CHROMIUM COMPLEXES OF BENZYLIC CATIONS

CHROMIUM COMPLEXES OF BENZYLIC CATIONS:
A SYNTHETIC, HIGH FIELD NMR SPECTROSCOPIC AND EHMO STUDY

by

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ABSTRACT

Treatment of chromium hexacarbonyl with a series of benzyl alcohols yields the corresponding $(R\text{-}C_6H_4CH_2OH)Cr(CO)_3$ complexes, where R = 3-methoxy, 3-methyl, 4-methoxy or 4-methyl. These complexes were characterized by NMR spectroscopy.

Protonation of the tricarbonylchromium alcohols with CF_3SO_3H at low temperature yields a benzyl cation complex which can be isolated and examined by variable-temperature ^{13}C NMR spectroscopy. The spectra show a splitting of the carbonyl carbons at low temperature, providing evidence of electronically restricted rotation of the tripodal ligand. Evaluation of the simulated spectra provides the rotational barrier for this dynamic process. These results are rationalized by means of EHMO calculations.

Evidence suggests tripodal rotation was also electronically hindered in the analogous fulvene complexes. Variable-temperature ^{13}C NMR spectra of (6,6-Diphenylfulvene)$Cr(CO)_3$ and (6-Methyl-6-phenylfulvene)$Cr(CO)_3$ show respective 2:1 and 1:1:1 splitting of the carbonyl carbons a low temperature. Barriers of 8.3 kcal/mol and 8.8 kcal/mol were obtained by spectral simulation and were explained by using EHMO calculations.

The calculated rotational barrier for the $[\alpha\text{-}(C_5H_5CH_2)Cr(CO)_2NO]^+$ cation suggests that NMR spectral evidence for hindered rotation may be difficult to obtain.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to my supervisor Dr. M.J. McGlinchey for the valuable guidance and enthusiasm that he provided throughout the course of this and previous work. He was willing to answer any question even when there was someone else already in his office. My apologies go out to Barbara who, as a result, suffered through late evenings and delayed lunches. In the past few years MJM has boosted my personal and academic confidence. Just when I'd decide to give up chemistry and join the circus, he would encourage me to remember how far I had come and what great things lay ahead in the future. I know that I will be remembered fondly as "that huge woman", now that my reign of terror has come to an end.

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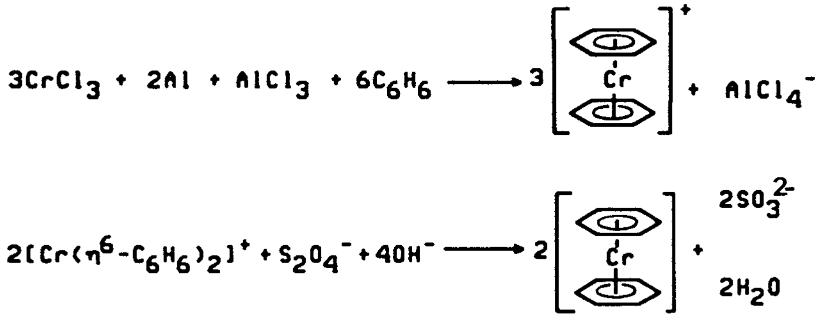
CHAPTER ONE

INTRODUCTION

1.1 Historical Background

The discovery in 1954 of bis(benzene)chromium, $[Cr(\eta^6\text{-}C_6H_6)_2]$, a sandwich compound like ferrocene, marked the starting point for the systematic investigation of chromium complexed hydrocarbons. Hein and his colleagues had been studying the interaction of aryl Grignards with $CrCl_3$ in diethyl ether[1] and were able to isolate what was subsequently shown to be the bis(benzene) complex, **1**.[2,3]

The general method for the preparation of bis(arene)chromium complexes was reported by Fischer and Hafner[4] which involved the reaction of benzene with anhydrous $CrCl_3$ in the presence of Al, which acts as a reducing agent, and with $AlCl_3$ as a halide acceptor. The salt was subsequently reduced to the neutral sandwich compound using aqueous sodium dithionate. The addition of a catalytic amount of mesitylene,[5] which rapidly forms $[Cr(\eta\text{-mes})_2]^+$ and is readily replaced by benzene, markedly reduced the reaction time, enabled the use of lower temperatures and improved the yields.



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The preparation of these bis(arene)chromium complexes was soon followed by the development of convenient routes to a wide variety of $Cr(CO)_3(\eta^6\text{-arene})$ molecules. Complexes of this type dominate π-arene chemistry primarily because of the wide range of synthetic routes available. The early realization that the coordination of the $Cr(CO)_3$ moiety modified the chemistry of the complexed arene led researchers to focus on the potential uses of these species in organic syntheses.

The first reported preparation of an arene tricarbonyl chromium complex involved the reaction of bis(benzene)chromium, **1**, and chromium hexacarbonyl in benzene in an autoclave at 220°C.[6] Yellow crystals were isolated and sublimed; they were diamagnetic, stable in air and found to be soluble in common organic solvents. The solutions were found to oxidize slowly in the presence of light. The preparation, however, was inconvenient and limited in scope, and has since been replaced by a variety of more straightforward and high-yield syntheses.

The most versatile approach was independently found by Nicholls and Whiting[7], by Natta[8] and by Fischer[9] when they heated $Cr(CO)_6$ anaerobically with the free arene under reflux. The liberation of CO gas was expected to drive the reaction to completion.

$$\textbf{Arene} + \textbf{Cr(CO)}_6 \longrightarrow \textbf{(Arene)Cr(CO)}_3 + \textbf{3CO}$$

A variety of solvents, ranging from the arene ligand itself, to inert (decalin) or polar (diglyme) have been employed, yet the yields of the metal arene complex are usually low because of the decomposition of the product as a result of the high temperatures and long reaction times involved. Faster reactions have been found with donor solvents such as THF,[10] α-picoline and 2,6-lutidine.[11] One problem associated with this preparation is that the $Cr(CO)_6$ readily sublimes out of the reaction vessel at these high temperatures and deposits onto the condenser. Strohmeier designed a "closed-cycle" apparatus in which the sublimed carbonyl is washed back into the reaction vessel by the condensed solvent vapours.[12] Studies have shown that a 10:1 ratio of di-n-butyl ether:THF was the most suitable solvent medium for a variety of arene chromium tricarbonyl species.[13,14] This modification improves upon previous synthetic routes by eliminating the problems of $Cr(CO)_6$ volatility (as it is soluble in warm THF) and the removal of high boiling point solvents or excess arene from the reaction product.

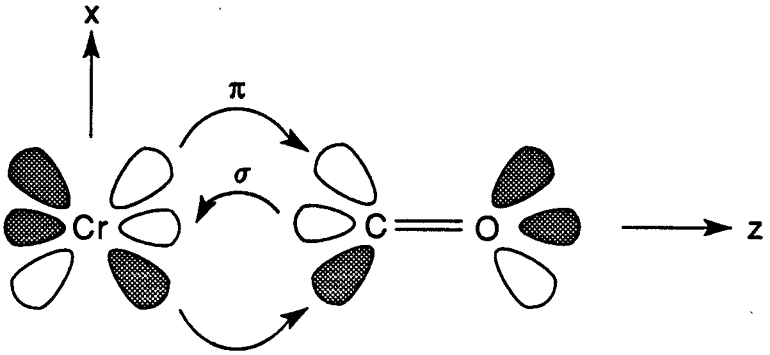
Although these reaction conditions provide a straightforward route to metal arene chromium complexes, they are limited by the substituents on the arene ring. It has been shown[7a,15] that these conditions are too drastic to permit isolation of the π-arene complexes with strongly electron withdrawing substituents such as NO_2, COOH, $CH{=}CH_2$, CHO or CN. The $Cr(CO)_3$ complexes of these arenes can be formed using a further modification to the general method. Rather than combining the substituted arene with $Cr(CO)_6$ (which requires a great deal of energy to remove CO ligands) it is combined with the complex $L_nCr(CO)_{6-n}$ (n=1-3). This method was studied when the L ligand was picoline,[16] pyridine,[17] or most often NH_3[18] or CH_3CN.[19,20] These ligands are better leaving groups than CO and are readily replaced by arenes in THF at lower temperatures than were required previously.

A detailed mechanism of the general method for the preparation of an (arene)$Cr(CO)_3$ is not well understood. Kinetic studies[21,22] on the related system of $Mo(CO)_6$ with the arenes shows the dissociative loss of one CO to form the $Mo(CO)_5$ intermediate to be the first step. The formation of $Mo(CO)_5(\eta^2\text{-arene})$ follows, and further intramolecular displacement of carbonyls to yield $Mo(CO)_3(\eta^3\text{-arene})$ has been proposed. Nicholls and Whiting questioned this mechanism for the similar chromium case early in the study of chromium carbonyl arenes.[7a]

1.2 Bonding and Structure

Arene metal carbonyls are unusual in that they contain metals in very low oxidation states compared to other transition metal compounds. The interaction of the metal with the σ-bonded arene is determined to be quite different than the interaction between the metal and the carbonyls, the latter of these is the better understood.

The linear M-C-O bond is conventionally described in terms of two interactions. Firstly, the filled carbon σ-orbital can donate electron density into suitable vacant chromium orbitals which are directed along the bond axis. Concomitantly, electrons are being transferred or "back-bonded" from filled metal d-orbitals of π-symmetry into the antibonding MO's of the carbonyl ligand.



The M-CO bonding described above is termed synergic, in that the metal has now become slightly more positive because of the loss of some electron density; the ability of the metal to attract the original ligand electrons in the formation of the σ bond is then subsequently enhanced. Therefore, to some extent, the effect of π back-bonding strengthens the σ bonding and vice-versa.[23,24]

The synergic bonding scheme has been used to explain the stability of arene chromium tricarbonyl.[25] The arene π electrons which are being donated to the chromium atom can assist in back donation into the π^* orbitals of the carbonyl ligands. Evidence for metal back-bonding can be found using infra-red spectroscopy.

The IR spectra of substituted and non-substituted benzene chromium tricarbonyl complexes have been studied extensively,[26] showing the inductive effect of the $Cr(CO)_3$ on the arene. In agreement with local C_{3v} symmetry, there are two IR active stretching vibrations for the terminal carbonyl ligands in most complexes. The two intense bands, one in the region 1900-1950 cm^{-1} and the other between 1970-2000 cm^{-1} are useful for rapid identification of a desired product. They have been assigned to a doubly-degenerate asymmetric vibration (E) and a non-degenerate symmetric vibration (A_1).[27] There are, however, some unsymmetrically substituted arenes which have been observed under high-resolution IR to exhibit splitting of the degenerate band, indicating that the local C_{3v} symmetry has some restricted validity. As electron density is back-donated into the CO antibonding orbital, the weakened C-O bond is expected to lengthen and the IR stretching frequency decreases. Concomitantly the σ bond between the metal and carbon is strengthened and shortened, resulting in an increase in Cr-CO stretching frequency.

The degree of this back-donation and in turn the IR absorptions are to a large extent, sensitive to the electronic effect of the substituent on the arene ring.[28] An electron-donating substituent on the arene ring increases the flow of electron density towards the metal, consequently enhancing the back-donation into π^*. Conversely, an electron-withdrawing group reduces the back-donation. It has been suggested[7a] that a π-bound $Cr(CO)_3$ group can withdraw electrons to the same extent as a para-nitro group since the pK_a values of $(C_6H_5CO_2H)Cr(CO)_3$ and *p*-NO_2-$C_6H_4CO_2H$ are the same.

The dipole moments of several tricarbonyl chromium complexes have been measured and confirm the re-allocation of electron density.[29,30] The positive end of the dipole points towards the benzene ring along the C_3 axis and increases with the addition of electron-releasing substituents.

TABLE 1.1 Dipole Moments of Selected $(Arene)Cr(CO)_3$ Complexes

Arene	Dipole Moment, D
C_6H_6	5.08
C_6H_5Me	5.26
p-$C_6H_4(Me)_2$	5.52
C_6Me_6	6.48

Numerous NMR studies on arene chromium tricarbonyls have been used to establish both the identity and steric arrangement of the organic moiety in these complexes. The most obvious characteristic of the proton and carbon spectra is the upfield shift of the corresponding resonance in the free ligand. The upfield shift of aromatic protons is of the order of 2 ppm, and protons on adjacent alkyl substituents shift 0.2 ppm.[31,32] This diamagnetic shift has been explained a number of ways. Originally it was believed that there was a reduction of the "ring current" and an overall withdrawal of the arene π electrons by the $Cr(CO)_3$ unit. The resultant effect is a reduction of the deshielding of the aromatic protons, and to a certain extent, of the alkyl substituent protons.[33] This theory has since been challenged.[34] Another hypothesis suggests that the magnetic anisotropy of the electrons in the ring-metal bond and the $Cr(CO)_3$ unit could produce an upfield shift of the same order of magnitude of the proton resonance. The carbon-13 resonances are also found to shift significantly by 30-40 ppm in the aromatic carbons and a down-field shift for the carbonyl-carbon (relative to the uncomplexed C≡O) is found.[35-37,99]

Extensive study[38-40] of the single crystal X-ray analyses of the π-(arene)$Cr(CO)_3$ complexes has provided a great deal of structural information, and in all compounds, the "piano-stool" conformation is adopted. The structures show that the $Cr(CO)_3$ group lies directly centered below the arene ring, with the chromium atom approximately equidistant from each aromatic carbon atom.

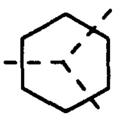
The $Cr\text{-}C_{\infty}$ bond lengths range from 1.76-1.85 Å and are always shorter than those found in $Cr(CO)_6$ (1.92 Å) which is consistent with the arene ligand being a weaker π acceptor than CO. The variability of these bond lengths reflects the relative electron-donating or electron-withdrawing ability of the substituents on the arene ring. The presence of an electron-donating group increases the donation of electron density into the C=O antibonding π orbital, lengthening the C-O bond and in turn shortening the metal to CO bond. The opposite occurs with an electron-withdrawing substituent, where there is more double bond character in the C=O bond due to the diminished back-bonding resulting in a subsequent elongation of the metal to CO bond.

The arene ring is essentially planar although slight folding is observed. The hydrogen atoms are found to be bent out of the plane towards the metal by 1.6° to afford better overlap of the carbon 2p orbitals with those on the chromium atom. The perpendicular distance from the chromium to the center of the arene ring plane is significantly longer (1.726 Å for (benzene)$Cr(CO)_3$) than the analogous bis(η^6-arene)chromium complexes (1.616Å). This suggests that the $Cr(CO)_3$ moiety has a greater ability to withdraw electrons than the $Cr(C_6H_6)$ unit. The chromium to ring back-bonding in the half-sandwich compound is then decreased so as to lengthen the bonding distance found in the full sandwich complex.

The distances from the aromatic carbons to the metal range from 2.20-2.25 Å and these values, as well as the distance from the metal to the aromatic protons, is independent of the electronic nature of the arene substituents.

The carbon-carbon bonds in the arene ring vary only slightly in the range 1.406-1.43 Å.[41] There is a controversy over whether or not these values are within experimental error or if the C-C bonds are fixed into single and double bonds due to the localized bonding of the $Cr(CO)_3$ unit. The longer bonds (by 0.02 Å) were found to lie above the projected Cr-CO bonds suggesting to some[39] that there was some loss of aromaticity of the arene upon complexation. This theory is supported by evidence in the NMR experiments which show the protons shifting upfield upon complexation.

The X-ray analyses have also revealed a variety of conformations that the "piano-stool" complexes can adopt. The two fundamental conformations are such that the projection of the carbonyl ligands onto the plane can either bisect a carbon-carbon bond (staggered, **2**) or the projection of the CO's may lie directly beneath an aromatic carbon (eclipsed, **3**).



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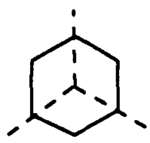

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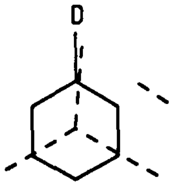

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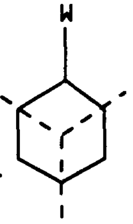
syn



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anti

Invariably, the unsubstituted arenes (benzene, naphthalene, phenanthrene, anthracene etc.)[38] as well as the fully substituted $Cr(CO)_3(C_6R_6)$ (R = methyl, ethyl)[42] adopt the staggered conformation.

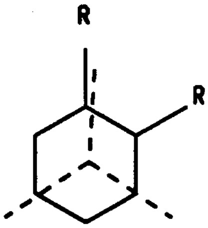
There are two possible conformations in a mono-substituted benzene, the syn-eclipsed, **4**, and the anti-eclipsed, **5**. The most common conformations found for these complexes are **2**, **4**, and **5**. The staggered structure for a mono-substituted benzene is very rare, although it has been found in (acetophenone)-$Cr(CO)_3$.[43] The syn- and anti-eclipsed conformations are most often found and the favouring of one over the other depends primarily on electronic factors.

Substitution of electron-releasing groups (ie. MeO or alkyl) indicates that the syn-eclipsed (**4**) conformation is favoured in the solid state, whereas the reverse holds true for the electron withdrawing groups (ie. CO_2Me) when the anti conformation (**5**) is favoured.[38,44,45]

Although the syn-eclipsed conformation of the π-alkyl benzenes is sterically disfavoured, there is a charge localization which explains the stability of this conformation. Since π electron density resides primarily on the ortho and para carbons the chromium retains its octahedral environment by forming stronger Cr-C bonds to these electron-rich positions, forcing one of the carbonyls to lie beneath the substituent.[46] By a similar argument, electron-withdrawing substituents are meta-directors and this effect causes the (arene)$Cr(CO)_3$ to adopt the preferred staggered conformation.

In di-substituted π-arene chromium complexes, the electron-releasing character again affects the conformation of the tripod.[47] There are three conformations of a di-substituted arene, where the substituents may be ortho, meta or para. Work in this area has been concentrated on the ortho substituted complexes. Although there are three possible orientations of the complexed molecules, (**6**, **7**, **8**) the first two are commonly observed; with (η^6-2-methoxy acetophenone)$Cr(CO)_3$ adopting conformation **6**.

Steric interaction of the substituents with the carbonyl ligands has also been shown to be important when determining the conformation of the metal complex. In the ortho-dialkyl benzene complexes (η^6-1-R-2-R'-C_6H_4)$Cr(CO)_3$ the Cr-CO bond eclipses the less bulky group.[47]



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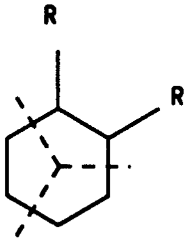

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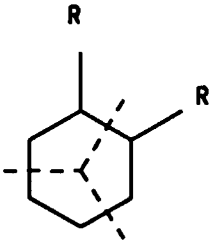

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1.3 Reactions of Arene Chromium Tricarbonyls

Thirty years have passed since the study of π-arene metal complexes began. In that time, hundreds of stable organometallic compounds with arene ligands have been prepared. Although it is known that almost every transition metal forms stable complexes with aromatic rings,[48,49] the arene tricarbonyls in particular have been studied the most extensively with a view to practical synthetic applications. They are readily prepared, found to be relatively stable in air and in protic solvents, easily purified by chromatography and are normally characterized by NMR spectroscopy and X-ray crystallography. It is the combination of these factors which makes the study of their reactivity so fruitful. Complexation of an arene to a $Cr(CO)_3$ can provide a temporary and powerful means of polarity inversion in aromatic rings and leads to interesting, synthetic applications.

A general method for the synthesis involving a π-arene metal complex begins with complexation of the metal to the aromatic moiety. Subsequent utilization of any alteration in steric or electronic factors or in the symmetry of the ligand leads to the desired reaction. Finally, it is necessary to remove the metal and isolate the new organic product.

There are five changes in arene reactivity observed upon complexation of a $Cr(CO)_3$ to a π-arene system.

(i) enhanced acidity of the arene ring hydrogens[50]

(ii) addition of nucleophiles to the arene π system leading to nucleophilic aromatic substitution[51]

(iii) stabilization of side chain cationic sites (benzyl and phenethyl cations)[52]

(iv) stabilization of side chain anionic sites (benzyl anion)[53]

(v) steric effects of the metal-ligand system[54]

These reactions can be grouped into the following categories:

a) reactions at the arene ring

b) reactions at the carbonyl group

c) reactions at the metal

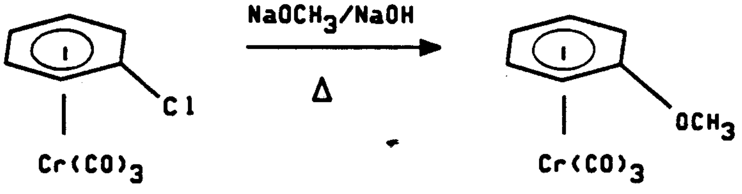
d) reactions at the exocyclic side chains

1.3.1 Reactions At The π-Complexed Ring

1.3.1.1 Nucleophilic Attack

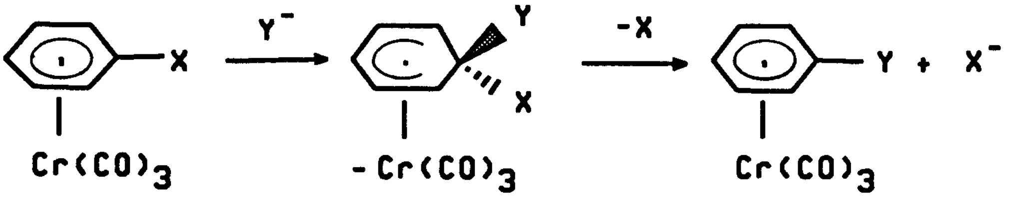
Benzene bears a slight positive charge when complexed, as evidenced by dipole moment measurements (Table 1.1) and the $Cr(CO)_3$ moiety supports the resulting negative charge. The partial positive charge on the benzene ligand leaves it susceptible to nucleophilic attack.

Shortly after the arene chromium tricarbonyls were first synthesized, it was reported that halobenzene complexes readily underwent nucleophilic substitutions.[55] For example in 1958, (η^6-ClC_6H_6)$Cr(CO)_3$, **9**, was found to react readily with sodium methoxide to give the corresponding anisole complex, **10**, in 80% yield.



9 10

Free chlorobenzene is relatively inert to the methoxide ion suggesting some interaction from the chromium tricarbonyl moiety. Kinetic studies followed which led workers to suggest that the coordination of chloro- or fluoro-benzene to the $Cr(CO)_3$ results in activation towards nucleophilic substitution on the same order as a 4-nitro substituent.[55b,56] This enhancement is explained by the electron-withdrawing ability of the $Cr(CO)_3$, stabilizing the intermediate, **11**, shown below in the addition-elimination mechanism proposed for these reactions.



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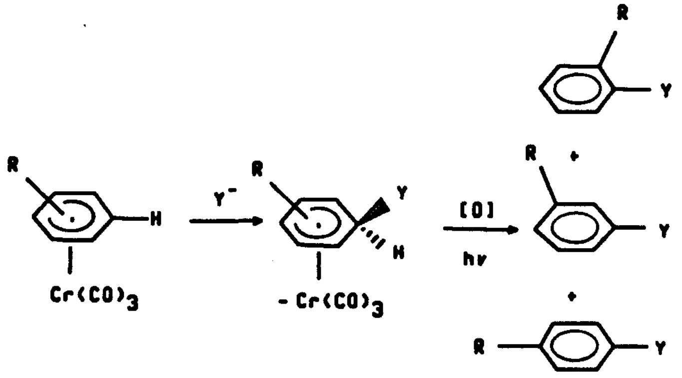
This bimolecular process does not seem to involve any aryne-type intermediates.

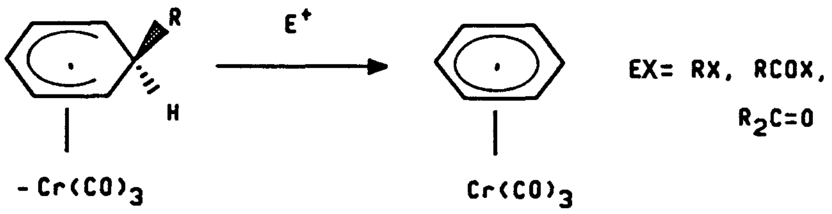
There is a great deal of synthetic potential for nucleophilic attack on complexes of these types. Generally, there are two synthetic routes employed, the first as mentioned previously, involves the replacement of a halide by various nucleophiles. Nucleophiles such as the reactive tertiary carbanions -C(Me)$_2$CN, -C(OR)(Ph)CN and -C(Me)CO$_2$Et and stabilized anions of phenoxide and malonate have been shown to react smoothly and in high yield via this route.[57] The alternative synthetic pathway is also an addition/oxidation route providing substitution of a nucleophile for a hydrogen.

The presence of directing substituents on the benzene ring has been investigated for carbanions (Y-) in the following process:



The regioselectivity is rationalized based on charge density arguments.[58] It has been shown that when R is a strong electron-withdrawing group (CF_3) carbanions attack the para position. When R is an electron-donating group (MeO, Me_2N) overall substitution is primarily in the meta position. It is interesting to note that while the meta-directing alkyl substituents (R = methyl, ethyl) show the expected meta attack of the nucleophile, reaction at the para position increases with increased steric bulk of the alkyl R group until it is the only position of attack when R = $CH\text{-}tBu_2$.[58a] This observation is rationalized in terms of the conformational preference of the $Cr(CO)_3$,[59] where the arene carbons which are eclipsed with a Cr-CO vector are preferentially attacked by the nucleophile. The approach of the nucleophile to a π-bound arene $Cr(CO)_3$ complex is considered to be trans to the metal tripod.[60]

Under the heading of Nucleophilic Attack; the addition/protonation process can also be discussed similar to the addition/oxidation routes previously outlined. Once the cyclohexadienyl intermediate, **12**, has been formed, the exo bond is cleaved when reacted with an electrophile,[61-63] with the nucleophile being transferred to the new electrophile.



