). The structure was solved by direct methods using 50

reflections with $|E| > 1.4$ and 12 sets of starting phases. The chromium atoms were

found in the resulting E map and the coordinates were refined. All non-hydrogen atoms

were revealed in a subsequent three-dimensional difference synthesis. Further refinement

using block-diagonal matrices terminated at a maximum shift/error of 0.1. Throughout

the refinement, the scattering curves were taken from ref. 163 and anomalous dispersion

corrections from ref. 164 were applied to the curve for chromium. The atomic positional

parameters are listed in Table A2. All calculations were carried out on a VAX 8600

computer and the structure was solved using programs from the SHELX package

(Sheldrick 1976).

Preparation of hexaphenylbenzene

Diphenylacetylene (0.4278 g, 2.4 mmol) and dicobaltoctacarbonyl (0.0787 g,

0.23 mmol) in 50 ml of dioxane were stirred at room temperature for about 1 hour until

no more carbon monoxide evolved. The reaction mixture was refluxed for 3 hours and

allowed to cool. Filtration under vacuum using a sintered glass filter and repeated

washings of the residue first with dioxane, then with conc. HCl and finally with distilled

water until the filtrate was neutral gave a white powdery material (0.3613 g, Yield

≈ 85%). Mass spectrum, m/z (%) 534 (100) $C_{42}H_{30}$ [M+]. The compound was characterized by comparison with an authentic sample.

Preparation of tricarbonyl(hexaphenylbenzene)chromium(O), **19**

Although hexaphenylbenzene itself is not readily soluble in any of the common solvents hexaphenylbenzene (0.677 g, 1.27 mmol) and $Cr(CO)_6$ (0.316 g, 1.44 mmol) were heated under reflux in n-Bu_2O (90 ml)/THF (10 ml) for 7 days. The initially milky yellow solution turned black. This black solution was allowed to cool and then filtered under vacuum to give a bright yellow filtrate. The solvent was removed on a rotary evaporator at 60°C. Thin layer chromatography on silica showed the product to contain a number of different yellow complexes. Reverse Phase High Pressure Liquid Chromatography using a Vydac 201TP C_{18} column and 80/20 methanol/water as eluent was used to isolate the various chromium complexes. The major yellow band was collected and identified as the mono-chromium complex of hexaphenylbenzene.

HPBCr(CO)₃, **19** : 43 mg, 5 %; m.p. > 300°C. FAB mass spectrum : m/z (%) 670 (10) $C_{45}H_{30}CrO_3$ [M]+, 586 (70) $C_{42}H_{30}Cr$ [M-3CO]+, 534 (26) $C_{42}H_{30}$ [HPB]+.

IR (CH_2Cl_2) : ν_{CO} 1975 and 1900 cm⁻¹. ¹³C NMR data are collected in Table 3.2.

Anal. Calcd for $C_{45}H_{30}CrO_3$: C, 80.6; H, 4.5. Found : C, 80.27; H, 4.22.

Preparation of tricarbonyl(η^6-hexaethylbenzene)chromium(O), **23**

Following the method reported in reference 28(a), hexaethylbenzene (2.40 g, 9.8 mmol) and chromium hexacarbonyl (2.2 g, 10 mmol) were refluxed in heptane (50 ml)/THF (10 ml) for 3 days. The orange solution gradually turned black. This was allowed to cool and then filtered using suction to give a deep yellow solution. The solvent was removed on a rotary evaporator and then column chromatography (silica gel)

was performed to purify the product. At first, the column was eluted with hexane until the starting materials were eluted and then methylene chloride was used to elute (HEB)Cr(CO)$_3$, **23** (0.2 g, 19.4%). **23** was recrystallised using CH$_2$Cl$_2$/hexane, m.p. 178.5-179°C.

