N.M.R. STUDIES OF THE BONDING IN ARENE CHROMIUM TRICARBONYL COMPLEXES

by

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ABSTRACT

The effects on the chemical and spectroscopic properties of an arene brought about by complexation to a chromium tricarbonyl moiety have been investigated by comparing the NMR chemical shifts of the free and complexed arenes.

The ^{19}F n.m.r. chemical shifts of a series of free fluoroarenes, FC_6H_4X where X = H, F, Cl, CH_3, CH_3O, NH_2 and CF_3, have been correlated with the Swain-Lupton field and resonance parameters. Comparison of these data with the corresponding $Cr(CO)_3$ complexes shows little change in the transmission of mesomeric effects by para-substituents. Meta-substituents which interact primarily by a field effect have very little influence on the fluorine chemical shift in the complexes suggesting that the σ framework of the ring interacts with the chromium. The constancy in the transmission of mesomeric effects implicates an unperturbed π system in the complexes. Conversely, participation of the chromium atom in this transmission would negate this latter conclusion. An investigation of the fate of the aromatic ring current upon complexation has been used to resolve these two possible conclusions.

[10]-paracyclophane has been used to reevaluate present ring current theories. The ^1H n.m.r. spectrum of [10]-paracyclophane has been recorded at 220 M Hz and the methylene protons assigned on the basis of homonuclear decoupled spectra. Local anisotropic contributions to chemical shifts for protons sited above or near the aromatic ring of [10]-paracyclophane have been calculated using a classical model previously proposed by Grant. The residual incremental shift was shown to follow the Waugh-Fessenden-Johnson-Bovey classical ring current model, but the loop

separation originally invoked was shown to be unnecessary. These corrected ring current contributions also correlate very well with the quantum-mechanical approach of Haigh and Mallion. This model has been tested with a series of cyclophanes. The ^{13}C n.m.r. spectrum of [10]-paracyclophane has also been recorded.

The ^{1}H n.m.r. of the chromium tricarbonyl complex of [10]-paracyclophane has also been recorded at 220 M Hz. Local anisotropic contributions were derived using ^{13}C shielding tensors from benzene $Cr(CO)_3$ and hexaethylbenzene $Cr(CO)_3$. The ring current was found to be reduced to approximately 50% of its former value upon complexation.

The ^{13}C n.m.r. spectrum of hexaethylbenzene chromium tricarbonyl is shown to exhibit two resonances for ring carbons, as well as for methylene and methyl carbons. Cessation of ring rotation is postulated. Activation energies of 53.1 ± 2.5, 44.8 ± 2.1 and 46.9 ± 1.7 kJ mol^{-1} for ring, methylene and methyl carbons are found.

The overall conclusions drawn are that there is a significant decrease in the aromatic ring current upon complexation and that, therefore, transmission of substituent effects between para positions of the ring may be mediated by the chromium atom.

ACKNOWLEDGEMENTS

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INTRODUCTION - ARENE CHROMIUM TRICARBONYL CHEMISTRY

1.1 HISTORICAL AND EXPERIMENTAL BACKGROUND

Since the first reported synthesis of the parent compound $(C_6H_6)Cr(CO)_3$ in 1957 (1,2), the field of arene chromium tricarbonyl chemistry has received much attention from researchers of widely differing disciplines largely due to the many new and unusual properties which these and related systems have exhibited.

This initial synthesis involved the reaction of chromium hexacarbonyl with dibenzenechromium in benzene at 220°C in an autoclave. A more versatile approach was independently developed at about the same time by Whiting (3,4), Natta (5) and Fischer (6,7) and was later modified by Ströhmeier (8). The aromatic compound of interest was heated, usually at reflux under nitrogen with $Cr(CO)_6$, either alone, or in an inert solvent such as decalin or diethylene glycol dimethyl ether. A wide variety of arene complexes were made in this manner:

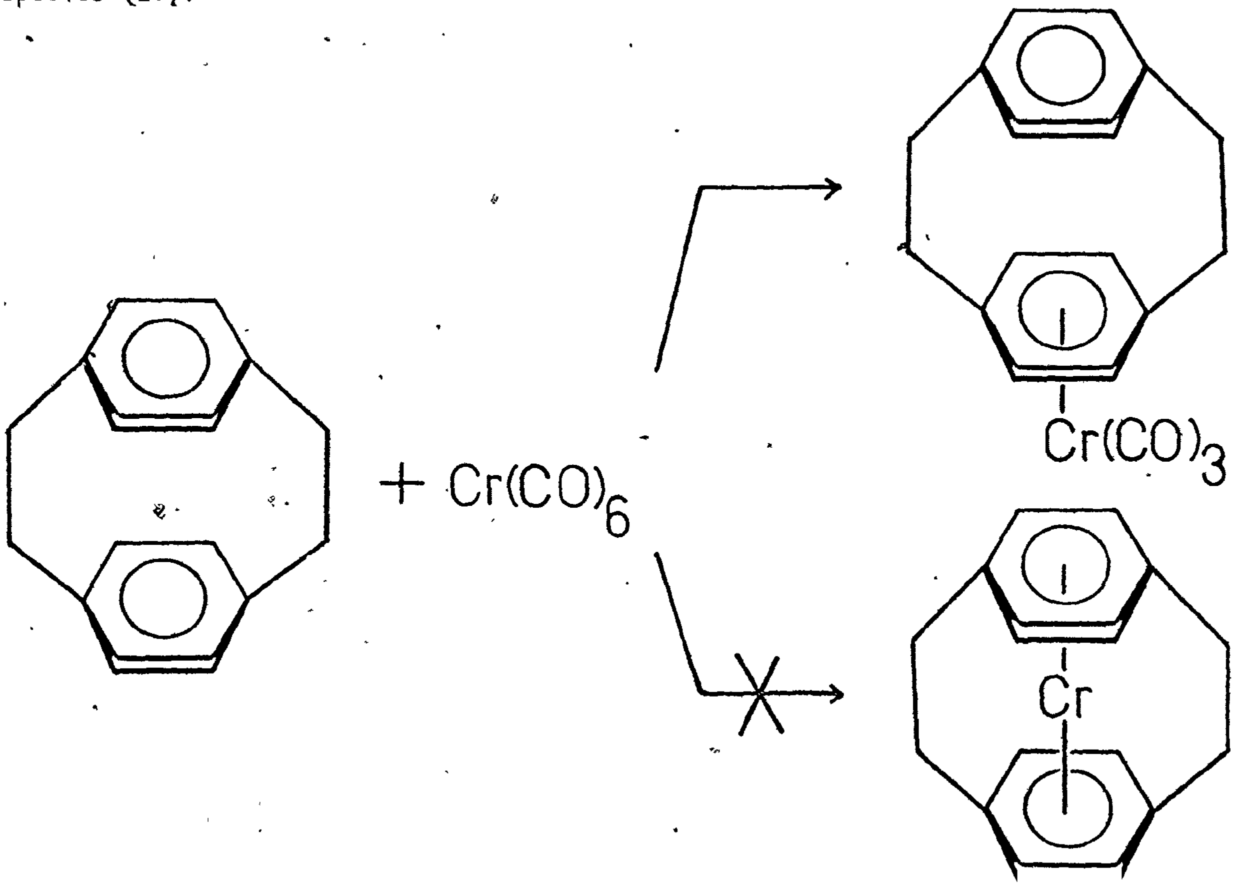
$$C_6H_5X \;+\; Cr(CO)_6 \xrightarrow{\text{Reflux}} \pi\text{-}(C_6H_5X)Cr(CO)_3 \;+\; 3CO$$

$X = CH_3, OCH_3, NH_2, N(CH_3)_2, F, Cl, COOH.$

However, the yields from use of this route were not always high and elevated temperatures and long reaction times were often required. A further refinement of this general method of synthesis, enabling milder conditions to be used and higher yields to be realized, was obtained by the prior formation of a complex of the type $X_nCr(CO)_{6-n}$ (n = 1-3) where X may be CH_3CN (9,10), NH_3 (11), pyridine (12) or picoline (13). Thus, complexes

Presumably formation of the intermediates of the type $X_nCr(CO)_{6-n}$ could follow a similar route with sequential loss of CO's giving rise to the trisubstituted, labile species which may then be readily converted to the final arene complex. Species of this type where X is CH_3CN, NH_3, or pyridine have actually been isolated (for n = 3) whereas the presence of the picoline intermediate has not been confirmed by isolation but merely implicated (13).

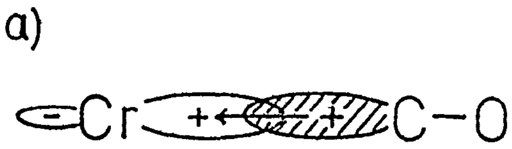
There can be little doubt that the trans influence accounts for the relatively facile loss of up to three carbonyl groups from chromium hexacarbonyl (20). An example of this is shown in the reaction of $Cr(CO)_6$ with [2,2]paracyclophane. Whereas it was hoped that formation of the sandwhich complex might result, the only complex formed was the tricarbonyl species (21).

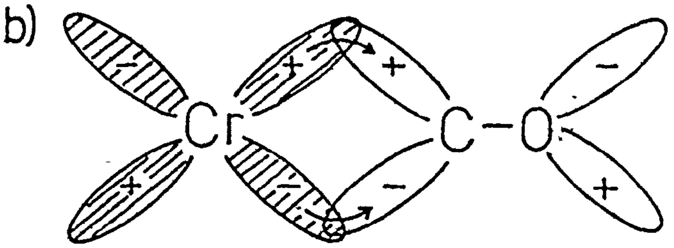


1.2 BONDING AND STRUCTURE

Obviously the major bonding interactions in arene chromium tricarbonyl complexes are those between the metal and the ring and the metal-carbonyl interplay. These two interactions are most certainly interdependent. Whilst the bonding mechanism between the metal and the three carbonyls is well understood,that between the π-bonded ring and the chromium atom is less so.

Filled σ orbitals on the carbon monoxide group overlap with empty orbitals of the chromium atom, as in situation (a). Further, the metal then back donates electron density from its filled "d" orbital into the antibonding π-orbital of the CO group to form a π bond, as shown in (b) (22).





This synergistic type of bonding scheme has been put forward to explain the stability of arene chromium tricarbonyls (23,24) in that electron density from the ring is donated to the chromium concommitantly enhancing the back donation by the metal into the π* orbitals of the carbonyl group.

The degree of this back donation is regulated to a large extent by the electronic requirements of the ring. Thus an electron-donating substituent on the ring causes an incremental increase in electron flow to the metal thereby enhancing the back donation to the carbonyl π^* orbitals, an electron withdrawing substituent acts in the opposite manner to reduce this back donation.

The above mentioned net re-allocation of electron density is evidenced by dipole moment measurements (25,26); Table 1.1 shows some representative values. As the substituent on the arene ring becomes more electron releasing the dipole moment increases; the arene ring is at the positive end of the dipole

Table 1.1 Dipole Moments of Selected Arene Chromium Tricarbonyl Complexes

Arene	Dipole Moment (D)
$C_6H_5N(CH_3)_2$	6.30
$C_6(CH_3)_6$	6.48
$p\text{-}C_6H_4(CH_3)_2$	5.52
$C_6H_5CH_3$	5.26
C_6H_6	5.08

Numerous crystallographic studies have been carried out (27-33) all of which show that the π-arene chromium tricarbonyl adopts a piano-stool configuration. A number of structurally and configurationally interesting features have been revealed by these investigations.

complex are equal, a neutron diffraction study (39) seems to support a localized bonding scheme.

1.3 REACTIONS OF π-ARENE CHROMIUM TRICARBONYL COMPLEXES

The π-arene chromium tricarbonyl system has been shown to undergo a wide variety of interesting reactions whereby the ligands around the metal centre are either exchanged or modified. Much of the chemistry of these systems has been satisfactorily explained by electron distribution and bonding considerations.

The more notable features of the chemistry of π-arene chromium tricarbonyl complexes may be related to:

(i) the electron withdrawing effect of the $Cr(CO)_3$ moiety, which modifies the receptiveness of the ring to nucleophilic attack, and of the metal atom itself which causes the carbonyl group to be susceptible to this type of attack.

(ii) the electron donating capacity of the metal atom which allows for creation and stabilization of carbonium ions adjacent to the arene ring or metal centre.

(iii) the steric bulk of the $Cr(CO)_3$ group which may be used to promote and effect stereoselective reactions at centres adjacent to the ring.

These reactions may be broadly grouped into the following categories:-

(a) reactions of the arene ring
(b) reactions of the arene ring side chain
(c) reactions at the metal centre
(d) reactions at the carbonyl group.

found that the acetyl benzene complex (31) is in a staggered form rather than the eclipsed conformation as would be expected in view of the meta-directing influence of the acetyl group.

The chromium-to-arene-carbon distance averages 2.22Å (ranging from 2.20 to 2.25Å) and does not appear to be affected by the electronic nature of the ring's substituents. An interesting comparison may be made of this metal-ring distance with that found in dibenzene chromium (37). This distance in the latter complex is somewhat shorter (2.14Å) than that in the half-sandwich complex. This may be readily explained by the strong π-bonding nature of the carbonyl group; they tend to decrease the extent of chromium to ring back bonding and so lengthen the bonding distance over that found in the full sandwich analogue.

The chromium-to-carbonyl-carbon bond lengths are of the order 1.76 to 1.88Å, this is to be compared to that in the hexacarbonyl (1.92Å). The shortening of these bonds in the arene tricarbonyl complex and the range of values reflects the net electron withdrawing or releasing characteristics of the ring's substituents. Thus with an electron withdrawing group such as acetyl there is a diminution of Cr-π^*_{CO} donation with a subsequent lengthening of the Cr-C_{CO} bond. Conversely, for electron donating substituents, enhancement of electron donation from the metal into the antibonding orbitals of the carbonyls causes more double bond character and a shortening of the Cr-C_{CO} bond.

The carbon-carbon bonds of the ring range in length from 1.40 to 1.43Å. Whilst the general opinion (27,38) seems to be that, within the limits of experimental error, all ring carbon-carbon bonds in the benzene complex are equal, a neutron diffraction study (39) seems to support a localized bonding scheme.

1.3 REACTIONS OF π-ARENE CHROMIUM TRICARBONYL COMPLEXES

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(c) reactions at the metal centre
(d) reactions at the carbonyl group.

1.3.1 Reactions at the π-complexed Ring

Dipole moment data previously cited and other accummulated evidence would seem to indicate that the arene ring supports a slight positive charge resulting from the apparent electron withdrawing character of the $Cr(CO)_3$ moiety. Indeed from a comparison of pK_a values for π-benzoic acid chromium tricarbonyl and p-nitrobenzoic acid it was concluded that the chromium tricarbonyl group exerts an electron withdrawing effect similar to that of a p-nitro group (4).

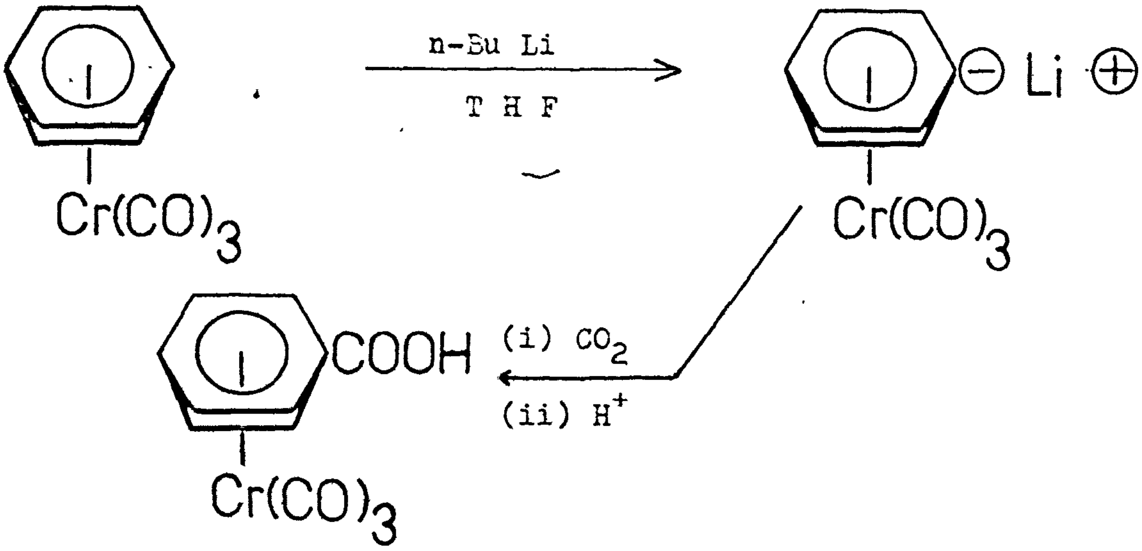
It is then not surprising to find that the complexed arenes are more susceptible to nucleophilic substitution than are their uncomplexed analogues. Fluorobenzene and chlorobenzene complexes react readily with sodium methoxide to give anisole chromium tricarbonyl in high yield (3,4, 40,41). This is in contrast to the free arenes which are relatively inert to such reactions.

$$\pi\text{-}(ClC_6H_5)Cr(CO)_3 \;+\; NaOCH_3 \xrightarrow[\Delta]{CH_3OH} \pi\text{-}(CH_3OC_6H_5)Cr(CO)_3$$

The kinetics of these substitution reactions both with $NaOCH_3$ and $NaNH_2$ have been studied (40;42,43). Comparison of the energetics of these reactions with those of the para-nitro analogues lead to the conclusion that the displacement reaction in the chromium tricarbonyl complexes is a bimolecular process (S_N2) and would seem not to involve an aryne-type intermediate.

An interesting observation arose from a similar nucleophilic substitution reaction with optically active derivatives of complexed methyl fluorobenzoate. Whereas the ortho compound $\pi\text{-}[2\text{-}FC_6H_4COOCH_3]Cr(CO)_3$ underwent partial racemization when treated with $NaOCH_3$ the meta analogue did not (42). This finding may be attributed to the participation in the mechanism of a 1,5 hydrogen shift or a "flipping" of the ring so as to change the side of complexation. Support has been gained for this latter rationale (44).

The ability of the chromium tricarbonyl group to dissipate excess electron density in the ring is evidenced again by the various direct metallation reactions that the complexed ring undergoes. Thus, π-benzene-chromium tricarbonyl reacts with n-butyl lithium in THF to give a phenyllithium complexed intermediate the subsequent quenching of which with CO_2 and acid results in the formation of benzoic acid chromium tricarbonyl in low yield (45).



This intermediate was also formed by the reaction of n-butyl lithium with bis(phenyl tricarbonyl chromium)mercury. Quenching the phenyl lithium complex with excess acetyl chloride led to a mixture of products including π-acetophenone chromium tricarbonyl (46). Similar quenching with chlorotrimethylsilane gave only small amounts of the trimethylsilyl benzene complex [however, good yields from this reaction have been reported (47)] but addition of diphenyl chlorophosphine to the system gave diphenylphosphinobenzene chromium tricarbonyl in 54% yield (46).

Figure 1.1

Addition of CH_3I or I_2 to the complexed phenyl lithium intermediate results in, respectively, toluene chromium tricarbonyl and iodobenzene chromium tricarbonyl (48). Reaction of toluene chromium tricarbonyl with n-butyllithium followed by quenching with CH_3I gave a mixture of xylene complexes (of which meta-xylene predominated) as well as small amounts of complexed ethylbenzene (48). The phenyl lithium chromium tricarbonyl intermediate has been observed by proton n.m.r. (48).

The net displacement of chloride in π-$(C_6H_5Cl)Cr(CO)_3$ by 2-lithio-2-cyanopropane in high yield has been studied as an example of a general, facile route of addition of carbon units to arene rings (the chromium tricarbonyl unit being subsequently oxidatively cleaved from the organic function) (49,50). The complete mechanism for this reaction is complex and has yet to be fully elucidated. It however appears to involve reversible attack of the complexed anion at all positions of the ring (except para) with subsequent irreversible loss of chloride from one or more of these intermediates.