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The anionic intermediate also reacts with strong acids leading to protonation of the ligand.[62,63]

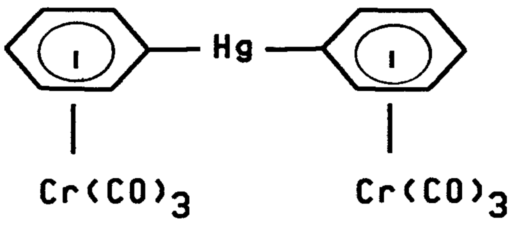
1.3.1.2 Electrophilic Attack

Theoretical calculations suggest that the presence of an electron-withdrawing unit (such as $Cr(CO)_3$) attached to an aromatic ring should reduce its susceptibility to electrophilic attack. It is difficult, however, to determine whether the free arene ring in (η^6-arene)$Cr(CO)_3$ is less reactive towards electrophiles than the complex because of the oxidative ability of the substrates towards Lewis acids and the classical electrophilic reagents.

While Nicholls and Whiting[7a] stated that benzene $Cr(CO)_3$ was inert to electrophilic substitution, a number of Friedel-Crafts acetylations and mercurations have been achieved.[64] The acetylation with $CH_3COCl/AlCl_3$ was found to be slower in the coordinated complex than the free alkyl benzenes.[65] It is noteworthy that while free alkyl arenes undergo para substitution, the π-arene complexes have ortho and meta substitution dominating with preferential meta attack found when the R group increases in bulk.

The mechanisms for these electrophilic reactions are not well understood, although Brown[66] suggests that the electron withdrawing ability of the $Cr(CO)_3$ favours coordination of the $AlCl_3$ to the metal.

The mercuration of (benzene)$Cr(CO)_3$ with $Hg(OAc)_2$ in refluxing ethanol



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probably involves direct electrophilic substitution on the benzene ring.[67] This reaction gives initially the π-acetoxy mercuration complex, which reacts with $CaCl_2$ to give (π-$ClHgC_6H_5)Cr(CO)_3$ in 43% yield. The same complex can be made in 80% yield[68] by direct chlorination of the above complex, **13**.

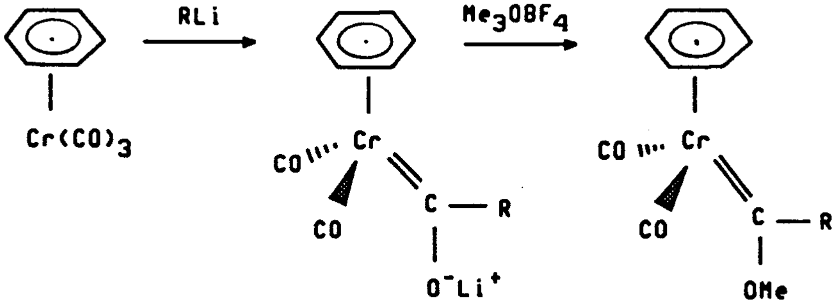
1.3.2 Reactions At Carbonyl Ligands

The carbonyl ligands of (π-arene)$Cr(CO)_3$ complexes can be exchanged for other σ or π donor ligands by either thermal or photochemical reactions to form complexes of the type (arene)$Cr(CO)L_2$ or (arene)Cr(CO)LL'.

$$\mathbf{(ARENE)Cr(CO)_3 + L \xrightarrow{UV} (ARENE)Cr(CO)_2L + CO}$$

Donor solvents such as cyclooctene and THF can be used to improve the yields.[69] Carbonyl ligands have been replaced by the following ligands; amines,[69] sulfides and sulfoxides,[70] olefins and acetylenes,[71] phosphines,[69,72] nitriles,[73] hydrogen and molecular nitrogen.[74] The hydride $(C_6H_6)Cr(CO)_2(SiCl_2)H$ has been prepared by addition of $SiCl_3H$ to the tricarbonyl complex under UV radiation.[75] Treatment of $(C_6H_6)Cr(CO)_3$ with NaCN gives the anion $(C_6H_6)Cr(CO)_2CN^-$[76] and treatment of $(C_6Me_6)Cr(CO)_3$ with the nitrosyl cation yields $(C_6Me_6)Cr(CO)_2NO^+$.[77]

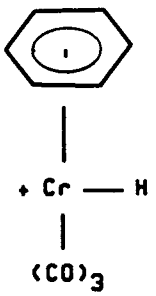
Reactions involving nucleophilic attack on the carbonyl carbon have also been studied. The reaction of (benzene)$Cr(CO)_3$ with alkyl or aryl lithium compounds[78,79] yields a carbene complex , **15**, after the cationic intermediate, **14**, has been quenched by $Me_3O^+BF_4^-$.



14 **15**

1.3.3 Reactions At The Metal Center

The electron distribution within the arene chromium tricarbonyl plays a significant role in determining its chemical reactivity. These compounds have a closed shell configuration with, formally, three unshared pairs of electrons associated with the chromium center. This arrangement should favour not nucleophilic, but electrophilic attack at chromium by strong Lewis acids such as $AlCl_3$,CF_3SO_3H or CF_3COOH. The structures of metal protonated[80a], **16**, and ring protonated[48a], **17**, complexes have been proposed.



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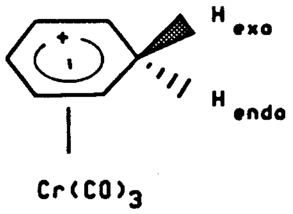

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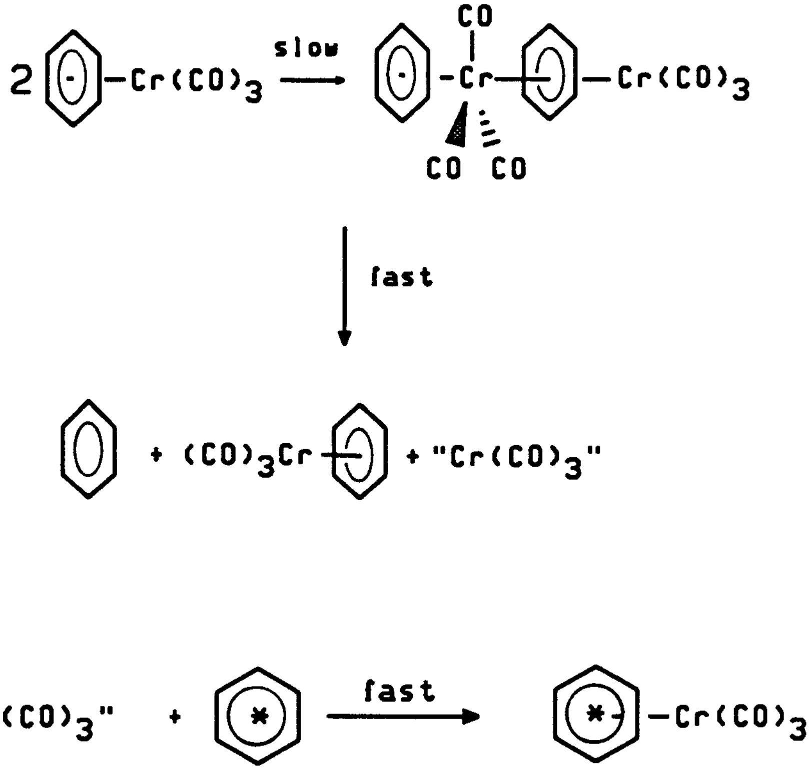
Mailvaganam et al.[80b] reported the protonation of $(C_6Et_6)M(CO)_3$, (M = Cr, W) at the metal center, with the $HM(CO)_3$ fragment adopting a square-based-pyramidal geometry. A study by Kursanov provided evidence that the metal had been protonated in a similar system, $(arene)Cr(CO)_2PPh_3$.[81,82]

Another reaction at the metal involves arene replacement reactions. This exchange is of great synthetic utility, in that some arenes cannot be complexed to the $Cr(CO)_3$ by the usual methods. The aromatic unit can be thermally replaced for another arene unit and the reaction process is enhanced by ultraviolet radiation.

$$(\mathrm{Arene})\mathrm{Cr(CO)_3} + \mathit{Arene}^{*} \longrightarrow (\mathit{Arene}^{*})\mathrm{Cr(CO)_3} + \mathrm{Arene}$$

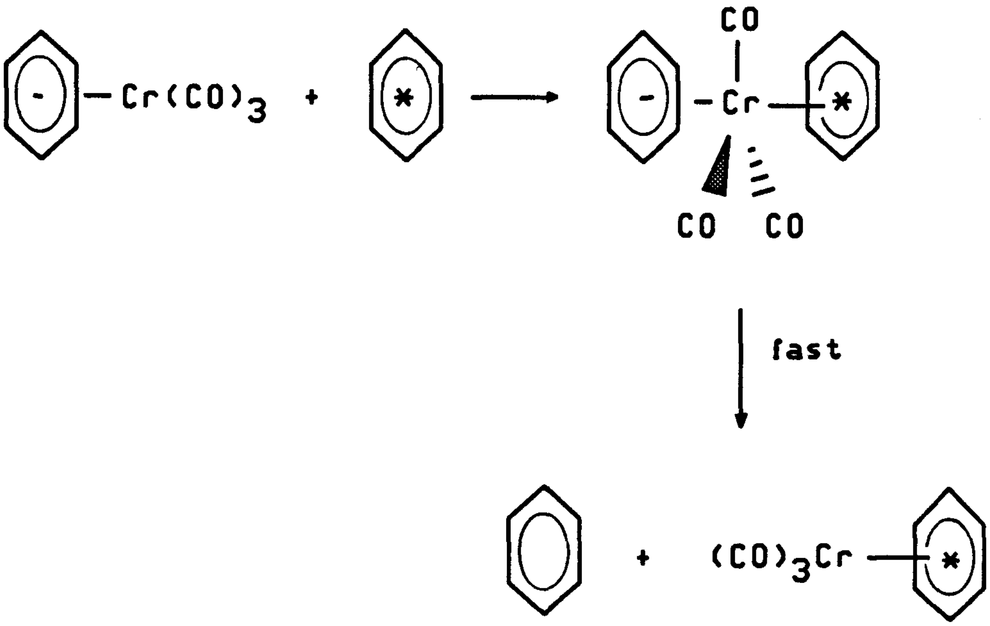
The mechanism for this reaction has been researched extensively using ^{14}C labelled arenes and the preliminary kinetic studies revealed a two term rate law.[83] The rate law was initially interpreted in terms of the following two paths.

PATH 1



The initial step involves the formation of a charge-transfer complex which then releases the active "Cr(CO)$_3$" fragment as well as benzene. The former then reacts with the new arene to form the desired product. The reaction rate was found to increase when there were electron-donating groups on the replacing arene.

PATH 2



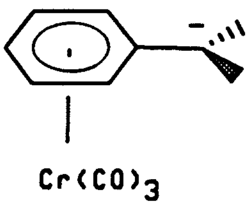
The second mechanism (Path 2) is an S_N2 type reaction which is much slower and involves direct displacement of the first arene ligand by the second.

1.3.4 Reactions At The Side Chain Of The Complexed Ring

A large number of reactions have been performed on the side chains of coordinated arenes and the effect of coordination with the $Cr(CO)_3$ moiety on ligand reactivity depends on the type of reaction occurring, be it S_N1, S_N2 or E2. The ability of an aromatic ring to coordinate to an organometallic unit allows novel and efficient routes to organic synthesis.

Chromium tricarbonyl derivatives appear as the leading series among the transition metal arene complexes employed in stoichiometric organic synthesis.[84] The popularity of these reactions is based not only on the fact that the complexation and decomplexation steps are simple, but because of the altered chemical properties of the ligand as a consequence of the complexed $Cr(CO)_3$.

Many groups have studied the capacity of the $Cr(CO)_3$ moiety to stabilize anions,[61,85] **18**, or cations,[86] **19**, at the benzylic position.



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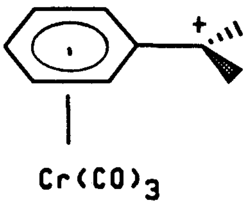

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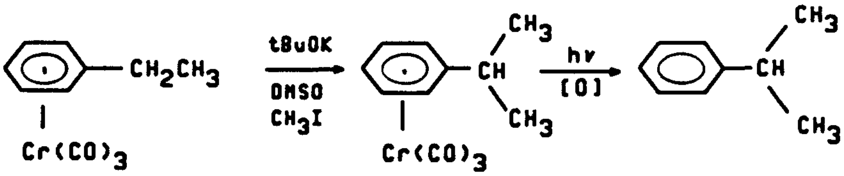
The synthetic potential of these species in organic syntheses is increased due to the unique hermaphroditic property of the complex. While there are two contrasting properties of the $Cr(CO)_3$ group (i.e. donor and acceptor with respect to an aromatic side chain) the inductive acceptor effect has been most widely explored with regard to its synthetic consequences.

The temporary complexation of the electron-withdrawing chromium tricarbonyl unit to an arene substrate increases its susceptibility to proton abstraction from the exocyclic carbon chain. The increased ability to form anions thus permits electrophilic attack of arene complexes for which the free arene has little or no reactivity.

Jaouen reported[87] the synthesis of isopropyl benzene, **21**, in 75% yield from the complex (ethylbenzene)$Cr(CO)_3$, **20**, in the presence of methyl iodide under basic conditions.



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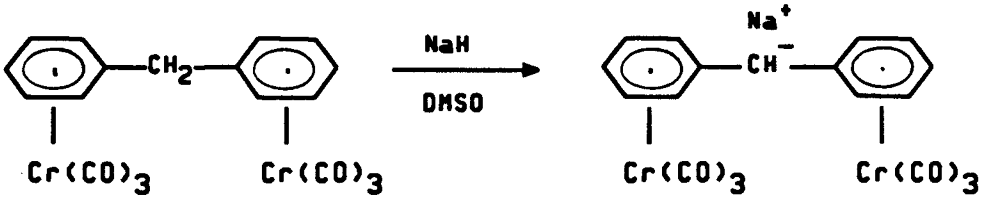
A stabilized anion has been isolated and reported.[88] (Diphenylmethane)$Cr_2(CO)_6$, **22**, was treated with NaH in DMSO forming the α-anion, **23**, which is shown to be more stable than the uncomplexed free arene analogue.



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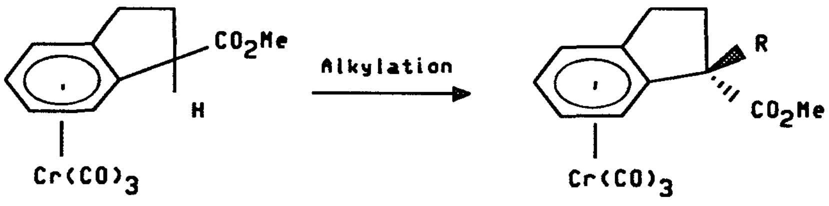
23

The proton and carbon NMR chemical shift changes once the complexed anion was formed suggest a stabilization of the negative charge throughout the metal-arene system.

Stabilization of the anion by the metal is also advantageous when attempting to alkylate the alpha-position. Alkylation of the exo- or endo-indane complexes, **24**, is stereospecifically exo with respect to the $Cr(CO)_3$ unit yielding **25** as the only product.



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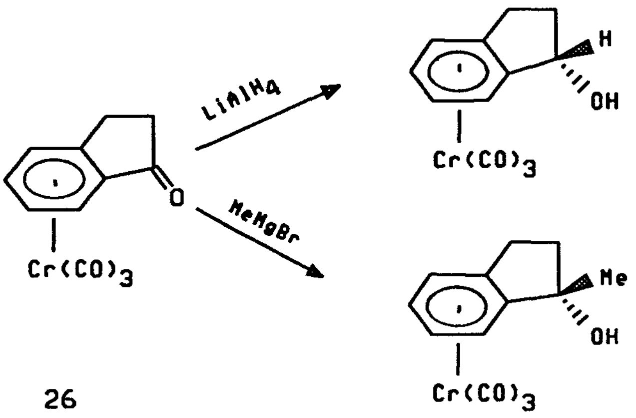
25

This stereospecificity of the attack at the side chain of the π-arene complex is a valuable synthetic tool. It arises from either specific electronic interaction of the reaction center with the $Cr(CO)_3$ moiety, or more commonly from steric blocking by the large chromium tricarbonyl beneath the arene unit.

The steric hindrance is responsible for the stereospecific reduction and alkylation of (η^6-indanone)$Cr(CO)_3$, **26**, and (η^6-tetralone)$Cr(CO)_3$[54d,91-93] where attack is always opposite from the face of chromium complexation.



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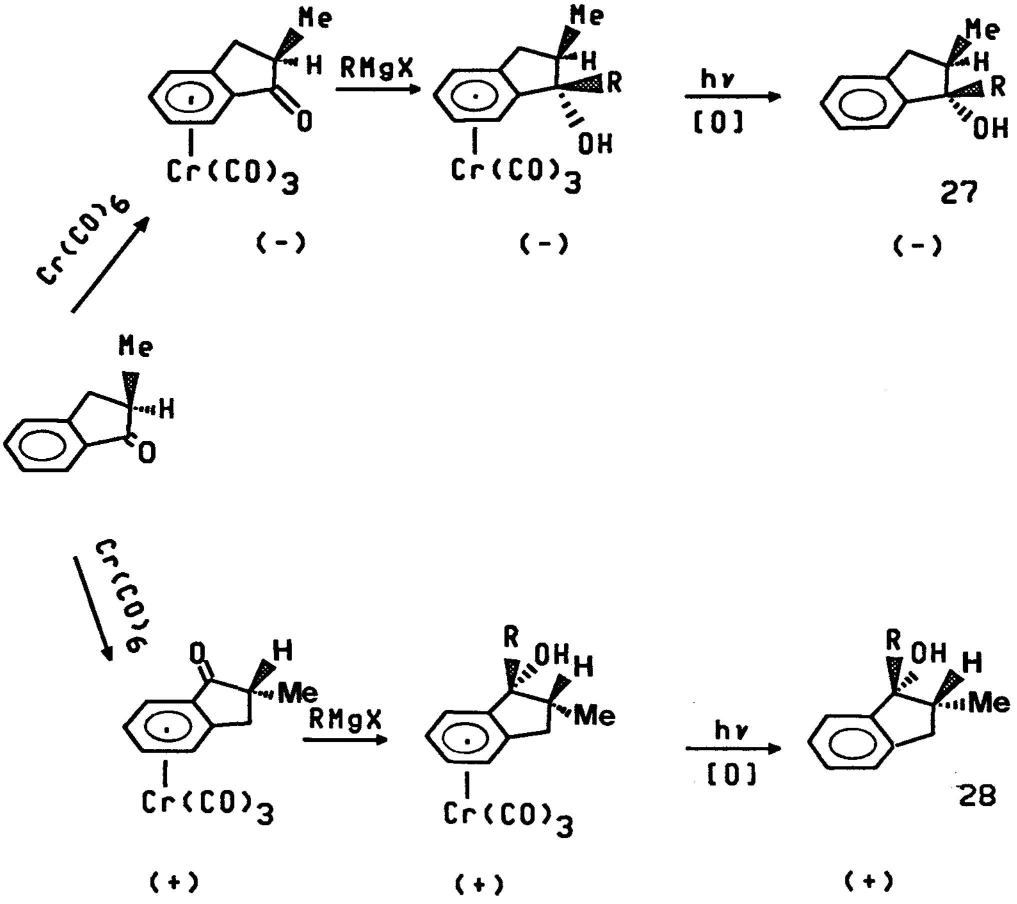
The ability to alkylate optically active ketones that are in an alpha position to an arene bound carbonyl is of significant chemical use. Pure tertiary alcohols such as **27** and **28** which are difficult or impossible to prepare by other means are produced in good yield[54e] with these techniques.



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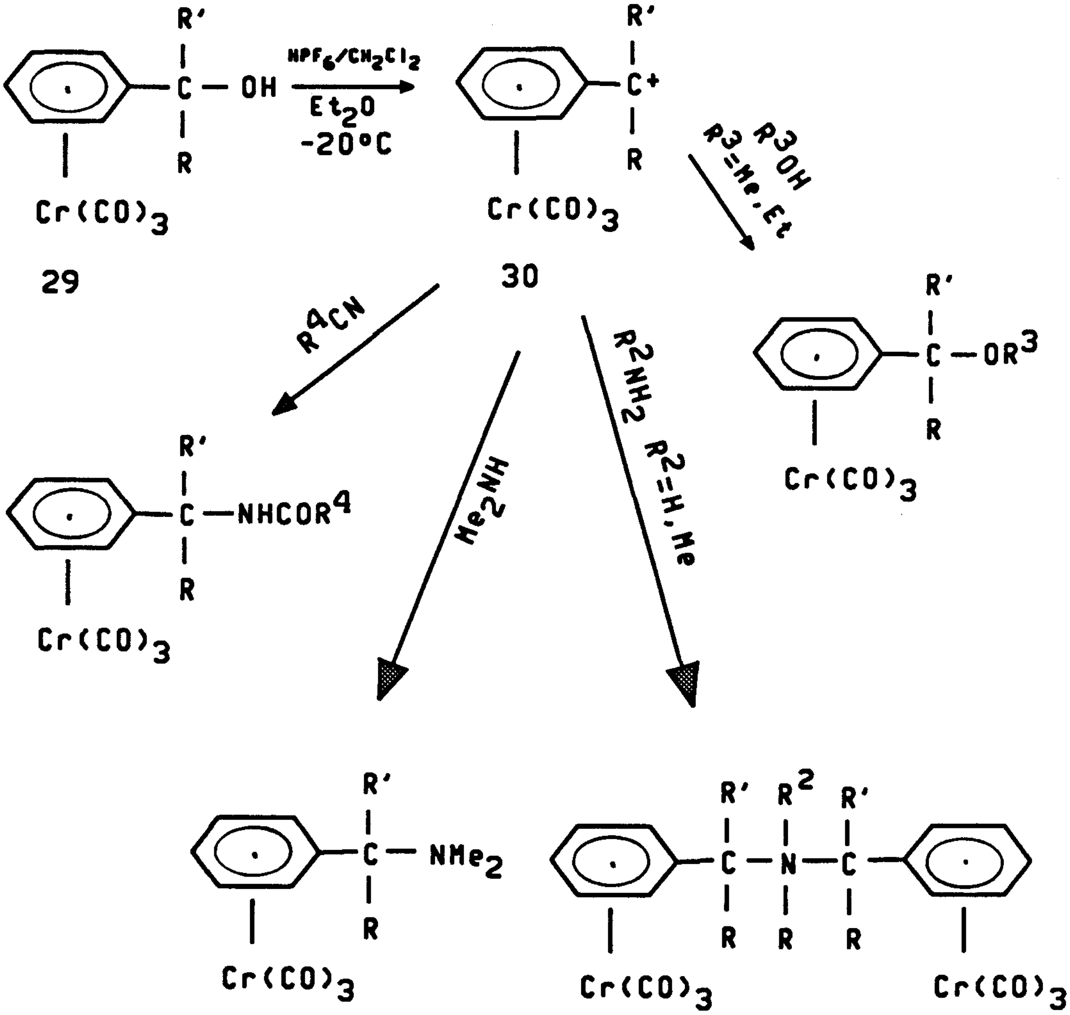
28

The ability of the metal carbonyl to stabilize a benzylic carbocation is also useful for synthetic purposes. Carbocations such as **30** are generated in situ by treatment of their corresponding alcohols, **29**, with HPF_6/CH_2Cl_2.[89,90]



CHAPTER TWO

RESTRICTED ROTATION ABOUT THE ARENE CHROMIUM BOND IN BENZYL CATION COMPLEXES

2.1 Chemical Exchange

The dynamic behaviour of arene chromium tricarbonyls in solution has been the subject of some debate for many years. It has been suggested[94] that the barrier to rotation about an (η^6-arene)-metal bond is normally too low to be observed directly by NMR spectroscopy. In principle, the barrier can be raised by exceptional electronic or steric effects and the rotation may be slowed on the observational time-scale at experimentally accessible temperatures.

The dynamic behaviour of a molecule in solution allows magnetic site exchange. This exchange leads to NMR spectra which are dependent on the rate of this dynamic process. The rate must be compared to the "NMR time-scale" where particular orientations of a molecule have lifetimes on the order of 1s to 10^{-6}s. Two types of NMR behaviour can be distinguished. If the exchange lifetime is longer than the NMR time-scale, the spectrum (at lower temperatures) will be at the slow-exchange limit. At higher temperatures, the exchange lifetime is shorter than the NMR time-scale and the fast-exchange regime results. The temperature at which fast and slow exchange meet is the coalescence temperature, T_c. The condition for slow exchange is that the exchange rate must be slower than the frequency difference between the two resonances.