Preparation of dicarbonyl(η^6-hexaethylbenzene)chromium(0)nitrosonium tetrafluoroborate, 29

HEBCr(CO)$_3$ (1.48 g, 3.9 mmol) and nitrosyl tetrafluoroborate (0.49g, 4.2 mmol) were dissolved in 1:1 methanol/toluene (20 ml) at ambient temperature under an atmosphere of nitrogen. The reaction mixture was stirred for about 2 hours until no more carbon monoxide evolved and then ether was added to precipitate the salt. The solid was then collected by suction filtration and washed with ether. Recrystallization from CH$_2$Cl$_2$/C$_6$H$_6$ yielded **29** as an orange solid (0.61 g, 1.3 mmol; 32%), m.p. 160° (dec.). Mass spectrum : m/z (%) 384 (100) C$_{20}$H$_{30}$CrNO$_3$ (M-BF$_4$)$^+$, 356 (5) C$_{19}$H$_{30}$CrNO$_2$ (M-BF$_4$-CO)$^+$, 328 (78) C$_{18}$H$_{30}$CrNO (M-BF$_4$-2CO)$^+$, 298 (24) C$_{18}$H$_{30}$Cr (M-BF$_4$-2CO-NO)$^+$, 246 (8) C$_{20}$H$_{30}$ (HEB)$^+$. IR (CH$_2$Cl$_2$): ν_{CO} at 2015 and 2062 cm^{-1}; ν_{NO} at 1765 cm^{-1}. ^{1}H and ^{13}C NMR data are collected in Tables 4.1 and 4.2. Anal. Calcd for C$_{20}$H$_{30}$BCrF$_4$NO$_3$: C, 50.98; H, 6.37; N, 2.97. Found: C, 50.69; H, 6.71; N, 2.94.

X-Ray crystallography of 29

The density of **29** was determined by flotation in aqueous zinc chloride solution. A well-formed orange parallelepiped crystal was sealed in a Lindemann capillary tube. Precession photographs revealed the symmetry of the crystals and unit cell parameters were obtained from a least-squares fit of X, Ø and 2Θ for 15 reflections in the range 15.4° < 2Θ < 21.6°. Data were collected on a Nicolet P3 diffractometer with the use of MoKα radiation (λ = 0.71069 Å at 22°C). Corrections for Lorentz and polarization

effects and absorption (ψ-scans) were applied to all reflections. Two standard reflections (0,2,-4; 1.84% and -1,-1,-2; 1.36%) monitored every 48 reflections showed no sign of crystal decomposition. Crystal data and other parameters related to data collection appear as Table A3 in the appendix.

Solution of the structure

The structure was solved by direct methods based on 404 reflections $|E| >$ 1.2 and 20 sets of starting phases with the use of the program SHELXS-86.[165] Full-matrix least-squares refinement of the coordinates of chromium followed by three-dimensional electron density difference synthesis revealed all the non-hydrogen atoms. After refinement the temperature factors of the non-hydrogen atoms which were previously isotropic were made anisotropic and further cycles of refinement revealed the positional parameters for most of the hydrogen atoms. These were included along with the calculated positions for the rest of the hydrogen atoms in subsequent cycles of refinement (U fixed at 0.08 Å^2). From a close examination of the Cr-CO and Cr-NO bond lengths it is evident that the $Cr(CO)_2NO$ tripod was probably disordered in a similar fashion to that reported for $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$[151] and a weighted scattering factor $(2/3f_c+1/3f_n)$ for the disordered atoms was used in subsequent cycles of refinement. Further refinement using full-matrix least-squares minimizing $\Sigma \ (|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached 0.018. Correction for secondary extinction was not necessary. Scattering curves obtained from ref. 166 and anomalous dispersion corrections from ref. 167 were applied to the curve for chromium during refinement. All calculations were performed on a VAX 8650 computer. Programs XTAL[168] for data reduction, TAPER[169] for absorption correction, SHELX-86[165] for structure solution, SHELX-76[170] for structure refinement, MOLGEOM[171] for molecular geometry and SNOOPI[172] for drawing diagrams were used. Atomic positional

parameters, selected bond lengths and bond angles appear in Tables A4, and A5 in the appendix.