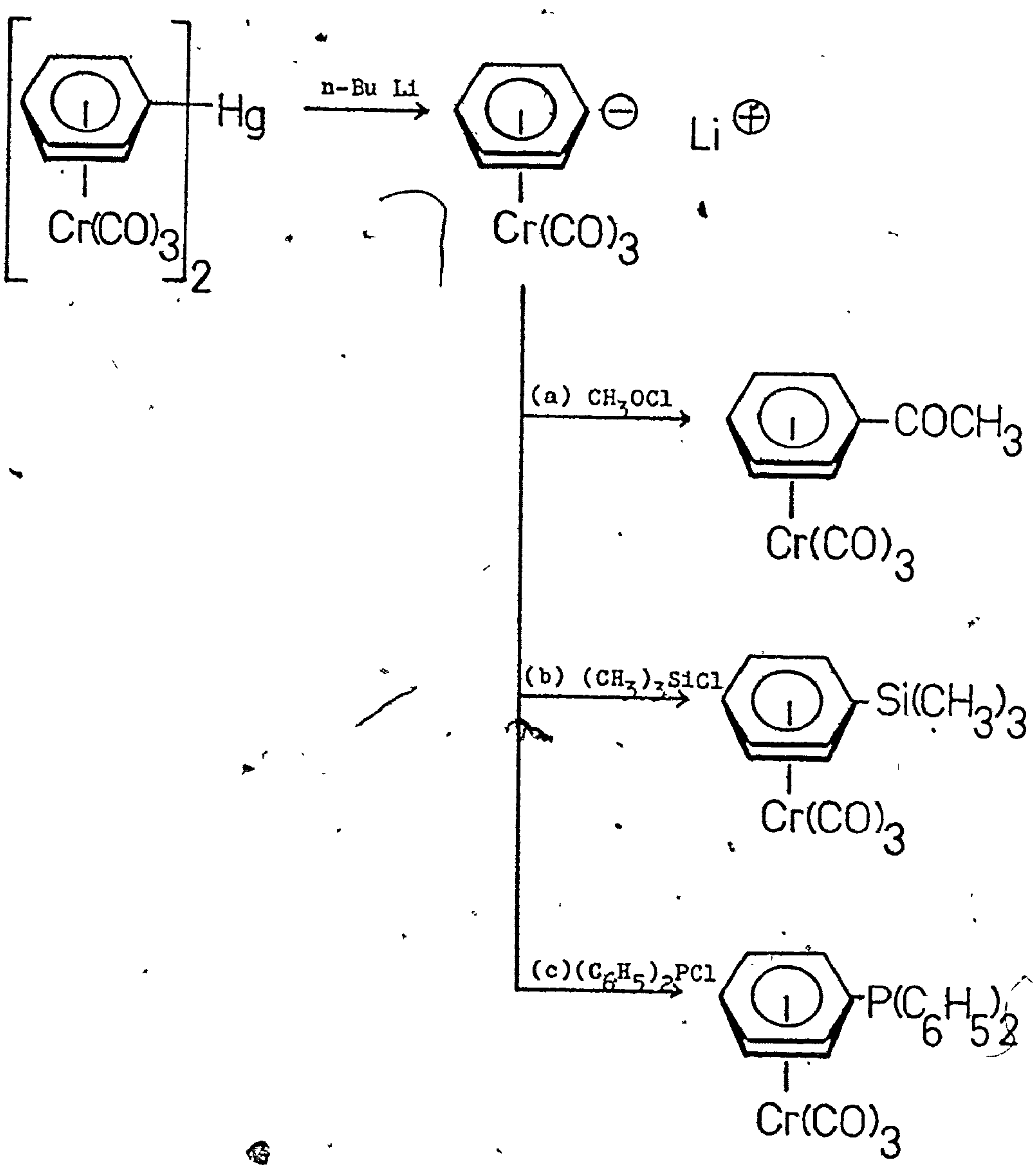
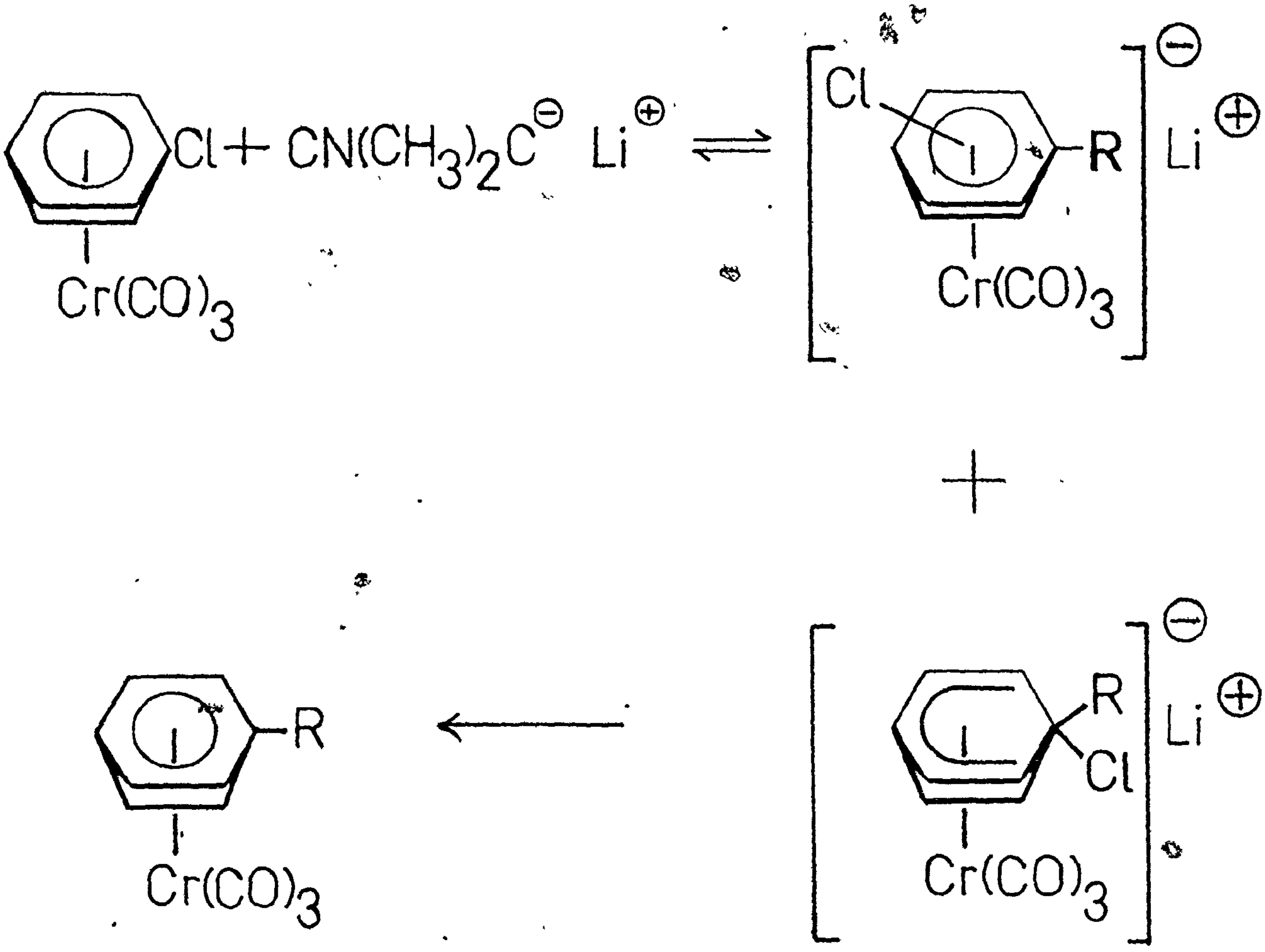


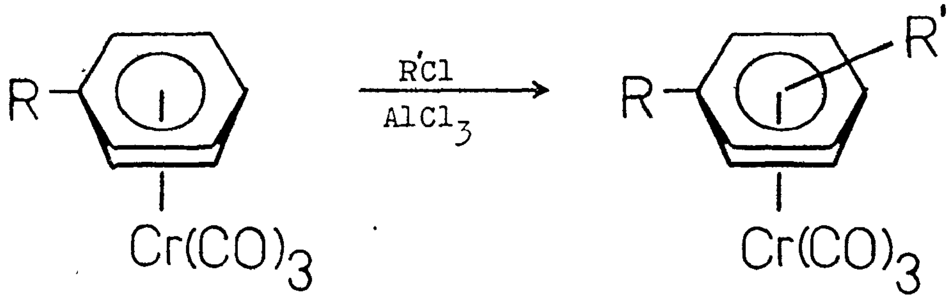
FIGURE 1.1 Some Reactions of a Lithiated Ring of an Arene Chromium Tricarbonyl Complex



$R = CN(CH_3)_2C—$

Although the inherent electron withdrawing effects of the $Cr(CO)_3$ unit can be expected to diminish the ring's susceptibility to electrophilic attack these systems do nonetheless undergo a number of such reactions.

Friedel-Craft acylations have been performed on a series of arene chromium tricarbonyls (40,51-53).



R= CH_3,H,CH_3CH_2,CH_3O,$(CH_3)_2CH$,$(CH_3)_3C$

The π-arene chromium tricarbonyl complexes have also been reported to undergo mercuration reactions with $Hg(OAc)_2$ followed by treatment with $CaCl_2$ to yield π-$(ClHgC_6H_5)Cr(CO)_3$ (54).

1.3.2 Reaction at the Side Chain of the Complexed Ring

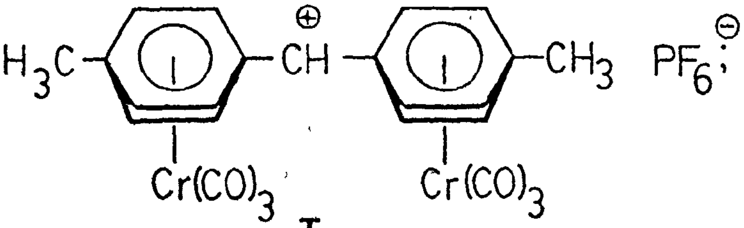
The evidence in support of the electron withdrawing capabilities of the chromium tricarbonyl moiety is well documented, however, its ability to stabilize electron deficient sites has also been illustrated. This latter aspect of the chromium tricarbonyl's dual nature has been implicated by a study of the rates of solvolysis of a number of systems.

Stabilization of the complexed benzyl cation by electron donation from the metal centre is believed to account for the increased rate of solvolysis of benzyl chloride chromium tricarbonyl over its uncomplexed analogue (55).

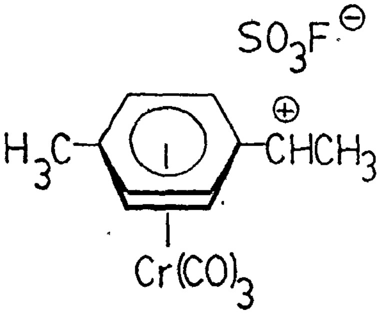
Similar arguments have been proposed to explain the enhancement of the rate of solvolysis of π-cumyl chloride chromium tricarbonyl over the free chloride (56) and of the rate of acetolysis of free and complexed aryl sulfonates (57,58).

Presumably direct interaction of the cationic sites with filled d orbitals of the chromium results in back donation of electron density to the deficient site.

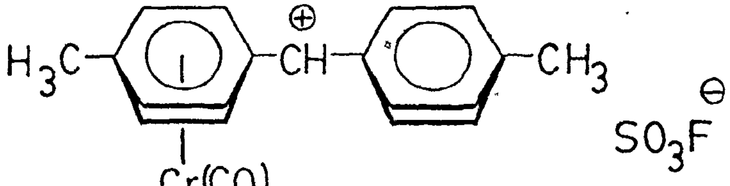
Spectroscopic evidence has been acquired for the existence of such complexed benzyl cations (59,60) and more recently a number of carbonium ion species, stabilized by a $Cr(CO)_3$ group, have been reported (61-63). Thus, the blue carbonium ion salt complex I (61) was formed by reduction of



I



II

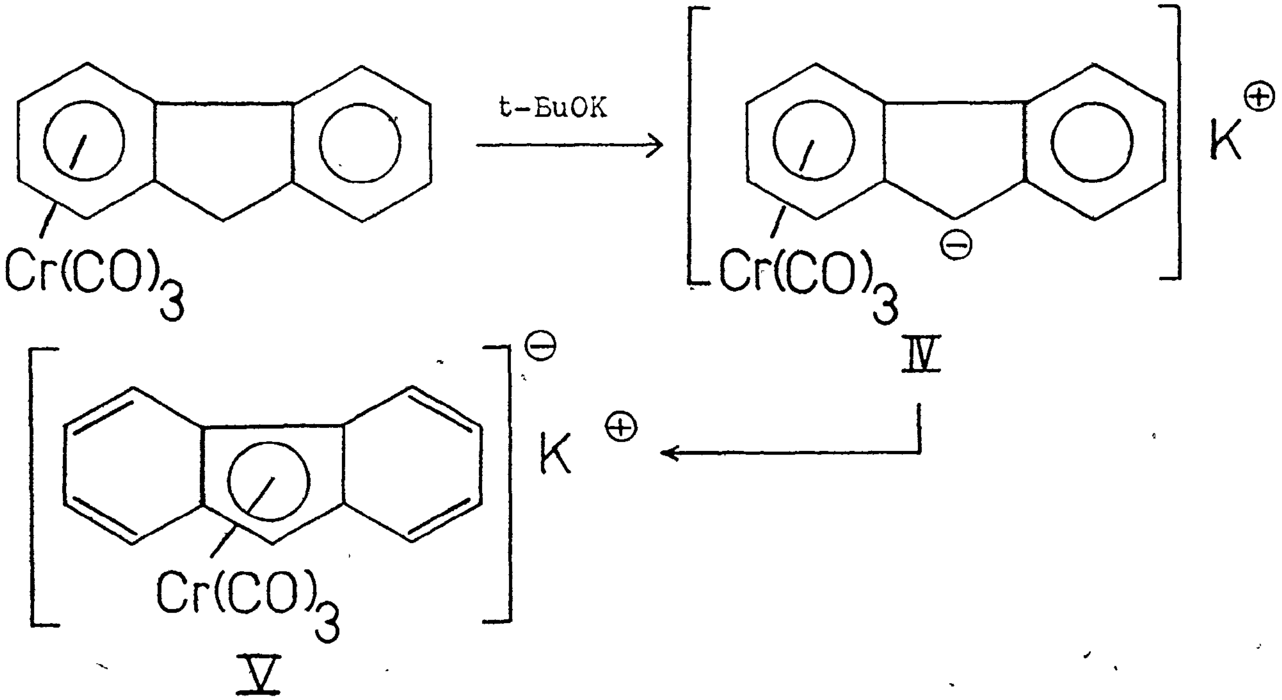


III

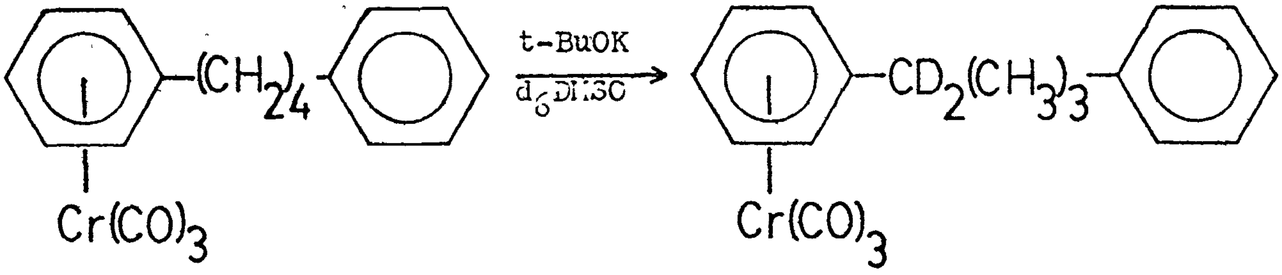
the corresponding diaryl ketone with $NaBH_4$ followed by treatment with HPF_6. Similarly, complex salts II (62) and III (63) have been isolated. Spectroscopic evidence for all of the above indicate that a considerable portion of the charge is transferred to the metal.

The diverse nature of the chromium tricarbonyl moiety is again evident in its promotion of α proton abstraction in (η^6-fluorene)$Cr(CO)_3$ by reaction with base (64,65).

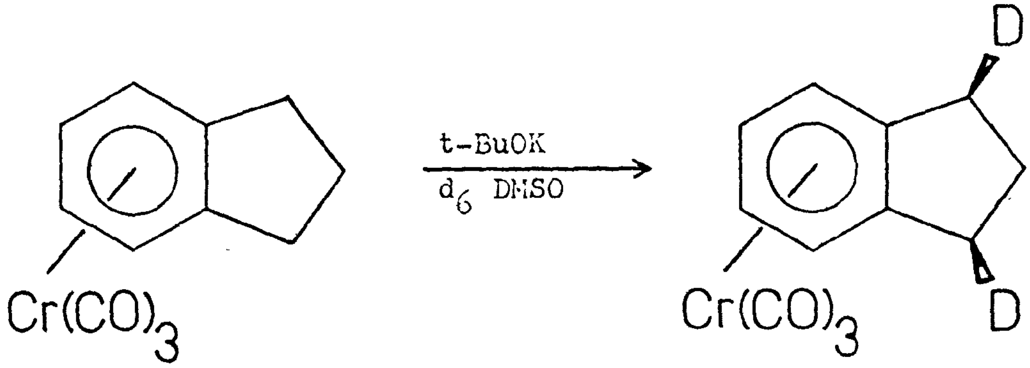
In the above cases it was justifiably argued that the aromatization of the five-membered ring by loss of a proton α to the complexed ring would tend to stabilize the anion (64). It was later shown (65) that the η^6-anionic intermediate (IV) is transformed into the η^5 isomer (V).



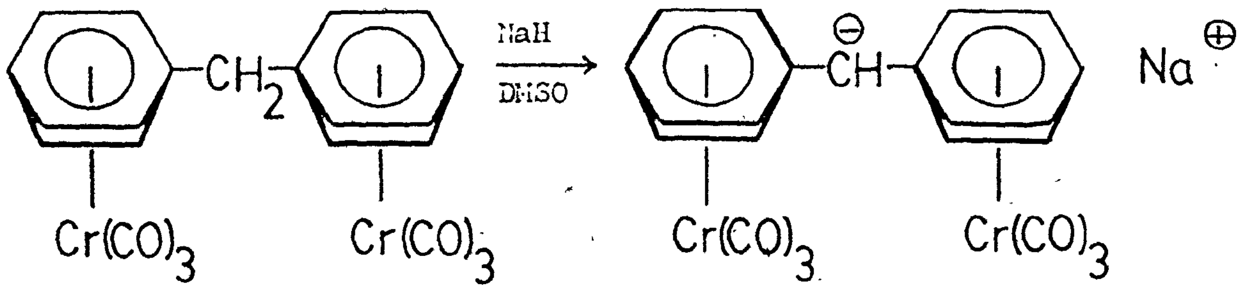
Indeed, α proton abstraction has been shown to occur even in the absence of other substituents to stabilize the α site (66).



Furthermore, in rigid systems such H/D exchange is stereoselective (66), more will be said on the rationale for this below.



Recently, a stabilized complex anion has been isolated (67). Thus the diphenylmethane chromium tricarbonyl complex, on treatment with NaH in DMSO, forms the corresponding α-anion which exhibits enhanced stability over the uncomplexed anion analogue.

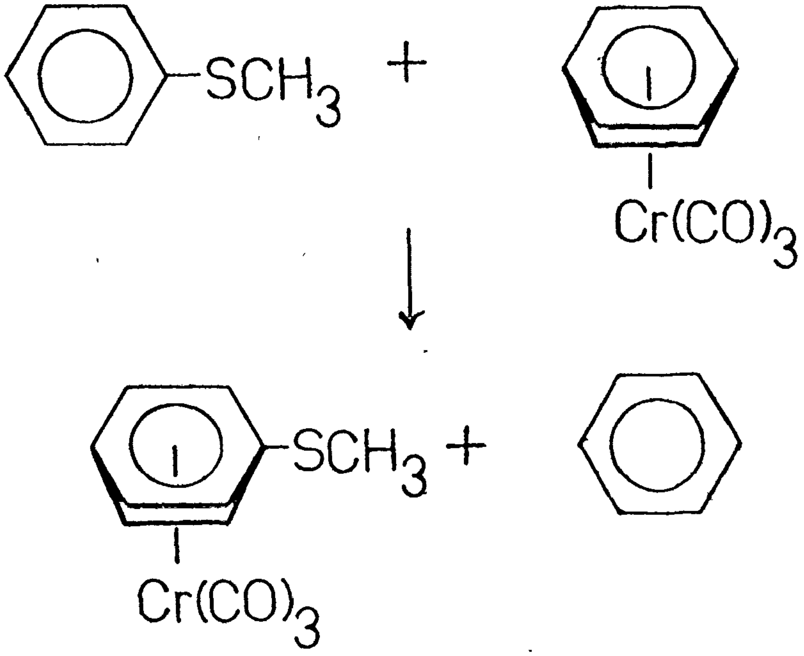


The ^1H and ^{13}C nmr and IR spectral changes upon complexed anion formation were interpreted as implicating a mechanism of stabilization whereby the negative charge became delocalized throughout the arene-metal tricarbonyl system.

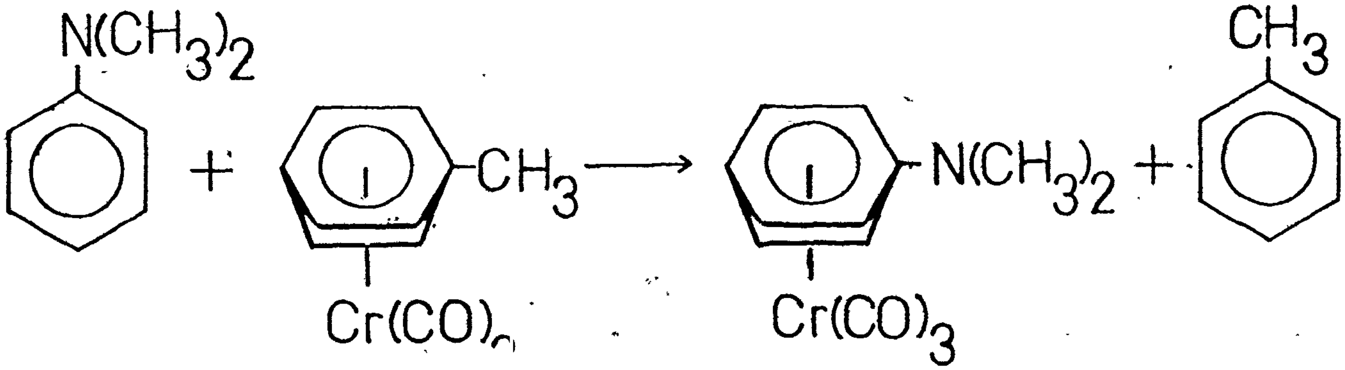
1.3.3 Reaction at the Metal Centre

This group of reactions includes those transformations where the reaction may be initiated at a ligand site but gives rise to a net change at the metal centre. These would then include, primarily, replacement of the arene and/or one or more carbonyl groups.

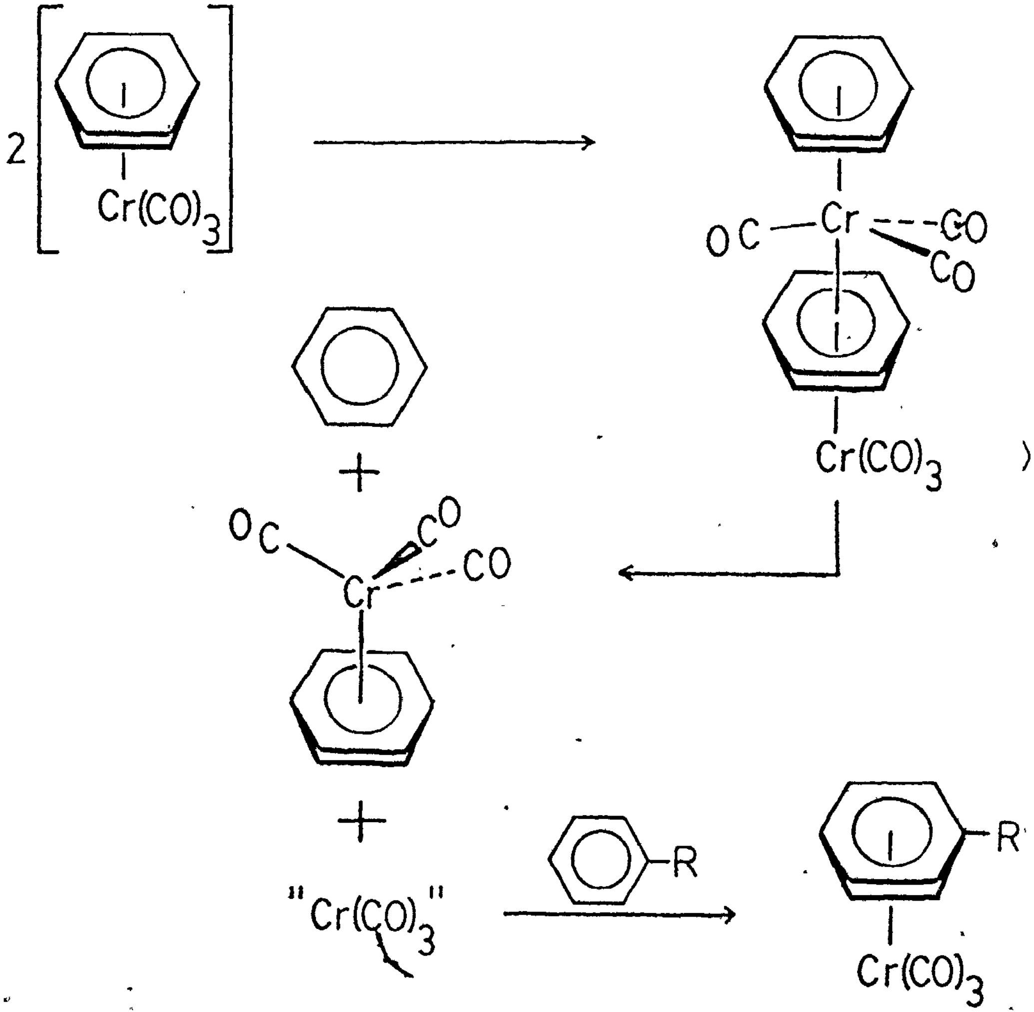
Arene replacement reactions have been shown to be of some synthetic utility. The complexed arene when reacted with another arene may be exchanged in the reaction for this second arene.