In NMR spectroscopy, the difference in frequencies is defined in hertz as $\Delta\upsilon$. At the coalescence point the rate constant, **k**, for the interconversion between two sites **A** and **B** is given by

$$\mathbf{k=1/\tau}$$

where τ, the lifetime of either nucleus A or B is defined

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

The rate of A interconverting to B is determined by the free energy of activation ($\Delta G^{\ddagger}$) where

$$k=(RT/Nh)\exp(-\Delta G^{\ddagger}/RT)$$

Therefore, at the coalescence temperature, the free energy of activation $\Delta G^{\ddagger}$ is

$$\Delta G^{\ddagger}/RT=\ln(\sqrt{2}R/\pi Nh) + \ln(T_c/\Delta\upsilon)$$

$$\Delta G^{\ddagger}/RT_c=22.96 + \ln(T_c/\Delta\upsilon)$$

This statement is valid only for a non-coupled mutually exchanging system of equal population.[95] In a multiple-site exchanging system the NMR spectra may be simulated using available computer programs such as DNMR3[96] or Exchange.[97] The results lead to a comparison of the line-broadened experimental spectra (at known temperatures) and the simulated spectra (with known rate constants). The activation energy E_a can be determined through an Arrhenius plot of ln k vs. 1/T. One can also estimate the activation enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ from an Eyring plot of ln(k/T) vs. 1/T.

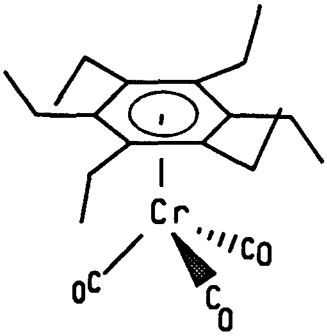
These techniques can be employed to determine the barrier to rotation of a chromium tricarbonyl moiety bound to an arene π system. Only when the interconversion of sites can be stopped on the NMR time-scale can the activation energy be obtained by examining the spectra over the slow and fast-exchange limits.

Fast exchange can only very rarely be achieved on the UV or IR time-scales since the frequency differences between peaks are 10^{14} and 10^{12} Hz respectively, compared with a 100 Hz separation for fast exchange in NMR. Diffusion rates place a limit of 10^9-10^{10} s^{-1} on most reaction rates, therefore NMR is the only technique of the three able to give information about these dynamic processes.

Valuable information about the structure and dynamics of a molecule can be gained by monitoring the change in chemical shifts over a range of temperatures. This technique prompted a number of researchers to devise ingenious experiments to determine whether the rotation of the chromium tricarbonyl moiety in (hexaethylbenzene)Cr(CO)$_3$ could be stopped on the NMR time-scale.

2.2 Steric Hindrance of Tripodal Rotation

Hexaethylbenzene (HEB) is known to have alkyl groups pointing alternately above and below the plane of the arene ring.[98] A solid-state ^{13}C NMR experiment on (HEB)Cr(CO)$_3$, **31**, suggested[99] that the same conformation of the ligand was adopted in the chromium complex, whereby the ethyl groups were alternately distal and proximal to the metal.



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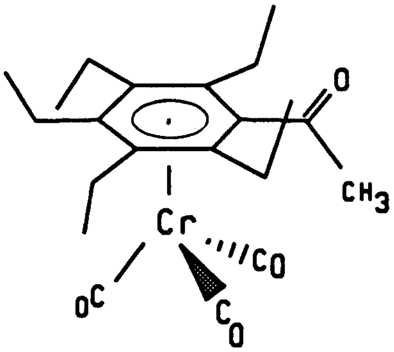
The methyl, methylene and ring carbons were split into pairs of equally intense lines, confirming the two different magnetic environments for each of the three carbon types. Subsequent X-ray crystallography studies[98,100] verified this 1,3,5-distal-2,3,6-proximal conformation for the HEB ligand. The organometallic tripod was oriented in such a way as to minimize steric interactions with the proximal alkyl chain by lying directly beneath the distal ethyl groups. This paper also established that the same conformation was adopted in solution at low temperature. At room temperature the methyl, methylene and ring carbons appear as singlets, but at low temperature as in the solid state spectra, these resonances were split. It had been suggested[101] that in the absence of any strong electronic effects, the rotational barrier of the chromium tricarbonyl moiety was calculated to be too low to be detected by NMR line-broadening methods.

While it is true that there is no electronic barrier to rotation,[94] the claim that the tripod acted as an unhindered rotor, passing by the bulky proximal ethyl groups was debated. Given the X-ray crystal structure of **31**, it is not possible to distinguish between a rotating or non-rotating tripod using NMR techniques, since the molecular symmetry is C_{3v} with or without tripodal rotation.

The three-fold symmetry of the tripod was then broken by incorporation of a thiocarbonyl to form $(HEB)Cr(CO)_2CS$[102] and a nitrosyl to form $(HEB)Cr(CO)_2NO^+$.[103] These molecules were expected to mimic $(HEB)Cr(CO)_3$ structurally. In both cases the X-ray crystal structure detailed the 1,3,5-distal-2,4,6-proximal conformation of the ethyl groups. As well, at low temperature the ^{13}C NMR spectra of both complexes exhibits a 2:1:2:1 pattern for both the methyl and methylene as well as the ring carbons in each compound. For both complexes the molecules have adopted a C_s conformation which can only occur if the tripod had slowed its rotation. Although Mislow and Hunter were not convinced that rotation had been stopped,[104,105] there appears to be a great deal of evidence to support the claim of restricted rotation.[102,103,106]

The original strategy to provide evidence of restricted rotation in (HEB)Cr$(CO)_3$ involved breaking the three-fold symmetry of the tripod by incorporating a ligand similar to a carbonyl in the tripod. The structural characteristics and NMR behaviour of these compounds were then used to compare with the highly symmetric tricarbonyl complex. Substitution of the new ligand provided a molecule with a single mirror plane with the distal ethyl groups in two distinct magnetic environments.

The next approach was to alter not the tripod, but the ligand itself. The formation of $(C_6Et_5COMe)Cr(CO)_3$,[106] **32**, provided a molecule which was also found to mimic (HEB)Cr$(CO)_3$ structurally. The restricted rotation of the Cr$(CO)_3$ in this low symmetry (C_s) complex could then be monitored by examining not the chemical shifts of the ligand as before, but by noting the changes in the chemical shift of the carbonyl carbon. Both the solid-state and solution (at -100°C) ^{13}C NMR spectra showed a 2:1 splitting of the carbonyl carbons which could only be explained in terms of a stationary tripod on the NMR time-scale.



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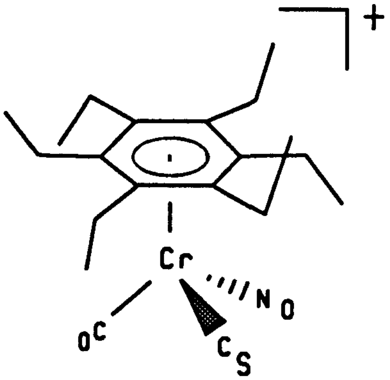
The excellent correspondence between these spectra, and the information available from the X-ray crystal structure left no doubt that the alternating distal-proximal arrangement of the ethyls was adopted. The barrier to rotation was found to be ≈ 9 kcal/mol.

Further confirmation that tripodal rotation could be stopped was recently published in an elegant paper by Mailvaganam et al.[103] By replacing two of the three carbonyls in (HEB)Cr(CO)$_3$ with different ligands, the chiral molecule (HEB)Cr(CO)(CS)(NO)$^+$, **33**, was formed.



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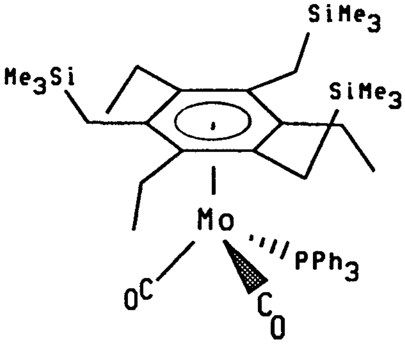
Since the 1,3,5-distal-2,4,6-proximal structure is favoured, only if the tripod were to stop its rotation would all six ethyls become magnetically non-equivalent as a consequence of this chirality. At -105°C, all the distal and proximal resonances were clearly separated and for each case they show three carbon environments. That is to say, all 18 carbons on the hexaethylbenzene ligand were readily differentiated. The barrier to tripodal rotation was calculated to be 9.5

kcal/mol. This evidence has resolved any controversy over whether or not cessation of the tripodal rotation could be attained on the NMR time-scale in hexaethylbenzene complexes.

Hunter and his group also have claimed to stop tripodal rotation in some similar systems. They were also trying to obtain unequivocal proof that rotation could be slowed due solely to steric hinderance. By examining the variable temperature ^{13}C NMR spectra of (η^6-$C_6Et_3(CH_2SiMe_3)_3$) $Mo(CO)_2(PPh_3)$, **34**,



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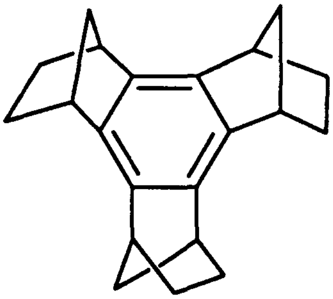
he found[107] the carbonyl carbons' splitting at 190K providing evidence for restricted rotation. The barrier was roughly estimated to be 35 kJ/mol.

As well, carbonyl decoalescence has been observed[108] in the tricarbonyl complex of the syn-anti-syn trimer of bicyclo[2.2.1]hept-2-yne, **35**, which has been explained in terms of a restricted rotation of the $Cr(CO)_3$ unit.



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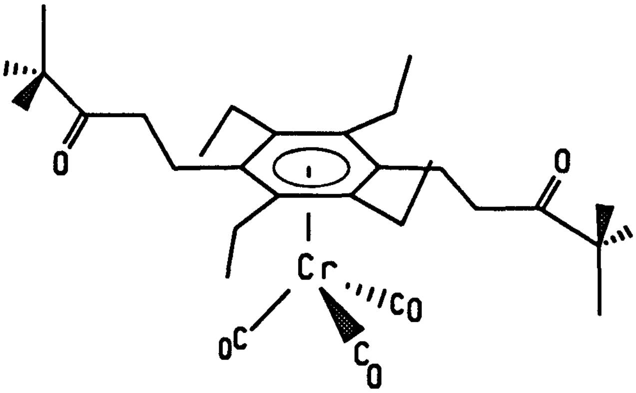
The barrier to rotation calculated from line shape fitting was determined to be ≈ 27 kJ/mol, lying very close to the experimental limit for direct observation of these processes on the NMR time-scale.

The most recent evidence for restricted tricarbonyl rotation was provided by Kilway and Siegel[109] when a 2:1 pattern for the carbonyl carbon was frozen out at 183K in [1,4-bis(4,4-dimethyl-3-oxopentyl)-2,3,5,6,-tetraethyl-benzene] tricarbonyl chromium(0), **36**. This corresponded to a barrier of 9.5 kcal/mol.



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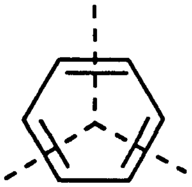
2.3 Electronically Controlled Restricted Rotation

As outlined already, much of the work on restricted tripodal rotation has concerned itself with sterically hindered arenes. Another approach involves determining whether or not the rotation could be slowed electronically. In other words, "can the bonding characteristics alone control the dynamic behaviour of the organometallic moiety?"

Hoffmann and his group have been studying these characteristics theoretically. They completely localized the pi-bonding in benzene to cyclohexatriene (one Kekule form) and examined its effect on the arene-chromium rotation barrier. Their calculations indicated barriers of 20 kcal/mol and 0 kcal/mol for the two extremes—completely localized, **37**, *vs* delocalized, **38**, bonding.



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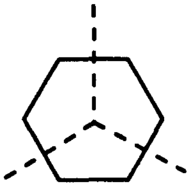

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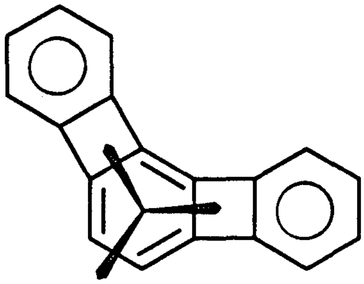
These extremes are trivial to obtain theoretically, but pose a challenge to the experimental chemist. Before 1988 there were no examples of restricted metal-arene rotations in an unencumbered neutral arene complex. Nambu and Siegel tested Hoffmann's predictions by synthesizing a molecule which gave the first example[110] of restricted rotation in a metal-arene complex due solely to the localized bonding of the metal to the arene π system. They obtained variable-temperature ^{13}C spectra of (terphenylene)$Cr(CO)_3$, **39**;



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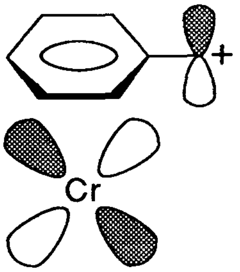
which displayed a 2:1 splitting of the carbonyl carbons at 170K, reflecting a rotational barrier of 9.3 kcal/mol. This value was 50% less than Hoffmann's theoretically calculated value. It was tentatively suggested[110] that barrier height correlates linearly with bond order, and since Hoffmann based his value on completely localized double and single bonds, the comparison between the experimental and calculated value was probably valid. Benzocyclobutanes are known to have considerable but not complete bond localization, consequently, their ability to slow tripodal rotation in this system suggests that the barrier is a good probe for the bonding in the central ring.

The capacity for the $Cr(CO)_3$ moiety to rotate depends on the strength of the bonding interaction between the metal and the ligand. Anything which strengthens this interaction should decrease the mobility of the organometallic unit. The formation of an aromatic chromium complex with a cation in the benzylic position allows electronic interaction between the metal and the ligand.

It is now well established that the $Cr(CO)_3$ group can stabilize an α-carbonium ion and there have been a number of papers detailing the synthesis of these complexed ions. A series of coordinated benzyl ($p\text{-}XC_6H_5CH_2^+$ X=H, Me, MeO)[52a,89] cumyl ($p\text{-}XC_6H_5CMe_2^+$ X=H, MeO)[89,113] and related carbonium ions ($p\text{-}XC_6H_5CHR^+$ X=H, Me, MeO, R=Me, Ph, $4\text{-}MeC_6H_4$)[86c,86d,89,112] have been prepared by protonating the corresponding complexed alcohols with acid (with a subsequent loss of water). The complexed ions have been characterized by their electronic, IR, ^1H and ^{13}C NMR spectra. A variety of solvent/acid mixtures have been employed such as H_2O/H_2SO_4, H_2O/CF_3SO_3H, CH_2Cl_2/HPF_6, CH_2Cl_2/CF_3SO_3H with reaction temperatures ranging from 25 to -60°C.

The pK_{R+} value (-logK of [cation + water $\rightleftharpoons$ alcohol + acid]) for the parent benzyl complex, $Cr(CO)_3C_6H_5CH_2+$, was determined spectroscopically to be -11.8.[52a] Since the pK_{R+} of the uncomplexed benzyl cation is <-17.3, there is evidence of significant stabilization of the carbonium ion upon complexation of the chromium tricarbonyl.

The mechanism by which $Cr(CO)_3$ stabilizes these carbonium ions has been debated. The initial mechanism (based on the analogous α-ferrocenyl carbonium ions) suggested that stabilization occurred via either a) by direct interaction between a filled chromium d orbital with a vacant p orbital on the carbenium ion, **40**, or b) metal-ring σ-π delocalization in which the α-carbenium ion is stabilized by π-conjugation with the ring, **41**.



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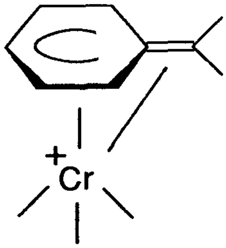


41

However, INDO[114] molecular orbital calculations on the free and complexed benzyl cation suggest that the stabilization arises by another mechanism, leading to an overall change in structure of the benzyl moiety. The stabilization occurs via back-donation from the chromium $d_{x^2-y^2}$ orbital into the non-bonding π-orbital of the benzyl ligand. The benzylic carbon is the most strongly affected since Ψ_n (the non-bonding orbital) has a high localization on this site (62%). The remainder of the back donation occurs equally into the ortho and para positions. A bending of the benzylic carbon towards the metal provides a more stable molecule; Albright et al.[111] finds an 11° bend is favoured, whereas Clack[114] suggests an angle of 40°.

If this electronic effect is significant, the metal would bind strongly to the ligand, slowing the rotation of the metal-arene bond, and the barrier to this rotation could then be found. Albright et al.[111] has calculated the barrier for $Cr(CO)_3(C_6H_5CH_2^+)$ to be 6.8 kcal/mol. It would be desirable to compare this result with an experimentally determined one, but it was reported[86e] that the complexed cation cannot be isolated, since rapid decomposition occurs when the complexed alcohol $(C_6H_5CH_2OH)Cr(CO)_3$ was treated with strong acid.

The synthesis of a more stable cationic complex was thus required. The next step would be to determine if indeed the presence of a cationic center was a strong enough electronic effect to result in slowed tripodal rotation.

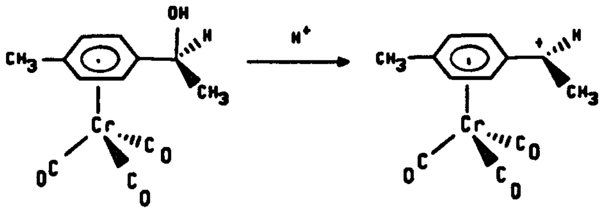
The incorporation of an electron-donating substituent (methyl, methoxy) onto the aromatic ring should provide a molecule better able to stabilize a cationic complex. Evidence of restricted rotation could then be obtained by monitoring the variable temperature ^{13}C NMR spectra of these complexes focusing primarily in the carbonyl region.

To that end, (4-methylbenzyl alcohol)Cr(CO)$_3$, **45**, (4-methoxybenzyl alcohol)-Cr(CO)$_3$, **43**, (3-methylbenzyl alcohol)Cr(CO)$_3$, **46**, (3-methoxybenzyl alcohol)-Cr(CO)$_3$, **44**, and (methyl-p-tolyl carbinol)Cr(CO)$_3$, **42**, were prepared, protonated and characterized.

2.4 Results and Discussion

2.4.1 Methyl-p-tolyl carbinol chromium tricarbonyl, **42**

In 1977 Ceccon[86d] and his co-workers reported the first relatively stable complexed benzyl cation when they characterized the p-tolylethyl tricarbonyl chromium cation, **47**.



42

47

At low temperature (-50°C) on a low-field instrument the authors claimed non-equivalence of the carbonyl resonance as evidenced by three signals in the carbonyl region. This was explained in terms of hindered rotation about the metal-arene bond. Once the $Cr(CO)_3$ tripod had stopped its rotation, the overall molecular symmetry would be lowered to C_1 and all three carbonyls would be in magnetically non-equivalent environments.

The authors were not able to estimate the activation energy of this rotation, nor did they provide any spectra for this system. It was decided, therefore, to repeat this experiment on a higher field NMR spectrometer to ensure that there was indeed complete non-equivalence of the carbonyl resonance, and that the three peaks were the real effect of hindered rotation and not an artifact.

The synthesis of this cation began with the formation of the complexed alcohol following a modification of the procedure outlined in the paper.[86d] The red-violet cation **47** was formed by protonation of the complexed alcohol, **42,** with triflic acid at -70°C. Variable-temperature ^{13}C NMR spectra were obtained on a 500 MHz spectrometer and the chemical shifts of the free alcohol, the complexed alcohol as well as the complexed cation are summarized in Table 2.1. Owing to the limited stability of the cation over a small temperature range, NMR spectroscopy was the favoured technique to study this cation. The ^{13}C NMR spectra at 125.8 MHz of cation **47** is shown as Figure 2.1, recorded at -60°C. The chemical shifts in this experiment are in agreement with the published values. As reported by Ceccon et al., the carbonyls have shown complete non-equivalence

TABLE 2.1

^1H NMR Data for (methyl-p-tolyl carbinol)$Cr(CO)_3$[a], **42**

Proton	Chemical Shift (ppm)[b]	Coupling Constant (Hz)
α-H	4.51 (q,1H)	$^3J=6.5$
α-Me	1.44 (d,3H)	$^3J=6.5$
H_o	5.67 (d,d,d,1H)	$^3J=6.4$, $^4J=1.7$
	5.50 (d,d,d,1H)	
H_m	5.24 (d,d,d,2H)	
p-Me	2.18 (s,1H)	

^{13}C Chemical Shifts (ppm) for (methyl-p-tolyl carbinol)$Cr(CO)_3$[a]

Carbon	Free Alcohol[b]	Complexed Alcohol[c]	Free Cation[b]	Complexed Cation[d], **47**
α-Me	25.2	25.2	25.4	16.7
α-C	70.4	68.2	218.0	127.3
C_1	143.2	115.0	139.2	106.2
$C_{2,6}$[e]	129.3	93.3	142.0	103.4
		92.3	152.9	107.0
$C_{3,5}$	125.3	93.6	133.8	101.4
		93.2	134.5	102.1
C_4	137.2	110.4	181.0	115.5
p-Me	21.2	20.6	24.7	21.0
CO	--	234.0	--	227.1 226.6 226.1

a) δ values relative to TMS in CD_2Cl_2 solution assuming an internal CH_2Cl_2 signal (5.32 ppm for proton, 53.8 ppm for carbon).

b) See also Reference 86d.

c) Recorded in solution at room temperature.

d) Recorded at -60°C in the presence of CF_3SO_3H.

e) Ortho and meta shifts may be reversed.

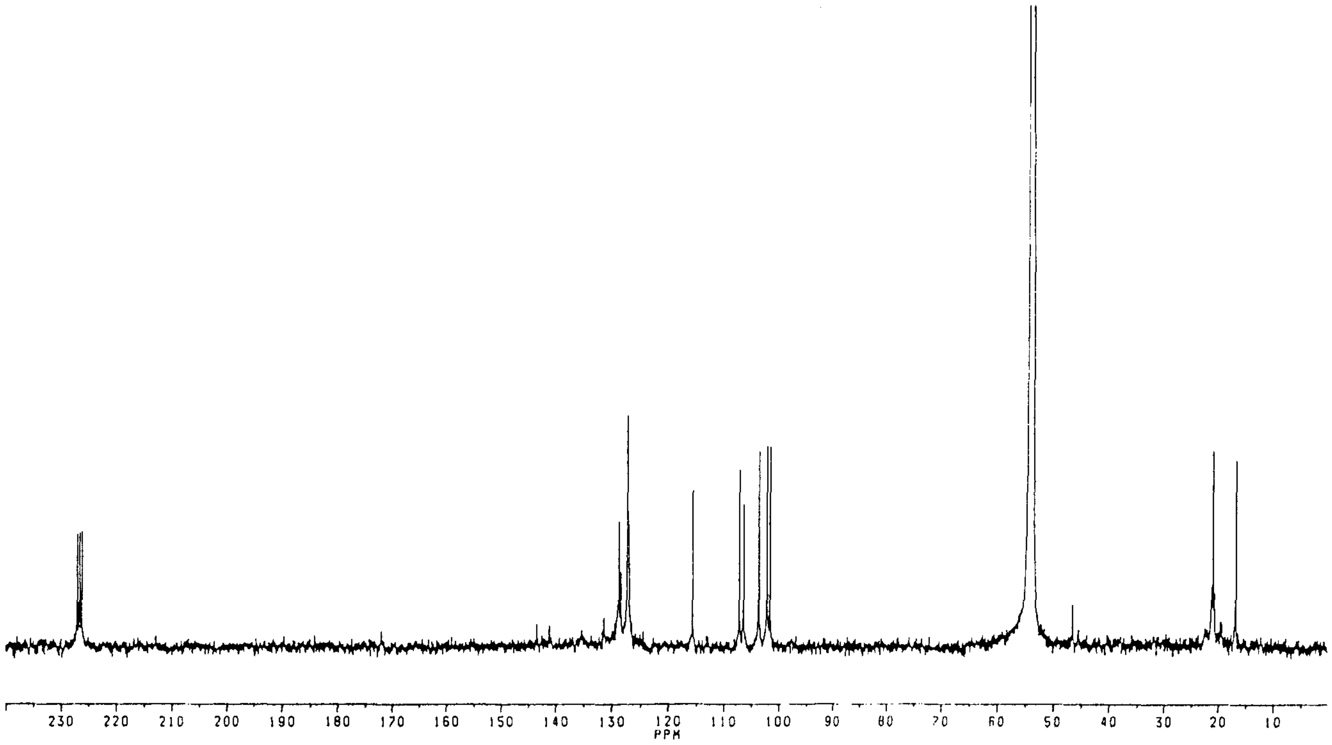


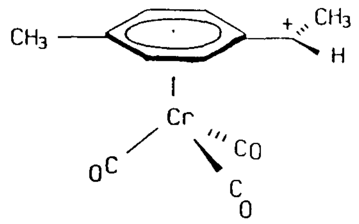
Figure 2.1: 125.8 MHz ^{13}C NMR spectrum of **47** recorded at -60°C in CD_2Cl_2.

at -60°C, providing evidence of electronically hindered $Cr(CO)_3$ rotation.