Preparation of dicarbonyl(η^6-hexaethylbenzene)thiocarbonyl chromium(0), 24

Following the method used in reference 141, HEBCr(CO)$_3$ (1.0 g, 2.64 mmol) was dissolved in benzene (70 ml) in a quartz vessel together with 20 ml of cyclooctene. The reaction mixture was degassed and then placed in a 250 nm Rayonet UV lamp. The solution was irradiated for about 2.5 hours while nitrogen was bubbled through the solution continuously. Triphenylphosphine (0.693 g, 2.64 mmol) in CS$_2$ (20 ml) was added to the irradiated solution and the resulting mixture was allowed to stand at room temperature for about 0.5 hours. This solution was then warmed to 50°C using a water bath and maintained at that temperature overnight. The solution was cooled and filtered to remove solid impurities and the solvent was removed from the filtrate using a rotary evaporator. Flash column chromatography using silica gel was performed to purify the product with hexane/CH$_2$Cl$_2$ (85/15) as the eluent. Four different bands were eluted, one of which was (HEB)Cr(CO)$_2$CS, 24 (0.12 g, 11%). m.p. 190°C.[141]

Preparation of carbonyl(η^6-hexaethylbenzene)thiocarbonylchromium(0)nitrosonium tetrafluoroborate, 35

(HEB)Cr(CO)$_2$CS (0.0955 g, 0.24 mmol) was dissolved in 4 ml of toluene: methanol (1:1 mixture) and the solution was degassed for 5 minutes. Nitrosyl tetrafluoroborate (0.03 g, 0.26 mmol, 10% excess) was added and then stirred at room temperature for 2 hours during which time the evolution of CO$_2$ was monitored. Anhydrous ether (60 ml) was added to the reaction flask and then allowed to cool in the refridgerator for 1 day. The maroon needle-like crystals that deposited upon cooling were collected by suction filtration and identified as 35 (0.0116 g, 10%). Sample decomposed at 150°C.

FAB mass spectrum (positive ion) : m/z (%) 400 (100) $C_{20}H_{30}CrO_2NS$ (M)$^+$, 372 (68)

$C_{19}H_{30}CrONS$ (M-CO)$^+$, 328 (12) $C_{18}H_{30}CrON$ (M-CO-CS)$^+$, 298 (11) $C_{18}H_{30}Cr$

(M-CO-CS-NO)$^+$.

FAB mass spectrum (negative ion) : m/z (%) 87 (100) BF_4 (M)$^-$IR(KBr) : ν_{CO} at 2015

cm^{-1}, ν_{CS} at 1752 cm^{-1}, ν_{NO} at 1300 cm^{-1}.

Anal. Calcd for $C_{20}H_{30}CrO_2NSBF_4$: C, 49.3; H, 6.16; N, 2.88; S, 6.57. Found: C,

49.57; H, 5.96; N, 2.82; S, 6.58.

Preparation of (η^6-hexaethylbenzene)tricarbonyltungsten(0), 31

Hexaethylbenzene (4.0 g, 16.3 mmol) and tungstenhexacarbonyl (11.2g, 31.7

mmol) in n-Bu$_2$O(50 ml) / THF(10 ml), were refluxed for six days. This was then

allowed to cool and filtered using suction to give a yellow filtrate. The solvent was

removed on a rotary-evaporator and then column chromatography (silica gel) was

performed to purify the product. At first, the column was eluted with hexane until the

starting materials were eluted and then CH$_2$Cl$_2$ was used to elute (HEB)W(CO)$_3$, 31

(1.1 g, 13%), m.p. 125°C.

Protonation of (HEB)M(CO)$_3$, M = Cr, 43; W, 44

(HEB)W(CO)$_3$ and (HEB)Cr(CO)$_3$ were each taken in NMR tubes and

cooled in a dry ice / acetone bath. A few drops of CF$_3$SO$_3$H were slowly added and the

sample was degassed on a vacuum line. SO$_2$ was transferred into the NMR tube which

was then sealed. The initially yellow solutions turned orange-red on protonation.

EHMO calculations

All calculations were performed *via* the extended Hückel method[173] using

weighted H_{ij}'s.[174] The parameters used are taken from Ref. 175. The following

distances were used: Mo-C(Ar) = 2.42 Å, Mo-CO = 2.0 Å, C-O = 1.14 Å, Mo-H = 1.7 Å, Mo-Cl = 2.47 Å.