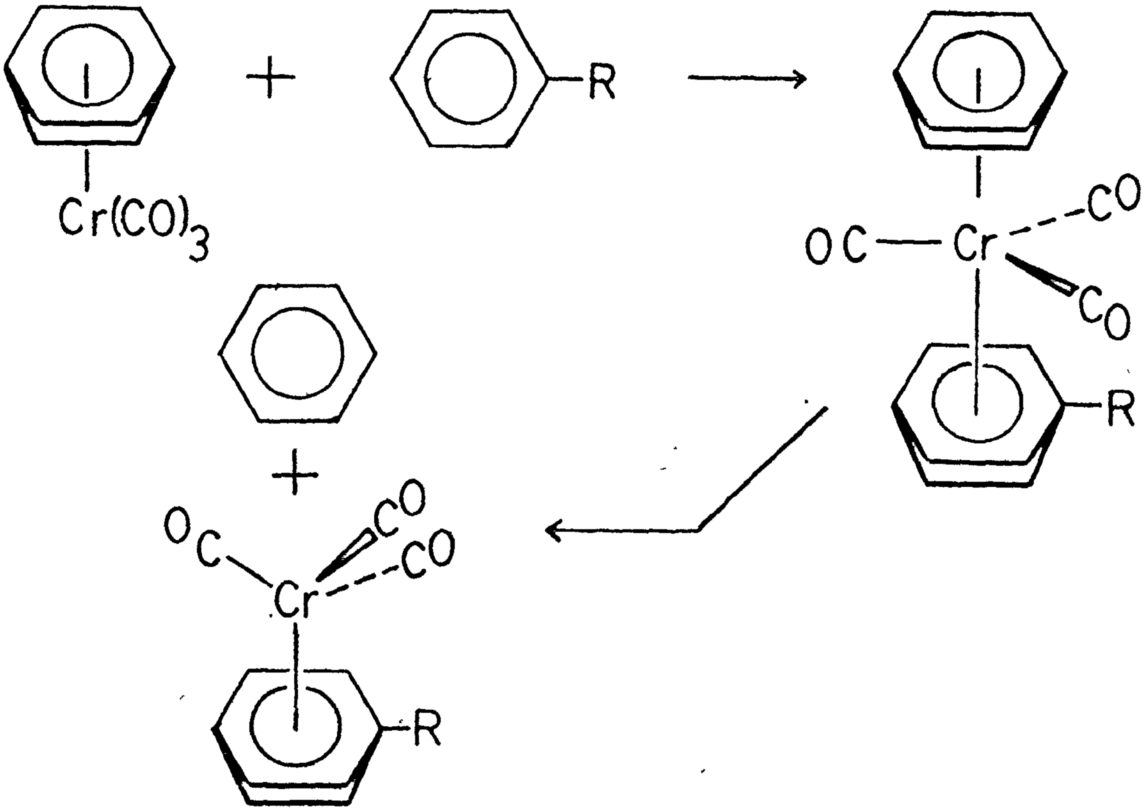
(68)



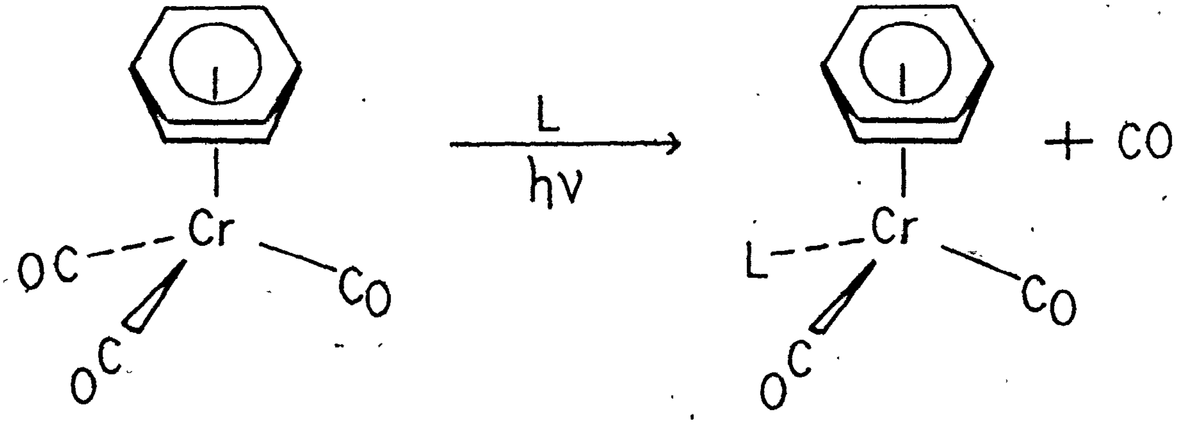
The mechanism for these reactions is believed to involve two processes; the initial one being the formation of a charge transfer complex.



This then fragments to release benzene and an active "Cr(CO)$_3$" group which goes on to react with the free arene. Not surprisingly, and in agreement with these proposed mechanisms, the reaction rate is enhanced by electron donor groups on the "replacing arene". The second process involves direct replacement by the free arene in a bimolecular reaction.

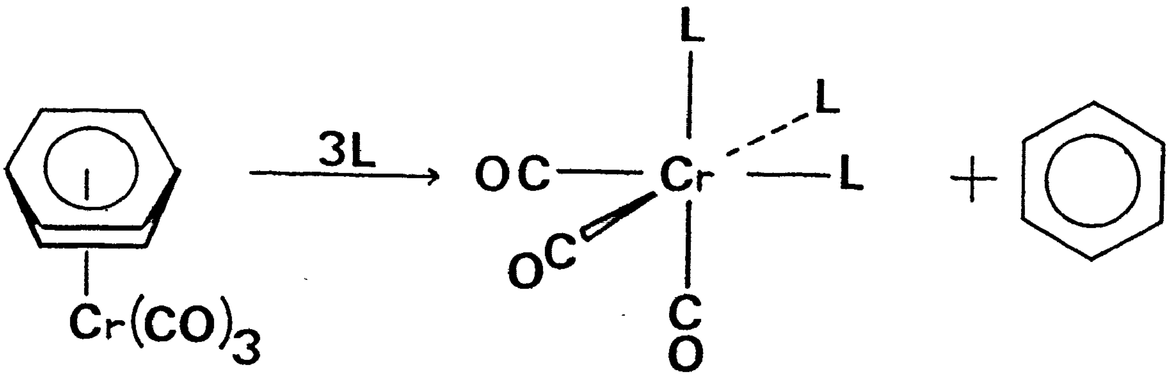


Replacement of a carbonyl ligand has been accomplished using a wide variety of ligands. Normally the reaction proceeds under U.V. irradiation, the general reaction being:-



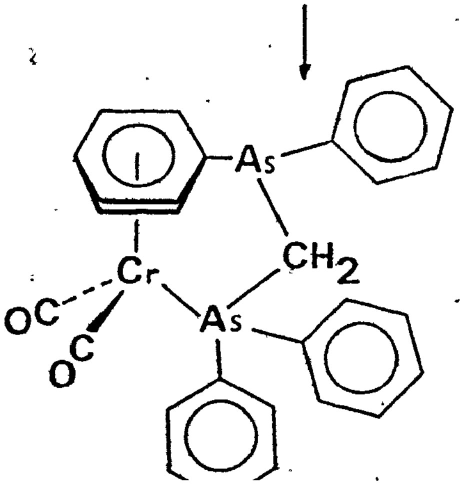
For example, L = phosphines (70,71), amines (70), nitriles (72), sulfides, sulfoxides (73,74) olefins, acetylenes (75), and molecular nitrogen (76).

Many of these ligands (those having strong σ donor properties) have been shown to replace the arene ring under conditions of a thermal reaction with π arene chromium tricarbonyls (4,77).



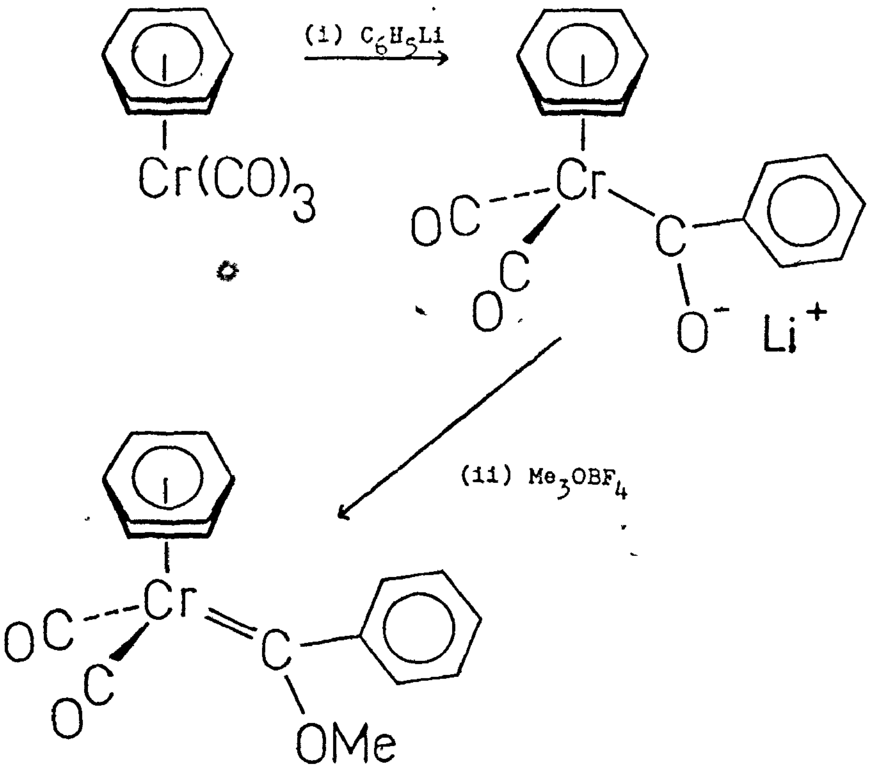
An interesting reaction involves that of $Cr(CO)_6$ with $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ and triaryl phosphines. The resulting complex is shown below:-

$(C_6H_5)_2As\ CH_2\ As(C_6H_5)_2\ +\ Cr(CO)_6$



1.3.4 Reaction at Carbonyl Ligands

By far the most prevalent reaction of this type involves the formation of a carbene species at a carbonyl by reaction with a nucleophile, commonly an alkyl or aryl lithium compound. For example, reaction of π benzene chromium tricarbonyl with phenyl lithium (followed by quenching with $Me_3O^+BF_4^-$) yields such a carbene complex (78). Similarly other arene complexes have been shown to react in an analogous manner (79).



The π-arene chromium tricarbonyl complexes are much less reactive towards nucleophiles than $Cr(CO)_6$ due mainly to the increase in electron density at the carbonyl carbons of the arene complex.

CHAPTER 2

SOME ASPECTS OF THE BONDING IN ARENE CHROMIUM TRICARBONYL COMPLEXES. A ^{19}F N.M.R. INVESTIGATION

2.1 INTRODUCTION

As previously mentioned the exact nature of the bonding of arenes to the chromium tricarbonyl moiety is not well understood and has been the subject of much speculation over the past few years.

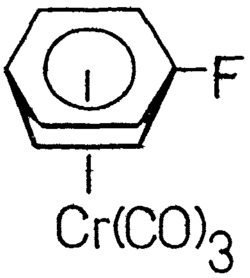
As has already been intimated much compelling evidence exists to suggest that the $Cr(CO)_3$ group is strongly electron withdrawing. Pioneering studies in this field showed that chlorobenzene chromium tricarbonyl undergoes rapid nucleophilic substitution with methoxide ion (4). Also, benzoic acid and phenol have been shown to be weaker acids than their complexed analogues (4,7,80,81), and similarly aniline is a stronger base than aniline chromium tricarbonyl (7). Benzene chromium tricarbonyl has been shown to undergo base catalysed deuterium exchange under conditions for which this reaction will not occur for the free arene (82,83). Semi-empirical molecular orbital calculations (23,24) and dipole moment measurements for benzene chromium tricarbonyl (25), both of which place a net positive charge on the arene ring, add further evidence to implicate the $Cr(CO)_3$ moiety as being electron withdrawing in its nature. N.m.r. chemical shift data (84-87) further support the above mentioned contention.

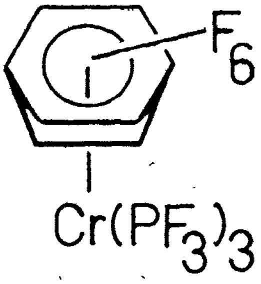
However, the transmission of π-substituent effects in complexed arenes has been shown to be largely unchanged from that in their respective free arenes (88-91).

Attempts have been made to resolve this apparent dichotomy and to probe the models of ring-metal bonding in arene chromium tricarbonyls by the investigation of ^{19}F n.m.r. chemical shifts of a series of substituted fluorobenzene chromium tricarbonyl complexes.

2.2 ^{19}F N.M.R.

The technique of ^{19}F n.m.r. as it applies to π-fluoroarene chromium systems has been sparingly exploited with fluorobenzene chromium tricarbonyl (92) and hexafluorobenzene-tris(trifluorophosphine) chromium (93) being the only compounds, to our knowledge, for which ^{19}F data has been gathered.





The fluorine nucleus offers several advantages over protons in terms of their usefulness as n.m.r. probes. The most obvious difference is the larger range of chemical shifts and coupling constants found for fluorine versus those for ^{1}H. The consequence of this is that interpretation of spectra is often less complicated for ^{19}F work due to the reduced frequency of band systems' overlap. Additionally, the "fall off" in values of coupling constants with increases in the number of intervening bonds is less pronounced for the fluorine nucleus. This greater propensity for

^{19}F coupling, whilst potentially very informative, can give rise to a more complicated spectra arising from the multiplet structure of bond systems.

Fluorine spectra are readily obtained, the resonance frequency at 14,090 gauss being 54.46 MHz with a relative sensitivity of 83.4% compared to that for protons.

It has long been recognized that the fluorine shielding constant is a sensitive probe of the electronic nature of substituted aromatic compounds (94). Further, it has been noted that changes in ^{19}F n.m.r. chemical shifts of para-substituted fluorobenzenes reflect changes in the π electron density at the C(4) position (94).

Thus a series of fluorobenzene chromium tricarbonyl complexes, of general formula π-(FC_6H_4X)$Cr(CO)_3$ where X = H, F, Cl, CH_3, CF_3, NH_2 or OCH_3, were prepared and their ^{19}F n.m.r. spectra, together with that of their uncomplexed analogues, were recorded.

2.3 CORRELATION OF INDUCTIVE AND RESONANCE PARAMETERS WITH ^{19}F N.M.R. CHEMICAL SHIFTS

Many workers have attempted to derive empirical relationships between structure and reactivity of organic molecules. Perhaps the best known of such relationships is that due to Hammett (95) who measured the ionization constants of a series of substituted benzoic acids. The familiar expression

$$\log (k/k_0) = \rho\sigma$$

resulted where σ is a substituent constant and relates to the electronic nature of the substituent in question.

This basic concept was employed by Gutowsky and coworkers in 1952 to investigate the substituent dependence of ^{19}F n.m.r. chemical shifts (96,97). The ^{19}F n.m.r. chemical shifts were determined for a series of monosubstituted fluorobenzenes, C_6H_4FX. The difference in ^{19}F shifts between fluorobenzene and the substituted fluorobenzene was used to define a δ parameter. An empirical correlation was found to exist between these experimental δ-values and the Hammett σ-constants for a considerable number of meta- and para- substituted fluorobenzenes.

Taft (98-100) later carried out work to refine Hammett's substituent constants and to apply this refinement to ^{19}F shielding data. He proposed (98) a quantitative separation of the Hammett σ-value to independent inductive and resonance contributions according to

$$\sigma \equiv \sigma_I + \sigma_R$$

where σ_I is the inductive contribution and may be regarded as a measure of the free energy effect of the substituent arising from its ability to attract or repel electrons through space and the sigma bonds of the benzene system. The resonance contribution, σ_R, may be taken as a measure of the free energy effect resulting from the power of the substituent to attract or repel electrons through a resonance interaction involving the π-orbital system of the benzene ring. Taft showed (101) that Gutowsky's δ^F values for meta- and para- substituted fluorobenzenes correlated precisely with the equations:

$$\delta_m^F = (0.583 \pm 0.026)\,\sigma_I - 0.02$$

$$\delta_p^F = (0.583)\,\sigma_I + (1.880 \pm 0.081)\,\sigma_R - 0.08$$

Rearrangement of these equations gives

$$\delta^F_m = (0.58)\,\sigma_I + (0.00)\,\sigma_R$$

$$\delta^F_p = (0.58)\,\sigma_I + (1.88)\,\sigma_R$$

These expressions are in keeping with classical thinking in that mesomeric effects are prevalent for para-substituents but not for those in the meta position.

It is thus apparent that ^{19}F n.m.r. shielding effects may be generally described by:

$$\delta^F = \alpha\sigma_I + \beta\sigma_R$$

where α and β are empirical constants and represent, respectively, the susceptibility of the magnetic shielding to the inductive and resonance interactions of the substituents.

McGlinchey and Tan (102) employed the above approach to draw correlations between the ^{19}F n.m.r. chemical shifts of a series of substituted bis(fluoroarene)chromium complexes and an appropriate combination of Taft's inductive and resonance parameters. In this way an interesting correlation evolved relating the ^{19}F n.m.r. shifts of these chromium sandwich compounds with those of a series of substituted pentafluorophenyl compounds.

This concept of weighting the resonance and inductive interactions may also be applied to Hammett's original sigma values (98,102) thus, in Hammett's terminology

$$\log (k^p/k_0) = \sigma_I + \sigma_R$$

$$\log (k^m/k_0) = \sigma_I + \tfrac{1}{3}\sigma_R$$

This overall approach, particularly as it was applied to Hammett's sigma values, was an attempt to overcome the overriding inadequacy of the substituent constants as derived by Hammett in that, contrary to initial beliefs, they were found not to be reaction independent and thus not to be applicable to the general case. As a direct consequence of this shortcoming there now exists more than 20 alternate sets of sigma values each having been derived or modified for a special system or application.

Swain and Lupton (104) addressed this problem and proposed a set of substituent parameters F and R such that each σ set may be expressed as a linear combination of these new parameters, thus:

$$\sigma = fF + rR$$

where F and R are, respectively, the field and resonance constants characteristic of particular substituents and f and r are weighting factors determined by optimizing the difference between experimental and calculated data using a standard linear regression program to maximize the correlation coefficients.

This approach was based on demonstrating that not more than two σ sets are significantly independent. Thus any substituent constant for a given substituent can be expressed as a linear combination of any other two constants (from different sigma sets) for the same substituents.

$$Z = aX + bY + i$$

The fitting was done with the above equation where X, Y and Z are the substituent constants. As an example, σ_p^+ (105) may be expressed in terms of σ_m and σ_p for a series of substituents:

$$\sigma_p^+ = a\sigma_m + b\sigma_p + i$$

then a, b and i are determined by means of a least squares fit.

The values for σ_m and σ_p were chosen as the basis set for the independent variables as they were deemed the most complete and accurate sets of data available. The principal deficiency of correlations with these constants were thought to result from their hybrid nature, i.e. σ_m still contained a degree of contribution from resonance, and field effects were still present in σ_p. It is this very problem that Swain and Lupton (104) implicate as being the reason why so many different sigma values have been made necessary.

In order to assess pure field and resonance effects they have made the assumptions that

(a) the effects of 4-substituents on the dissociation constants of bicyclo (2.2.2) octane-1-carboxylic acids is entirely a field effect, and

(b) the resonance potential of the trimethylammonium ion substituent is negligible.

Thus with these assumptions and working from a basic set of σ_m and σ_p values for F and R were calculated. The relative importance of field versus resonance effects, i.e. the magnitude of f and r respectively, in different reaction series was then determined by optimizing the correlation coefficient within a given sigma set according to

$$\sigma = aF + bR + i$$
$$(a = f; \quad b = r)$$

Whilst these substituent parameters (F and R) have the same qualitative characteristics as σ_I and σ_R they have the added usefullness of being independent of position in the aromatic ring, reaction, solvent and temperature. Additionally, F and R values have been determined for 42 substituents (104).

Correlations of ^{1}H (105), ^{11}B (106) and ^{13}C (107) n.m.r. chemical shifts with these field and resonance parameters of Swain and Lupton (104) have been made. In the work to be presented similar correlations will be attempted for the ^{19}F n.m.r. chemical shifts of the aforementioned series of substituted fluoroarenes and their chromium tricarbonyl derivatives.

2.4 ^{19}F AND ^{13}C NUCLEAR MAGNETIC RESONANCE DATA

Swain and Lupton (104) proposed that an empirical relationship exists between ^{19}F n.m.r. chemical shifts in meta- or para- substituted fluorobenzenes and their previously mentioned field and resonance parameters according to

$$\Delta^{F} = fF + rR$$

The originally quoted values for f and r (104) for para-substituted fluorobenzenes are 35% and 65% respectively, which are calculated to have a low linear correlation coefficient using the substituents H, F, Cl, CH_3, CH_3O, NH_2 and CF_3. A better fit is obtained (correlation coefficient, $\bar{r}$, of 98.8%) for f = 9% and r = 91%. These values seem intuitively more reasonable and are in keeping with the idea of a predominance of the resonance substituent effect for such a para-substituted series. Application of the same technique to the ^{19}F n.m.r. chemical shifts of the corresponding para-substituted fluorobenzene chromium tricarbonyl complexes (see Table 2.1 for relevant data) yields f and r values of 6% and 94% respectively, $\bar{r}$ = 99.4% (see Figure 2.1). This remarkable constancy of the dominance of the resonance parameter in the transmission of substituent effects is most gratifying as it is in direct agreement with the findings of a similar ^{13}C n.m.r. study (107). In this work the C(4) ^{13}C n.m.r. chemical shifts (corrected by the method of Maciel and Natterstad (108)) for a series of monosubstituted arenes was shown to have maximum correlation with the Swain and Lupton (104) parameters when f and r were 3% and 97% respectively. In the corresponding complexes the optimum correlation resulted when f and r were, respectively, 1% and 99%.

The correlation between the ^{19}F chemical shifts in para-substituted fluorobenzenes and the ^{13}C chemical shift of the C(4) carbon in the corresponding monosubstituted arenes is well established (108-110) and this relationship still holds in most cases when the arenes are complexed (see Figure 2.2).

The ^{13}C n.m.r. chemical shifts at the meta position in monosubstituted arenes show no recognizable correlation with substituent parameters (109) or indeed with ^{19}F chemical shifts in the corresponding meta-substituted fluorobenzenes (108). However, in contrast to the para isomers, meta-substituted fluorobenzenes show a greater than 95% dependence of the ^{19}F chemical shift on F, the field parameter, (or as Taft (101) showed, Δ_m^F is

TABLE 2.1 N.m.r. and Infrared data for <u>para</u>-substituted arenes and complexes.

SUBSTITUENT	ΔF^*		$\Delta C^\dagger$		6% $\mathcal{F}$ + 94% $\mathcal{R}$	ν_{CO} #	
	COMPLEX	FREE	COMPLEX	FREE		E	A_1
H	135.9	113.1	-93.50	-127.97	0.0	1930	1936
CH_3	137.8	118.8	-90.21	-125.05	-0.136	1926	1994
OCH_3	142.4	124.4	-85.95	-120.22	-0.445	1911	1992
Cl	137.2	116.1	-88.74	-126.02	-0.109	1938	2002
NH_2	146.2	127.1	-83.80	-117.85	-0.638	1909	1990
F	134.0	120.0	-86.97	-123.58	-0.273	1930	1997
CF_3	133.5 60.5	108.3 62.5	-94.34	-131.45	+0.213	1950	2006

* ^{19}F chemical shifts of <u>para</u>-substituted fluorobenzenes and $Cr(CO)_3$ analogues, measured as 2% solutions in benzene relative to internal $CFCl_3$.