As there had been no previous attempt to ascertain the barrier to this rotation, a spectral simulation of the carbonyl region corresponding to a range of experimental temperatures was carried out. Figure 2.2 displays the decoalescence of the carbonyl resonace. Since the cation decomposed at the higher temperatures, a sharp resonance representing the interconversion of freely rotating carbonyls was not observed. The rates corresponding to each temperature were incorporated into an Arrhenius plot shown as Figure 2.3. Each data point shows the temperature (in °C) to the left and the rate constant (in s^{-1}) to the right. Evaluation of the slope revealed a rotational barrier of 8.8 kcal/mol. This value is well within the range of rotational barriers found in sterically hindered molecules. The results outlined above have confirmed the claim that the rotation of a $Cr(CO)_3$ tripod can be slowed on the NMR time-scale attributable solely to electronic interactions.

2.4.2 EHMO Calculations on the $(Benzyl)Cr(CO)_3^+$ Cation, **52**

The next step in this research was to understand the factors controlling the $Cr(CO)_3$ rotation, and to determine the conformation of the complex once the tripod had stopped. Mentioned previously was the work done by Hoffmann et al.[111] suggesting that the anti-eclipsed tricarbonyl conformation was energetically favoured over the syn-eclipsed. This is a result of the charge delocalization of the



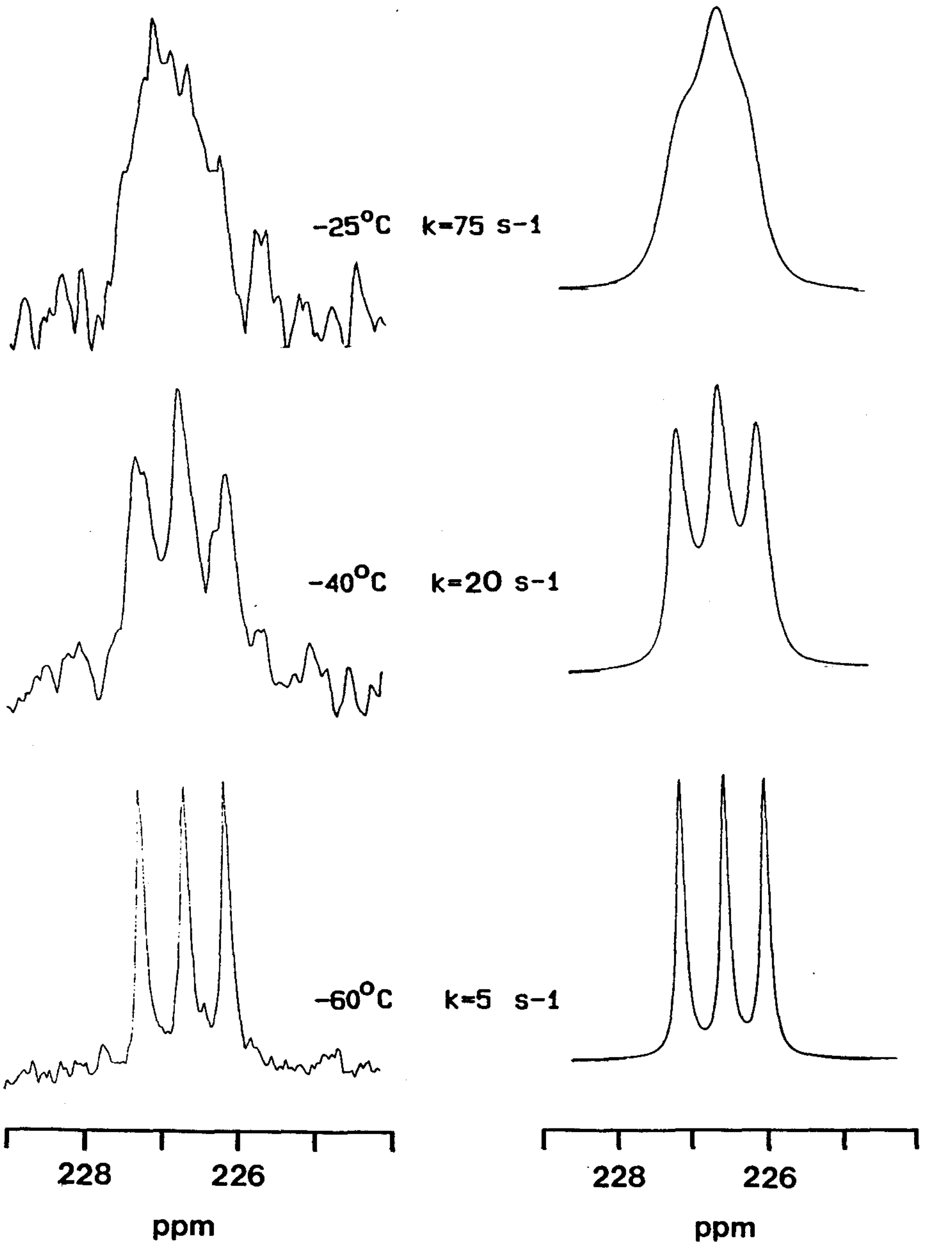


Figure 2.2: 125.8 MHz variable-temperature ^{13}C NMR solution spectra and the corresponding simulated spectra of **47**.

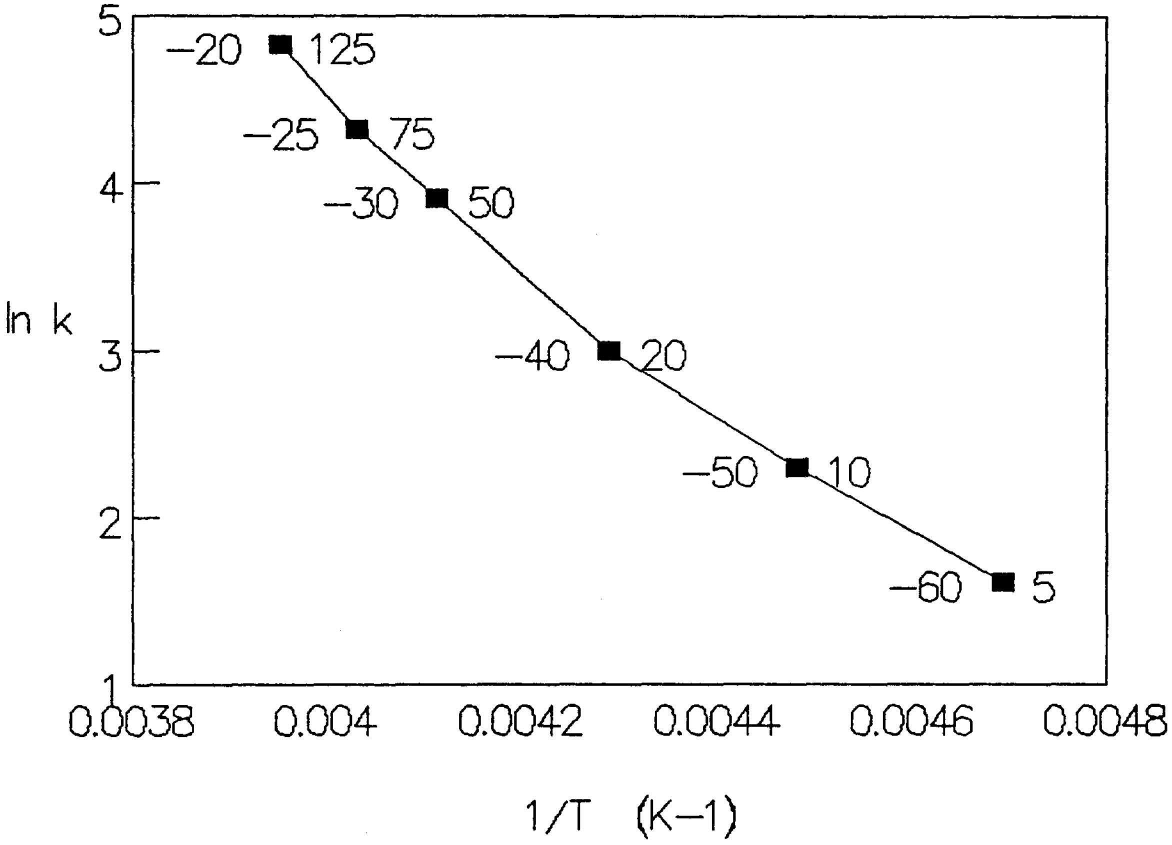


Figure 2.3:

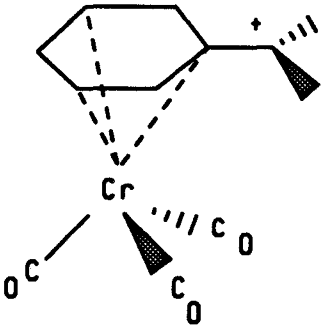
The Arrhenius plot of ln k *vs* 1/T for the (p-tolylethyl)Cr(CO)$_3^+$ cation, **47**.

cationic charge throughout the aromatic π-system. Table 2.2 outlines the cationic charge distribution in the (benzyl)Cr(CO)$_3^+$ complex, determined by our EHMO calculations.

Table 2.2 Carbon Atomic Charges for (benzyl)Cr(CO)$_3^+$, **52**

Atom	**Charge**
C(1) *ipso*	+0.12
C(2) *ortho*	+0.14
C(3) *meta*	+0.01
C(4) *para*	+0.11
C(5) *meta*	+0.01
C(6) *ortho*	+0.14
C(7) *benzyl*	+0.44

Clearly, the positive charge is built up on the α-carbon, and is localized onto the ortho and para positions, leaving carbons 1, 3 and 5 relatively electron-rich for the chromium to bind. Chromium orbitals are known to be arranged in an octahedral fashion. To maintain its octahedral environment, the metal is bound to C(1), C(3) and C(5), the carbonyl ligands are forced to eclipse carbons 2, 4 and 6.



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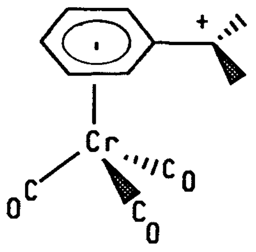
Thus the anti-eclipsed conformation, **53**, is energetically favoured when the tripod stops its rotation. The barrier to this rotation is the difference between the favoured conformation **54**, and the high energy conformation **55**.



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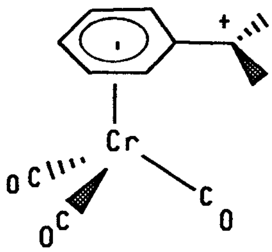


55

It cannot be forgotten, that the metal can stabilize the charge on the exocyclic carbon, causing a bend of the external bond towards the chromium. This bend lowers the overall energy of the system, in turn, raising the barrier to produce a more stable molecule. Figure 2.4 is a space-filling model of the (benzyl)$Cr(CO)_3^+$ cation. This view clearly illustrates the ability of the metal to aid in cation stabilization because of its proximity to the benzylic carbon. A slight bend of the carbon towards the metal center enhances the chromium 3d ↔ carbon 2p orbital interaction, resulting in an overall net energy loss.

Figure 2.5 graphically demonstrates the energy barrier that the (benzyl)$Cr(CO)_3^+$ molecule must surmount to achieve rotation of the tripodal ligand (one carbonyl is labelled * for clarity). The lowest energy conformation is the bent, anti-eclipsed conformation which then requires 0.2 kcal/mol to adopt the planar

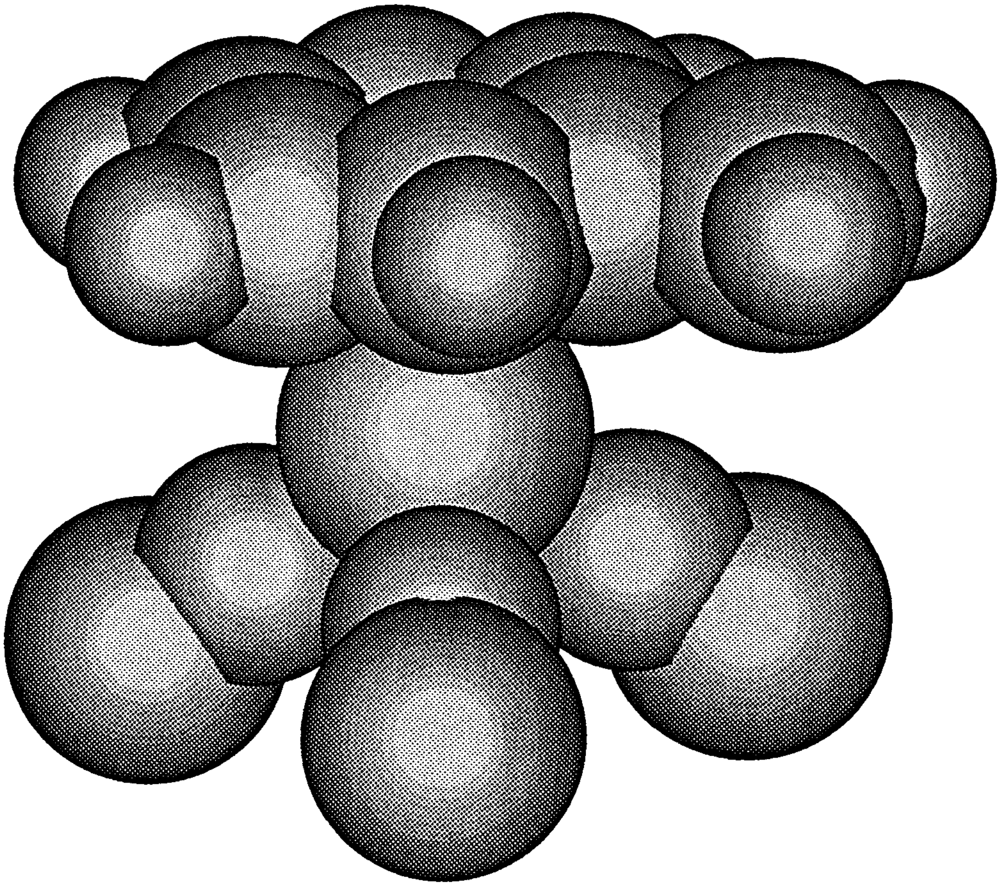


Figure 2.4:

Space-filling model of the (benzyl)Cr(CO)$_3^+$ cation, **52**, showing the proximity of the metal to the α-carbon.

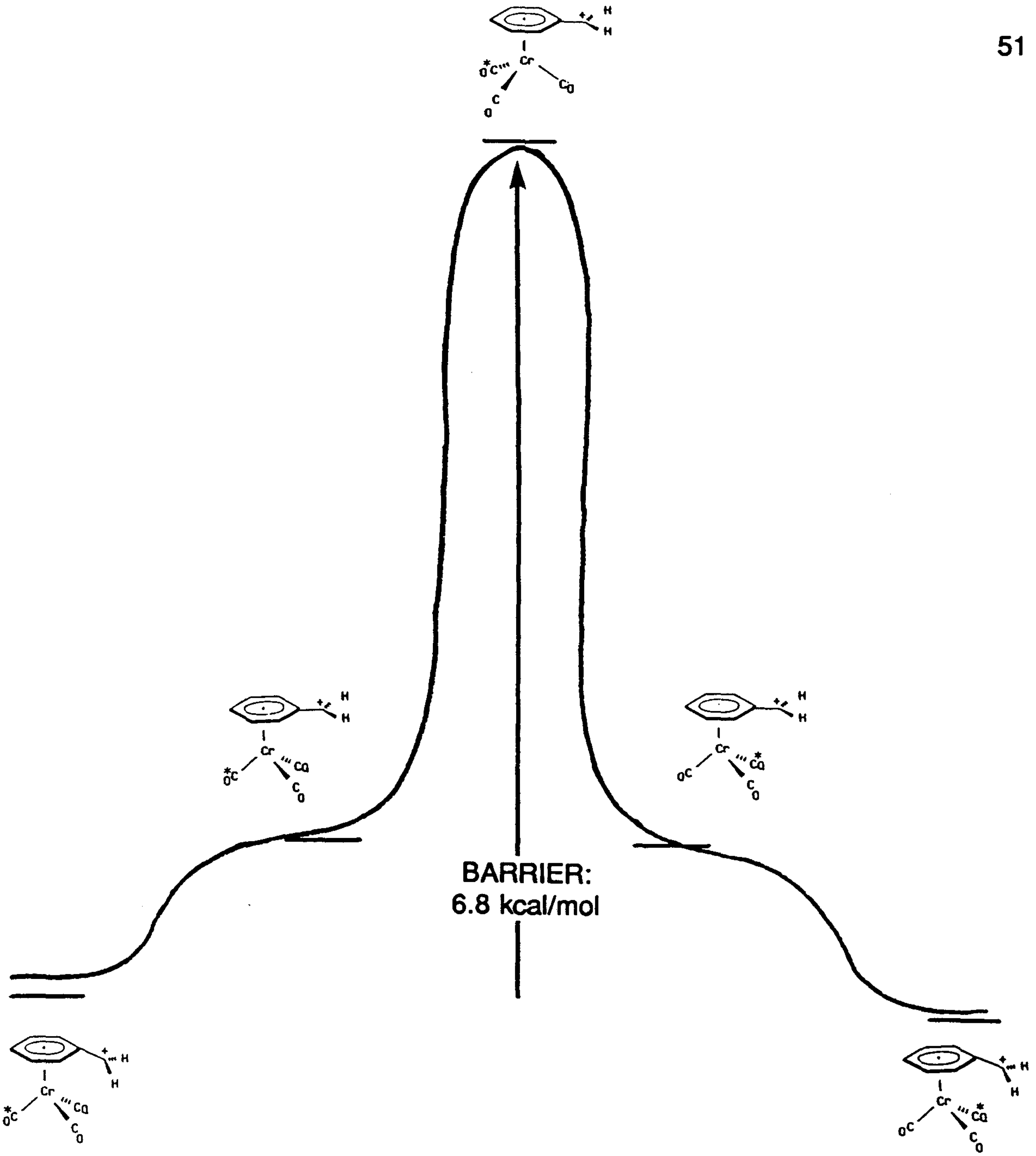


Figure 2.5: Calculated energy barrier to rotation for the (benzyl)Cr(CO)$_3$$^+$ cation, **52**.

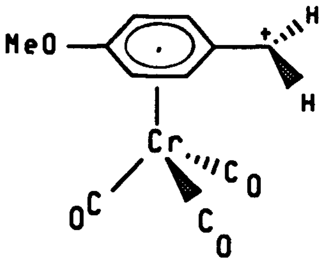
arrangement of the aromatic ligand. The tripodal ligand then rotates 120° about the metal-arene bond into the highest energy conformation with one carbonyl group lying directly beneath the benzylic substituent. It is the height of this barrier and the ability to surmount it which is determined in an NMR experiment. The tripod then rotates another 120°, and the benzylic carbon bends down to return to the lowest energy conformation; indistinguishable from its starting conformation. Kinetic theory utilizing the Boltzman distribution can be used to argue that the lifetime of the high energy conformer is actually negligible on the NMR time-scale, hence there is no contribution from this conformation in the spectra.

It has been shown that charge distribution on the arene ring localizes the bonding of the metal, therefore it should be possible to fix the geometry of the tripod if the proper conditions could be found. That is to say, anything which accentuates this charge localization should "lock" the $Cr(CO)_3$ tripod in place, raising the rotational barrier. The latter can be accomplished by adding a substituent to the arene ring.

2.4.3 An EHMO and NMR Study of Substituted (Benzyl)$Cr(CO)_3^+$ Complexes

As outlined in Chapter 1, a large number of X-ray crystal structures has been solved for substituted benzene chromium tricarbonyls (without the presence of a benzyl substituent). These studies have demonstrated that while the parent compound, (benzene)$Cr(CO)_3$, favours the staggered conformation, substitution of electron donating groups indicates the syn-eclipsed conformation is favoured, whereas the anti-eclipsed structure is found in complexes with electron-withdrawing substituents.

It was of interest in this study to determine the effect on tripodal rotation when both a cationic benzyl substituent as well as a second substituent were incorporated onto the arene ring of the complex. For example, if a methoxy group was situated para to the benzylic substituent, it would be expected to donate electrons into the arene π system resulting in the following resonance forms.



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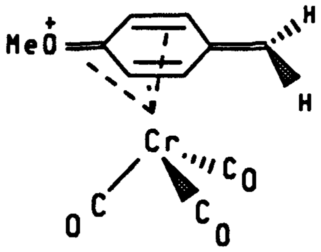

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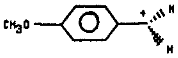
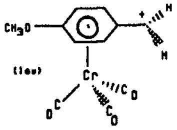
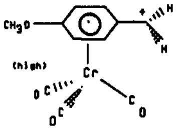
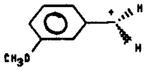
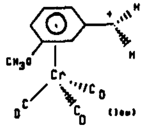
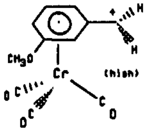
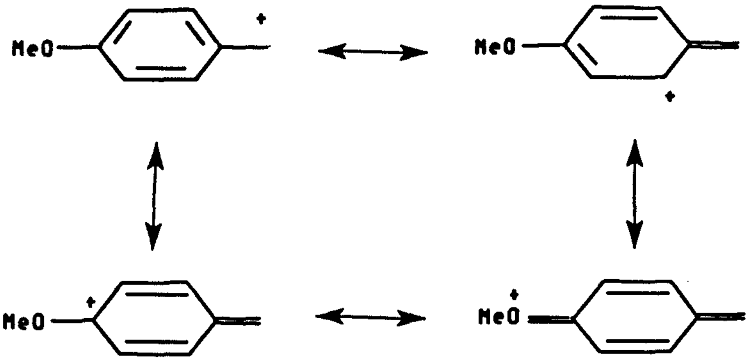
Given this resonance stability, it was proposed that the rotational barrier could be more easily determined in this molecule than the unsubstituted, very unstable, (benzyl)Cr(CO)$_3$$^+$ cation. To test this proposal, a series of EHMO calculations were done to examine and compare the charge localization on each carbon in the free and complexed 3-methoxybenzyl, **49**, and 4-methoxybenzyl, **48**, cations. These results are summarized in Table 2.3. The Table shows a comparison between the free cation and the two conformations of the complexed cation which are the lowest and highest energy conformers.

Focusing on the 4-methoxybenzyl cation complex, **48**, both the high and low

TABLE 2.3
Carbon Atomic Charges on the (3-Methoxybenzyl)Cr(CO)$_3^+$ and (4-Methoxybenzyl)Cr(CO)$_3^+$ cations

Compound	α-C	C_1 *ispo*	C_2 *ortho*	C_3 *meta*	C_4 *para*	C_5 *meta*	C_6 *ortho*	α-$\underline{C}H_3$	α-$\underline{O}$Me	Barrier
	0.265	0.087	0.103	-0.098	0.672	-0.078	0.102	0.323	-0.684	
	0.330	0.119	0.147	-0.063	0.612	-0.044	0.147	0.324	-0.728	
	0.471	0.157	0.089	0.005	0.569	0.024	0.088	0.324	-0.724	7.5 kcal/mol
	0.366	0.098	0.017	0.504	0.062	-0.023	0.080	0.323	-0.733	
	0.327	0.127	0.072	0.517	0.037	0.008	0.133	0.324	-0.741	
	0.497	0.167	0.017	0.576	-0.033	0.078	0.067	0.324	-0.739	5.1 kcal/mol

energy structures show positive charge build up on the benzylic and para carbons. This is consistent with the suggestion that the molecule has resonance stability in that it may delocalize the cationic charge through the π system onto the ortho and para positions.



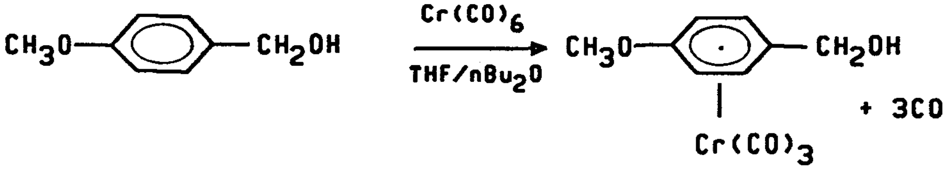
The localized positive charge on the ortho carbons and negative charge on the meta carbons is more pronounced in the lower energy conformation of **48**. The charge localization favours attachment of the chromium to the relatively electron-rich sites as in **53**; the octahedral arrangement of ligands about the metal center thus places the carbonyls under positions 2,4 and 6. The preferential attachment of the metal to the three carbons on the arene ring as a result of this charge localization, raises the barrier to $Cr(CO)_3$ rotation.

The energy difference between the high and low energy conformation was found to be 7.5 kcal/mol, which is the theoretical value for the rotational barrier in this molecule.

With the methoxy group situated para to the benzylic cation, the substituent has helped to increase the localization of cationic charge onto the ortho and para positions. It was of interest, therefore, to examine the case when the substituent effect counteracts the charge distribution pattern laid out by the cation at the benzylic position. Table 2.3 also shows the charge distribution of the free and complexed 3-methoxybenzyl cation, **49**, with its low and high energy complexed conformations. As expected, there is significant positive charge remaining at the benzylic position in all three cases, but there is substantial charge at the meta carbon where the methoxy group resides. The charge localization from the α-cation onto the ortho and para positions is again more pronounced in the lower energy conformation. The localization of charge, however, is not to the same extent as in cation **48**. As a result of incorporating an electron-rich substituent at the meta position, the metal has no tendency to bind specifically to the ortho and para positions. This suggests that there is less preference for the complex to adopt either geometry, and thus the tripod would be expected to rotate more readily. That is to say, the barrier to rotation in **49** would be lower than the barrier for **48**, with a greater number of molecules having sufficient energy to surmount the barrier. As a result, it should be more difficult to stop the rotation of the tripod under the same experimental conditions. The difference between the low and high energy conformations of (3-methoxybenzyl)Cr(CO)$_3^+$ was calculated to be 5.1 kcal/mol; this value is 2.6 kcal/mol less than the value for the (4-methoxybenzyl)-Cr(CO)$_3^+$ complex. Assuming the same chemical shift separations, the 3-methoxybenzyl cation complex would be expected to begin decoalescence at an even lower temperature because of the lower rotational barrier.