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APPENDIX

TABLE A1

Crystal Data for (1,3,5-Triphenylbenzene)[Cr(CO)$_3$]$_3$, **12.**

compound	Cr$_3$C$_{33}$H$_{18}$O$_9$
fw (daltons)	714.5
crystal size, mm.	0.27 x 0.17 x 0.17
systematic absences	h0l, h+l = 2n, 0k0, k = 2n
space group	P2$_1$/n
unit cell	
a, Å	8.316(2)
b, Å	15.498(5)
c, Å	22.254(4)
β, deg	92.18(2)
V, Å^3	2865.8(11)
Z	4
ρ_{calcd}, g/cm^3	1.65
ρ_{obsd}, g/cm^3	1.65
temp, °C	22
linear abs coeff μ, cm^{-1}	12.22
no. of reflctns measd	4245
no. of independent reflections	3469
max 2Θ reflctns measd	45°, +h, +k, ±l
no. with I > 3σ	2830
std reflctns (esd, %)	1.53, 1.42
final R$_1$, R$_2$[a] for I > 0	0.0528, 0.0526
final shift/error, max (av)	0.1 (0.024)
Χ (secondary extinction)	-0.00002
final diff map max peak, eÅ^{-3}	0.40
valley, eÅ^{-3}	-0.39
weighting scheme	w = (σ$_F^2$ + 0.00073F$_o^2$)$^{-1}$
error in an observn of unit wt	1.15

[a]$R_1 = (\Sigma \mid F_o \mid - \mid F_c \mid /\Sigma \mid F_o \mid)$;　$R_2 = [\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma wF_o^2]^{1/2}$.

TABLE A2

Atomic positional parameters and temperature factors (Å²) for molecule 12.

Atom	x	y	z	U_{eq}
CR1	0.21959(8)	0.13974(4)	0.09907(3)	0.03225(4)
CR2	-0.35268(8)	0.86544(4)	0.56864(3)	0.02884(4)
CR3	0.37842(8)	0.61037(4)	0.76438(3)	0.02719(4)
C1	0.34887(6)	0.68946(3)	0.33193(2)	0.05488(3)
O1	0.39770(6)	0.72127(3)	0.28883(2)	0.11817(3)
C2	0.49323(6)	0.63117(3)	0.42403(2)	0.04488(3)
O2	0.62785(5)	0.62422(3)	0.43795(2)	0.03503(3)
C3	0.27360(5)	0.74835(3)	0.43463(2)	0.02778(3)
O3	0.26562(4)	0.81542(4)	0.45636(2)	0.05870(3)
C4	-0.37946(6)	0.86521(3)	0.48620(2)	0.03266(3)
O4	-0.39592(5)	0.86535(3)	0.43473(2)	0.06708(3)
C5	-0.56417(6)	0.89938(3)	0.57162(2)	0.04028(3)
O5	-0.69637(4)	0.92070(3)	0.57348(2)	0.03558(3)
C6	-0.42715(6)	0.75316(4)	0.57044(2)	0.04287(3)
O6	-0.47514(5)	0.68368(3)	0.57267(2)	0.08758(3)
C7	0.36803(7)	0.72319(4)	0.74263(3)	0.06124(4)
O7	0.36584(7)	0.79597(3)	0.72901(2)	0.14181(4)
C8	0.59006(7)	0.61734(4)	0.75118(3)	0.04053(4)
O8	0.72586(5)	0.62149(4)	0.74156(3)	0.04340(5)
C9	0.42083(6)	0.64319(4)	0.84253(2)	0.04409(3)
O9	0.44719(6)	0.66175(3)	0.89239(2)	0.09739(3)
C11	0.10889(5)	0.59483(3)	0.46923(2)	0.02961(2)
C12	0.01998(5)	0.62671(3)	0.41763(2)	0.02692(3)
C13	0.04745(6)	0.59630(3)	0.35999(2)	0.04302(3)
C14	0.16287(6)	0.53134(3)	0.35123(2)	0.05150(3)
C15	0.24632(6)	0.49782(3)	0.40052(2)	0.05249(3)
C16	0.22196(5)	0.52934(3)	0.45920(2)	0.03968(3)
C21	-0.10732(5)	0.82602(3)	0.60170(2)	0.02528(3)
C22	-0.20689(6)	0.83983(3)	0.65099(2)	0.03986(3)
C23	-0.28614(6)	0.91842(3)	0.65828(2)	0.04355(3)
C24	-0.27305(6)	0.98394(3)	0.61670(2)	0.04448(3)
C25	-0.17731(6)	0.97163(3)	0.56724(2)	0.04274(3)
C26	-0.09528(5)	0.89312(3)	0.56004(2)	0.02901(3)
C31	0.19536(5)	0.57531(3)	0.69193(2)	0.02391(2)
C32	0.32937(5)	0.52037(3)	0.68813(2)	0.03510(3)
C33	0.38580(6)	0.47257(3)	0.73875(2)	0.04472(3)
C34	0.31098(6)	0.47951(3)	0.79257(2)	0.05433(3)
C35	0.17757(6)	0.53405(3)	0.79724(2)	0.04149(3)
C36	0.11967(5)	0.58186(3)	0.74822(2)	0.02364(3)
C41	0.08517(5)	0.63142(3)	0.52973(2)	0.02432(2)
C42	0.14785(5)	0.59011(3)	0.58108(2)	0.02431(3)
C43	0.13055(5)	0.62367(3)	0.63830(2)	0.02446(2)
C44	0.04601(5)	0.70020(3)	0.64482(2)	0.03036(3)
C45	-0.02087(5)	0.74235(3)	0.59446(2)	0.02451(2)
C46	0.00086(5)	0.70740(3)	0.53869(2)	0.03438(2)