† ^{13}C chemical shifts of C_4 in monosubstituted benzenes and $Cr(CO)_3$ analogues; all values taken from ref. 107 except for CF_3 substituent (this work) and measured relative to internal T.M.S.

\# Carbonyl stretching frequencies (cm^{-1}) for <u>para</u>-substituted fluoroarene complexes.

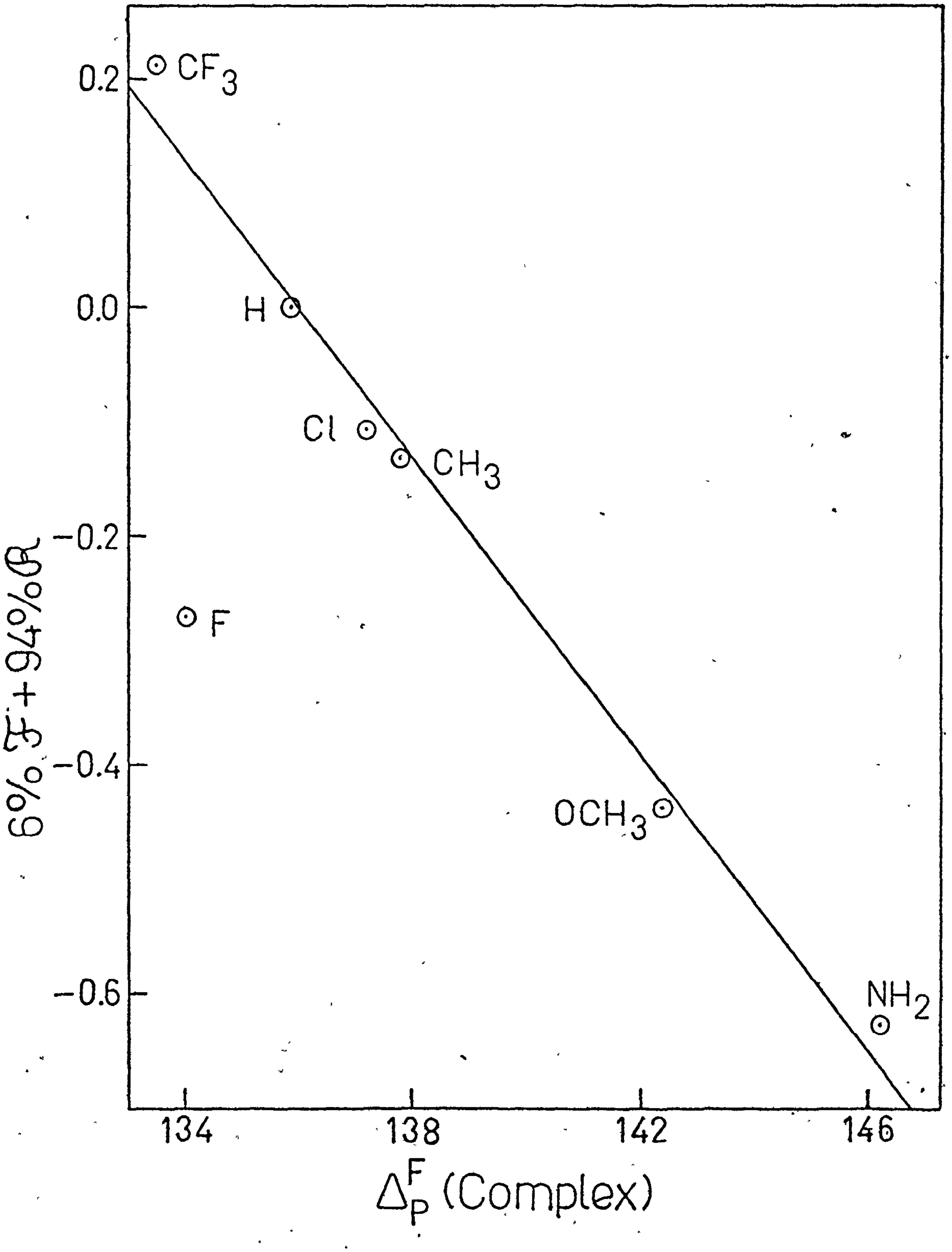


FIGURE 2.1 Plot of ^{19}F chemical shifts of <u>para</u>-substituted fluorobenzene chromium tricarbonyls (measured in p.p.m. to high field of $CFCl_3$) against 6% $\mathcal{F}$ + 94% $\mathcal{R}$.

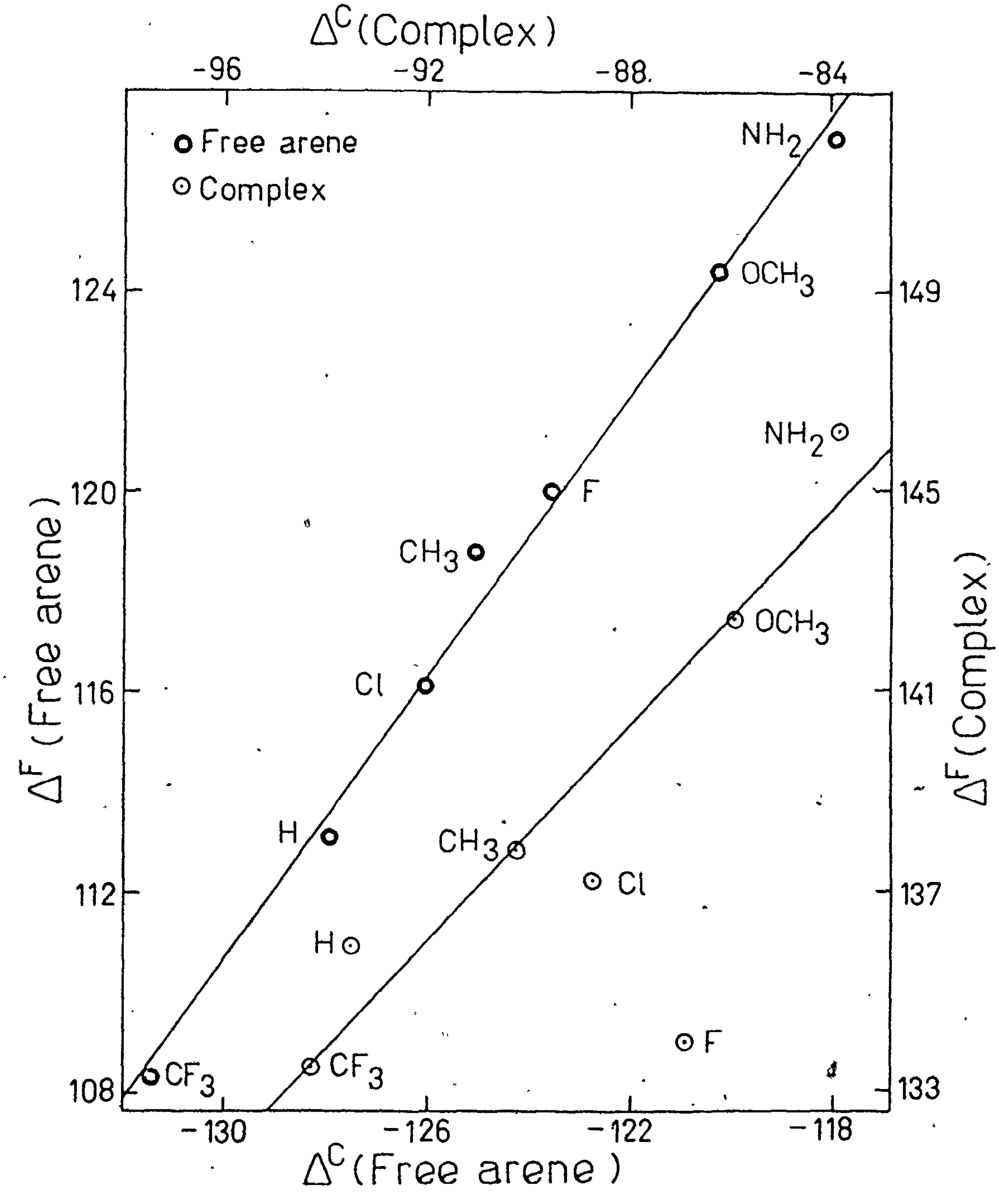


FIGURE 2.2: Plot of ^{13}C chemical shifts of C_4 in monosubstituted benzenes and chromium tricarbonyl analogues against ^{19}F chemical shifts of para-substituted fluorobenzenes and tricarbonyl analogues. ^{19}F chemical shifts are in p.p.m. to high field of $CFCl_3$ and ^{13}C chemical shifts are in p.p.m. to low field of T.M.S.

directly proportional to σ_I). Upon complexation, however, a dramatic change occurs in that the ^{19}F chemical shifts of a wide variety of meta-substituted fluoroarenes (including ones of vastly differing electronic characteristics, such as CF_3 or NH_2) are almost all the same. The chemical shifts all fall within a narrow range of rather less than 2 ppm (see Table 2.2) and show no obvious correlation with the electronic properties of the meta-substituent, whereas the free arenes cover a range almost five times as large as this (101). Thus, the fluorine atom in the complex seems hardly able to distinguish any other meta-substituent from hydrogen, and is completely different to the para isomers where substituent dependence is very pronounced.

TABLE 2.2 N.m.r. and infrared data for meta-substituted complexes.

SUBSTITUENT	ΔF^* COMPLEX	ν_{CO} † E	A
H	135.9	1930	1996
CH_3	135.3	1924	1993
OCH_3	136.7	1910	1993
Cl	136.6	1939	2003
NH_2	136.3	1901	1991
F	136.4	1937	1999
CF_3	135.8 62.4	1950	2008

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* ^{19}F chemical shifts of meta-substituted fluorobenzenes and $Cr(CO)_3$ analogues. measured as 2% solutions in benzene relative to internal $CFCl_3$.

† Carbonyl stretching frequencies (cm^{-1}) for meta-substituted fluoroarene complexes.

A fundamental change has clearly occurred in the arene ring upon complexation and, making the usual assumptions that mesomeric effects are transmitted predominantly via the π system while inductive effects primarily concern the σ framework, the following conclusions may be drawn.

The chemical shifts of the fluorine atoms in the complexes reveal an indifference to the identity of the meta-substituent; thus it would seem that since this effect is transmitted almost entirely via the σ system, then the σ system itself must have been drastically modified. Indeed this would suggest participation by the σ framework of the ring in the arene-metal bond formation such as has been suggested by Drago and Anderson (110) from molecular orbital calculations. The observed upfield shift of about 20-25 ppm relative to the uncomplexed arenes has been attributed to apartial sp^2-sp^3 rehydridization (92) which seems reasonable in light of the above evidence.

Since the transmission of substituent effects from the para position is scarcely changed upon complexation, and it has further been shown that this effect is transmitted predominantly by a resonance effect, then, if this goes entirely via the π system of the ring, the π system must be essentially unperturbed by complexation. Conversely, if one could consider that the chromium atom were involved in the mechanism of transmission of the substituent effect, then it is not necessary to assume that the π-electron density remains unchanged. Furthermore, any modification of the π system would certainly affect the aromatic ring current and work to elucidate this point will be presented subsequently.

So it is clear that, upon complexation, there still remains an effective pathway by which a para-substituent can deliver its mesomeric effect while the net withdrawal of electron density from the σ framework seriously curtails the ability of a meta-substituent to bring about its inductive effect. Neither of these conclusions are inconsistent with any of the experimental findings cited in the introduction.

Bodner and Todd (107) reach much the same conclusions, i.e. complexation results in a net withdrawal of electron density from the σ framework of the arene ring whilst the π system remains essentially unchanged. The former point is implicated by comparison of the C(1) ^{13}C chemical shifts in free and complexed systems and by consideration of the changes in the $^{1}J_{CH}$ coupling constants upon complexation.

2.5 INFRARED DATA

The infrared spectra of the meta- and para- substituted fluorobenzene chromium tricarbonyl complexes reveal, as one might have anticipated from the work of Brown et al. (89-91) and Reeves, Biehl and Wu (88), a good correlation between corresponding ν_{CO} stretching vibrations and a measure of the overall electron-accepting or -donating capability of a substituent whether it be meta or para to the fluorine. Thus a plot of ν_{CO} (E mode) against Hammett's σ_p, or against (35%F + 65%R) using Swain's parameters, shows a linear correlation of 96.3% (See Figure 2.3). Furthermore, as previously noted by Brown and Ragu (91), substituent effects are approximately additive, thus a plot of corresponding carbonyl stretching frequencies in the fluorinated and nonfluorinated complexes is linear with a slope very close to unity and an intercept of ~ 10 cm^{-1}. That is, the additional fluoro substituent raised the carbonyl frequency by an approximately

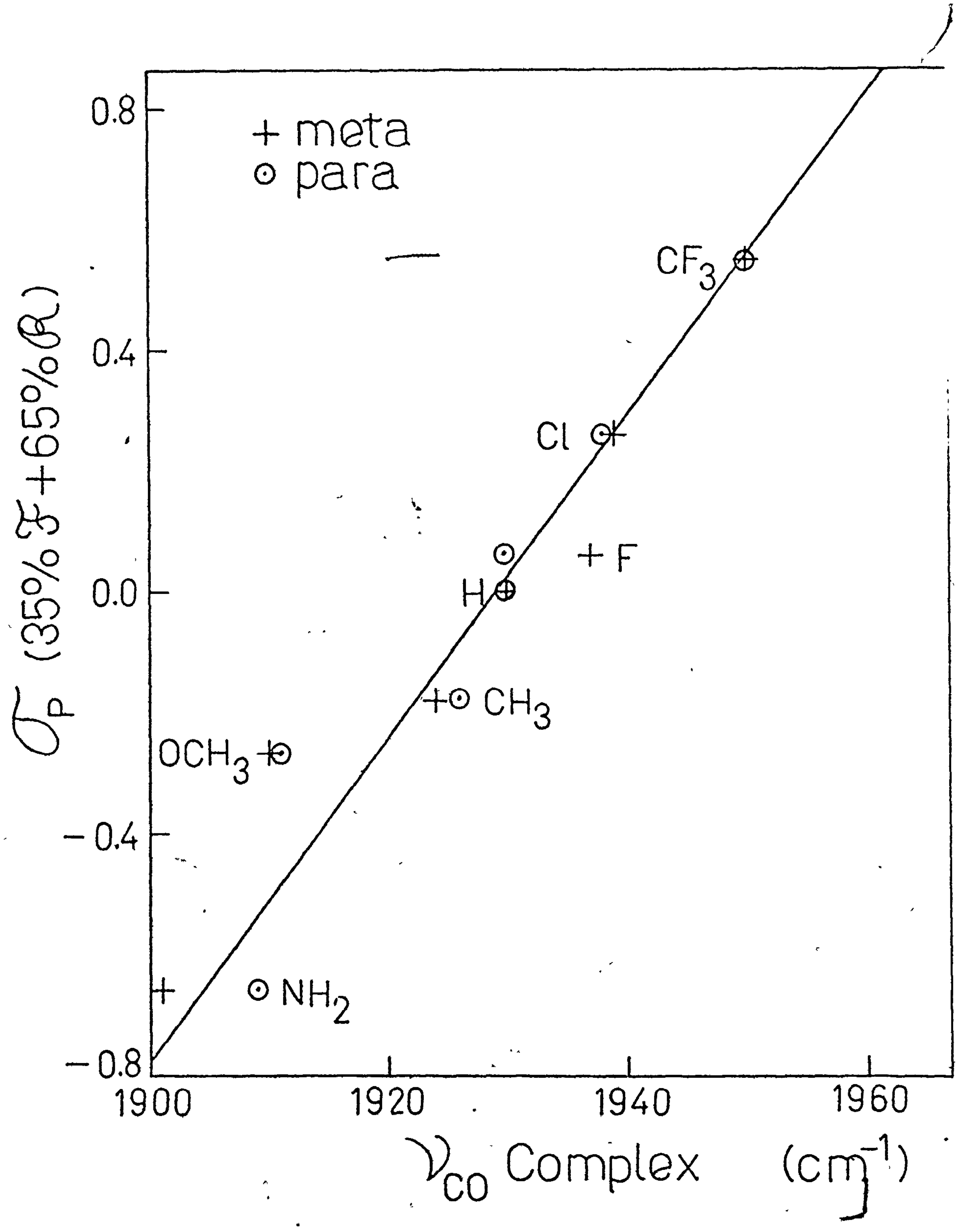

FIGURE 2.3: Plot of carbonyl stretching frequencies (E mode) for meta and para-substituted fluorobenzene chromium tricarbonyls against Hammett's σ_p values, (95) 35% $\mathcal{F}$ + 65% $\mathcal{R}$ (104)

constant amount and is thus behaving as an acceptor of electron density in these systems.

Despite repeated syntheses of the p-difluorobenzene chromium tricarbonyl complex, an anomalous ^{19}F chemical shift was obtained (see Figures 2.1 and 2.2) while its infrared and mass spectra were quite normal. The para-fluoro substituent would only fall on the line of Figure 2.1 if one assumed an $(f\mathcal{F} + r\mathcal{R})$ value of +0.13, i.e. fluoro would need to be a much stronger electron-withdrawing substituent in these systems than implied by both Taft and Swain-Lupton values. As mentioned above, the carbonyl infrared data support the contention of fluorine as a relatively strong electron-withdrawing group in these instances. It is also worth noting that the ^{19}F chemical shift of the para-fluoro substituent in the bis(arene)chromium system was anomalously low (102).

The electronic environment in the complexed ring of arene chromium tricarbonyls appears to be considerably different from that in the corresponding bis(arene)chromium complexes. In the latter case there is a marked dependency of fluorine chemical shifts on both meta- and para- substituents (102) and this is presumably a reflection of the lack of carbonyl groups which act as an electron buffer (111). Thus, in the chromium tricarbonyl complexes an electron-donating substituent makes the ring electron rich and so electron density is siphoned off via the chromium into the π^* orbitals of the carbonyl ligands leading to a decrease in ν_{CO}; vice versa, electron-withdrawing groups produce an increase in ν_{CO}. This self-compensating mechanism is not available in symmetrically substituted bis(arene)chromium complexes (102) and thus the arene ring itself must accommodate the relative excess or deficit of electron density; this in turn is reflected in the n.m.r. chemical shifts of nuclei such as ^{13}C or ^{19}F in the ring.

Interestingly, in the bis(arene)chromium systems, the ^{19}F n.m.r. spectra of CF_3 groups directly bonded to complexed arene rings exhibit downfield shifts of 4-6 ppm relative to those of the uncomplexed arenes (102). In the $Cr(CO)_3$ analogs[1] this trend is also observed but the downfield shifts are approximately one-third the magnitude (see Tables 2.1 and 2.2)

2.6 CONCLUSIONS

The ^{19}F n.m.r. studies of meta- and para-substituted fluoroarene chromium tricarbonyl complexes indicate that transmission of resonance effects within the ring differs little from the free arenes but inductive effects are greatly diminished. This is rationalizable on the basis of withdrawal of σ-electron density from the ring with either little change in π-electron density of the ring or diminution of π-electron density in the ring if one invokes the concept of participation by the chromium atom in transmission of substituent effects between para positions.

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[1] $(CF_3{\cdot}C_6H_5)Cr(CO)_3$ shows ^{19}F absorption at 61.7 ppm and ν_{CO} at 1940 and 1980 cm^{-1}.

CHAPTER 3

RING CURRENTS AND LOCAL ANISOTROPIES IN AROMATIC SYSTEMS: A CRITICAL REEVALUATION OF CLASSICAL RING CURRENT MODELS BASED ON THE PROTON N.M.R. SPECTRUM OF [10]-PARACYCLOPHANE

3.1 INTRODUCTION

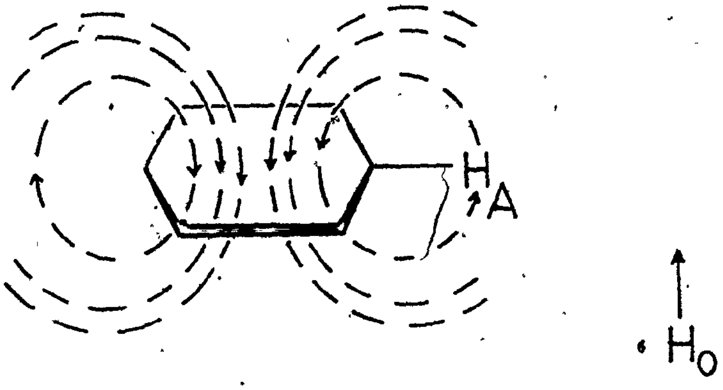
The two alternatives put forward in Chapter 2 as being possible rationales for the findings cited therein should be subject to differentiation on the basis of the fate of the aromatic ring current when an arene is complexed to a chromium tricarbonyl moiety. If indeed the π-system of the ring is essentially unchanged upon complexation then the ring current - which classically at least is due to circulating π-electrons (112-115) - should still be operative. Conversely, it is expected that any change in the π-electron density of the arene ring will be reflected in a modification of the ring current.

Consequently, an independent probe for the existence of a ring current is required, and the (n)-paracyclophanes, whose chemistry was pioneered by Cram and Allinger (116), provide the ideal systems since their methylene protons are situated in both shielding and deshielding regions of the ring current. Thus, the n.m.r. shifts of these protons should provide a sensitive, panoramic probe for any perturbations in the ring current on going from the free to the complexed system. Therefore, [10]-paracyclophane and its chromium tricarbonyl complex were examined by high resolution (220 MHz)p.m.r. spectroscopy.

However, since much of the ensuing work had a pronounced dependence of the interpretation of the ring current concept it was deemed appropriate, critically to reevaluate the present state of the art as it relates to ring current theories.

3.2 THE RING CURRENT EFFECT

Ehrenfest (117) recognized that an interatomic circulation of electrons would cause large diamagnetic anisotropies. Pauling (118), in order to explain the observed diamagnetic anisotropy of cyclic conjugated hydrocarbons, envisaged the concept of circulating π-electrons. As a consequence of this physical picture, the secondary fields arising from the magnetically induced electronic circulation have been viewed as important factors in explaining the proton chemical shifts of aromatic molecules (119). Thus, in an external magnetic field, H_0, as would be encountered in an n.m.r. experiment, the π-electrons of the aromatic compound will circulate in such a manner as to set up a field in opposition to the applied field. The net result of this for the proton H_A is to move its resonance to very low field, i.e. it is deshielded.



The problem was first approached semi-classically by Pople (120) who proposed a simple model to explain the deshielding of the protons in benzene. To estimate the magnitude of the secondary field, Pople chose to equate the induced current to a simple point dipole located at the centre of the ring. Although the agreement with the experimental data is quite good it does suffer from several drawbacks. Firstly, this point dipole approach is not valid for the proximate protons of benzene and is only applicable to points far removed from the centre of the ring (121). Also, the method does not predict upfield shifts for protons inside the ring as has been experimentally proven for [4n + 2]-annulenes (122), where $n > 2$ (benzene being a [6]-annulene).

Waugh and Fessenden (114), in a now classic paper, improved upon Pople's method by developing a "Free Electron Model" in which the π-electrons were regarded as being analogous to a simple current loop and, using the well-established methods of classical electrodynamics (123), they were able to evaluate the induced field at any point whether in or out-of the plane of the ring.