Although EHMO calculations play an informative role in defining and evaluating rotational barriers, it is of greater interest to find experimental proof of restricted $Cr(CO)_3$ rotation. To that end, both (4-methoxybenzyl alcohol)$Cr(CO)_3$ and (3-methoxybenzyl alcohol)$Cr(CO)_3$ were synthesized and protonated.

Initially, the respective free alcohol was heated under reflux in n-butyl ether/THF for four days with chromium hexacarbonyl.



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In both experiments, bright yellow crystals were obtained after purification of the crude product by flash column chromatography. The yields were modest, (4-MeO, 41% ; 3-MeO, 30%) typical for many of the reactions involving the coordination of $Cr(CO)_3$ to an arene ring. No attempt was made to maximize these yields. Both complexed alcohols displayed two IR peaks at 1890 and 1970 cm^{-1} which identify the terminal carbonyls on the $Cr(CO)_3$ tripod adopting local C_{3v} symmetry. Mass spectra of each complex show peaks at successive losses of 28 mass units from the molecular ion, confirming the presence of the $Cr(CO)_3$ on the aromatic ligand. Further conformation that the metal had complexed to the alcohol was provided by ^1H and ^{13}C NMR spectra, the results summarized in Tables 2.4

TABLE 2.4

^{1}H NMR Data for (4-methoxybenzyl alcohol)Cr(CO)$_3$[a], **43**

Proton	Chemical Shift (ppm)	Coupling Constant (Hz)
α-H	4.21 (s,2H)	
$H_{2,6}$ *ortho*	5.67 (d,2H)	$^3J_{2,3}$=7.0
$H_{3,5}$ *meta*	5.17 (d,2H)	
p-OMe	3.69 (s,3H)	
OH	2.75 (br.s,1H)	

^{13}C Chemical Shifts (ppm) for (4-methoxybenzyl alcohol)Cr(CO)$_3$[a]

Carbon	Free Alcohol	Complexed Alcohol[b]
α-C	64.5	62.8
C_1	114.0	105.2
$C_{2,6}$ *ortho*	128.8	94.9
$C_{3,5}$ *meta*	128.8	78.4
C_4 *para*	133.8	143.6
p-MeO	55.4	55.6
CO	--	233.7

a) δ values relative to TMS in CD_2Cl_2 solution assuming an internal CH_2Cl_2 signal (5.32 ppm for proton, 53.8 ppm for carbon).

b) Recorded in solution at room temperature.

TABLE 2.5

^1H NMR Data for (3-methoxybenzyl alcohol)$Cr(CO)_3$[a], **44**

Proton	Chemical Shift (ppm)	Coupling Constant (Hz)
α-H	4.55 (s,2H)	
H_2 *ortho*	5.27 (s,1H)	
H_6 *ortho*	5.66 (d,d,1H)	
H_5 *meta*	5.15 (d,d,1H)	$^3J_{4,5}={}^3J_{5,6}=6.8$
H_4 *para*	4.99 (d,1H)	
m-OMe	3.73 (s,3H)	
OH	2.08 (br.s,1H)	

^{13}C Chemical Shifts (ppm) for (3-methoxybenzyl alcohol)$Cr(CO)_3$[a],

Carbon	Free Alcohol[b]	Complexed Alcohol[c]	Complexed Cation[d], **49**
α-C	64.7	63.5	144.7
C_1	142.9	114.4	106.3
C_2 *ortho*	112.4	77.6	86.3
C_6	119.2	84.6	89.7[e]
C_3 *meta*	159.9	144.2	116.0
C_5	129.4	95.8	99.5,89.1
C_4 *para*	113.1	78.1	
m-MeO	55.1	56.2	57.9
CO	--	234.0	226.9 broad at -100°C

a) δ values relative to TMS in CD_2Cl_2 solution assuming an internal CH_2Cl_2 signal (5.32 ppm for proton, 53.8 ppm for carbon).

b) See also Reference 133.

c) Recorded in solution at room temperature.

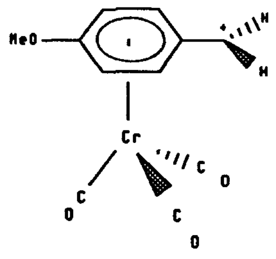
d) Recorded at -80°C in the presence of CF_3SO_3H.

e) Ortho and meta shifts may be reversed.

and 2.5.

Confident that the $Cr(CO)_3$ had complexed to the alcohols, the protonation to form the benzylic cations was then carried out. Addition of CF_3SO_3H to a filtered yellow solution of the respective complexed alcohol resulted in the formation of a red-violet solution of the cation.

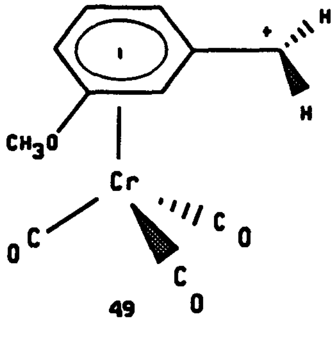
Several attempts were made to obtain variable-temperature 125.8 MHz ^{13}C NMR spectra of the (4-methoxybenzyl)$Cr(CO)_3^+$ cation. The solution containing the freshly made cation rapidly decomposed with the evolution of CO gas to form a green solution. As a result, the NMR spectra in the arene region of the cationic complex could not be satisfactorily obtained. There was, however, a noticeable change in the carbonyl region upon protonation of the (4-methoxybenzyl alcohol)$Cr(CO)_3$ complex. At low temperature (-70°C) a 2:1 splitting of the carbonyl carbon was found. This can only be explained in terms of a stationary tripod on the molecule adopting C_s symmetry with the carbonyls resting in the lower energy conformation, **58**.



58

The plane of symmetry passing through the benzylic carbon as well as carbons 1 and 4, renders two of the carbonyls chemical shift equivalent and clearly different from the third.

Fortunately, the protonation of (3-methoxybenzyl alcohol)$Cr(CO)_3$ was much more successful, and the chemical shifts of the cation could be determined. Figure 2.6 displays the 125.8 MHz ^{13}C NMR spectrum of the $(3\text{-}MeOC_6H_4CH_2)Cr(CO)_3^+$ cation at -70°C. At this temperature there is still a single resonance at 226.9 ppm in the carbonyl region, indicating that the tripod has still not stopped its rotation. This result agrees with the postulate that a lower coalescence temperature would be found for the rotation of **49** as compared to **48** which had already decoalesced to 2:1 at -70°C. Even at -100°C the carbonyl peak is just beginning to decoalesce, the broadened, decreased intensity peak is shown as the inset to Figure 2.6. Unfortunately, the sample froze out of solution at lower temperatures. As a result of complete cessation of tricarbonyl rotation, one expects to see three signals for the carbonyl carbons in accordance with a molecule possessing C_1 symmetry. All three carbonyls would be magnetically non-equivalent.



49

Closer examination of the chemical shifts of $(4\text{-}MeOC_6H_4CH_2)Cr(CO)_3^+$ reveal similar characteristics to those reported by Ceccon et al.[86d] Upon protonation,

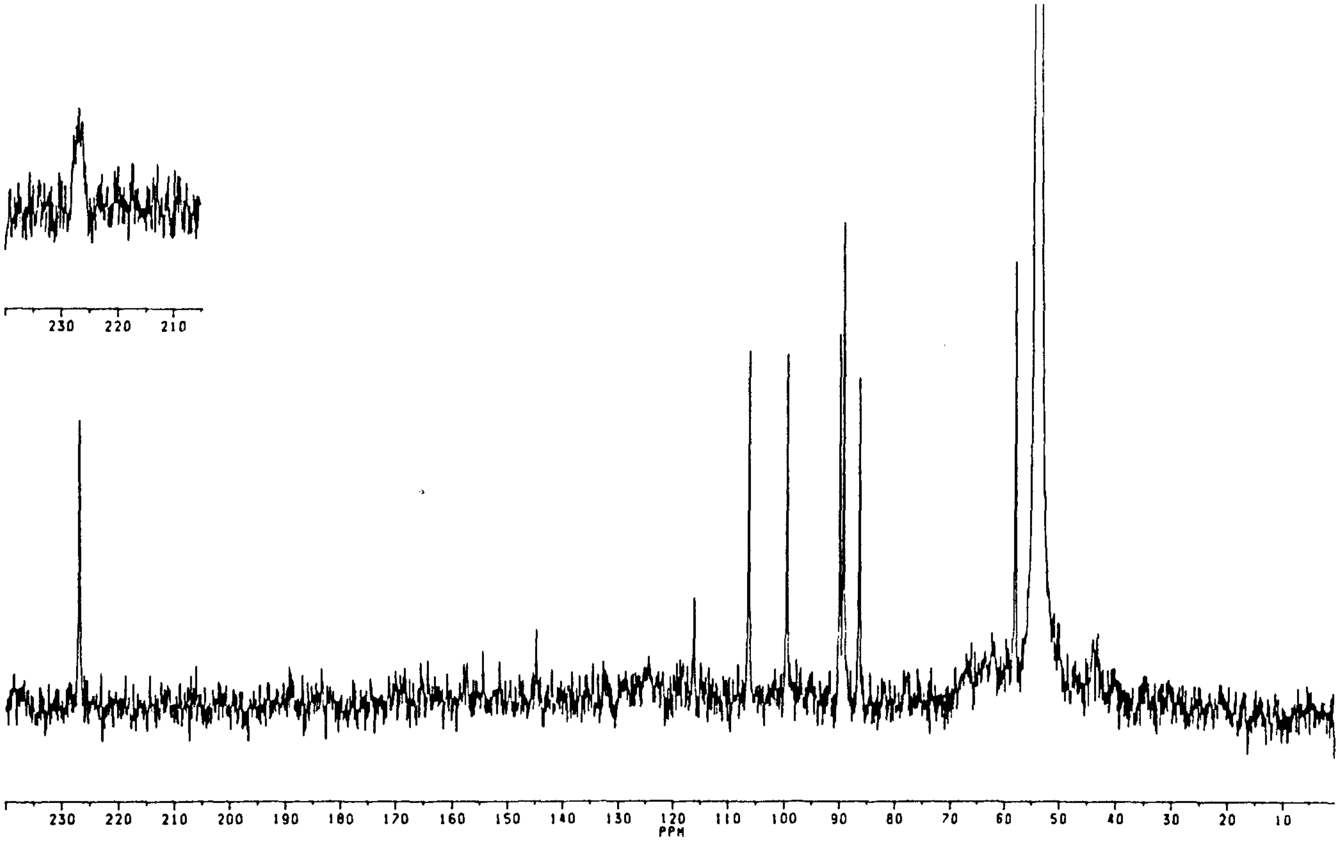


Figure 2.6: 125.8 MHz ^{13}C NMR spectrum of (3-Methoxybenzyl)Cr$(CO)_3H^+$, 49, recorded at -70°C. The -100°C spectrum shows the start of decoalescence.

the carbonyl resonance has shifted upfield from 234.0 ppm to 226.9 ppm. This upfield shift may upon first glance appear contradictory to what is well known about the correlation between charge density and chemical shift.

A great deal of research has examined the change in carbon chemical shifts when a molecule becomes positively or negatively charged. There is a general consensus that the chemical shifts of carbons in ionic complexes are indicative of the extent of charge delocalization, and of ion stability, since they are correlated with electron density. Evidence of a metal having the ability to stabilize an α-positive charge has been explained by comparing the chemical shifts in the free and complexed cations. As the positive charge increases on a carbon, its resonance is found to shift downfield. Olah et al.[115] while studying phenyl carbenium cations found that the shifts of C-4 were correlated linearly with charge much better than the ipso, ortho and meta carbon atoms. Though Olah and many others place a great deal of confidence in the importance of $\Delta\delta$ values, one must be cautious and remember that the correlation between charge density and chemical shift may vary from series to series.

The prevailing opinion is that the charge density at the carbonium center is the central factor controlling its shielding.[116] It is important the recall, however, that ^{13}C chemical shifts are not based solely on charge density at the carbon atom, but also on hybridization as well as anisotropic, paramagnetic and diamagnetic effects. The fact that the carbonyl resonance in **49** has shifted upfield suggests that charge localization is not the only factor that must be considered.

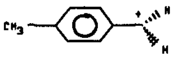
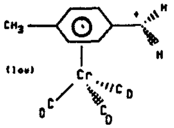
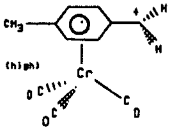
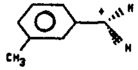
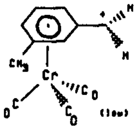
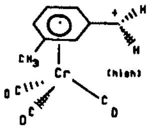
Interestingly, the opposite occurs in a similar system when a benzyl anion is formed. The change in carbonyl chemical shift of the anion is found to be equal but of opposite sign to the cation,[85g] shifting downfield from 233.8 to 237.4 ppm upon ionization.

Although the focus of this research was in the carbonyl region of the ^{13}C NMR spectra, examination of the aromatic chemical shifts cannot be ignored. Evidence that the (3-methoxybenzyl)$Cr(CO)_3^+$ cation was the only molecule in solution was provided by the arene carbon resonances. As with the cation formed initially by Ceccon, the aromatic carbons were all found to shift downfield upon protonation, with no evidence of any remaining unprotonated alcohol. No attempt was made to assign unambiguously the primary aromatic carbons. The methoxy-substituted carbon was found to shift upfield from 144.2 ppm to 116.0 ppm, providing evidence of the positive charge as described in the corresponding EHMO calculation. The methoxy carbon was shifted slightly downfield (1.7 ppm) indicating little effect from the benzylic charge.

To compare these results with Ceccon's early work, and to obtain more complete information about the characteristics of electronically hindered chromium tricarbonyl rotation, EHMO calculations on two additional cations were undertaken.

Table 2.6 details the charge distribution for the free cation, as well as the low and high energy conformation for the (3-methylbenzyl)$Cr(CO)_3^+$, **51**, and (4-methylbenzyl)$Cr(CO)_3^+$, **50**, cations. These data are in excellent agreement with the results generated from the 3-methoxy and 4-methoxy substituted benzyl cation complexes. One expects to see similar results even though the methyl group will

TABLE 2.6
Carbon Atomic Charges on the (3-Methylbenzyl)$Cr(CO)_3^+$ and (4-Methylbenzyl)$Cr(CO)_3^+$ cations

Compound	α-C	C_1 *ispo*	C_2 *ortho*	C_3 *meta*	C_4 *para*	C_5 *meta*	C_6 *ortho*	α-$\underline{C}H_3$	Barrier
	0.336	0.091	0.113	-0.050	0.244	-0.050	0.109	-0.075	
	0.337	0.123	0.145	-0.012	0.192	-0.014	0.144	-0.083	
	0.493	0.162	0.086	0.058	0.136	0.057	0.083	-0.081	6.1 kcal/mol
	0.370	0.095	0.077	0.068	0.122	-0.028	0.105	-0.076	
	0.332	0.123	0.119	0.093	0.089	0.004	0.141	-0.081	
	0.496	0.164	0.059	0.159	0.020	0.075	0.076	-0.083	6.8 kcal/mol

not donate electrons into the system to the same extent as the methoxy group.

Focusing on the (4-methoxybenzyl)$Cr(CO)_3^+$ cation, again there is significant charge localized onto the ipso and benzylic carbons as expected, and the low energy conformation has the ortho and para positions more positively charged than in the high energy conformation. At the same time, both the meta positions in the low energy conformation are negatively charged. Thus the octahedral environment of chromium whereby it binds to carbons 1, 3 and 5 and projects the carbonyls below carbons 2, 4, and 6 is again the most stable conformation. The energy difference between the two conformations was calculated to be 6.1 Kcal/mol which, as discussed earlier, is the barrier to tripodal rotation.

Returning to Table 2.6, the values calculated for (3-methylbenzyl)$Cr(CO)_3^+$ are now not surprising. The ortho positions in both conformations have significant positive charge as well as at carbon 1 and the benzylic carbon in the low energy complex. A 6.8 kcal/mol barrier has been calculated for the rotation of the tricarbonyl moiety in this cation. Compared to a value of 6.1 kcal/mol in the (4-methylbenzyl)$Cr(CO)_3^+$ and 6.8 kcal/mol in the unsubstituted (benzyl)$Cr(CO)_3^+$, there does not appear to be a significant change in the barrier when the benzyl cation is substituted with a methyl group at either the para or meta position. Previously, the different decoalescence temperatures of the para-methoxy and meta-methoxy substituted cation complexes provided evidence for the 2.6 kcal/mol difference in their calculated rotational barriers. As there is no significant difference in the calculated rotational barriers for the 3-methyl and 4-methyl complexes, the decoalescence temperatures were expected to be nearly identical in the NMR experiment.

The next stage of this research set out to determine the experimental rotational barriers of the two cations, under the assumption that it was possible to stop their rotations on the NMR time-scale.

The (3-methylbenzyl alcohol)$Cr(CO)_3$ and (4-methylbenzyl alcohol)$Cr(CO)_3$ complexes were first synthesized, and then protonated following standard procedures to form the desired cations.

Characterization of the complexed alcohols by IR and mass spectral techniques confirmed the presence of the $Cr(CO)_3$ moiety, as described earlier for the complexes **43** and **44**. Although the yields of the products were low, enough of each pure product was isolated so that NMR spectra of the protonated complexes could be obtained.

Protonation (by acidification with CF_3SO_3H) of a CD_2Cl_2 solution of each complexed alcohol at -70°C was successful in the production of a red-violet solution for both cations.

The 125.8 ^{13}C NMR spectra of the (4-methylbenzyl)$Cr(CO)_3^+$ cation recorded at -70°C is displayed as Figure 2.7. The chemical shifts of the free alcohol, the complexed alcohol, in addition to the $(4\text{-}MeC_6H_4CH_2)Cr(CO)_3^+$ cation are listed in Table 2.7. Although this cation appeared to be almost as unstable as the (4-methoxybenzyl)$Cr(CO)_3^+$ cation, there was sufficient time to obtain chemical shift information about the system before it decomposed. On Figure 2.7 the decoalescence of the carbonyl resonance to a 2:1 pattern at 226.1 ppm and 225.2

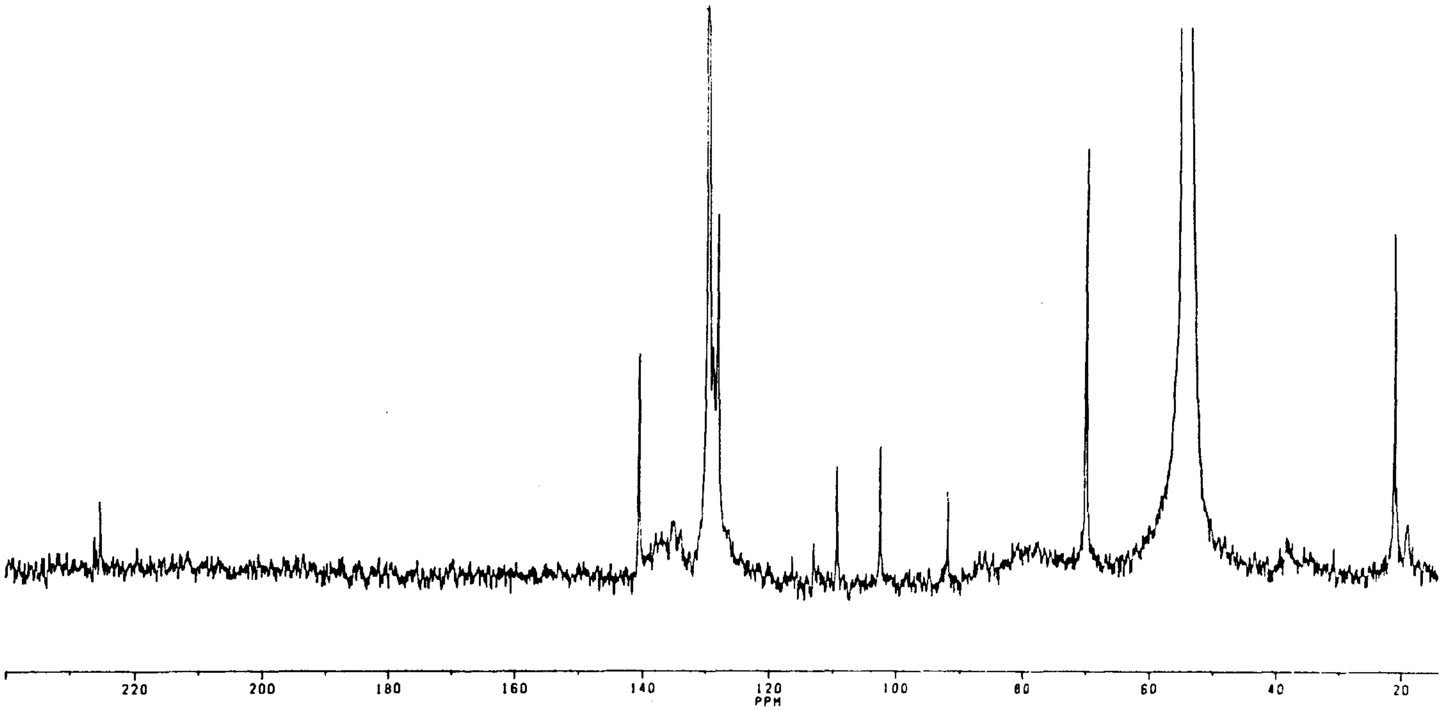


Figure 2.7: 128.5 MHz ^{13}C NMR spectrum of (4-Methylbenzyl)$Cr(CO)_3^+$, **50**, recorded at -70°C showing a 2:1 splitting of the carbonyl carbons.

TABLE 2.7

^{1}H NMR Data for (4-methylbenzyl alcohol)$Cr(CO)_3$[a], **45**

Proton	Chemical Shift (ppm)	Coupling Constant (Hz)
α-H	4.34 (s,2H)	
$H_{2,6}$ *ortho*	5.53 (d,2H)	^3J_o=6.5
$H_{3,5}$ *meta*	5.26 (d,2H)	^3J_o=6.5
p-Me	2.17 (s,3H)	

^{13}C Chemical Shifts (ppm) for (4-methylbenzyl alcohol)$Cr(CO)_3$[a], **45**

Carbon	Free Alcohol[b]	Complexed Alcohol[c]	Complexed Cation[d], **50**
α-C	64.8	63.2	140.5
C_1	138.5	109.5	91.7
$C_{2,6}$ *ortho*	127.1	93.7	102.3[e]
	127.1	93.7	102.3
$C_{3,5}$ *meta*	129.1	93.7	109.1[e]
	129.1	93.7	109.1
C_4 *para*	137.6	109.8	113.0
p-Me	21.0	20.6	21.0
CO	--	233.8	225.2[1], 226.1[2][f]

a) δ values relative to TMS in CD_2Cl_2 solution assuming an internal CH_2Cl_2 signal (5.32 ppm for proton, 53.8 ppm for carbon).

b) See also Reference 133.

c) Recorded in solution at room temperature.

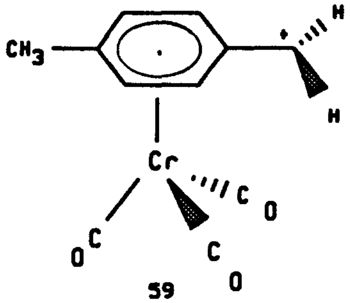
d) Recorded at -70°C in the presence of CF_3SO_3H.

e) Ortho and meta shifts may be reversed.

f) Intensities in parentheses.

ppm provides further evidence of electronically hindered rotation about the metal-arene bond.

As with the para-methoxy cation, this splitting can only describe a stationary tripod on the molecule adopting the lowest energy conformation, **59**, and C_s molecular symmetry.



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Again, because of the presence of the mirror plane, two of the carbonyls are magnetically equivalent, though different from the third. As expected, the spectrum looks very similar to Figure 2.1, the spectrum for the (p-tolylethyl)$Cr(CO)_3^+$ cation. These molecules differ only in that the latter has a methyl group on the benzylic carbon. In fact, this cation was initially synthesized in order to make this very comparison.

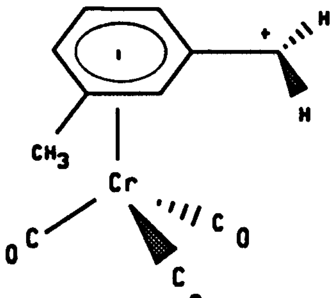
It is well known that the stability of cations follows the order 3°>2°>1°. The p-tolylethyl cation is a secondary cation which has a $Cr(CO)_3$ unit available to accept positive charge; providing a certain degree of stability. The 4-methylbenzyl cation, however, is a primary cation, which needs as much help from the metal as it can get to remain stable. The unsubstituted (benzyl)$Cr(CO)_3^+$ is known to be very unstable, thus it was interesting to examine the ability of the metal to aid in a variety of benzylic cations.