TABLE A3

Crystal data for [(C$_6$(C$_2$H$_5$)$_6$)Cr(CO)$_2$NO]$^+$ BF$_4$, 29.

compound	C$_{20}$H$_{30}$O$_3$NBF$_4$Cr
fw (daltons)	471.26
system	orthorhombic
crystal size, mm	0.15 x 0.20 x 0.30
systematic absences	h00, h=2n, 0k0, k=2n, 00l, l=2n
space group	P2$_1$2$_1$2$_1$, No. 19
unit cell	
a, Å	8.995(3)
b, Å	14.144(6)
c, Å	17.825(5)
V, Å^3	2268(1)
Z	4
ρ_{calcd}, g/cm^3	1.38
ρ_{obsd}, g/cm^3	1.38
temp, °C	22
F(000)	985.6 (984)
μ(MoKα), cm^{-1}	5.84 (5.06)
final R$_1$, R$_2$[a,d]	0.0893, 0.0786
weighting scheme	w = (σ^2F + 0.0013F^2)$^{-1}$
error in observn of unit wt[b]	1.1086
highest peak, eÅ^{-3}; location	0.40; -0.042,0.002,-0.480[c]
lowest peak, eÅ^{-3}	-0.64

[a]R$_1$ = (Σ | F$_o$ | - | F$_c$ | /Σ | F$_o$ |);   R$_2$ = [Σw(| F$_o$ | - | F$_c$ |)^2/ΣwF$_o^2$]$^{1/2}$.
[b]S = (Σw(| F$_o$ | - | F$_c$ |)^2/(m-n))$^{1/2}$, m = no. of reflections, n = no. of variables.
[c]1.05 Å from Cr.
[d]R$_1$, R$_2$ for 1795 reflections with I>3σ(I) 0.0522, 0.0508 respectively.

TABLE A4

Positional parameters (x10^4) and U$_{eq}$ (x10^4) for 29 with standard errors in parentheses.

Atom	x	y	z	U$_{eq}$
Cr	8487(1)	9913(1)	5388(1)	304
C(1)	8957(6)	9642(5)	6634(3)	212
C(11)	10336(9)	9288(6)	7040(4)	424
C(12)	10055(10)	9257(6)	7877(5)	564
C(2)	7852(9)	8992(5)	6404(4)	258
C(21)	8011(9)	7937(5)	6566(4)	409
C(22)	8818(11)	7386(6)	5935(5)	655
C(3)	6554(8)	9325(5)	6063(3)	230
C931)	5338(8)	8638(5)	5819(4)	323
C(32)	4269(9)	8455(6)	6468(5)	485
C(4)	6309(9)	10328(5)	5970(4)	289
C(41)	4808(8)	10685(5)	5647(4)	367
C(42)	4741(10)	10783(6)	4812(4)	564
C(5)	7425(6)	10968(5)	6188(4)	287
C(51)	7158(9)	12029(5)	6109(5)	428
C(52)	6428(11)	12432(5)	6826(5)	554
C(6)	8729(9)	10645(5)	6527(4)	325
C(61)	9918(9)	11333(5)	6821(4)	397
C(62)	11093(10)	11619(6)	6253(6)	649
X(1)	7762(8)	9193(5)	4616(4)	605
X(2)	10349(9)	9489(5)	5240(4)	352
X(3)	8752(9)	10899(6)	4770(4)	407
O(1)	7259(6)	8746(5)	4120(3)	789
O(2)	11555(6)	9223(5)	5164(3)	703
O(3)	8886(8)	11571(5)	4398(4)	811
B	9274(13)	4505(8)	1867(6)	539
F(1)	10532(10)	4878(8)	2139(5)	1739
F(2)	9607(6)	3752(3)	1451(3)	775
F(3)	8632(10)	5187(4)	1446(4)	1361
F(4)	8740(11)	4293(6)	2460(6)	1641