The downfield shift of the benzene protons predicted by an in-plane current loop was 2.79 ppm and, in order to correlate with the then accepted shift of ∿ 1.5 ppm (i.e. the difference between benzene and the vinylic protons of 1,3-cyclohexadiene), Waugh and Fessenden separated the π current into two loops, one above and one below the ring plane; the separation between the loops was empirically adjusted to be 1.28 Å, and a very convenient tabulation of chemical shift increments calculated on this basis has been provided by Johnson and Bovey (124). It should be stressed that this separation, and its magnitude, has no theoretical basis but rather is an arbitrary parameter chosen by the judicious assessment of the experimental and calculated data.

A quantum mechanical treatment of the ring current calculation was initiated by McWeeny (125) who extended London's (126,127) molecular orbital method for the ring current effect on diamagnetism to its effect on chemical shifts. Basically this treatment involved consideration of the vector potential due to a magnetic dipole sited at the proton in question. Hall and Hardisson (128) improved upon McWeeny's (125) method by using a self-consistent field (SCF) MO method.

All these approaches gave estimates for benzene protons of about 2.5 ppm, hence to fit the accepted value of 1.5 ppm a scale factor of about 0.6 has commonly been used to relate the calculated and experimental data (129).

More recently Haigh and Mallion (130-132) have made further improvements one being to account for protons situated out of the plane of the ring. Haigh and Mallion (130,131) have presented a tabulation of their results similar to that of Johnson and Bovey (124).

3.3 RESULTS AND DISCUSSION

3.3.1 The ^{1}H Nuclear Magnetic Resonance Spectrum of [10]-Paracyclophane

As previously mentioned, a number of models have been proposed to account for the shifts of aromatic protons. The now widely-accepted free electron model, as presented by Waugh and Fessenden (114) was used in an attempt to rationalize the shifts of the out-of-plane protons in (10)-paracyclophane. In their original paper (114) they presented experimental and calculated n.m.r. shift data on [10]-paracyclophane. Although their 40 MHz spectrum, as expected, showed clearly the presence of high field protons in the methylene chain, the resolution was insufficient to allow any definitive assignments to be made and consequently quantitative verification of the theory was somewhat hazardous. Nevertheless, constant application to a variety of aromatic systems has almost bestowed an imprimatur upon the theory. However, with the technological advances of two decades, a number of discrepancies are now apparent. Thus in 1957 there was no method of reliably determining the structure of [10]-paracyclophane (or at least the most populated conformation in solution) and the authors had to estimate the proton positions relative to the aromatic ring by using Fisher-Hirschfelder models and trying to allow for the twisting motions of the decamethylene bridge. It is perhaps not surprising that the original assignment of the methylene protons as following the sequence: α, β, δ, γ, ε is incorrect. The 220 MHz spectrum of [10]-paracyclophane is presented (Figure 3.1, Table 3.1) in which the five aliphatic resonances are clearly resolved. This, together with the homonuclear decoupling data, unequivocably established the order of the proton resonances as: α, β, γ, δ, ε with the ε protons at highest field.

3.3.2 The Structure of [10]-Paracyclophane

The apparent inconsistency discussed above prompted these investigations to be directed towards a quantitative appraisal of the ring current tabulations (124, 131). Consequently, it was essential to know the structure of the molecule. In the absence of crystallographic data, it is necessary to

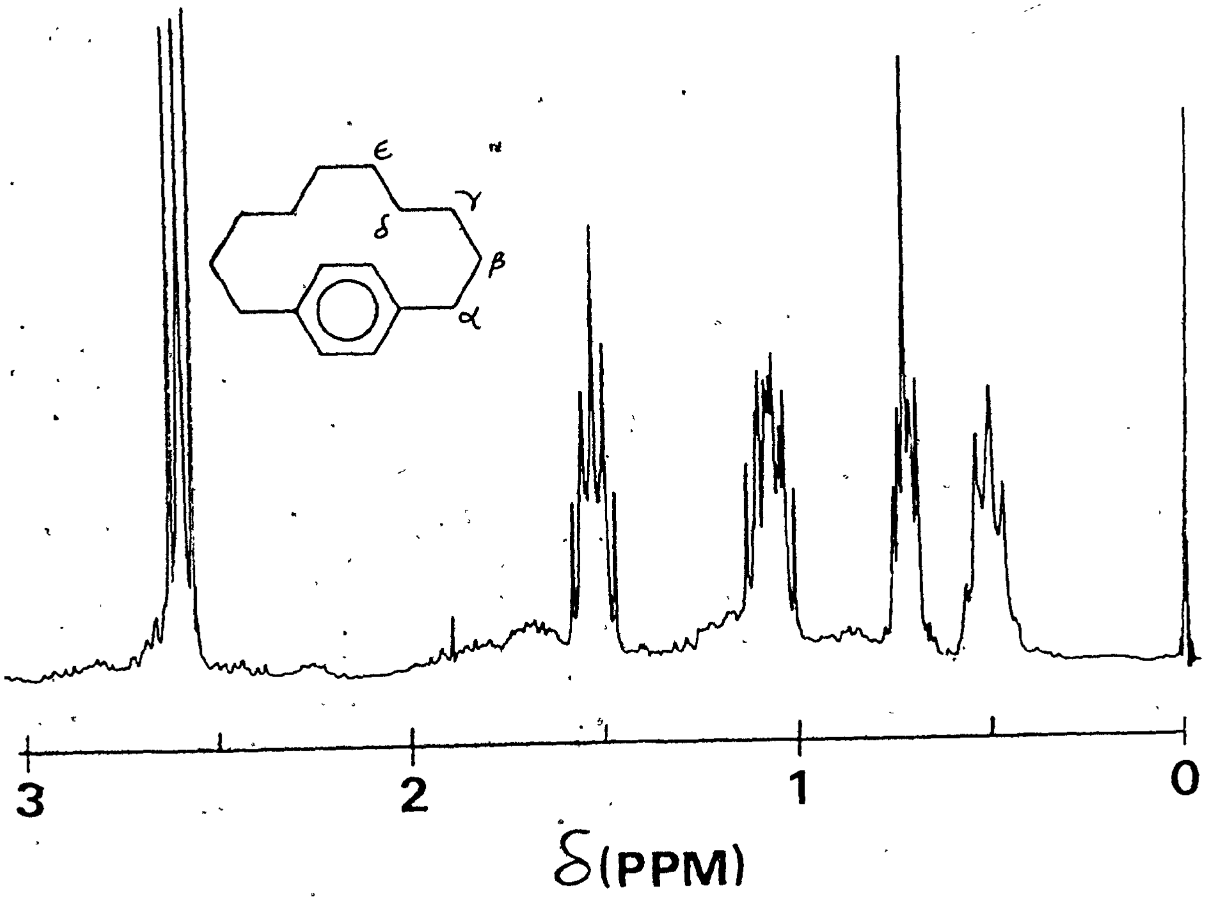


FIGURE 3.1 220 M Hz ^{1}H N.M.R. Spectrum of High Field Resonances of [10]-Paracyclophane'

Table 3.1 ^{1}H n.m.r. data for [10]-Paracyclophane. (δ values).

	Exptl 220 MHz	Calc'd J-B (124)	Calc'd H-M (131)
Ar	7.04		
α	2.62	1.66	1.60
β	1.54	1.55	1.36
γ	1.08	1.30	1.23
δ	0.73	0.82	1.13
ε	0.51	0.59	1.10

calculate the molecular conformation of lowest energy, and for such systems a high degree of success has been achieved using Allinger's molecular mechanics calculations (133,134). Thus, the correlation between the predicted and observed structures of [8]-paracyclophane is very good and so one can confidently use this approach as the best available at present. Since the ^{1}H n.m.r. spectrum shows only five methylene environments, the molecular is conformationally mobile on the n.m.r. time scale; indeed Allinger calculated that the molecule would have a rather flat potential energy minimum allowing considerable amplitude of ring oscillation. The preferred conformation for [10]-paracyclophane was calculated to have a non-planar aromatic ring in which the para-carbons were displaced upwards through 8.4°, while the α-carbons were displaced downwards through 4.4° (134). The molecular mechanics method also predicted the conformation of the decamethylene chain, and an attempt to verify these predictions was undertaken using the Karplus theory (135,136) relating vicinal coupling constants ($^3J_{HH}$) and dihedral angles which has been extensively used in structure determinations (137).

The dihedral angles of the most populated conformation were determined from the coupling constants obtained from the homonuclear decoupled spectra using the following relationship:

$$J = A + B\cos\phi + C\cos 2\phi \qquad [3\text{-}1]$$

where A = 7 Hz, B = -1 Hz, C = 5 Hz, a set of empirically derived parameters which refer to an H-C-C-H fragment in a carbon chain (138). The observed coupling constant is in fact an average of four coupling constants whose dihedral angles of interaction are ϕ, $120 + \phi$, ϕ, and $|120 - \phi|$. Then,

$$J_{obs} = 0.25(2J_{\phi} + J_{\phi+120} + J_{120-\phi}) \qquad [3\text{-}2]$$

with this consideration, eq. 3.1 becomes:

$$J_{obs} = 2.5 \cos^2 \phi - 0.25 \cos \phi + 5.75 \qquad [3\text{-}3]$$

The calculated dihedral angles are listed in Table 3.2. In this analysis it was assumed that each -CH_2-CH_2- unit could be regarded as an $[AX]_2$ system, since the chemical shifts of the protons in a given methylene group are dynamically averaged to give only one value and the chemical shift differences between adjacent methylene groups are relatively large. While this simplification is justifiable for the $J_{\alpha\beta}$, $J_{\beta\gamma}$, and $J_{\gamma\delta}$ couplings such is not the case for the $J_{\delta\varepsilon}$ case which is more correctly regarded as $[[AB]_2]_2$; consequently the dihedral angle predictions from $^3J_{H_\delta H_\varepsilon}$ are distinctly less reliable than are the others. Of course, the dihedral angle between the aromatic ring and the α-carbon-β-carbon bond is not evaluable directly as there is no appropriate coupling constant. This angle was approximated from a Fieser model and refined as outlined below. Now, accepting the values for the non-planarity of the ring and C_α atoms as calculated by Allinger (134), use of molecular models made it relatively easy to decide the unique combination of dihedral angles which allowed the construction of the decamethylene bridge. Finally, a molecular geometry programme (139) was used empirically to adjust not only the dihedral angles (within the calculated error limits) but also the aliphatic C-C-C bond angles (to parallel the behaviour of the corresponding angles

Table 3.2 Experimental Vicinal Coupling Constants and Calculated Dihedral Angles.

	$\underline{J}$ (Hz)	φCalc (Karplus)	φCalc (Refined)
Ring - α			155.5°
α - β	6.2 ± 0.1	62° ± 3° or 112° ± 3°	62°
β - γ	6.0 ± 0.1	68° ± 4° or 106° ± 4°	106°
γ - δ	7.1 ± 0.1	38° ± 2° or 133° ± 2°	133°
δ - ε	7.6 ± 0.1	24° ± 3° or 144° ± 3°	141.3°

in [8]-paracyclophane) such that the ε-carbon coordinates (x,y,z) corresponded to the ε'-carbon coordinates $(\bar{x},\bar{y},z)$ as required by C_2 symmetry. Throughout these calculations, the aromatic ring carbon-carbon bond lengths were taken as 1.39 Å. The exocyclic sp^2-sp^3 bond as 1.50 Å and the C-C and C-H bonds in the polymethylene chain as 1.54 and 1.08 Å respectively. Each H-C-H plane was positioned orthogonally to the appropriate C-C-C plane. It is gratifying that these experimental data, viz., coupling constants, reinforce Allinger's theoretically predicted molecular geometry as shown by comparing Figure 2 in Ref. (134) (reproduced here in Figure 3.2) with Figure 3.3.

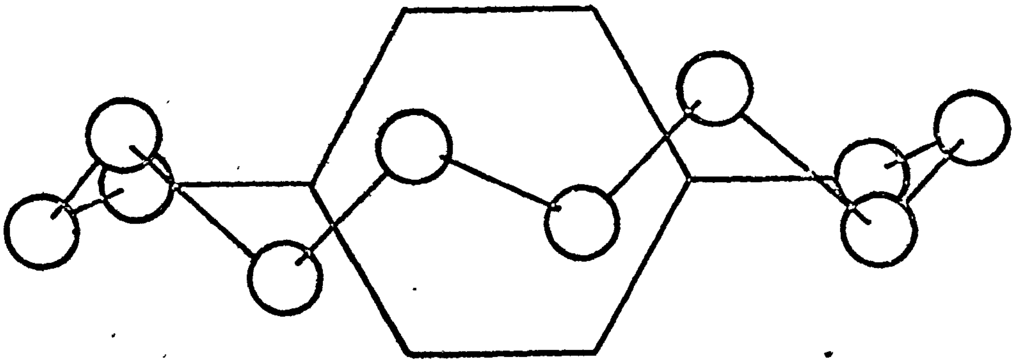


FIGURE 3.2 Theoretically Predicted Molecular Geometry of [10]-Paracyclophane - from Ref. 134.

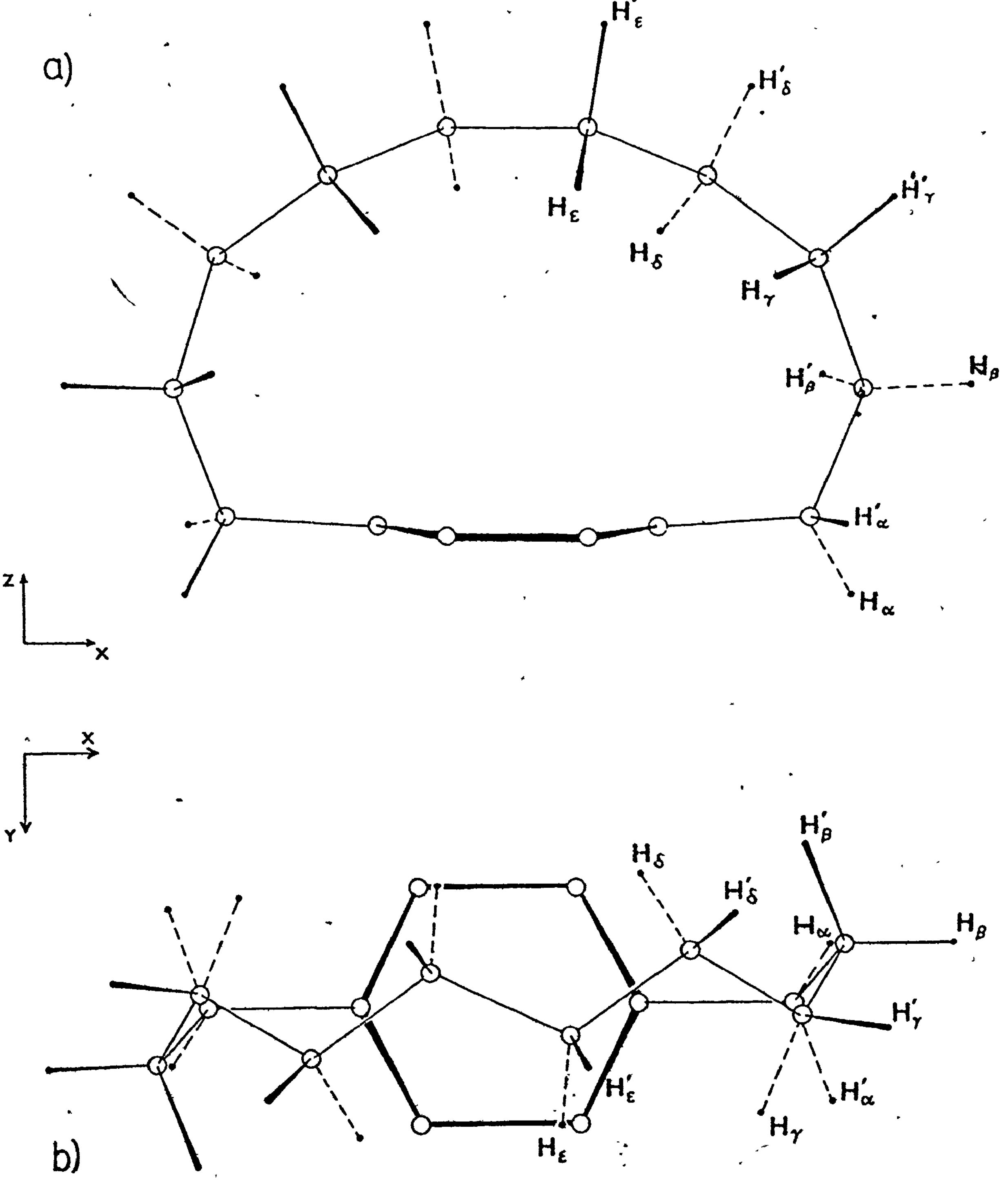


Fig. 3.3

Preferred conformations of [10]-paracyclophane.

(a) plan

(b) elevation

The hydrogen atom positions are shown in perspective relative to the carbon atom to which they are attached.

3.3.3 Comparison of Ring Current Theories

These structural data allow the evaluation of incremental shifts for the methylene protons lying out of the aromatic ring plane using both the semiclassical (124) and quantum mechanical (131)approaches. In order to predict chemical shifts relative to TMS it is necessary to select the "standard methylene shift" appropriate to the system. Typical values for large cycloalkanes average to 1.30 ppm (140), and this is the standard that has been used. The chemical shifts thus predicted by the Johnson-Bovey (124) and Haigh-Mallion (131) tabulations for the α, β, γ, δ, and ε protons are presented in Table 3.1, and may be compared with the experimental values in the same table. It is apparent that, while both methods are qualitatively very useful, the quantitative agreement with the experimental shifts is not uniform throughout all positions which experience the effect of the ring current. The semi-classical method shows good agreement for protons held over the centre of the ring, but becomes less reliable as the value of ρ increases and z decreases. However, the quantum mechanical approach gives adequate agreement in these latter regions but seriously underestimates the upshield shifts of the protons directly above the ring, as was originally inferred (130,141). The work of Rose (142) on pyridylphenanthrenes also supports this generalization.

3.3.4 Local Anisotropic Contributions

It was apparent that the present ring current theories did not provide a complete rationale for the experimentally observed shifts and that some other important contribution had been overlooked. It had earlier been suggested by Pople (143,144) that local anisotropic effects were a large contributing factor to the deshielding of the protons in benzene.

In an externally applied magnetic field, H_0, a secondary field is induced at atom X by circulation of electrons. If this field is anisotropic then it can have the effect of changing the screening constant of a neighbouring hydrogen atom. This effect may be deshielding or shielding depending on the orientation of the H-X bond relative to the applied field. Barfield, Grant and Ikenberry (145) have now successfully demonstrated that local anisotropic contributions to chemical shifts may be evaluated using the ^{13}C chemical shielding tensors so painstakingly obtained by Waugh (146,147) using proton-enhanced nuclear induction spectroscopy (148). Grant's data (145) clearly show that local anisotropic contributions cannot be ignored for in-plane protons in condensed aromatic systems,[1] and these calculations are now extended to out-of-plane protons.

Using the analogy of a current circulating in a loop of wire (145), the proton shielding component, σ_{ii}^{H}, is given by

$$\sigma_{ii}^{H} = \frac{a}{\pi\,[(a+\rho)^2 + z^2]^{1/2}} \times \left[K + \frac{a^2 - \rho^2 - z^2}{(a-\rho)^2 + z^2}\cdot E\right]\cdot\sigma_{ii}^{C} \qquad [3\text{-}4]$$

where a is the radius of circulation about each carbon atom taken as 0.47 Å (145), ρ and z are the usual cylindrical coordinates, and K and E are

---

[1] A dipolar approximation presented in Ref. 145 contains an algebraic error due to mis-evaluation of the elliptical integral power series. However, this does not materially affect the conclusions drawn previously, i.e., it is unsafe to calculate chemical shifts for proximate protons using only a dipolar formula. For the situation in Ref. 145 the correct dipolar formula is

$$(\sigma^{H}) = \frac{a^2}{3r_{CH}^{2}}\left(\sigma_{11}^{C} + \frac{a}{r_{CH}}\cdot\sigma_{22}^{C} + \sigma_{33}^{C}\right)$$

complete elliptical integrals of the first and second type with the argument

$$k^2 = \frac{4a\rho}{(a + \rho)^2 + z^2}$$

More simply, $\sigma_{ii}{}^{H} = G\sigma_{ii}{}^{c}$ where $\sigma_{ii}{}^{H}$ and $\sigma_{ii}{}^{c}$ are the proton and carbon shielding components and G is a geometric factor. The isotropic shielding, as measured in solution, is given by averaging the components

$$(\sigma^H) = 1/3[\sigma_{11}{}^{H} + \sigma_{22}{}^{H} + \sigma_{33}{}^{H}]$$

Figure 3.4 gives a schematic representation of the components of local anisotropic shielding at the carbon atoms with respect to the induced orientation of electron circulation.

The ^{13}C shielding tensors used in this study are taken from Refs. 146 and 147; values used for aromatic carbons bearing alkyl chains are those listed by Waugh for hexaethylbenzene, while those for aromatic carbons with hydrogen substituents are the average of the appropriate values from pentamethylbenzene and durene. To convert the values from shifts relative to benzene into absolute shifts, it is necessary to add 71 ppm to each ^{13}C shielding tensor (145). The actual values used for each of the respective carbon environments together with an interpolated value for C-H are listed in Table 3.3. The local anisotropic contributions for each methylene proton brought about by circulations about each ring carbon in [10]-paracyclophane are presented in Table 3.4.

3.3.5 Experimentally Determined Ring Currents

The ring current contribution (ΔRC) to the chemical shift can now

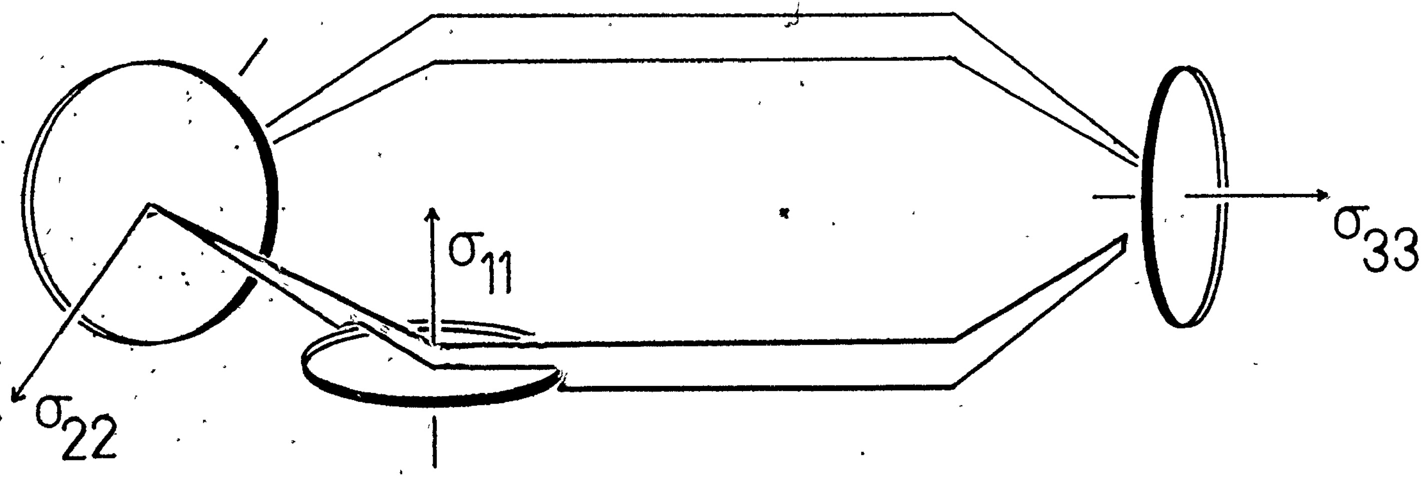


FIGURE 3.4 The Components of Local Anisotropic Shielding at the Carbon Atoms with Respect to the Induced Orientation of Electron Circulation

Table 3.3: ^{13}C Shielding Tensors for the Various Substituents on the Ring Carbon.