A direct comparison of the variable-temperature ^{13}C NMR spectra between the secondary and primary cation shows the extent of this stabilization. Since the structures of these two molecules are almost identical, a comparison of the coalescence temperatures may provide insight into the extent of metal stabilization. Complete decoalescence of the carbonyls on the secondary cation occurred at -60°C as compared to -70°C for the primary cation. The expectation was that as the primary cation required more assistance from the metal, the bonding interaction would increase, resulting in a decrease in the rotational ability of the $Cr(CO)_3$ tripod. If the tripod was held in place due to the stronger metal-carbon bond in the 1° as compared to the 2° cation, the decoalescence temperature should be higher in the 1° case. On the contrary, however, the secondary cation was found to decoalesce sooner, suggesting that decoalescence temperature cannot solely explain the mechanism of metal-cation stabilization. Unfortunately, ^{13}C NMR spectra could not be obtained over a range of temperatures due to the decomposition of the cation, so this first approximation of a correlation between decoalescence temperature and 1° vs 2° metal stabilization is tenuous at best.

Once the information regarding carbonyl rotation was obtained from the ^{13}C NMR spectra, the assignment of the aromatic carbons was of less importance. Although no attempt was made to unambiguously assign each peak, the pattern of the change in chemical shift was in agreement to that of the methyl-p-tolyl cation complex.

The α-carbon was seen to shift quite far downfield ($\Delta\delta_{\text{alcohol-ion}}$=77.3 ppm) whereas the ipso carbon shifted upfield (7.8 ppm). As in previously synthesized cations, the carbonyl carbon in (4-methylbenzyl)$Cr(CO)_3^+$ appeared ≈ 8 ppm upfield from its original position, which insured that it was the cation, not the unprotonated alcohol under investigation.

Finally, the ^{13}C NMR of the protonated (3-methylbenzyl alcohol)$Cr(CO)_3$ complex, recorded at 125.8 MHz at -60°C, can be viewed on Figure 2.8. Relevant chemical shifts for the complex can be found in Table 2.8. At -60°C the tripod begins to coalesce, evidenced by a broadening of the single peak at 224.0 ppm, but is frozen out at -90°C in a 2:1 pattern at 225.2 ppm and 225.9 ppm. Examination of the lowest energy conformation of the (3-methylbenzyl)$Cr(CO)_3^+$ cation suggests that as a result of the C_1 symmetry adopted by the complex, **60,** the carbonyls should all be in different environments, displaying 3 peaks in the carbonyl region.



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The peak with an intensity of two represents two non-equivalent carbonyls which happen to resonate at the same chemical shift; this is not an uncommon

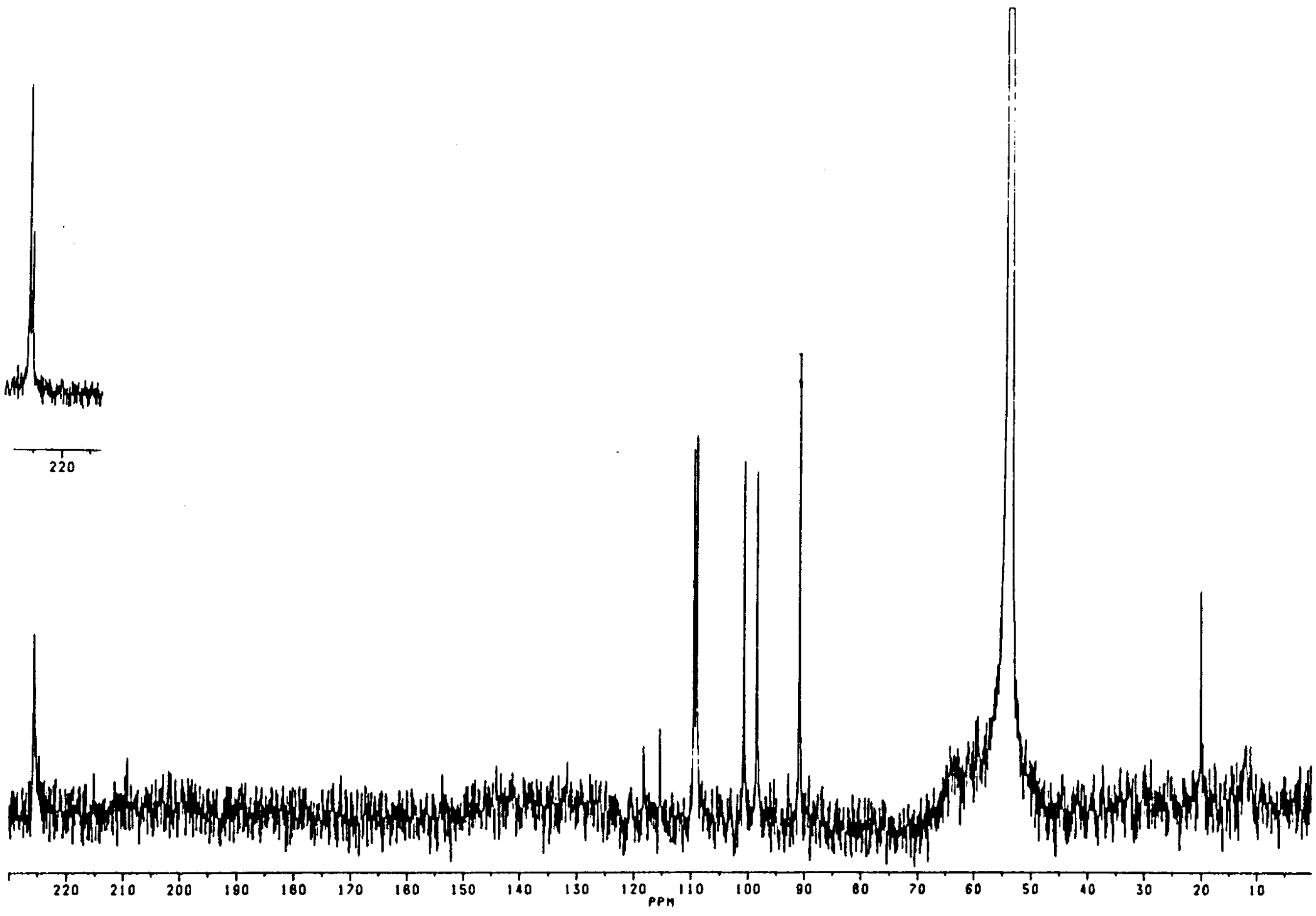


Figure 2.8: 125.8 MHz ^{13}C NMR spectrum of (3-Methylbenzyl)Cr$(CO)_3^+$, **51**, recorded at -60°C showing one peak for the carbonyl carbon. The -100°C spectrum shows a 2:1 splitting in the carbonyl region.

TABLE 2.8

^1H NMR Data for (3-methylbenzyl alcohol)$Cr(CO)_3$[a], **46**

Proton	Chemical Shift (ppm)	Coupling Constant (Hz)
α-H	4.46 (d,2H)	$^3J=5.8$
H_2 *ortho*	5.28 (s,1H)	
H_6 *ortho*	5.17 (d,1H)[b]	$^3J_o=6.3$
H_5 *meta*	5.53 (d,d,1H)	$^3J_o=6.3$
H_4 *para*	5.25 (d,1H)[b]	$^3J_o=6.3$
p-Me	2.20 (s,3H)	

^{13}C Chemical Shifts (ppm) for (3-methylbenzyl alcohol)$Cr(CO)_3$[a], **46**

Carbon	Free Alcohol	Complexed Alcohol[c]	Complexed Cation[d], **46**
α-C	65.0	63.5	118.0
C_1	141.6	113.6	90.6
$C_{2,6}$ *orthO*	128.4, 128.7	92.6, 95.3	109.3, 108.8[e]
C_3 *meta*	138.4	110.8	115.2
$C_{5,4}$ *m,p*	124.4, 128.1	92.2, 88.8	100.6, 98.6[e]
p-Me	21.5	20.8	20.7
CO	--	224.0	225.2[1], 225.9[2][g]

a) δ values relative to TMS in CD_2Cl_2 solution assuming an internal CH_2Cl_2 signal (5.32 ppm for proton, 53.8 ppm for carbon).

b) Ortho and para shifts may be reversed.

c) Recorded in solution at room temperature.

d) Recorded at -90°C in the presence of CF_3SO_3H.

e) Ring carbons are not unambiguously assigned.

f) Ortho and para shifts may be reversed.

g) Intensities in brackets.

phenomenon in organometallic carbonyls.

Again the carbonyl carbons were found to shift upfield by ≈ 9 ppm and the remaining carbons behaved in a fashion similar to the four other cations prepared previously, hence there was no doubt that the cation had indeed been formed. Assignments of the cationic carbons was based by comparison to spectra obtained in earlier experiments. No attempt was made to further identify the cation. The cation was sufficiently stable to obtain a series of spectra over a limited temperature range and a rotational barrier could then be calculated. The coalescence of the two carbonyl peaks were simulated and these spectra are compared in Figure 2.9. With the aid of an Arrhenius plot, the rotational barrier was calculated to be ≈ 10 kcal/mol.

For many years researchers have attempted to find evidence of restricted chromium tricarbonyl rotation on the NMR time-scale. The great body of research involved sterically hindering arenes to facilitate slowed rotation. The effort in this work focused on electronically hindering $Cr(CO)_3$ rotation. By examining the low-temperature NMR behaviour of (p-tolylethyl)$Cr(CO)_3^+$, (4-methoxybenzyl)-$Cr(CO)_3^+$, (3-methoxybenzyl)$Cr(CO)_3^+$, (4-methylbenzyl)$Cr(CO)_3^+$ and (3-methylbenzyl)$Cr(CO)_3^+$, it has been clearly shown that chromium tricarbonyl rotation can be slowed due solely to electronic interactions between the metal and the arene ring, without the necessity for steric hinderance.

A number of factors controlling this rotation have been suggested. The geometry of the molecule, the position of the carbonyls, the effect and position of a substituent as well as the 1° vs 2° character of the cation have played an

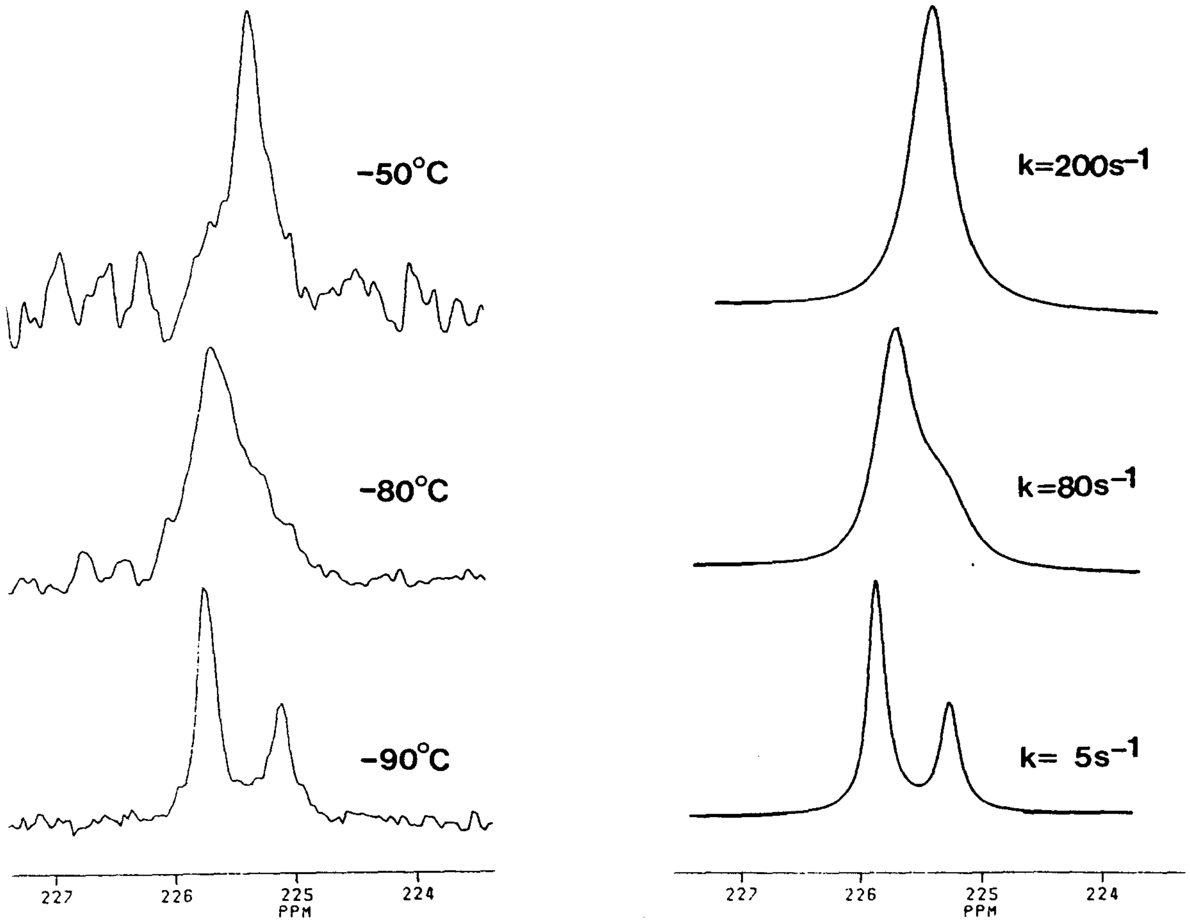
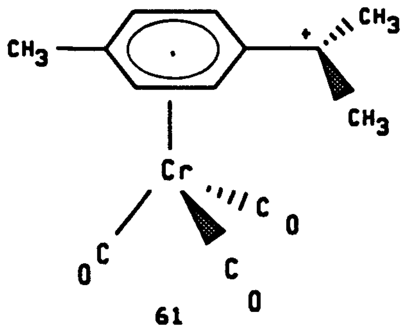


Figure 2.9: 125.8 MHz variable-temperature ^{13}C NMR solution spectra and the corresponding simulated spectra of (3-methylbenzyl)Cr(CO)$_3^+$, **51**.

important role in the understanding of the $Cr(CO)_3$ rotational barrier.

2.5 Future Work

A follow up to this work could involve the study of the variable-temperature spectra of the tertiary cation, **61**, shown below.



61

It would be of interest to determine if the 3° cation requires less stabilization from the metal than the 2° or 1° cations, as reflected in the rotational barriers for each complex. EHMO calculations on each cation could provide a theoretical answer to this question.

Secondly, interaction of the metal with the benzylic position could also be examined by a different approach. By incorporating a $W(CO)_3$ unit onto a benzylic cation, a long-range coupling between the tungsten and the α-hydrogens could provide evidence of metal-cation interaction.

Finally, it would be interesting to examine the effect of placing a boron at the benzylic position. Boron has an empty 2p orbital which may interact with an electron-rich metal, and may provide insight into the solid state structures of these complexes, in that the boron complex would be expected to be a stable, neutral molecule. The neutral molecule could then be analyzed by X-ray diffraction techniques. Benzyl cation complexes decompose far too quickly to be characterized in this manner, and thus the extent of the benzylic carbon bending towards the metal cannot be directly observed.

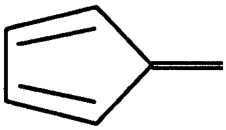
CHAPTER THREE

ROTATIONAL BARRIERS IN SUBSTITUTED FULVENE COMPLEXES

3.1 Introduction

As an extension of the work involving rotational barriers of metal stabilized benzyl cations, it was of interest to determine if the bonding interaction between the benzylic carbon and metal orbitals could be enhanced. Any enhancement would restrict the tripodal rotation and a barrier could then be determined. To that end, an investigation of some previous work on a similar system involving fulvenes rather than arenes was undertaken.

A fulvene ligand may be represented by two resonance forms, one with localized bonds (ylene, **62**) and one written in a zwitterionic form (ylide, **63**).



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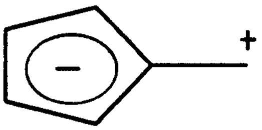
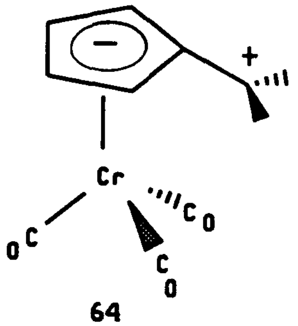


63

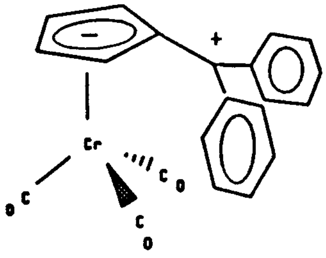
If a chromium tricarbonyl moiety could be bonded to the cyclopentadienide ion, the metal would be in a position to stabilize the exocyclic cation. A bending of the exocyclic bond towards the metal, **64**, would provide evidence of ligand-metal interaction and of ligand stabilization.



64

The fulvene complex is a neutral molecule with a zwitterionic contribution and is expected to have greater stability than the benzylic cation. E. O. Fischer et al.[117] were the first to synthesize complexes of this type when they formed (6,6-diphenylfulvene)Cr(CO)$_3$, **65**. The air-stable brown crystals were found to be monomeric and soluble in most organic solvents. The preliminary ^{1}H NMR spectra show a clearly resolved pair of triplets (of equal intensity) suggesting an A_2B_2 system representing the four protons on the cyclopentadienyl ring, with the ring π-bonded to the metal. The upfield shift of these protons upon complexation indicates interaction of the metal with the five membered ring and not the phenyl rings. It is well known, however, that Cr(CO)$_3$ readily forms stable complexes with aromatic ligands. The benzyl alcohol complexes discussed in Chapter 2 are perfect examples of how the chromium moiety preferentially binds to a ligand that can donate six π-electrons. In the fulvene system then, the Cr(CO)$_3$ interacts not only with the double bonds in the five membered ring, but with the exocyclic double bond.

The structure proposed as a result of Fischer's NMR studies was confirmed by Adrianov et al.[118] who solved the X-ray crystal structure of (6,6-diphenylfulvene) $Cr(CO)_3$, **65**. They found that indeed, the metal carbonyl was bound to the five membered ring and the molecule had almost perfect C_s symmetry with the exocyclic bond bisecting the projection of the carbonyl ligands.



65

The interaction of the metal with the fulvene system led to a significant distortion in the ligand geometry compared to the planar, non-coordinated dimethyl fulvene complex where pronounced double and single bonds were observed. The $Cr(CO)_3$ fragment had lost its C_{3v} symmetry evidenced by three carbonyl peaks in the IR spectra. The degenerate E band had been split due to the deformation of the tripod as a result of the steric hindrance of the two phenyl groups. These IR spectra are often found to be temperature dependent.[119]

In the diphenylfulvene complex, the fulvene ligand is not planar and the expected ≈ 30 degree bend of the exocyclic bond towards the metal was found. Coplanarity of the phenyl and fulvene groups is not possible due partially to the steric interaction between the ortho hydrogens on the phenyl group with the fulvene hydrogens.

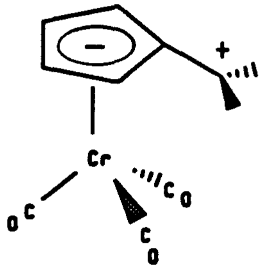
The bending of the external bond increases the overlap between the external carbon and the d_{z^2} orbital of the metal.[120] Adrianov[118] explains that the interaction between the chromium atom with the fulvene ligand can be represented by the ylene and ylide resonance forms. The percentage of the contribution of the zwitterionic resonance form can be increased as electron-donating substituents are incorporated at the 6,6- positions on the fulvene. These groups provide a mechanism for cation stabilization such that the olefinic character of the C_5-C_6 bond decreases.

Using ^{13}C NMR spectroscopy Behrens[121] and his group examined the change in chemical shift ($\Delta\delta$) of the exocyclic carbon upon complexation to the chromium tricarbonyl unit. They found an excellent correlation between the $\Delta\delta$ values and the Cr-C_6 bond lengths (determined crystallographically) for a number of 6,6-substituted fulvenes. The downfield shift of carbon-6 suggested greater zwitterionic character resulting in a shorter bonding distance between the metal and the carbon. This report provided further evidence for metal stabilized cationic centers. NMR spectroscopy can then be used as a tool to determine the olefinic character of the C_5-C_6 bond.

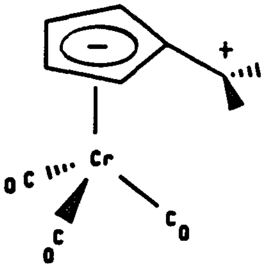
The fulvene systems, therefore, were expected to provide a valid comparison with the previously discussed metal complexed benzyl cations which show the bending of the benzylic position to be energetically favoured.

It was of interest to examine how the bend in these neutral fulvene complexes affected the barrier to rotation of the $Cr(CO)_3$ tripod. Any increased interaction of the metal with the exocyclic bond should restrict the tricarbonyl rotation and raise the barrier.

The barrier to be measured is the energy difference between the lowest (**64a**) and highest (**64b**) energy conformations.



64a



64b

EHMO calculations[111] on unsubstituted (fulvene)$Cr(CO)_3$, **65**, show this difference to be 7.3 kcal/mol when the olefinic bond is coplanar with the ring, and 9.3 kcal/mol when the exocyclic carbon has bent down. Experimental evidence by Behrens[119] suggests that restricted rotation of this molecule does occur. Decoalescence of the single carbonyl carbon resonance at 229K was followed by a 2:1 splitting at 190K. The authors claim this process reflects an 11.3 kcal/mol activation enthalpy.

Through a "personal communication" Hoffmann[111] had learned about Kreiter's work on (6,6-dimethylfulvene)Cr(CO)$_3$. Kreiter claimed that the carbonyl exchange had been frozen out at 183K and suggested that this probably corresponded to a 7-9 kcal/mol barrier. Since that communication there have been no data available on this system.

It was of interest, therefore, to synthesize and characterize the symmetric (6,6-diphenylfulvene)Cr(CO)$_3$, **65**, and non-symmetric (6-methyl-6-phenylfulvene)Cr(CO)$_3$, **66**, and to examine their variable-temperature ^{13}C NMR spectra to determine their rotational barriers.

3.2 Results and Discussion

3.2.1 (6,6-Diphenylfulvene)Cr(CO)$_3$, **65**

The generation of this molecule began with the synthesis of the free ligand. The reaction of benzophenone with freshly distilled cyclopentadiene occurs during a 45 minute reflux in a basic solution of sodium in ethanol. Upon cooling, a bright orange precipitate falls out of solution. The solid was recrystallized in hot ethanol to obtain pure 6,6-diphenylfulvene in good yield (80%). The identity of the product was confirmed by mass spectral and NMR data. The 200 MHz ^{1}H and 50.3 MHz ^{13}C NMR spectra revealed peaks consistent with the literature values,[117,121,122] and have been summarized in Tables 3.1 and 3.2. The higher field instrument has provided additional information such that the coupling constants for the fulvenic hydrogens could be determined. Since the chemical shifts agreed well with the

TABLE 3.1

^{1}H NMR Data (in ppm) For 6,6-diphenylfulvene and its Cr(CO)$_3$ complex, **65**, recorded at 200.13 MHz

	$H_{1,4}$ / $H_{2,3}$	H_o,H_m,H_p
Free Ligand[a]	6.27 (d,d,d,2H) 6.56 (d,d,d,2H) ^3J=4.0 Hz, ^4J=2.6 Hz	7.31 (m,10H)
Complex[b]	4.66 (t,2H) 5.44 (t,2H)	7.28 (m,6H) 7.33 (m,4H)

TABLE 3.2

^{13}C NMR Chemical shifts (ppm) for 6,6-diphenylfulvene and its Cr(CO)$_3$ complex, **65**, recorded at 62.9 MHz

Carbon	Free Ligand[c]	Complex
C_1,C_4	124.3	89.5
C_2,C_3	132.1	94.1
C_5	144.1	107.7
C_6	151.7	128.2
C_7 *ipso*	141.3	141.2
$C_{8,9,10}$ *o,m,p*	128.5, 128.7	128.5, 123.9
CO	--	238.4 at RT 236.5[1], 240.8[2][d] at -80°C

a) Recorded in CDCl$_3$, see also Reference 117.

b) Recorded in CH$_2$Cl$_2$, see also Reference 122.

c) See also Reference 121.

d) Intensities in brackets.

literature values, no attempt was made to distinguish the hydrogens at the 1,4 positions from those at positions 2,3. As well, the ortho and meta carbons on the phenyl groups were not unambiguously assigned.

The free ligand was then combined with chromium hexacarbonyl during a 48 hour reflux in heptane.[117] The solution was cooled and the precipitated brown crystals of **65** were filtered, washed with pentane and purified by sublimation to remove excess $Cr(CO)_6$. The 61% yield was more than adequate for use in the NMR experiment. One-half the length of the usual reaction time for a $Cr(CO)_3$ complexation was found to be sufficient to complex the $Cr(CO)_6$ unit to the fulvene. The mass spectrum of the complex showed a successive loss of carbonyl ligands indicating that the $Cr(CO)_3$ tripod had coordinated to the free fulvene. The IR spectra were consistent with the structure of the product with two strong vibrations in the terminal carbonyl region. The degenerate E band at 1910 cm^{-1}, however, showed slight splitting to indicate a divergence of the $Cr(CO)_3$ tripod from local C_{3v} symmetry.