$U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$

TABLE A5

Selected bond lengths (Å) and bond angles (°) for 29 with estimated standard deviations in parentheses.

Chromium coordination

Cr-C(1)	2.293(6)	Cr-X(1)	1.831(8)
Cr-C(2)	2.303(7)	Cr-X(2)	1.798(8)
Cr-C(3)	2.273(7)	Cr-X(3)	1.793(8)
Cr-C(4)	2.294(8)	X(1)-O(1)	1.178(9)
Cr-C(5)	2.275(7)	X(2)-O(2)	1.157(9)
Cr-C(6)	2.290(7)	X(3)-O(3)	1.165(9)
Cr-Ctrd[a]	2.293(6)		
Cr-X(1)-O(1)	178.0(7)	Ctrd-Cr-X(1)	124.1
Cr-X(2)-O(2)	178.2(7)	Ctrd-Cr-X(2)	123.2
Cr-X(3)-O(3)	176.2(7)	Ctrd-Cr-X(3)	124.5

Hexaethylbenzene

C(1)-C(2)	1.415(9)	C(4)-C(41)	1.552(10)
C(2)-C(3)	1.398(10)	C(5)-C(51)	1.526(10)
C(3)-C(4)	1.445(9)	C(6)-C(61)	1.539(10)
C(4)-C(5)	1.407(10)	C(11)-C(12)	1.515(10)
C(5)-C(6)	1.397(10)	C(21)-C(22)	1.550(10)
C(6)-C(1)	1.445(9)	C(31)-C(32)	1.526(10)
C(1)-C(11)	1.521(10)	C(41)-C(42)	1.496(10)
C(2)-C(21)	1.526(10)	C(51)-C(52)	1.544(10)
C(3)-C(31)	1.526(10)	C(61)-C(62)	1.518(10)

C(6)-C(1)-C(2)	120.0(7)	C(3)-C(4)-C(5)	119.4(7)
C(11)-C(1)-C(2)	119.8(6)	C(41)-C(4)-C(5)	120.9(6)
C(11)-C(1)-C(6)	120.1(7)	C(41)-C(4)-C(3)	119.6(7)
C(1)-C(11)-C(12)	110.0(6)	C(4)-C(41)-C(42)	115.7(7)
C(1)-C(2)-C(3)	119.6(6)	C(4)-C(5)-C(6)	120.5(6)
C(21)-C(2)-C(3)	119.4(7)	C(51)-C(5)-C(6)	119.6(7)
C(21)-C(2)-C(1)	121.0(7)	C(51)-C(5)-C(4)	119.7(6)
C(2)-C(21)-C(22)	113.4(7)	C(5)-C(51)-C(52)	110.7(6)
C(2)-C(3)-C(4)	120.5(7)	C(5)-C(6)-C(1)	119.8(7)
C(31)-C(3)-C(4)	118.9(7)	C(61)-C(6)-C(1)	118.6(7)
C(31)-C(3)-C(2)	120.5(6)	C(61)-C(6)-C(5)	121.6(6)
C(3)-C(31)-C(32)	110.1(6)	C(6)-C(61)-C(62)	115.1(6)

Tetrafluoroborate anion

B-F(1)	1.340(13)	F(1)-B-F(2)	109.1(9)
B-F(2)	1.331(11)	F(1)-B-F(3)	106.3(10)
B-F(3)	1.353(12)	F(1)-B-F(4)	105.2(10)
B-F(4)	1.316(13)	F(2)-B-F(3)	111.0(9)
F(2)-B-F(4)	113.0(9)		
F(3)-B-F(4)	111.9(10)		

[a]centroid of the ring obtained by averaging the coordinates of atoms C(1) through C(6).