Group Attached to C	σ_{11} ppm	σ_{22} ppm	σ_{33} ppm
* H	153	73	-19
** CH	177	32	-20
* CH_2	178	36	-20
* CH_3	179	40	-20

* From References 146, 147.

** Estimated from values for CH_2 and CH_3 groups.

be defined as the difference between the experimental shift (δ) and that calculated by adding the local anisotropic contribution to the standard, i.e.,

$$(-\delta)_{expt} = -1.30 + \text{LA term} + \Delta RC_{expt} \qquad [3\text{-}5]$$

These "experimentally determined ring current shifts" are listed in Table 3.4 together with ring current shifts calculated using the equation

$$\Delta = \frac{C}{[(a+\rho)^2 + z^2]^{1/2}} \times \left[K + \frac{a^2 - \rho^2 - z^2}{(a-\rho)^2 + z^2} \cdot E\right] \qquad [3\text{-}6]$$

where $C = ne^2/6\pi M_e c^2 = 8.970$, where n is the number of circulating electrons of charge e and mass M_e, c is the velocity of light, ρ and z are the usual cylindrical coordinates, and a is the radius of circulation about the ring taken as 1.39 Å. In this case ρ and z are measured in Å rather than ring radii.

The quoted shifts are the average of two shifts Δ_1 and Δ_2 obtained by taking $z_1 = z + S/2$ and $z_2 = z - S/2$, where S is the separation of the current loops. It is necessary to accept that any ring current contribution calculated semi-classically must follow an equation of the type [3-6] where the only adjustable parameters are C and S. Waugh and Fessenden chose to adjust the separation of the loops, while Barfield, Grant, Ikenberry adjusted both C and S. The approach of this work is to adjust the separation between the loops to get the best correlation between the "experimental ring current shifts" and the calculated shifts, and then to evaluate C empirically.

It is now apparent from the data presented that the arbitrary separation into two loops is not only unnecessary but is actually detrimental to the optimum fit. Now a plot (Figure 3.5) of the ΔRC_{expt} values vs.

	RING CURRENT INCREMENTS[a]										
	SEMI-CLASSICAL THEORY						QUANTUM MECHANICAL THEORY		EXPERIMENTAL	LOCAL ANISOTROPY INCREMENTS	
	S=0		S=1.28[b]		S=1.63[c]						
H_α	-0.729	-0.786	-0.379	-0.360	-0.228	-0.203	-0.278	-0.300	-0.905	-0.295	-0.415
H'_α	-0.842		-0.340		-0.178		-0.321			-0.535	
H_β	-0.173	-0.171	-0.171	-0.252	-0.161	-0.256	-0.069	-0.063	-0.155	-0.104	-0.086
H'_β	-0.169		-0.332		-0.351		-0.057			-0.067	
H_γ	0.265	0.177	-0.030	-0.002	-0.248	-0.132	0.102	0.068	0.095	0.193	0.125
H'_γ	0.088		0.026		-0.015		0.034			0.057	
H_δ	0.643	0.446	0.692	0.479	0.652	0.462	0.246	0.171	0.329	0.348	0.241
H'_δ	0.248		0.266		0.271		0.095			0.134	
H_ε	0.717	0.515	1.014	0.710	1.232	0.852	0.274	0.197	0.538	0.347	0.252
H'_ε	0.313		0.405		0.472		0.120			0.157	

[a] Units: ppm.A minus sign indicates a downfield effect.

[b] Johnson-Bovey separation, (Å), ref. 124

[c] Barfield-Grant-Ikenberry separation, (Å), ref. 145

TABLE 3.4: Calculated and Experimental Ring Current and Local Anisotropy incremental contributions to the shifts of protons in the decamethylene bridge of [10]-paracyclophane. H' represents the proton of any given methylene pair having the larger positive Z value.

calculated ring current by the Johnson-Bovey (124) method ($\Delta RC_{J\text{-}B,S\,=\,0}$) provides a value for C, and follows the equation

$$\Delta RC_{expt} = 1.04\ \Delta RC_{J\text{-}B,S\,=\,0} - 0.06 \qquad [3\text{-}7]$$

The correlation coefficient, $\bar{r}$, was found to be a maximum (0.9928) at S = 0; the correlation worsened very rapidly on invoking loop separation. Typically, S = 1.0 Å, $\bar{r}$ = 0.9461; S = 1.28 Å (Reference 114), $\bar{r}$ = 0.8883; S = 1.63 Å (Reference 145), $\bar{r}$ = 0.7634; S = 2.0 Å, $\bar{r}$ = 0.6161. Therefore, the data make apparent the conclusion that the arbitrary separation of the ring current into two loops is unnecessary; furthermore, the ring current increments derived by a semi-classical approach and those determined experimentally show good agreement.

A plot of measured chemical shift ($-\delta$) vs. calculated ring current ($\Delta RC_{J\text{-}B,S\,=\,0}$) also shows an interesting correlation, viz.,

$$(-\delta) = 1.57\ \Delta RC_{J\text{-}B,S\,=\,0} - 1.36 \quad (\bar{r} = 0.9974) \qquad [3\text{-}8]$$

Combining eqs. 3.5, 3.7 and 3.8, we see that

$$LA = 0.53\ \Delta RC_{J\text{-}B,S\,=\,0} \qquad [3\text{-}9]$$

indicating that the ring current contribution to the incremental shift is of the order of 65%.

This whole postulate receives strong support from Dailey's work on magnetic anisotropy which showed that the ring current only contributes to the extent of ∿60% to the chemical shifts of aromatic hydrocarbons (149).

Having shown that the experimental ring current shifts are readily

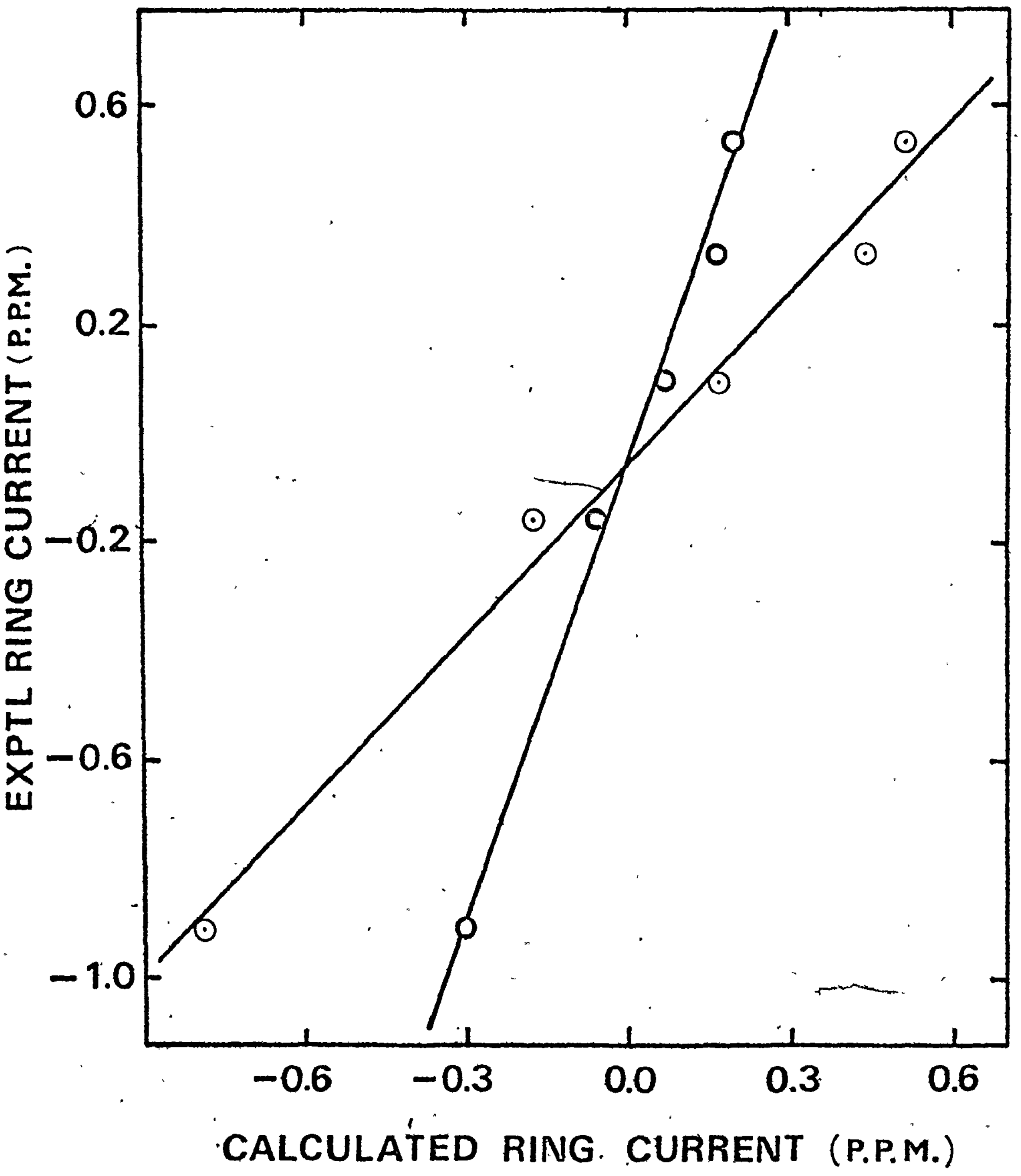


Fig. 3.5

Plot of Experimental Ring Current (ΔRC_{Expt}) vs. Calculated Ring Current ($\Delta RC_{J-B,S=0}$ = ⊙ and ΔRC_{H-M} = ○).

rationalizable from the semi-classical viewpoint, it is of interest to determine whether any analogous correlation exists for the quantum mechanical theory. This latter theory has only one variable parameter which was obtained from a linear regression analysis of data for planar polycyclic aromatics.

A plot of the experimental ring current shifts against those predicted from the quantum mechanical approach shows excellent agreement ($\bar{r} = 0.9932$) and follows the equation

$$\Delta RC_{expt} = 2.73\ \Delta RC_{H\text{-}M} - 0.06 \qquad [3\text{-}10]$$

It will be noted that the predictions of the Johnson-Bovey (124) and Haigh-Mallion (131) tabulations differ by a factor of ∿2.6 in the limit (131). Using our data (see Table 3.4) the following relationships were found

$$\Delta RC_{J\text{-}B,S = 0} = 2.60\ \Delta RC_{H\text{-}M} \qquad [3\text{-}11]$$

$$\Delta RC_{J\text{-}B,S = 1.28} = 2.02\ \Delta RC_{H\text{-}M} \qquad [3\text{-}12]$$

where $\bar{r} = 0.9998$ and 0.8938 respectively, thus reinforcing our earlier arguments dispelling the necessity for loop separation.

It is especially gratifying to see that the two entirely different models are compatible with the experimental data. Previous statements (131, 142) that the two theories are only applicable to specific spatial regions of the aromatic molecule are nullified when the correct ring current increments are evaluated. Thus, previously published experimental ring currents which did not allow for the local anisotropic corrections would not be expected to fit either ring current model, except fortuitously.

One would have anticipated that eqs. [3-7] and [3-10] should have zero intercept since the overall chemical shift of any given methylenic proton is assumed to be a composite of only three terms, viz., LA and RC terms, which are of course position dependent, and the standard shift, which is the same for all protons in the chain. Since one obtains the identical non-zero intercept from both the semi-classical and quantum mechanical approaches, it is proposed that the standard methylene shift in chloroform be taken as 1.36 ppm rather than the initially chosen value of 1.30 ppm.

In the previous treatment of [10]-paracyclophane (114), the predicted shifts of the protons α to the ring gave such poor agreement that they were ignored, and these shifts were merely compared to the corresponding protons in ethylbenzene. However, the present approach adequately accounts for the α-CH_2 shift without invoking an inductive effect of the phenyl ring; that is, the inherent standard shift for the α-proton can still be taken as 1.36 ppm. Thus, it would seem that the so-called inductive effect of the phenyl ring can be wholely attributed as being a manifestation of the anisotropic nature of the electron distribution within the ring.

In calculating incremental methylene proton shifts using a combination of local anisotropic and ring current contributions from the aromatic ring it has been assumed that local anisotropic contributions from atomic neighbours in the polymethylene chain are allowed for by suitable choice of a standard. One should point out that whilst the determination of the local currents involves the use of the total carbon shielding tensor (the effect of the delocalised current being ignored), comparison of the isotropic ^{13}C shifts in benzene and the C-2, C-3 resonances in cycloheptatriene shows that the delocalised effect must be relatively small.

Having established a model for predicting chemical shifts of protons sited in close proximity to an arene ring it is now of interest to apply this theory to a series of molecules of known structures. Thus it is possible to make an independent comparison of the predictions of the Johnson-Bovey semi-classical approach with those of the Haigh-Mallion quantum mechanical formalism and with the model set forth here.

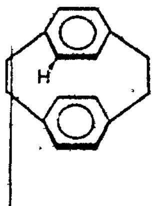
For this purpose a series of cyclophanes were chosen for which chemical shift data have been obtained (150). In each of these systems there exists a monitor proton situated above the plane of an arene ring.

Table 3.5 lists the series of cyclophanes together with the coordinates of the proton of interest relative to the centre of the ring from which local anisotropic and ring current contributions arise. To relate these coordinates to those used in the Johnson-Bovey and Haigh-Mallion tabulations, the y coordinate in Table 3.5 corresponds to the z coordinate in the published tabulations and ρ in the Johnson-Bovey or Haigh-Mallion tables is obtained from the relationship $\rho = [x^2 + z^2]^{1/2}$. The standard shifts, following Lehner's approach (150), were obtained from p-xylene, for the paracyclophanes I and II, and from 1,3-diethylbenzene, for the metacyclophanes, III, IV and V. The internal monitor protons of V are compared to those of durene. The coordinates were taken from crystallographic data for I, II and IV (151, 152,153) and, for III, from a force-field calculation (154) and a partial crystal structure (155). In V the

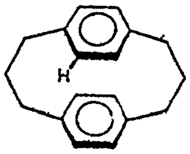
Table 3.5 Calculated and Experimental Chemical Shifts of a Series of Paracyclophanes Comparing Johnson-Bovey and Haigh-Mallion Predicted Shifts with those of the Proposed Model

	Coordinates of H				Johnson-Bovey		Haigh-Mallion		Proposed Model				
	X	Y	Z	Standard	Incremental Shift	δ Calculated	Incremental Shift	δ Calculated	LA	RC	Total Incremental Shift	δ Calculated	δ Experimental
I	0.695	3.086	2.374	6.97	0.38	6.59	0.15	6.82	0.22	0.40	0.62	6.35	6.46
II	0.695	3.294	2.374	6.97	0.37	6.60	0.15	6.82	0.20	0.38	0.58	6.39	6.60
III	0.0	2.700	1.376	7.10	1.38	5.72	0.45	6.65	0.52	1.22	1.74	5.36	5.35
IV	0.792	2.488	0.0	7.10	2.39	4.71	0.76	6.34	0.70	1.99	2.69	4.41	4.23
V (H)	0.792	2.488	0.0	7.10	2.39	4.71	0.76	6.34	0.76	1.99	2.75	4.35	4.40
V (H')	0.792	2.488	0.0	6.85	2.39	4.46	0.76	6.09	0.70	1.99	2.69	4.16	4.03

I



; II



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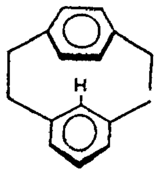
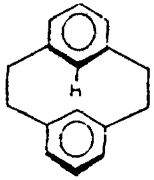
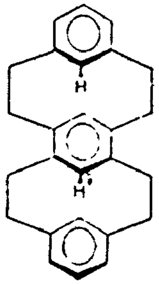


; IV



; V



central ring is known to adopt the chair conformation (156).

Table 3.5 then gives the respective standards for each system, the calculated incremental shift and predicted total chemical shift for Johnson-Bovey, Haigh-Mallion and proposed models together with the experimentally determined shift. It is readily apparent from these data that for protons above the plane of the arene ring the Haigh-Mallion calculations always underestimate the shielding and that the proposed model allows, in general, a more accurate prediction of the chemical shift than does the Johnson-Bovey tabulation.

Thus, in conclusion it can be stated that the present ring current tabulations do not allow for the local anisotropic contributions to the chemical shifts of protons in aromatic environments; independent calculation of these local anisotropic contributions allows the evaluation of corrected (experimental) ring current shifts. These corrected shifts were found to show simple relationships to both the quantum mechanical and semi-classical approaches; in each case, the correlation coefficients were excellent. However, the separation of the current loops in the semi-classical approach was shown to be unnecessary.

An extension of the concepts developed here allows a study of ring currents ~~in~~ arene-metal π-complexes and this will be dealt with subsequently.

3.4 ^{13}C N.M.R. SPECTRA OF [10]-PARACYCLOPHANE

The ^{13}C data on [10]-paracyclophane was also obtained. Details of the resulting spectrum are given in Table 3.6. The bridging methylene carbons were assigned on the basis of heteronuclear decoupling data ~~(Figure 3.6)~~ using the proton resonances already obtained. The sequence

Table 3.6 ^{13}C N.M.R. Data for [10]-Paracyclophane

Carbon Atoms	Shift
Ar (1,4)	139.7
(2,3,5,6)	129.4
α	35.4
β	29.3
γ	25.1
δ	27.0
ε	28.5

α, β, ε, δ, γ, obtained experimentally agrees with that predicted using Woolfenden and Grant's (157) empirically derived additivity relationship; this also reinforces the original proton assignments.

When viewing the role of the ring current in aromatic systems the probe of choice has most often been ^{1}H n.m.r. chemical shifts. Little application has been made of carbon magnetic resonance spectroscopy. The large inherent shifts in ^{13}C spectra, their great sensitivity to changes in electronegativity and strain and the lack of a suitable model are just some of the reasons why ^{13}C n.m.r. has not found favour in these areas of investigation. The magnitude of the changes in chemical shift that can be expected to occur due to ring current aberrations is such that they are usually wholly overshadowed by even minor changes in electronegativity or strain effects. Furthermore, the requirements of a model compound, for which all factors other than the ring current effect are nullified, have been difficult to achieve.

Nonetheless, a number of investigators have attempted to use ^{13}C to observe ring current effects (158-166).

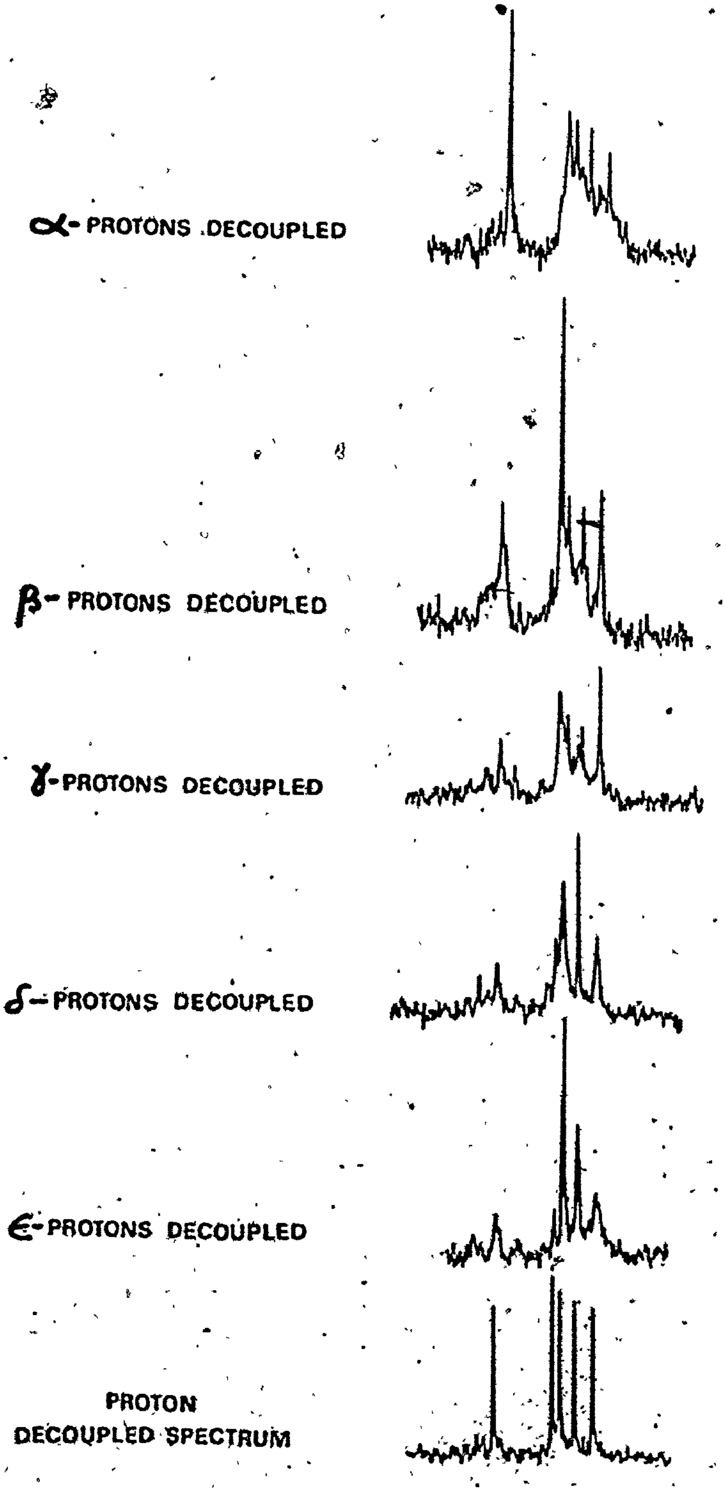
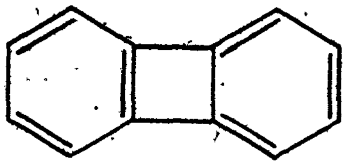


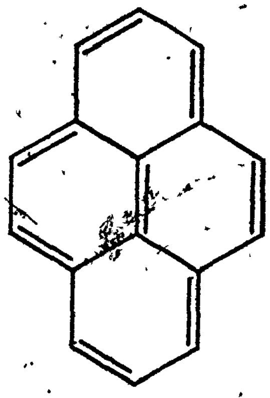
FIGURE 3.6 ^{13}C Heteronuclear Decoupled Spectra of [10]-Para-Cyclophane. High Field Resonances

A number of studies have involved macrocyclic systems, oftentimes bridged annulenes (158-163,164). The rationale in each case being that the more extensive peripheral π-system of these large rings would enhance the ring current effect and make any resulting effects more easily observable.