The 200 MHz ^1H NMR results can also be found in Table 3.1 and are in good agreement with those presented elsewhere.[117,121] A 50.3 MHz ^{13}C NMR spectrum of (6,6-diphenylfulvene)$Cr(CO)_3$ is shown in Figure 3.1, with the relevant chemical shifts (as recorded at 62.6 MHz) listed in Table 3.2. There is no doubt that complexation of the metal occurred at the five-membered ring. The upfield shift of the fulvenic protons (>1 ppm) and carbons (>30 ppm) upon complexation is a result of the well known shielding ability of the π-complexed chromium atom.

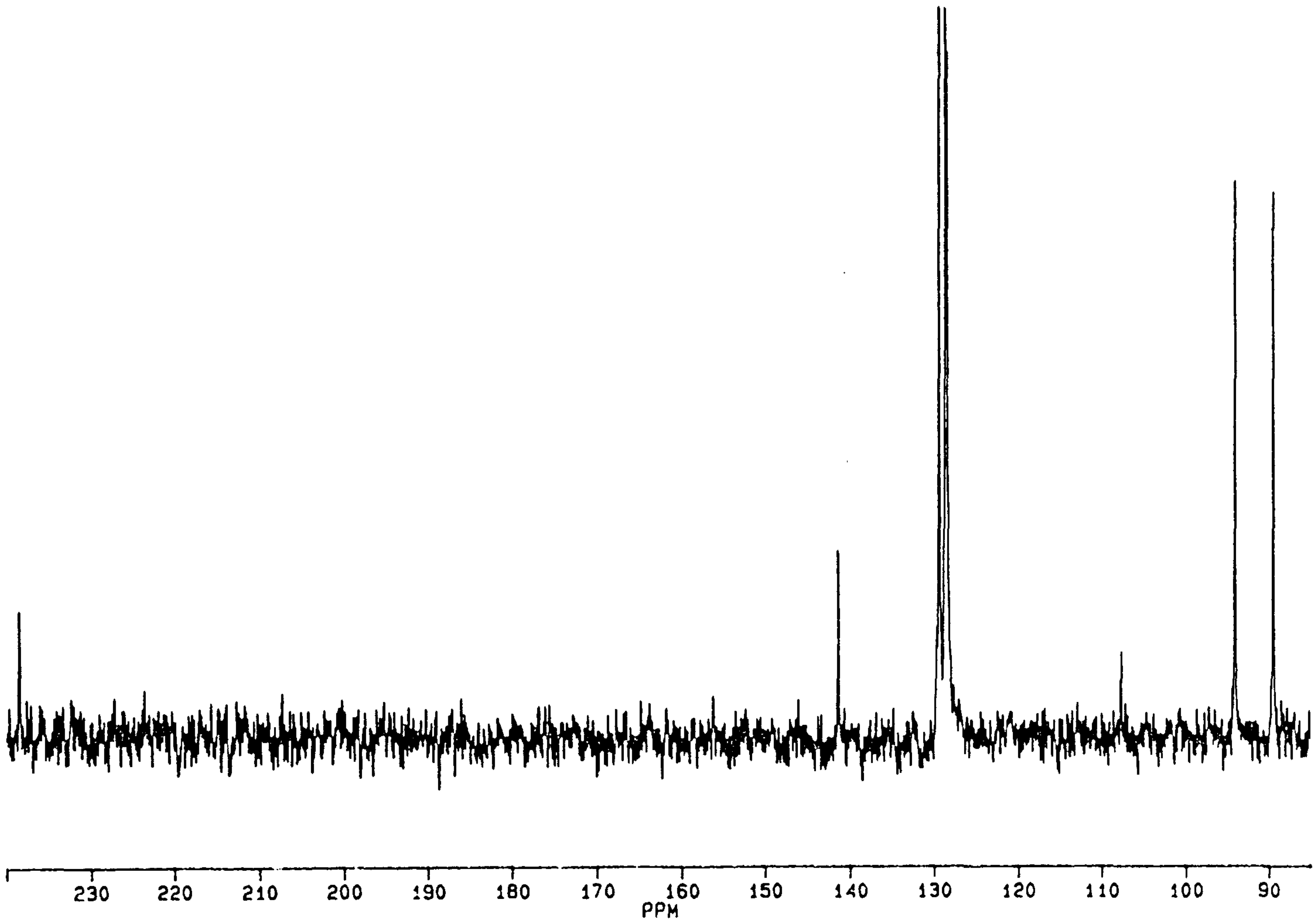
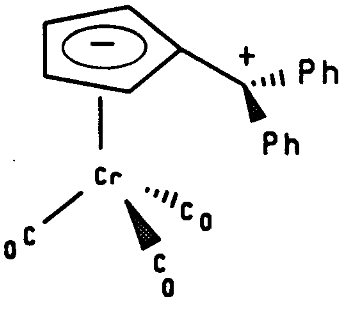


Figure 3.1: 50.3 MHz ^{13}C NMR spectrum of (6,6-Diphenylfulvene)Cr(CO)$_3$, **65**.

Once the purity of the (6,6-diphenylfulvene)Cr(CO)$_3$ complex had been confirmed, a variable-temperature ^{13}C NMR experiment followed. The chemical shifts of all carbons were found to remain constant over a temperature range of -100°C to +25°C except for the carbonyl carbon. The single resonance at 238.4 ppm began to decoalesce at -20°C as the rotation of the Cr(CO)$_3$ tripod began to slow. At -30°C The resonance began to split into two peaks and at -100°C two very narrow, intense peaks at 240.8 ppm and 236.5 ppm in the ratio 2:1 were clearly displayed. Further evidence for restricted chromium tricarbonyl rotation has again been provided.

By examining the conformation of **67** below;



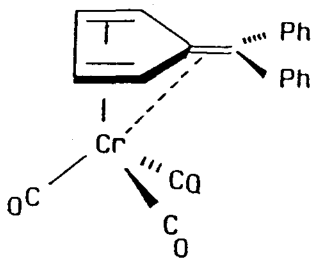
67

the 2:1 splitting of the carbonyls occurs as a result of a stationary tripod on the molecule which possesses a plane of symmetry bisecting the two phenyl rings. This conformation is consistent with the solid state structure whereby two of the carbonyl ligands are found to project out towards the phenyl rings, while the third points in the direction opposite to carbon 5. In the solid state, the phenyl rings are known to be symmetrical about this mirror plane. Assuming the molecule adopts the solid state conformation at low temperature, two of the carbonyls are magnetically non-equivalent to the third in the NMR experiment.

Once this rotation had been stopped on the NMR timescale, its barrier could then be calculated. A simulation of the experimental spectra is presented as Figure 3.2. The calculated rates corresponding to a number of experimental temperatures were incorporated into an Arrhenius plot revealing a rotational barrier of 8.3 kcal/mol. This result is well within the 7-9 kcal/mol range predicted by Kreiter[111] for the barrier of the analogous (6,6-dimethylfulvene)$Cr(CO)_3$ complex, which to this date has yet to be satisfactorily determined.

The fact that the rotation of the chromium tricarbonyl moiety can be slowed in this molecule suggests that there must be some electronic interaction between the metal and the fulvene ligand. The solid state structure indicates that the proximity of the phenyl rings to the $Cr(CO)_3$ unit should not provide a significant deal of steric hindrance. The bending of the α-carbon towards the metal (seen in the solid state) is a result of the molecule attempting to lower its overall energy by allowing the metal to stabilize the exocyclic carbon.

Recalling that i) the fulvene ligand can be written in a zwitterionic form and ii) that the $Cr(CO)_3$ units are known to stabilize α-carbons, it is proposed that the metal-carbon interaction in the (6,6-diphenylfulvene)$Cr(CO)_3$ molecule can be compared to that of the benzyl cation complexes discussed in Chapter 2. By increasing the interaction with the α-carbon by the metal, the probability of tripodal rotation has been subsequently decreased. In solution, at low temperature, this interaction can be indirectly observed for **65** as evidenced by the 2:1 splitting in the



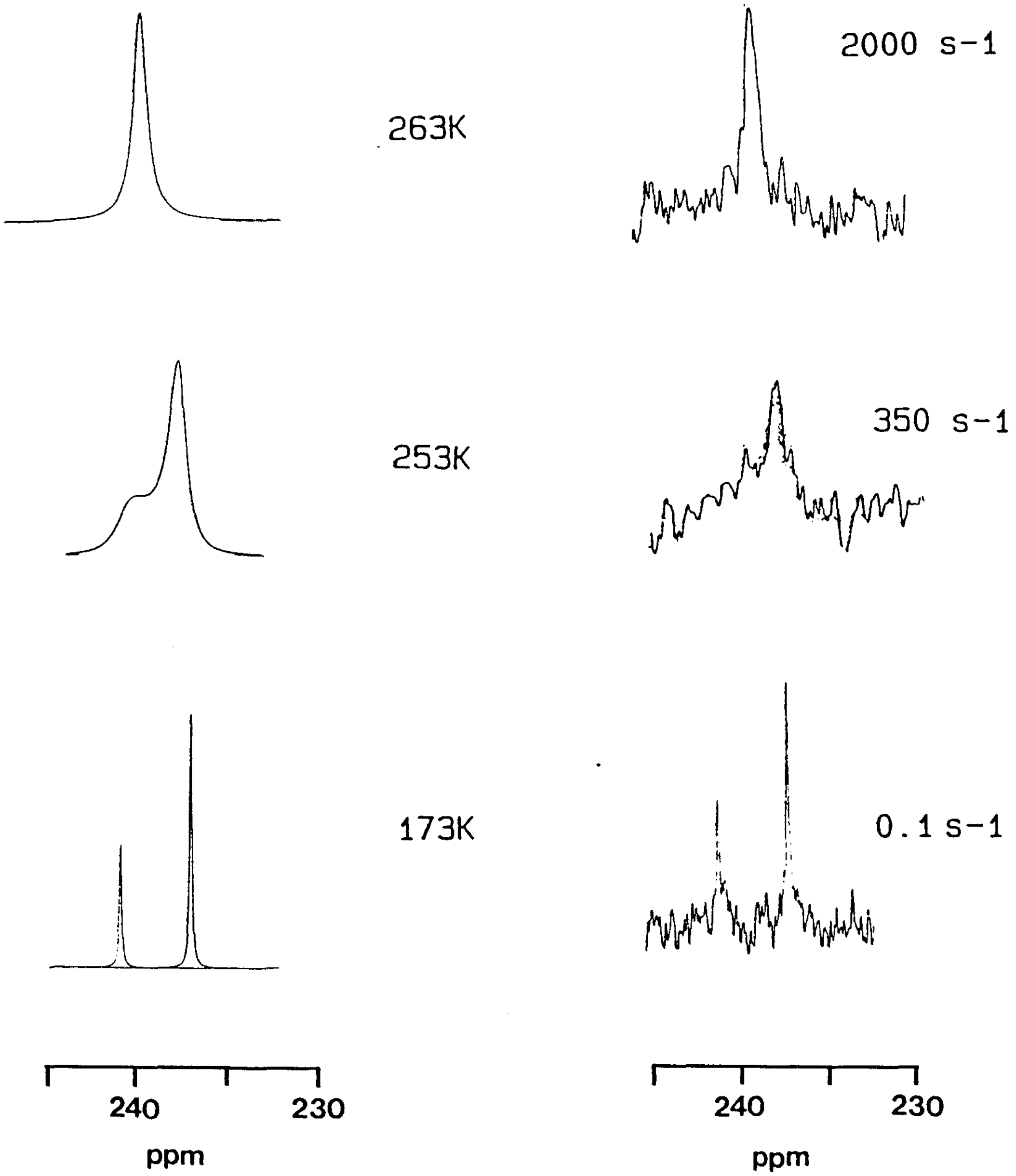


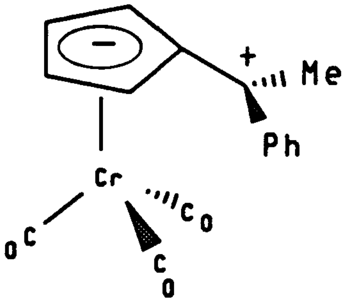
Figure 3.2: 62.9 MHz variable-temperature ^{13}C NMR spectra of (6,6-Diphenylfulvene)$Cr(CO)_3$, **65**, with the corresponding simulated spectra.

aforementioned NMR experiment.

To quell any doubts that this hindered rotation was brought about by electronic rather that steric effects, a less hindered, asymmetric complex was formed to provide unequivocal proof of electronically hindered $Cr(CO)_3$ rotation.

3.2.2 (6-Methyl-6-phenylfulvene)$Cr(CO)_3$,**66**

By replacing one of the phenyl groups of **65** with a methyl group, the synthesis of (6-methyl-6-phenylfulvene)$Cr(CO)_3$ allowed for a second attempt to compare how the metal-cation interaction affects the barrier to tripodal rotation in a fulvene complex. If the chromium tricarbonyl tripod were to stop on the NMR time-scale in this molecule, all three carbonyls would be in different magnetic environments as a consequence of the lack of symmetry in the molecule.



66

Before the complex could be formed, the free 6-methyl-6-phenylfulvene ligand was synthesized, following modifications of the methods by Kice and

Parham[123], Kresze and Goetz[125]. Mass spectral and NMR techniques were utilized to identify the fulvene. The molecular ion, as well as the methyl and phenyl fragmented ions were clearly visible in the mass spectrum. Both the carbon and proton spectra of the uncomplexed 6-methyl-6-phenylfulvene were recorded and the results are summarized within Tables 3.3 and 3.4. As with 6,6-diphenylfulvene, obtaining a 200 MHz spectrum of the free ligand allowed the observation and identification of the fulvenic protons' coupling constants. The chemical shift for each specific fulvenic proton or carbon was not rigorously defined. Similarity to the reported value was deemed sufficient enough evidence for confirmation that the synthesized molecule was the desired one. Of greater interest was the NMR behaviour of the chromium complexed fulvene, hence the synthesis of the (6-methyl-6-phenylfulvene)$Cr(CO)_3$ soon followed.

Edelmann et al.[124] had originally synthesized **65** photochemically by the reaction of either (benzene)$Cr(CO)_3$ or (mesitylene)$Cr(CO)_3$ in the presence of the free 6-methyl-6-phenylfulvene. They found that the reaction went almost quantitatively, and were thus the first to report a photochemical reaction of an (arene)$Cr(CO)_3$ complex.

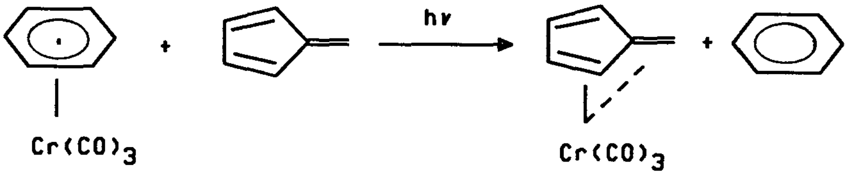


TABLE 3.3

^{1}H NMR Data (in ppm) For 6-methyl,6-phenylfulvene and its Cr(CO)$_3$ complex, **66**, recorded at 200.13 MHz

	$H_{1,4}$	$H_{2,3}$	Phenyl	Methyl
Free Ligand[a]	6.57 (d,d,d,1H) 6.46 (m,1H)	6.16 (d,d,d,1H) 6.64 (d,d,d,1H) ^3J=5.2 Hz, ^4J=2.0 Hz	7.37 (s,5H)	2.54 (s,3H)
Complex[b]	4.75 (t,2H)[d]	4.69 (t,2H)[d]	7.27 (m,5H)	2.51 (s,3H)

TABLE 3.4

^{13}C NMR Chemical shifts (ppm) for 6-methyl,6-phenylfulvene and its Cr(CO)$_3$ complex, **66**, recorded at 62.9 MHz

Carbon	Free Ligand[c]	Complex
C_1,C_4	123.4/120.9	87.4/90.4
C_2,C_3	131.6/131.3	95.2/92.4
C_5	143.3	104.3
C_6	149.3	130.5
C_7 *ipso*	141.7	141.8
C_8 *ortho*	129.0	129.4[e]
C_9 *meta*	127.9	128.0[e]
C_{10} *para*	127.6	126.9[e]
Me	22.6	25.4
CO	--	238.0 at RT 240.2, 236.7 and 235.5 at -80°C

a) Recorded in $CDCl_3$.

b) Recorded in CD_2Cl_2, see also Reference 124.

c) See also Reference 126.

d) These chemical shifts may be interconverted.

e) The ortho and meta carbons may be reversed.

Although the fulvene complex had been characterized by IR and proton NMR spectra, there was no attempt to obtain ^{13}C NMR chemical shifts at any temperature.

Rather than forming **66** photochemically, the complex was formed in the present study using a more familiar preparative technique. Chromium hexacarbonyl and 6-methyl-6-phenylfulvene were stirred under reflux for four days in an n-butyl ether/THF solution. After cooling and filtering the brown solution to remove excess $Cr(CO)_6$, the solvents were removed under high vacuum, leaving a sticky brown solid. Flash column chromatography on the impure product yielded brown (6-methyl-6-phenylfulvene)$Cr(CO)_3$ (23%).

Chemical shifts provided by the 200 MHz ^1H NMR spectrum of the complex are consistent with those found by Edelmann et al.[124] As expected, the fulvenic protons have shifted upfield and a great deal more splitting was observed at this high field. To observe the behaviour of the tripodal carbonyl carbons at low temperature, a series of 62.9 MHz ^{13}C NMR spectra were recorded over the temperature range -80°C to +25°C. Similar to the (6,6-diphenylfulvene)$Cr(CO)_3$ complex, the fulvenic carbons were found to shift downfield upon complexation, yet there was little effect on the methyl or phenyl resonances upon complexation. As before, there was no change in the spectra over the range of temperatures, except for a change in the carbonyl region.

The variable-temperature spectra in the carbonyl region of **66** together with the simulated spectra appears as Figure 3.3. The spectrum recorded at -80°C

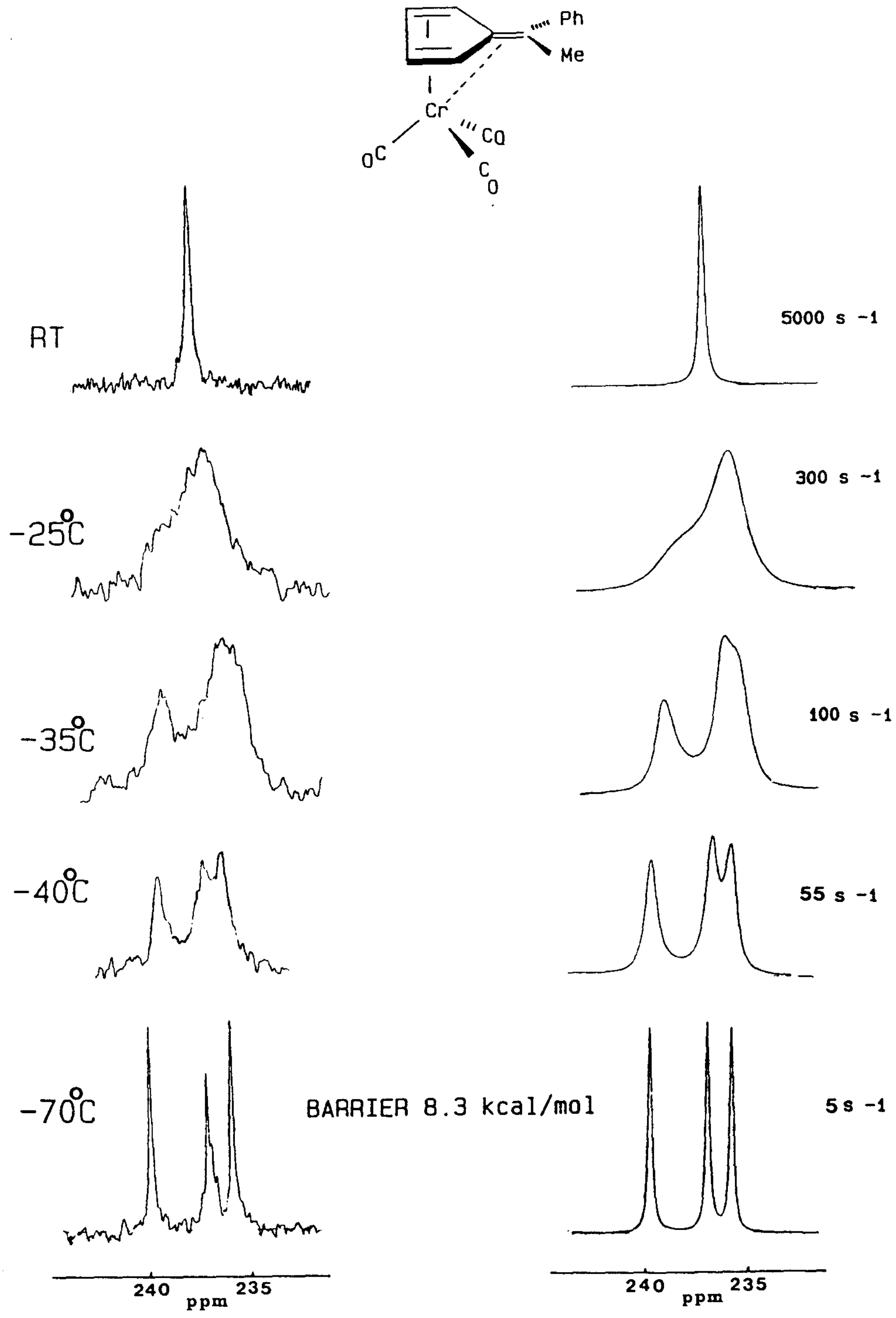


Figure 3.3: 62.9 MHz variable-temperature ^{13}C NMR spectra of (6-Methyl-6-phenylfulvene)Cr(CO)$_3$, **66**, with the corresponding simulated spectra.

shows three sharp signals at 240.2, 236.7 and 235.5 ppm as compared to the single peak at 238.0 ppm found at room temperature.

This dramatic decoalescence beautifully illustrates the effect of hindered chromium tricarbonyl rotation on the NMR time-scale. As proposed, the complete non-equivalence of the carbonyl carbons provides evidence that there is, in fact, some electronic interaction between the metal and the exocyclic carbon. This interaction results in an electronic barrier which the molecule must surmount if the carbonyl intends to rotate about the metal-fulvene bond. The experimental temperatures were incorporated into an Arrhenius plot of lnk vs 1/T shown as Figure 3.4. Analysis of the slope led to the determination of a 8.3 kcal/mol rotational barrier, similar to that of (6,6-diphenylfulvene)$Cr(CO)_3$ and again in the 7-9 kcal/mol range predicted by Kreiter.

The hypothesis that the fulvene complexes would provide an interesting, insightful and relevant comparison to the benzylic cation complexes has been shown to be quite valid.

3.2.3. α-(η^5-Cyclopentadienyl)dicarbonyl nitrosyl chromium cations

While researching the NMR behaviour of chromium complexed fulvenes, a paper by Rausch et al.[127] was discovered. These authors were interested in the stabilization of carbonium ions in (η^5-cyclopentadienyl)$Cr(CO)_2NO^+$ compounds. Protonation of the complexed alcohols such as **68** led to the production of a cation

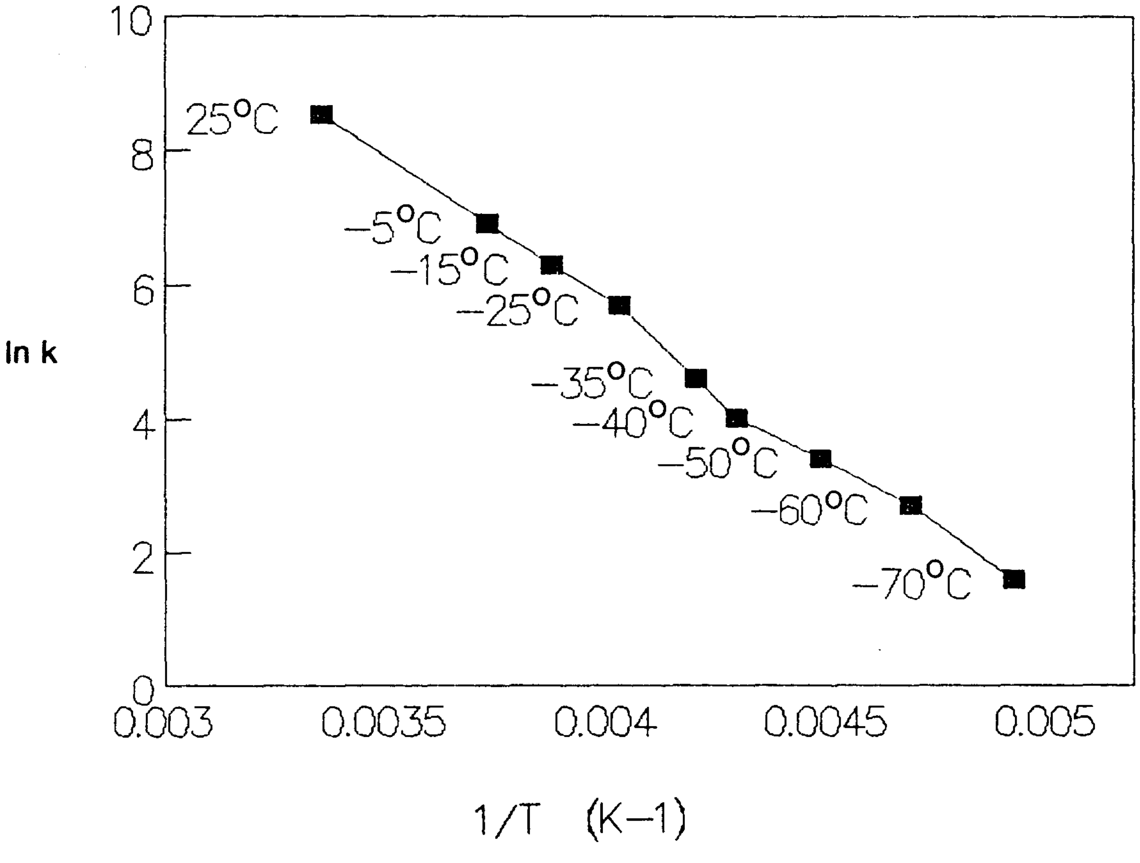
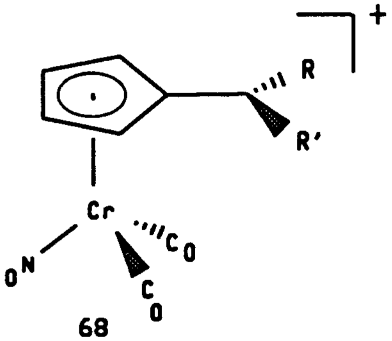


Figure 3.4: The Arrhenius plot of ln k vs 1/T for (6-methyl-6-phenylfulvene)Cr(CO)$_3$, **66**.

similar both to the benzylic and fulvene complexes discussed earlier.