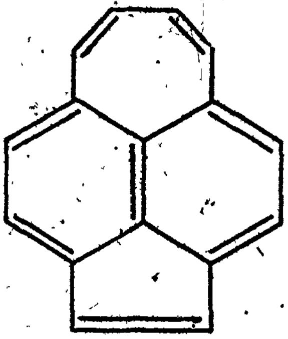
Thus, Jones and Grant have attempted to explain the low field ^{13}C shift of the quaternary carbons of biphenylene (VI) (158) and the large upfield shifts of the internal carbon of pyrene (VII) and acepleiadylene (VIII) (159,160) in terms of a ring current effect. Quite conceivably ring strain is a predominant factor here, also suitable models were not available.



VI



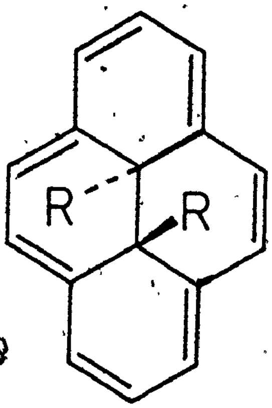
VII



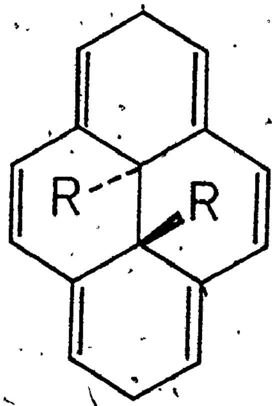
VIII

Bridged annulenes have also been used for similar studies (161,162). Both 1,6-methano(10)annulene and bridged (14)annulenes were investigated, with the bridging species being utilized as ^{13}C probes. The conclusion was that the ring current effect was small when compared to other factors thought to be affecting the total shift.

Du Vernet and Boekelheide undertook a study which employed alkyl derivatives of dihydropyrenes (IX) (a bridged (14)annulene) with tetrahydro analogues as model compounds (X) (164).



IX



X

These authors found that the upfield shifts, in going from X to IX, in both ^{13}C and ^{1}H spectra for alkyl group carbons and the hydrogen atom in the same respective region, were essentially the same. Their conclusion then was that these observed shifts were due solely to the aromatic ring current, all other factors remaining constant by virtue of the geometric similarities of the model compound (X) with the corresponding aromatic species (IX).

Changes in the local anisotropic contributions to the ^{1}H chemical shifts between the two systems (IX and X) has not been considered. It was earlier shown that such effects cannot be ignored when accounting for the observed chemical shifts.

Other workers have looked at bridged benzene ring systems (163,165,166). The common conclusion has been that the ring current effect is not an important factor in these systems relative to the other influences on overall shifts.

Levin and Roberts (163) investigated the ^{13}C n.m.r. of (12)paracyclophane, a close analogue of the (10)paracyclophane currently being considered, with a view to isolating the ring current effects. They acknowledged the difficulties involved in choosing a suitable model compound but decided on cyclopentadecane. This study also suffered from the inability to specifically assign the γ, δ, ε, and ζ bridging methylene shifts.

If the same standard shift were to be adopted (27.6 ppm) for (10)paracyclophane then the ε carbon shift would appear to be in a deshielded region of the ring current, if one assumes that electronegativity and strain effects are negligibly different from those of the standard.

This observation and the prior findings of numerous other investigators make it readily apparent that any attempts to draw definitive conclusions, concerning the ring current effect, from the ^{13}C data generated for (10)paracyclophane would be futile.

CHAPTER 4

[10]-PARACYCLOPHANE CHROMIUM TRICARBONYL: THE EFFECT OF COMPLEXATION ON THE RING CURRENT AND LOCAL ANISOTROPY IN AN ARENE RING

4.1 INTRODUCTION

In Chapter 2, the fate of the π-system, (which of course affects the electronic environment of the arene ring) was discussed. This is now extended to include the complexed ring.

The unusual approximate 1.5-2.0 ppm upfield chemical shift of the aromatic protons in the proton magnetic resonance spectra of arenes upon being complexed to a chromium tricarbonyl moiety has been viewed with intrigue by numerous workers (17,23,24,85-92,106,167-172).

The origin of this phenomenon has been ascribed to a combination of factors viz. decrease in the aromatic ring current (17,24,85-92,167,168, 170), the magnetic anisotropy of the arene bond (87) and the electron withdrawing effect of the metal carbonyl moiety (86,87). Whilst the initial suggestion of a decrease in the aromatic ring current has its attractive features there are still a number of apparent anomalies.

Thus, although dipole moment measurements (25,26), reactivity data (4,7,80-83), M.O. calculations (23,24) and h.m.r. chemical shifts (84-87) seem to suggest that the chromium tricarbonyl group is electron withdrawing, various n.m.r. studies (84,88,92,106) have shown that resonance effects are transmitted from a para substituent almost equally well in the π-(arene)-chromium tricarbonyl complex as in the corresponding free arene. Whilst the former evidence lends credence to the ring current diminution concept the latter does not. Still, the fate of the ring current on complexation has been central to many of the various explanations of the origin of the observed upfield shift of the aromatic protons in a complexed system.

Emmanuel and Randall (87) from their ^{1}H n.m.r. investigation of polymethylbenzenes and their chromium tricarbonyl complexes concluded that this observed upfield shift was due to a combination of:

a) reduction in the π-electron density, resulting in a downfield shift,

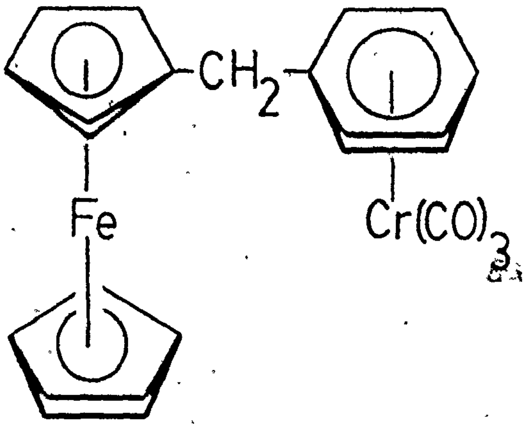
b) an upfield contribution arising from the magnetic anisotropy of the $Cr(CO)_3$ group,

c) quenching of the ring current to give rise to a further upfield shift.

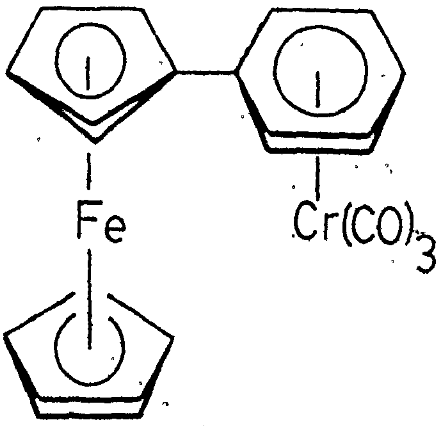
This work followed a similar ^{1}H n.m.r. investigation, also of polymethylbenzenes and their complexes, by Price and Sorensen (86) who suggested, based on their findings, that the upfield shift is a result of a suitable combination of the electron withdrawing effect of the chromium tricarbonyl moiety and a reduction in the aromatic ring current.

In contrast to the above findings much support has been generated for the view that, upon complexation, the ring current is little altered.

Infra-red and far infra-red studies (89-91) [illegible]ve indicated that the π system of the ring is essentially unperturbed by complexation. McFarlane and Grim (84) concluded, from their n.m.r. study of polymethylbenzenes and the analogous chromium tricarbonyl complexes, that the ability of the aromatic nucleus to transmit mesomeric effects is little affected by association with a $Cr(CO)_3$ moiety. This conclusion is in agreement with the findings of KhandKarova, Gubin and Kvasov (92) from a ^{19}F n.m.r. study of fluorinated biphenyls and their complexes. Gubin and KhandKarova (172) also carried out polarographic studies on ferrocenylphenylchromium tricarbonyl methane (I) and ferrocenylphenylchromium tricarbonyl (II) in order to determine a σ-constant for the C_6H_5-$Cr(CO)_3$ group. From an analysis of the results it was concluded that no decrease



I



II

in the π-electron density in the benzene molecule occurred upon its complexation.

Further, Wu, Biehl and Reeves (88,181), from their correlation of Hammett substituent constants with the pK_a values of phenoltricarbonyl chromium complexes (171) and with the amine protons' n.m.r. chemical shifts in meta and para substituted aniline complexes (88), concluded that the π-electron cloud of the complexed arenes can function in much the same way as that of an uncomplexed arene in the transmission of resonance effects.

More recently Bodner and Todd's ^{13}C investigation of monosubstituted benzenes (107) results in the hypothesis that the π-system of the arene is undisturbed upon complexation.

It is apparent that more exact knowledge of the ring current in the complexed arene system would aid in resolving the conflicting speculation and, more importantly, would shed light on the exact nature of the π-system in the bonding of an arene ring to a chromium tricarbonyl moiety. To this end it was deemed highly desirable to consider a system in which the ring current was directly observable and isolable from other influences. Recent publications by Keller (169) and Langer and Lehner (168) have attempted to accomplish this but they too have drawn conflicting conclusions; their results will subsequently be discussed further.

An attempt has been made to clarify the situation. The basic approach used for the free [10]-paracyclophane has been extended to the chromium tricarbonyl complex. Thus, [10]-paracylophane chromium tricarbonyl was synthesized and the proton magnetic resonance spectrum obtained together with the relevant selectively decoupled spectra. In this way, by monitoring any changes in the chemical shifts of the bridging methylene protons, the total perturbations arising from complexation should be directly observable.

Also, the ^{13}C n.m.r. spectrum was obtained.

4.2 RESULTS AND DISCUSSION

4.2.1 The ^{1}H Nuclear Magnetic Spectrum of [10]-paracyclophane chromium tricarbonyl

The data from the 220 MHz proton n.m.r. spectrum is listed in Table 4.1 and the high field section of the spectrum is shown in Figure 4.1 together with that of the free cyclophane for comparative purposes. The α, β and γ resonances were easily assigned by homonuclear decoupling.

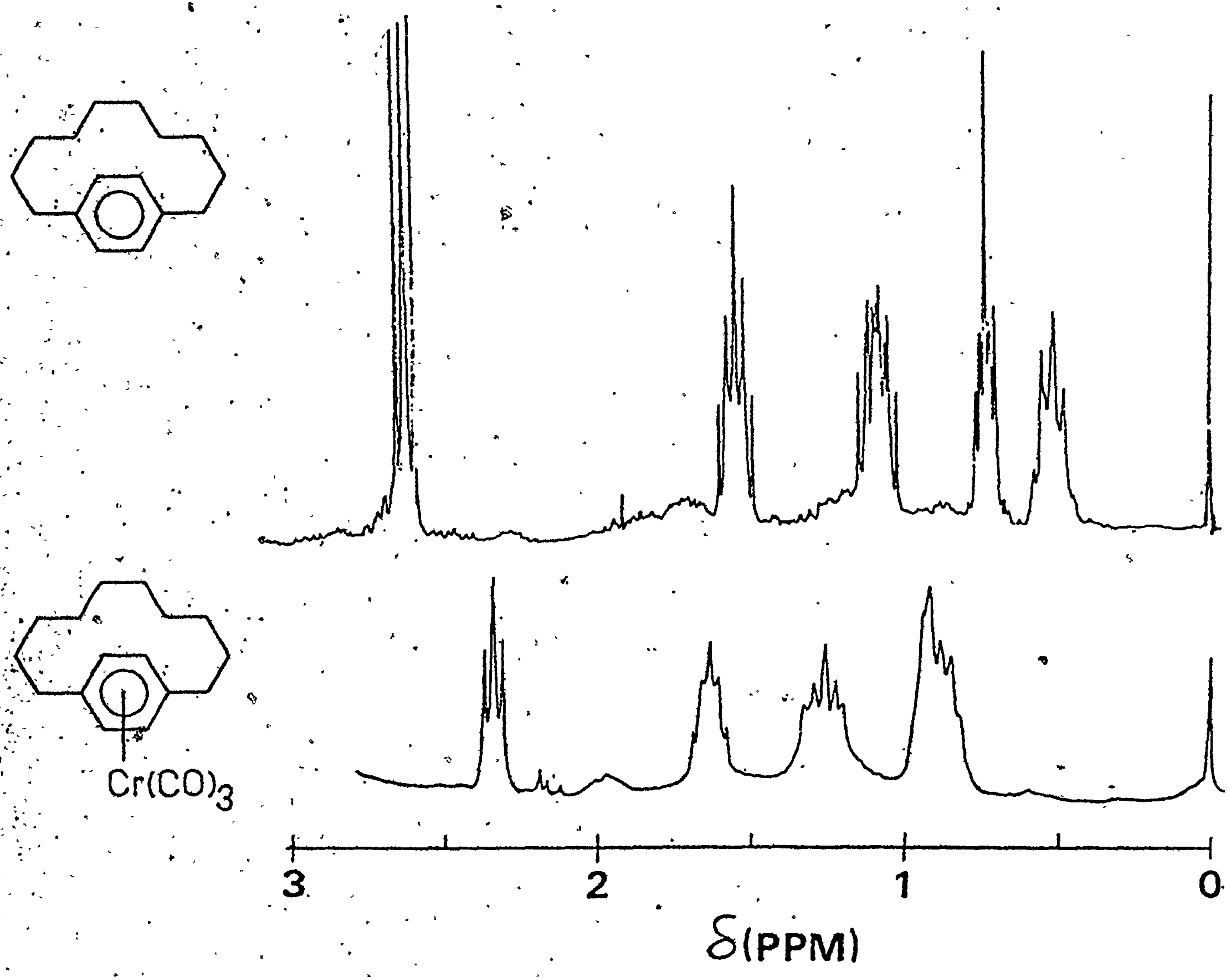


FIGURE 4.1 220 M Hz ^{1}H N.M.R. Spectrum of High Field Resonances of [10]-Paracyclophane Chromium Tricarbonyl

The δ and ε methylene groups are too close to be clearly decoupled, but the ε resonance is still recognizable as a distorted triplet. As can be seen the protons of the arene ring and the α protons are shifted upfield upon complexation whereas β, γ, δ and ε methyl protons undergo a downfield shift; Table 4.1 lists the magnitude of these shifts.

Determination of the vicinal coupling constants in the complex showed them not to differ from the corresponding values in the free paracyclophane. From these data it was thus assumed that there were no major changes in the geometry of the decamethylene chain upon complexation.

Table 4.1 ^{1}H N.M.R. Data for [10]-paracyclophane chromium tricarbonyl

Position	shift (δ values)	$\delta_{free}-\delta_{complex}$
Ar	5.20	+ 1.84
α	2.34	+ 0.29
β	1.63	- 0.08
γ	1.26	- 0.18
δ	0.92	- 0.22
ε	0.85	- 0.34

4.2.2 Experimentally Determined Ring Current of the chromium tricarbonyl complex of [10]-paracyclophane

With the objective of quantifying the fate of the ring current in [10]-paracyclophane on its complexation to a $Cr(CO)_3$ group, the myriad of influences which are thought to affect the observed chemical shift have been assembled. An approach analogous to that used for the free paracyclophane is deemed appropriate with the exception that an additional term has been introduced to describe the anisotropic influence of the $Cr(CO)_3$ group. This latter idea follows that suggested by Emmanuel and Randall (87); the importance of such a term to explain the chemical shifts of protons in π-complexes has been cited by other workers (173).

The ring current contribution to the observed shift is then defined as the difference between the experimental shift and that calculated by adding the local anisotropic term and the anisotropic contribution of the $Cr(CO)_3$ group, $\chi\Delta G$, to the standard shift, i.e.,

$$(-\delta)_{complex,expt} = -std + LA_{complex} + \Delta RC_{complex,expt} + \chi\Delta G \qquad [4\text{-}1]$$

where χ is the magnetic susceptibility and G is the geometric term associated with the anisotropic contribution from the $Cr(CO)_3$ moiety. In this expression it is anticipated that the ring current contribution, $\Delta RC_{complex,expt}$, is directly related to that calculated for the free arene ($\Delta RC_{J-B,S=0}$) but adjusted by a factor "n" to reflect any change in the ring current resulting from complexation. Thus, a simple relationship

$$\Delta RC_{complex,expt} = n\Delta RC_{J-B,S=0} \qquad [4\text{-}2]$$

is expected.

4.2.3 Local Anisotropic Contributions

In order to evaluate the local anisotropic contribution to the observed shift it is necessary to know the anisotropic ring-carbon shielding components. To this end benzene chromium tricarbonyl and hexaethylbenzene chromium tricarbonyl (and for comparative purposes hexamethylbenzene chromium tricarbonyl were prepared and the principal tensor elements of the ring carbons obtained (176); these are presented in Table 4.2. These data were obtained (175) from powder samples using Waugh's technique of proton-enhanced n.m.r. (176).

Table 4.2: Principal Shielding Values (σ) in $ArCr(CO)_3$, (ppm from Liquid Benzene) and Changes in These Values ($\Delta\sigma$) on Going from Free Ligand to the Corresponding Complex (All values ± 5 ppm).

arene	$\sigma_\perp$	σ_t	σ_r	$\Delta\sigma_\perp$	$\Delta\sigma_t$	$\Delta\sigma_r$	$\Delta(\sigma_t + \sigma_r)/2$
C_6H_6	122	- 9	-23	+2	*	*	+44
$C_6(CH_3)_6$	104	- 9	-41	-6	+17	+57	+37
$C_6(C_2H_5)_6$	100	-32	-41	-7	+ 4	+50	+27
$C_6(C_2H_5)_6$	107	-17	-39	0	+19	+52	+36

* σ_t and σ_r in benzene are know known individually because of averaging over rapid C_6 rotation.

As before, the shielding contributions are split into perpendicular, tangential and radial components. The values of Table 4.2 are for the ring carbons of their respective systems. An interesting feature emerges in the hexaethylbenzene complex. The ring carbon resonance, as well as the methylene and methyl resonances, is split into two components. The six-fold symmetry of the ring appears to be broken to C_3 making three alternating ring positions inequivalent to the intervening ones. This will subsequently be discussed further.

Table 4.2 also lists the increases in shielding, denoted by $\Delta\sigma_i$, of the complexes over the parent molecules (147). A comparison of these values reveals striking changes. Whilst the perpendicular and tangential elements are little changed by complexation there is a very large change (> 50 ppm) in the shielding when the external field is in the radial direction. It is noteworthy that the lowest energy electronic spectral band in $(C_6H_6)Cr(CO)_3$ has been calculated to be a 5e→6e transition and to be xy polarized (23). One might thus naively have anticipated that the in-plane elements would be more affected upon complexation than the perpendicular element. It is interesting that in the free arenes the radial element is almost insensitive to the identity of the substituent but this suffers the predominant change on π complexation. One could view this shielding, when the external field is directed radially, as requiring greatly enhanced circulation about an axis parallel to the C-H bond, and as a corollary the marked upfield shift of the aromatic protons upon complexation can also be rationalized. Hitherto, this latter result has been attributed solely to a quenching of the aromatic ring current (167).

The ^{13}C shielding tensors used for the paracyclophane complex were as follows; values used for ring carbons bearing hydrogens were those of benzene chromium tricarbonyl whereas averaged values from the hexaethylbenzene complex were used for the aromatic carbons bearing alkyl chains. As before the shifts were converted to absolute shifts (by adding 71 ppm to each tensor value), the resulting values are cited in Table 4.3.

Table 4.3: ^{13}C Shielding Tensors for the Various Substituents on the ring carbons of $Cr(CO)_3$ π-complexed Rings.

Group attached to C	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)
H	193.0	62.0	48.0
* CH	175.0	31.0	32.0
** CH_2	175.0	46.5	31.0
CH_3	175.0	62.0	30.0

* Estimated from CH_2 and CH_3 values

** Average

Using these data the local anisotropic term for the complex ($LA_{complex}$ in equation 4.1) is directly calculable for each methylene group using the expression, as before:

$$\langle\sigma^H\rangle = 1/3[\sigma_{11}^H + \sigma_{22}^H + \sigma_{33}^H]$$

where, in each case,

$$\underset{i=1-3}{\sigma_{ii}^{H}} = \frac{a}{\pi}\frac{1}{[(a+\rho)^2+Z^2]^{1/2}} \times \left[K + \frac{a^2-\rho^2-Z^2}{(a-\rho)^2+Z^2} \cdot E\right]\sigma_{ii}^{C}$$

4.2.4 Magnetic Anisotropy of a $-Cr(CO)_3$ Moiety

To evaluate the expression for the anisotropic effect of the chromium tricarbonyl group it was deemed appropriate to treat it as being the sum of the individual effects arising from each of the carbonyl groups. Somewhat simplistically perhaps; these effects were represented by a set of point dipoles with their origin at the geometric centres of each carbonyl group. Thus a McConnell relationship (177),

$$\sigma = \frac{\chi}{3R^3}\ (1 - 3\cos^2\theta)$$

suitable for computation of the shielding constant due to a group having axial symmetry, was used. In this expression σ is the chemical shift (in ppm), R is the distance from the chosen origin of the point dipole to the monitor nucleus (in meters) and θ is the angle made by R with the C-O bond axis. It is felt that the carbonyl groups reflect sufficiently the electronic nature of the $Cr(CO)_3$ group as a unit so as to make the direct inclusion of the chromium atom not essential.

In order to be able to evaluate χ, the magnetic susceptibility of a C-O group, it is necessary to consider a system in which, for two given protons, all influences except that due to the $Cr(CO)_3$ anisotropy are constant. The methylene protons of hexaethylbenzene chromium tricarbonyl afford such a situation. Thus, as will be seen subsequently, in the limit, the ^{13}C spectrum of the hexaethylbenzene complex shows two methylene shifts, one associated with the "up" or carbonyl-eclipsed ethyl groups and one for the "down" or non-eclipsed ethyls. Furthermore, the corresponding protons of the two $-CH_2-$ types will then be, respectively, "down" and "up". These protons then can be expected to feel identical ring current and local anisotropic effects but, by virtue of their different spatial positions relative to the $Cr(CO)_3$ moiety, will experience unequal contributions from the chromium tricarbonyl anisotropy. The requirements for calculating χ then are the ^1H chemical shift difference of the two sets of protons and their spatial positions relative to each of the CO groups.

The 100 MHz proton n.m.r. spectrum shows a separation of 0.20 ppm (at -70°C) for the "up" and "down" methylene protons. The "down" protons are assumed to be those at lower field; a complete rationale for this will be presented in Chapter 5.

With these basic structure-related assumptions and using average arene chromium tricarbonyl bond lengths and angles the positions of the methylene carbons (and their corresponding protons when normal tetrahedral geometry is assumed) and each of the carbonyl groups in the $Cr(CO)_3$ unit were determined.

Thus, evaluation of the geometric terms and knowledge of the chemical shift difference enables χ to be determined from the following expression:

$$\sigma_{up} - \sigma_{down} = \chi \ (G_{up} - G_{down})$$

where σ's are the chemical shifts and G's the geometric terms according to the McConnell relationship for each set of "up" and "down" methylenic protons. Assuming a [illegible]-rotating ring (relative to the $Cr(CO)_3$ group) the value of χ, averaged over the three carbonyl groups, is found to be -31.0 m^3/molecule.

Use of this value for molecules under conditions where internal rotation is fast on the n.m.r. time scale requires that more than one relative position of each of the carbonyl groups must be considered. Since, in theory, for a given methylene proton each CO group may have an infinite number of relative positions it was decided to average these effects from four positions. These positions were defined by the angle made by the CO group in question and the arene-αcarbon bond when viewing the molecule along the metal to ring-centre axis. These angles were varied from zero to 120° at 30° intervals, and the values averaged for each position of all carbonyl groups.