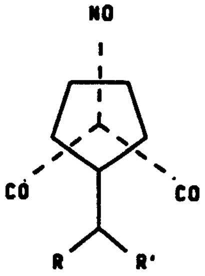


68

As evidenced by ^{1}H and ^{13}C NMR studies, they claimed to be the first to report metallo-aromatic carbonium molecules such as these which exhibit diastereotopic carbonyl resonances at ambient temperature. They went on to claim that this diastereotopic behaviour was a result of hindered rotation of the $Cr(CO)_2NO$ tripod. That is to say, Rausch et al. have suggested that the rotation of the two carbonyls in the substituted title complex have stopped on the NMR time-scale such that they are in different magnetic environments which results in the two observed peaks.

The research on the benzyl and fulvene complexes discussed within describe the dynamic behaviour of molecules which are nearly identical to those described by Rausch. We viewed this claim of ambient-temperature hindered tripodal rotation with some skepticism since temperatures well below zero are required to stop the rotation in all previously discussed systems. The following simple explanation clearly illustrates why their assumptions were incorrect.

There are three lowest energy conformations that the $Cr(CO)_2NO$ moiety can adopt once the tripodal rotation has been stopped. All three conformations are represented below with the view looking along the metal-ring bond.



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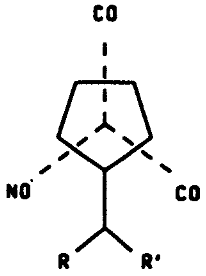

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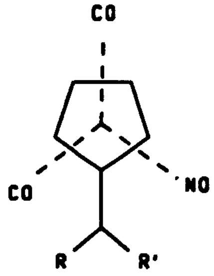
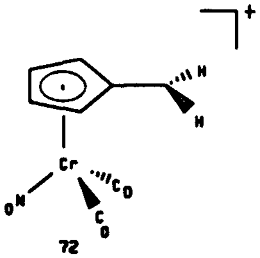


71

The nitrosyl group may come to rest directly opposite to the exocylic bond, **69**, or it may lie beneath C-1, **70**, or C-4, **71**. In **69**, the R groups are non-equivalent and an absence of any symmetry elements in the molecule leaves the carbonyls in different magnetic environments. The carbonyls thus exhibit two distinct resonances in the NMR spectrum. A similar argument can be used to explain the two carbonyl peaks observed for orientations **70** and **71**. In fact, any conformation of the tripod, whether it stops at **69**, **70**, **71** or any place in between should result in two peaks in the NMR spectra. The carbonyls will *always* be different whether the tripod rotates or not because they are *diastereotopic*. The authors of this paper were therefore incorrect when they claimed that they had stopped tripodal rotation on the NMR time-scale at ambient temperature using the two carbonyl resonances as evidence for the claim. The carbonyls are always non-equivalent at any temperature.

After some thought it was decided that it would be interesting to determine if evidence of restricted tripodal rotation could be found in a system such as this. A system had to be cleverly designed, however, which could provide evidence of this in an NMR experiment. A molecule was needed, therefore which would model those studied by Rausch et al., but would not significantly differ in structure. More importantly, it must be possible to distinguish between a rotating versus a non-rotating tripod in the NMR specta.

The hydrogen substituted model, **72**, was expected to provide information about the rotational barriers in these types of systems.



72

By ensuring that both substituents (hydrogens) on the carbonium center were equivalent, there would be no confusion as to the presence of diasterotopic carbonyls. To determine if the $Cr(CO)_2NO$ tripod has stopped rotating in **72** could be a challenge for the following reason. If orientation **69** was found to be energetically favoured, such that the rotation would stop in this conformation, the two carbonyls are related by a mirror plane and would exhibit one peak in the carbonyl region. This is not desirable for an NMR experiment, since there is also only one peak when the tripod is still rotating. No information about hindered rotation could be observed in the model compound if the tripod stopped in conformation **69**. If, however, the tripod could be stopped in orientation **70** (or **71**), the carbonyls would be non-equivalent and would exhibit two peaks at low temperature compared to the one peak observed at higher temperature when the tripod is rotating. Only in the second case could a variable-temperature ^{13}C NMR experiment be used to determine if the interaction of the metal with the exocyclic carbon provides a significant electronic effect to hinder the tripodal rotation.

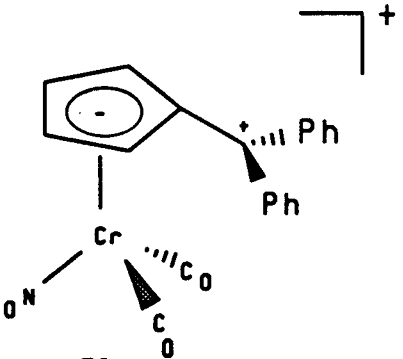
To ascertain whether or not the NMR experiment should be attempted, a series of EHMO calculations were undertaken on **72** to determine which of the conformations **69** or **70/71** was energetically favoured. In the tricarbonyl as well as the two dicarbonylnitrosyl complexes, a 20° bend (from the plane of the five-membered ring) of the exocyclic carbon towards the metal was found to lower the overall energy of all three complexes. To increase metal d orbital ↔ carbon 2p orbital overlap, the bend allows the metal to stabilize the cationic center as evidenced in the previous benzyl and fulvene complexes.

The symmetric conformation (**69**) of the $Cr(CO)_2NO$ complex was found to be 2.2 kcal/mol more stable than the asymmetric one (**70/71**). Unfortunately, this was the conformation that would give no information in the variable-temperature NMR experiment. A 2.2 kcal/mol difference would favour this rotamer greatly but one might perhaps see a small percentage of the asymmetric molecule present at low temperature. One expects to see one predominant peak for the more stable complex (**70** or **71**) whether it is rotating or not. It is possible, that the two peaks representing the non-equivalent carbonyls in conformation **69** may straddle the predominant peak at low temperature. The carbonyl region on the ^{13}C NMR spectrum would look very much like an intense resonance with satellites.

3.4 Future Work

Although the results of the EHMO calculations were not as hoped, there is the possibility that the symmetrical carbonium ion may freeze out in solution in the variable-temperature ^{13}C NMR experiment. If this were to occur, a rotational barrier could be determined and another molecule could then be added to the growing list of complexes which show electronically hindered tripodal rotation.

Since the symmetric (6,6-diphenylfulvene)$Cr(CO)_3$ has already been synthesized, the next logical step would be to replace one of the carbonyl ligands with a nitrosyl ligand.



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This would provide another model for Rausch's system and the variable-temperature ^{13}C NMR behaviour could then be examined. Perhaps the presence of the phenyl groups would act favourably towards lowering the energy difference between the symmetric and asymmetric $Cr(CO)_2NO$ conformations. The preliminary attempts to replace one of the carbonyls with a nitrosyl have failed to produce a cation which would remain stable long enough to obtain variable-temperature ^{13}C NMR spectra. Since the carbonyl carbon has no attached proton, its signal builds up relatively slowly in the NMR experiment. Enrichment of the carbonyls with isotopically labelled $^{13}C{\equiv}O$ could facilitate a more rapid increase in the signal to noise ratio.

It may also be of interest to study similar systems involving organometallic moieties such as $Mo(CO)_3$, $W(CO)_3$, $Fe(CO)_3$ or $Mn(CO)_3$ which are also expected to stabilize cationic centers.

CHAPTER FOUR

EXPERIMENTAL

4.1 General Procedures

All reactions were carried out in reduced light, under an atmosphere of dry nitrogen and solvents were dried according to standard procedures.[128] Solvents were removed under reduced pressure by using a vacuum line or rotary evaporator. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. NMR spectra were recorded on a variety of spectrometers. ^{13}C NMR spectra were obtained using Bruker AM500, WM250 and AC200 spectrometers at 125.7 MHz, 62.9 MHz and 50.3 MHz respectively. Proton NMR were recorded using Bruker AM500, WM250, AC200 and Varian EM390 spectrometers. ^{13}C and ^{1}H chemical shifts reported were referenced to tetramethyl silane and samples were diluted with CD_2Cl_2, $CDCl_3$ or Acetone-d_6. Field/frequency stabilization was achieved by locking to the deuterium solvent. Infrared spectra were obtained on a Perkin-Elmer 283 instrument using KBr solution cells. Electron impact and chemical ionization (NH_3) mass spectra were performed on a VG Micromass 7070F spectrometer. Fast atom bombardment

(FAB) spectra were obtained from a reverse-geometry double-focusing VG ZAB-E spectrometer with an accelerating potential of 8 Kv. Xenon was the bombarding species with 3-Nitrobenzyl alcohol used as the sample matrix. Thin layer chromatography (TLC) was performed on silica gel 60F. Purification by flash column chromatography used silica gel with a variety of solvents as the eluent. The preferred method of introducing the impure sample to the packed column began with its dissolution in suitable solvent and adding five grams of silica. When the solvent was evaporated, the dry coated silica was then introduced onto the packed column.

Preparation of the arene tricarbonyls followed a general approach which is detailed below.

4.2 Experimental Procedures

Preparation of 3-methoxybenzyl alcohol chromium tricarbonyl, **44**

A typical preparation involves the use of a 250 ml one-neck round bottom flask which was connected to a water cooled condenser. A side arm of the flask was equipped with a stopcock to ensure positive nitrogen flow when required. The top of the condenser was then joined by tygon tubing to an empty flask, then to a paraffin bubbler to monitor the evolution of CO gas. The intermediate empty flask was a safeguard to ensure that no paraffin oil was drawn back into the reaction vessel under adverse experimental conditions. In the round bottom flask

5.3 ml (42.6 mmol) of 3-methoxybenzyl alcohol and 11.461 g (52.1 mmol; 1.2-fold excess) of chromium hexacarbonyl were stirred under reflux with freshly distilled n-butyl ether (35 ml) for 15 minutes under a heavy stream of nitrogen from the side arm on the flask. Tetrahydrofuran (THF) (25 ml) was then added through the condenser and the side arm nitrogen flow was turned off so as not to evaporate this lower boiling solvent. A positive flow of dry nitrogen was, however, maintained over the condenser. The flask was wrapped with aluminum foil to shield the reaction mixture from unwanted light. After 4 days, the solution was allowed to cool to room temperature with the stream of N_2 from the side arm passing over the reaction mixture. Unreacted $Cr(CO)_6$ falls out of solution and deposits on the condenser as the THF evaporates off. When the reaction vessel had cooled, the unreacted $Cr(CO)_6$ was filtered off using a Schlenk tube under high vacuum and unreacted alcohol and solvent were subsequently removed under high vacuum. Heating the flask with a water bath accelerated the removal of the high boiling point solvent. Purification of the resultant solid by flash chromatography on silica gel (eluent CH_2Cl_2) yielded bright yellow crystals. The solid (3.52 g, 30%) was recrystalized with CH_2Cl_2/Hexanes, m.p.102-103°C. Mass spectrum (EI): m/z(%) 274(25) $C_{11}H_{10}O_5Cr$ $[M]^+$, 218(10) $C_9H_{10}O_3Cr$ $[M-2CO]^+$, 190(100) $C_8H_{10}O_2Cr$ $[M-3CO]^+$, 172(10) C_8H_8OCr $[M-3CO-H_2O]^+$, 121(40) C_8H_90 $[M-Cr(CO)_3-OH]^+$. IR(CH_2Cl_2):υ_{CO} 1890 and 1970 cm^{-1}. NMR data have been collected in Table 2.5.

Protonation of (3-MeOC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$, **49**

A typical preparation of the cation by alcohol protonation follows. In a glove bag under a dry nitrogen atmosphere, 50 mg of 3-methoxybenzyl alcohol chromium tricarbonyl was dissolved in 1 ml of CD_2Cl_2. The bright yellow solution was then filtered through glass wool into an NMR tube. The tube was then placed in a CO_2(s)/Acetone bath maintained at -70°C. When the sample was cool, a few drops of triflic acid (CF_3SO_3H) were added to the tube producing a red-violet coloured solution. The sample was introduced to the NMR spectrometer at -70°C. The cation was unstable, decomposing over time or if the temperature was increased. As a result this great instability, the cation was characterized solely by NMR spectroscopy. NMR data have been collected in Table 2.5.

Preparation of 3-methylbenzyl alcohol chromium tricarbonyl **46**

3-Methyl benzy alcohol (4 ml, 36.2 mmol), $Cr(CO)_6$ (8.78 g, 39.9 mmol; 1.1 excess) in n-butyl ether (25 ml) and THF (25 ml) were heated under reflux for 4 days in an atmosphere of dry nitrogen. The solution was then allowed to cool and the reaction mixture was both filtered and evaporated under high vacuum. The resultant yellow oil was purified by flash column chromatography (silica gel) with petroleum ether/ether 1/5 used as the eluent. The product was recrystalized with ether/hexane to give yellow crystals (1.76 g, 19%), m.p. 79-80°C(lit.m.p.81°C)[120]. Mass spectrum (FAB$^+$): m/z(%) 258(100) $C_{11}H_{10}O_4Cr$ $[M]^+$, 241(12) $C_{11}H_9O_3Cr$ $[M-OH]^+$, 202(100) $C_9H_{10}O_2Cr$ $[M-2CO]^+$, 174(55) $C_8H_{10}OCr$ $[M-3CO]^+$, 122(35)

$C_8H_{10}O$ [M-Cr(CO)$_3$]$^+$, 105(95) C_8H_9 [M-Cr(CO)$_3$-OH]$^+$. IR(CH_2Cl_2): υ_{CO} 1890 and 1970 cm^{-1}. NMR data are summarized in Table 2.8.

Protonation of (3-MeC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$, **51**

Following the protonation procedure as outlined earlier, the yellow solution of the complex turned violet upon protonation with triflic acid. NMR data are listed in Table 2.8.

Preparation of 4-methoxybenzyl alcohol chromium tricarbonyl **43**

4-Methoxybenzyl alcohol (5.0 ml, 40.1 mmol) was heated under reflux in n-butyl ether/THF 40/30 ml with $Cr(CO)_6$ (10.25 g, 46.6 mmol; 1.2 excess) for 4 days in a dry nitrogen atmosphere. The yellow solution was then cooled, filtered and the solvents removed under high vacuum. The resultant yellow oil was purified by flash column chromatography (silica) with ether:petroleum ether 3:1 eluent. Yellow crystals were obtained (4.5 g, 41 %), m.p. 55-57°C. Mass spectrum (FAB$^+$): m/z(%) 274(55) $C_{11}H_{10}O_5$ Cr[M]$^+$, 218(60) $C_9H_{10}O_3$ Cr[M-2CO]$^+$, 190(35) $C_8H_{10}O_2Cr$ [M-3CO]$^+$, 121(43) C_8H_9O [M-Cr(CO)$_3$-OH]$^+$,107(20) C_7H_7O [M-Cr(CO)$_3$-CH$_3$O]$^+$ or [M-Cr(CO)$_3$-CH$_2$OH]$^+$, 89(20) C_7H_6 [M-Cr(CO)$_3$-CH$_3$O-H$_2$O]$^+$. IR(CH_2Cl_2):υ_{CO} 1890 and 1970 cm^{-1}. NMR data can be found in Table 2.4.

Protonation of (4-MeOC$_6$H$_4$CH$_2$OH)Cr(CO)$_3$, **48**

The 4-methoxybenzyl cation was prepared as described to form a red-violet solution at -70°C. The sample was characterized by NMR spectroscopy.

Preparation of 4-methylbenzyl alcohol chromium tricarbonyl, **45**

As with earlier procedures, $Cr(CO)_6$ (5.04 g, 22.9 mmol) and 4-methylbenzyl alcohol (2.779 g, 22.7 mmol) were heated under reflux for 4 days in a nitrogen atmosphere in n-butyl ether (45 ml)\THF (25 ml). The solution was cooled, filtered and the solvents evaporated on a vacuum line, forming a yellow solid. The product was purified by column chromatography (silica, flash) with ether/CH_2Cl_2 7/3 as the eluent. Bright yellow crystals (1.171 g, 20%) were obtained, m.p. 72-73°C. Mass spectrum(FAB$^+$): m/z(%) 258(60) $C_{11}H_{10}O_4Cr$ $[M]^+$, 241(10) $C_{11}H_9O_3Cr$ $[M\text{-}OH]^+$, 202(65) $C_9H_{10}O_2Cr$ $[M\text{-}2CO]^+$, 174(40) $C_8H_{10}OCr$ $[M\text{-}3CO]^+$, 122(17) $C_8H_{10}O$ $[M\text{-}Cr(CO)_3]^+$, 105(100) C_8H_9 $[M\text{-}Cr(CO)_3\text{-}OH]^+$. IR($CH_2Cl_2$):$\upsilon_{CO}$ 1890 and 1970 cm^{-1}. Relevent NMR chemical shifts are available in Table 2.7.

Protonation of $(4\text{-}MeC_6H_4CH_2OH)Cr(CO)_3$, **50**

A red-violet solution was produced upon addition of CF_3SO_3H to the complexed alcohol. NMR spectroscopy was used to confirm the structure with the chemical shifts outlined in Table 2.7.

Preparation of methyl-p-tolyl carbinol chromium tricarbonyl, **42**

Following a modified method by Acampora[86d], methyl-p-tolyl carbinol (4.0 ml, 30 mmol) and $Cr(CO)_6$ (7.77 g, 35.3 mmol;1.2 excess) in n-butyl ether(25 ml)/THF (35 ml) were heated under reflux for 4 days. The reaction mixture was cooled, filtered and the solvents were evaporated by high vacuum, leaving a yellow-orange oil. The oil was recrystallized with ether/n-hexane and purified by flash column chromatography (silica) with ether/petroleum ether 30/60 as the eluent. A bright yellow solid was isolated, (2.48 g, 31%) m.p. 56-57°C (lit.m.p. 56.5-57°)[86d]. Mass spectrum(FAB$^+$): m/z(%) 272(32) $C_{12}H_{12}O_4Cr$ $[M]^+$, 255(9) $C_{12}H_{11}O_3Cr$ $[M\text{-}OH]^+$, 216(35) $C_{10}H_{12}O_2Cr$ $[M\text{-}2CO]^+$, 188(20) $C_9H_{12}OCr$ $[M\text{-}3CO]^+$, 136(17) $C_9H_{12}O$ $[M\text{-}Cr(CO)_3]^+$, 128(100) C_6H_4Cr $[M\text{-}CH_3\text{-}CHCH_3OH\text{-}3CO]^+$. IR($CH_2Cl_2$):$\upsilon_{CO}$ 1890 and 1970 cm^{-1}. NMR data are collected in Table 2.1.

Protonation of (p-Me$C_6H_4CHCH_3OH)Cr(CO)_3$, **47**

Upon addition of triflic acid, the yellow solution of the chromium complex turned violet. Variable-temperature ^{13}C NMR spectra were then obtained. See Table 2.1 for NMR data.

Preparation of 6,6-diphenylfulvene

In a 250 ml round bottom flask, benzophenone (20.6 g, 113 mmol) and freshly cracked cyclopentadiene (9.3 ml, 113 mmol) were stirred in 95% ethanol (75 ml). To this was added a solution of sodium metal (2.6 g, 113 mmol) in ethanol (50 ml). The previously clear solution turned dark brown upon addition of the base. The reaction mixture was heated under reflux for 45 minutes, allowed to cool to room temperature then cooled in an ice bath. A bright orange precipitate fell out of solution and was recrystallized from hot ethanol, yielding 20.8 g (80%), m.p. 82°C. Mass spectrum(EI): m/z 230 $C_{18}H_{14}$ $[M]^+$, 229 $C_{18}H_{13}$ $[M-H]^+$, 152 $C_{12}H_8$ $[M-H-Ph]^+$, 77 C_6H_5. NMR data are in Tables 3.1 and 3.2.

Preparation of 6,6-diphenylfulvene chromium tricarbonyl, **65**

Following a procedure by Cooper[117] $Cr(CO)_6$ (5.01 g, 22.8 mmol;1.5 excess) and 6,6-diphenylfulvene (3.5 g, 15.2 mmol) were heated under reflux together for 48 hours in heptane (60 ml, distilled over P_2O_5). The reaction mixture was then cooled and the brown crystals were filtered under high vacuum and washed with pentane. The unreacted $Cr(CO)_6$ was removed by sublimation (70°C, water pump pressure) and the brown solid (3.4 g, 61%) was recrystallized in THF, m.p. 208°C (lit.m.p.209°).[122] Mass spectrum(FAB^+) m/z (%) 366(25) $C_{21}H_{14}O_3Cr$ $[M]^+$, 310(55) $C_{19}H_{14}OCr$ $[M-2CO]^+$, 230(35) $C_{18}H_{14}$ $[M-Cr(CO)_3]^+$. IR(CH_2Cl_2):υ_{CO} 1910 and 1990 cm^{-1}. NMR in Tables 3.1 and 3.2.

Preparation of 6-methyl-6-phenylfulvene

Following a modification of the method of Kice and Parham[123], Kresze and Goetz[125], to a solution of sodium (2.78 g, 0.12 mol) in 95% ethanol (100 ml) was added acetophenone (14 ml, 0.12 mol) and freshly cracked cyclopentadiene (10 ml, 0.12 mol). The reaction mixture was stirred and heated to reflux for 30 minutes in a nitrogen atmosphere. The dark brown solution was then cooled and poured over 100 ml of distilled water. The dark orange product was extracted (5 x 50 ml) into ether. The organic layer was dried over anhydrous calcium sulfate, filtered and the solvent was removed by rotary evaporator to produce and dark orange oil. The oil was purified by flash column chromatography (silica) with CH_2Cl_2 as the eluent. Yield (14.4 g, 72%). Mass spectrum(EI): m/z(%) 168(100) $C_{13}H_{12}$ $[M]^+$, 167(32) $C_{13}H_{11}$ $[M-H]^+$, 153(85) $C_{12}H_9$ $[M-CH_3]^+$, 152(25) $C_{12}H_8$ $[M-CH_3-H]^+$, 89(7) C_6H_5C, 77(10) C_6H_5. Proton and carbon chemical shifts are outlined in Tables 3.3 and 3.4.

Preparation of 6-methyl-6-phenylfulvene chromium tricarbonyl, **66**

6-Methyl-6-phenyl fulvene (7.0 g, 41.6 mmol) and chromium hexacarbonyl (10.1 g, 45.9 mmol; 1.1 excess) in n-butyl ether (30 ml)/THF (20 ml) were heated under reflux for 66 hours. The mixture was then cooled, filtered and the solvents evaporated off using the high vacuum line. The sticky brown solid was purified by flash coloumn chromatography (silica) using CH_2Cl_2/Hexane 3/2 as the eluent to form the product (2.91 g, 23%), m.p.116-118°C lit.m.p. 119°C)[124]. NMR in tables 3.3 and 3.4.

EHMO Calculations

All calculations were performed using the extended Hückel method[130] using weighted H_{ij}'s.[131] Parameters used can be found in Reference 132. The distances used were as follows;

(Benzyl)Cr(CO)$_3$H$^+$ and Substituted (Benzyl)Cr(CO)$_3$$^+$ Cations

C-H 1.09Å, C-C 1.41Å, Cr-(Ar) 1.73Å, Cr-CO 1.84Å, C-O 1.14Å, C_{Ar}-OMe 1.33Å, O-Me 1.47Å.

(Fulvene)Cr(CO)$_3$,[119] (Fulvene)Cr(CO)$_2$NO

C-H 1.09Å, C_5-C_6 1.37Å, C_1-C_5 and C_4-C_5 1.45Å, C_1-C_2 and C_3-C_4 1.36Å, C_2-C_3 1.31Å, Cr-Ring Centroid 1.754Å, Cr-CO and Cr-NO 1.853Å, C-O and N-O 1.146Å.

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