4.2.5 The Ring Current in the Complex

The total shift of the protons in 10-paracyclophane chromium tricarbonyl may now be evaluated by use of expression (4-1), by inserting the appropriate values χ, G, LA and δ for each proton type, α through ε. Each of these values is either directly measurable or calculable; the standard shift, however, is not and, whilst it is anticipated that its value will be close to that of the free system i.e, 1.36, it is felt more appropriate to allow this to be determined by the method of treatment.

From (4-1) the expression for the ring current then becomes:

$$\Delta RC_{complex,expt} = std - (\delta_{complex,expt} + LA_{complex} + \chi\Delta G) \qquad [4\text{-}3]$$

Now, combining (4-2) and (4-3) an expression as follows is obtained:

$$-(\delta_{complex,expt} + LA_{complex} + \chi\Delta G) = n\Delta RC_{J-B,S=0} - C \qquad [4\text{-}4]$$

where C reflects the standard shift plus any additional constant residuals.

The values for the total observed shift (δ), the local anisotropic contribution (LA) and the effect from the $Cr(CO)_3$ moiety ($\chi\Delta G$) may now be used for each set of protons (α through ε) in the decamethylene chain. In this way a series of expressions of the type (4-4) is obtained. A plot (Figure 4.2) was then made of $-(\delta + LA + \chi\Delta G)$ versus the calculated ring current ($\Delta RC_{J-B,S=0}$).

The slope, n, in equation (4-4) was found to be 0.499 and the intercept was 1.44. A good correlation was found ($\bar{r} = 0.991$).

Thus, these data indicate that the aromatic ring current, upon complexation with a chromium tricarbonyl unit, has been reduced to approximately 50% of its former value. Gratifyingly, given the limitations and assumptions of the model, the value of the intercept is very close to the anticipated value of 1.36, the standard shift for the corresponding free system. This would seem to suggest that either the model for the complexed system has adequately accounted for the majority of changes that are the result of complexation and this small discrepancy (0.08) represents the inherent experimental error or, that there is a small factor affecting the overall shift which has been ignored. Emmanuel and Randall (87) suggest that, by application of Buckingham's equations (178), a small contribution to the overall shift (of about 0.2 ppm for ring protons) may be expected owing to the electric field gradient as arising from the metal-ring dipole. This influence would be a down-field effect which is consistent with the direction of the 0.08 ppm difference found in the above treatment. Whilst the magnitude of the observed difference is somewhat less than that calculated using Buckingham's approach this is perhaps not surprising since the latter value relates to ring protons whereas the smaller value is for the more distant protons of the decamethylene chain.

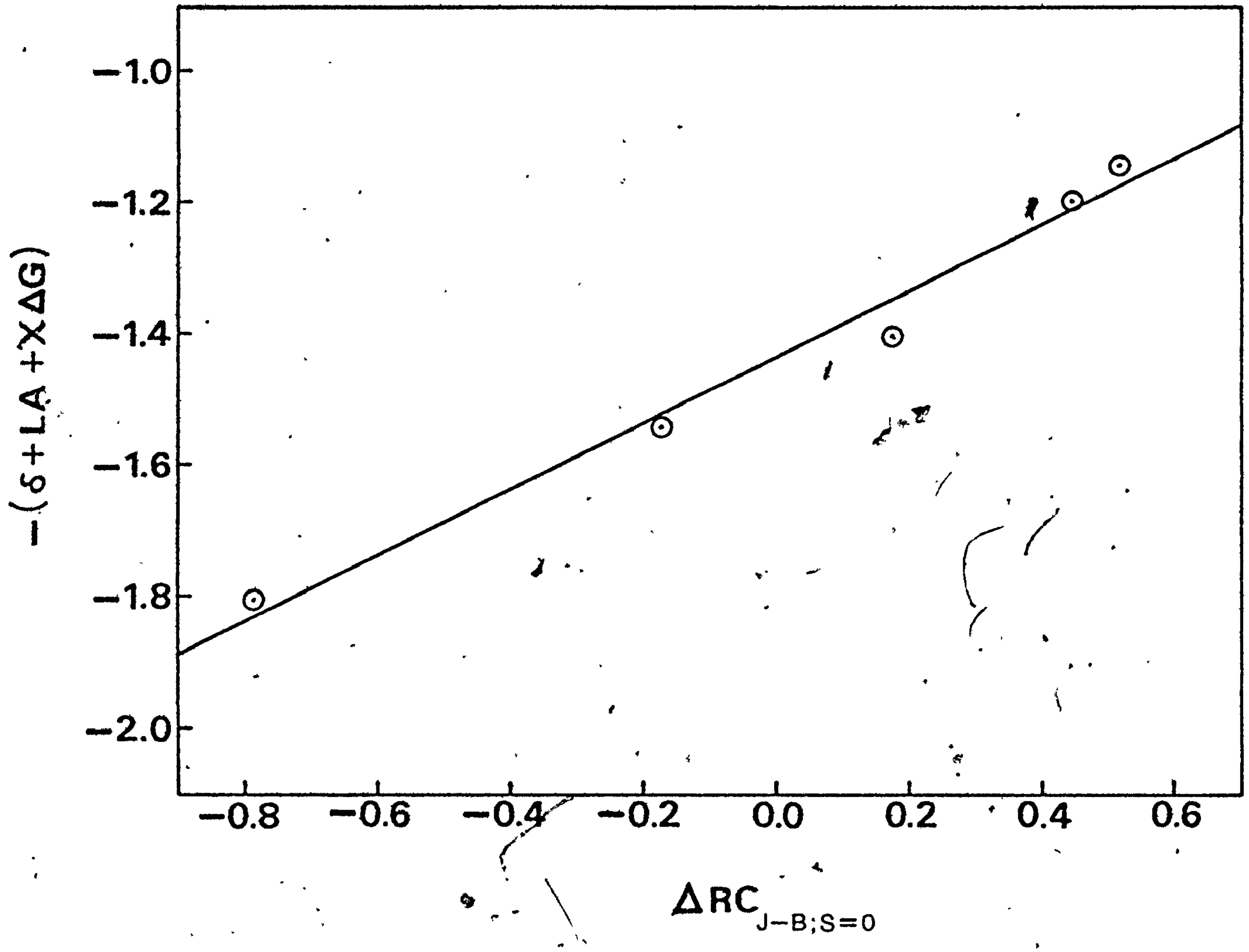


FIGURE 4.2 Plot of $-(\delta + LA + \chi\Delta G)$ versus the Calculated Ring Current ($\Delta RC_{J-B,S=0}$), in the $ArCr(CO)_3$ System, based on the Data for [10]-Paracyclophane Chromium Tricarbonyl

The complete expression for the total shift now becomes:

$$-\delta_{complex} = -1.44 + LA_{complex} + 0.499\ \Delta RC_{J\text{-}B,S=0} + 31.0\ G \qquad [4\text{-}5]$$

It is of interest to compare the relative magnitudes of each of the effects which contribute to the overall shift in the paracyclophane complex. Table 4-4 summarizes these data.

Table 4-4: Components of the calculated shift in [10]-paracyclophane chromium tricarbonyl.

Proton	Standard	Ring Current	Local Anisotropy	Chromium tricarbonyl anisotropy	Calculated shift (-δ)	Experimental shift (-δ)
α	-1.44	-0.392	-0.449	-0.085	-2.37	-2.34
β	-1.44	-0.085	-0.097	0.013	-1.61	-1.63
γ	-1.44	0.088	0.107	0.036	-1.21	-1.26
δ	-1.44	0.222	0.232	0.048	-0.94	-0.92
ε	-1.44	0.257	0.249	0.049	-0.88	-0.85

As can be seen from Table 4-4 the local anisotropic and ring current terms are of a similar magnitude in the complexed system. This is in contrast to the free cyclophane in which the ring current contributions were dominant (Table 3.4). The effect arising from the anisotropic nature of the $Cr(CO)_3$ unit is relatively small. This is perhaps not too surprising in light of the distance of the protons from the source of the effect.

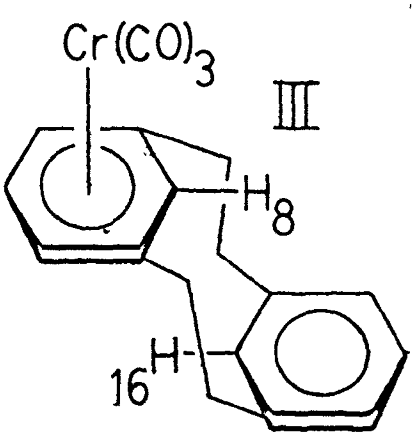
The result of a diminution of the ring current, whilst not entirely surprising, is in conflict with the majority of prior opinion (84,88-92, 107,169,172). A number of these investigations have been concerned with the transmission of substituent effects between para positions across the ring (84,88-91,107,171). As was stated in Chapter 2 the constancy of the transmission of such effects on going from free to complexed systems need not necessarily arise from an unchanged π-system if there were an alternate route by which these effects could be transmitted. In light of the above findings it would seem reasonable to propose such a mechanism whereby orbitals of the chromium atom itself are able to interact directly between para positions of the ring thereby aiding in the transmission of these electronic variations across the ring. The ability of the orbitals of the central metal atom to interact directly with sites α to the ring is evidenced in the stabilization of both anionic and cationic species (61-63).

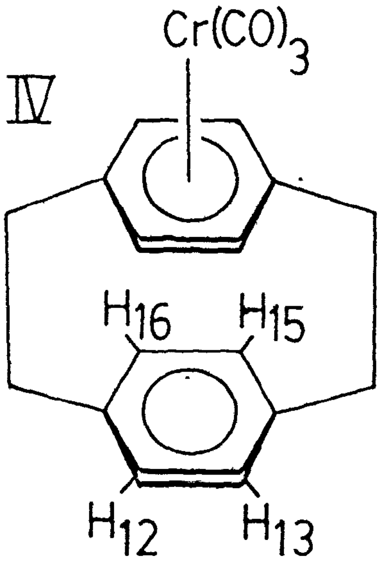
4.3 TESTING OF THE MODEL

In order to evaluate the usefulness of this model it is of interest to determine its appropriateness in other chromium tricarbonyl systems. For such evaluations to be possible the requirements of the system to be tested should be that the chemical shifts of the protons of interest must be known and that the relevant structural data should be available.

Langer and Lehner (168) chose to look at the proton n.m.r. of a series of [2,2]-meta and [2,2]-para-cyclophanes and their chromium tricarbonyl complexes (Figures III and IV).

These systems are considered rigid, furthermore the lack of any change in geometry was thought to be confirmed by the constancy of chemical


III

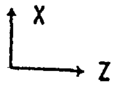
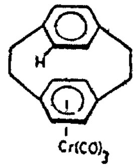
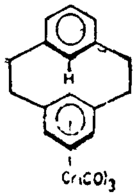
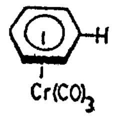
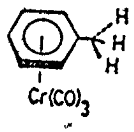

IV

shift differences between H-8 and the remaining protons of the ring in both the free and complexed systems. Protons H-16 (in III) and H-12,13, 15,16 (in IV) were then used to monitor directly any changes in the respective ring currents on going from the free arene to the Cr(CO)$_3$ complexes. An overall donwfield shift of these proton probes upon complexation was interpreted as being due to a diminution of the aromatic ring current.

Following the approach of Chapter 3, the standards for III and IV were taken to be, respectively, 1,3-diethylbenzene and p-xylene. The sources of the structural data are as stated previously. Table 4.5 lists the components of the incremental shift and the calculated shift. As can be seen relatively good agreement is found between calculated and experimental values for III and IV.

Table 4.5: Calculated and Experimental ^{1}H N.M.R. Chemical Shifts for a Series of Arene Chromium Tricarbonyl Complexes.

TABLE 4.5 Calculated and Experimental ^1H N.M.R. Chemical Shifts for a Series of Arene Chromium Tricarbonyl Complexes

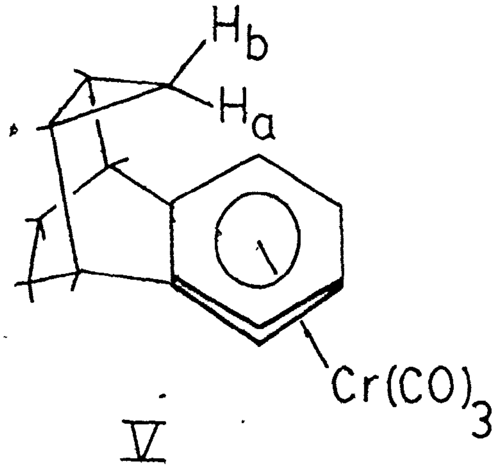
	Coordinates of H				Proposed Model (complex)					
	X	Y	Z	Standard	LA	RC	xG	Total Incremental shift	δ Calculated	δ Experimental
	0.695	3.086	2.374	-7.01	0.226	0.20	0.053	0.479	-6.53	-6.77
	0.792	2.488	0.0	-7.20	0.730	1.00	0.135	1.865	-5.34	-5.45
	2.470	0	0	-0.23	-4.09	-1.40	-0.145	-5.635	-5.87	-5.30
	3.250 3.250 3.250	0 0.885 -0.885	1.018 0.509 -0.509	-1.32	-0.435	-0.338	-0.081	-0.854	-2.17	-2.18

A similar approach was used for benzene and toluene. The standard for benzene was taken as the chemical shift of methane which is an isotropic system, lacking a ring current.

In the case of toluene the predicted shift is taken as an average resulting from imagining the three methyl hydrogen atoms to be positioned such that one is in the plane of the ring and the other two are positioned equidistantly above and below the plane. The standard shift for toluene was derived by consideration of $^1J_{CH}$ for a series of molecules of the type CH_3-X where the X group is widely varied (179).

As is apparent from Table 4.5 the agreement of the calculated shifts with the experimental values is quite good for benzene and very good for toluene.

A relatively recent publication (169) involving a barrelane $Cr(CO)_3$ complex V concluded that there is no reduction of the aromatic ring current upon complexation.



V

Protons H_a (and H_b) are used as probes. Shift differences of only -0.05 ppm and -0.02 ppm are seen, for H_a and H_b respectively, on going from the free to the complexed system.

Whilst the explanation (168) that these probe protons are accidentally on the zero field gradient is not valid, the concern (168) that adequate consideration was not given to the effects of possible conformation changes is justified.

Construction of a model of the complex form makes it readily apparent that the pendant portion of the barrelane function and the carbonyl groups would be prone to steric interactions. A possible outcome of this would be to force the barrelane substituent to twist away from the $Cr(CO)_3$ group. This in turn might result in the cyclopropyl function (and H_a and H_b) being pushed down further into the cone of influence of the ring current. The close proximity of these probe protons to the plane of the ring would then result in an increased local anisotropic and chromium diamagnetic anisotropic effect which could be coincidentally almost exactly offset by the reduction in the ring current arising from complexation. It should be reiterated that, without more exact knowledge of the relative conformations of the barrelane function in the free and complexed systems this, and indeed any other interpretation of the observations, must be viewed as speculative.

It has been shown that, upon complexation with chromium tricarbonyl, the aromatic ring current of an arene is reduced to approximately 50% of its former value. It is then suggested that the chromium atom itself must play a part in the transmission of resonance effects between para positions in an arene ring. Further, using the approach of Chapter 3, a model has been developed which, with a careful and knowledgeable choice of standards, enables the chemical shifts of protons both in and out of the plane of a complexed arene ring to be predicted.

4.4 ^{13}C N.M.R. SPECTRA OF [10]-PARACYCLOPHANE CHROMIUM TRICARBONYL

The ^{13}C n.m.r. spectrum of the $Cr(CO)_3$ complex of [10]-paracyclophane is presented in Table 4.6 and Figure 4.3. As for the free arene the carbons of the decamethylene bridge were assigned by heteronuclear decoupling experiments.

Whilst there have been a number of studies of the ^{13}C n.m.r. shifts of aromatic rings complexed to $Cr(CO)_3$ units (180-187) little attention has been given to the effects of complexation on an alkyl side chain.

Table 4.6: ^{13}C N.M.R. Data for [10]-Paracyclophane Chromium Tricarbonyl.

Carbon Atoms	Shift
Ar (1,4)	113.5
(2,3,5,6)	93.0
α	34.2
β	29.0
γ	24.6
δ	27.0
ε	29.3

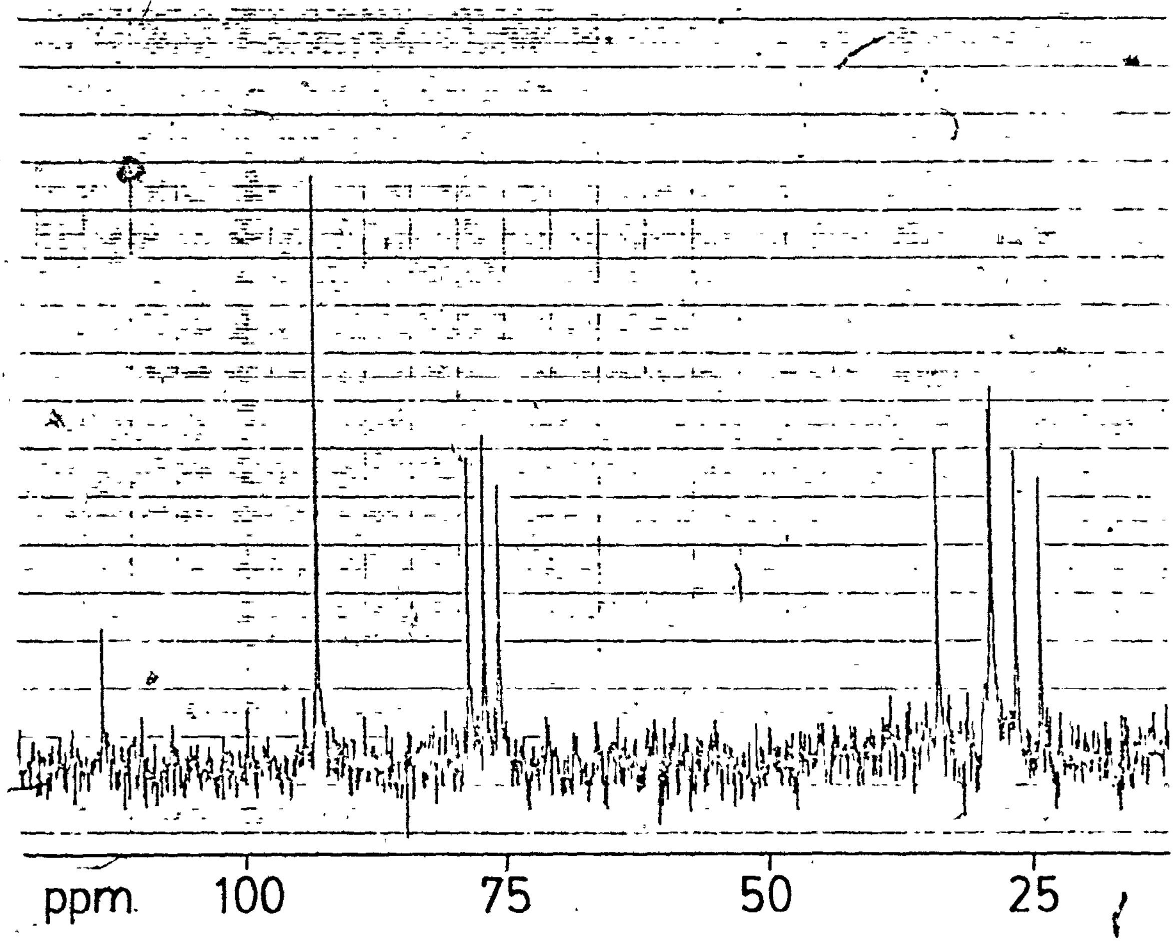


FIGURE 4.8 ^{13}C N.M.R. Spectrum for [10]-Paracyclophane Chromium Tricarbonyl

The α-carbon resonance of [10]-paracyclophane, on complexation, is shifted slightly upfield as would be expected from the reported data for methyl-substituted benzene chromium tricarbonyls (107,187,189). The β, γ and δ ^{13}C resonances are scarcely affected at all, while the ε-carbon undergoes a downfield shift of 0.8 ppm. Bearing in mind the cautions cited in Chapter 3 it is not thought to be meaningful to attempt to interpret such changes as arising from a single given influence.

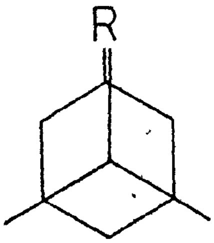
The ^{13}C resonances of the ring carbons show the usual approximately 25-35 ppm upfield shifts upon complexation.

CHAPTER 5

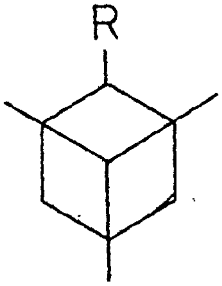
INTERNAL ROTATION IN ARENE CHROMIUM TRICARBONYLS

5.1 INTRODUCTION

The relative conformation of the $Cr(CO)_3$ moiety with respect to the arene ring has been the focal point for numerous investigations (27,28, 31,32,34-36,190-193). The more important determinants of these conformations were cited in Chapter 1. Recapping briefly, the preferred conformations are believed to be determined by (i) steric effects, where a substituent on the ring can create spatial constraints by its interaction with the carbonyl groups of the $Cr(CO)_3$ group, and (ii) electronic effects of the substituent on the ring which, because of the chromium orbitals' preference to overlap with the sites of greatest electron density, directly affects the relative conformation and may be reinforcing or counteracting. A specific example of the latter has been shown in studies of a series of monoalkylbenzene chromium tricarbonyls (180,181,190-192,194,195). Whilst the electronic influences of the substituent favors conformation I as the alykl group becomes more sterically demanding this conformation is thought to become less favored and II becomes preferred.



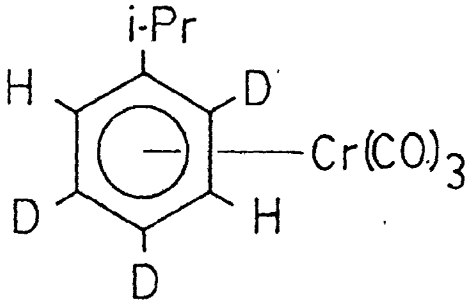
I



II

The rotation of the arene ring with respect to the three-fold axis of the chromium tricarbonyl moiety, thereby resulting in an interconversion of I and II, has been the subject of a number of n.m.r. spectroscopic investigations and the conformational equilibria involved have aroused some debate (180-182,190,191,196,197).

The n.m.r. spectrum of isopropylbenzene chromium tricarbonyl was initially shown to be temperature dependent (195) however, this was refuted by Jula and Seyforth who failed to see such a temperature dependence (191). Further work was carried out on this system using a specifically deuterated arene so as to simplify the spectra (194).



At -40° the ring protons were found to give two singlets which were reported to coalesce upon warming. It was further concluded that, by comparison of these shifts with those of the ring protons in (2,3,4,5-tetradeuterioisopropylbenzene) tricarbonylchromium(0), the preferred conformation was such that the isopropyl group was eclipsed by a carbonyl group (conformation I). It was also found that the eclipsed protons of the ring were deshielded relative to the non-eclipsed protons. The mechanism which results in this deshielding was not thought to be a through-space effect caused by the magnetic anisotropy of the carbonyl groups as they are remote (193), but rather a consequence of directed ring-metal bonding (193,198). Additionally, the n.m.r. spectra of (t-butylbenzene,1,3-di-t-butylbenzene, 1,4-t-butylbenzene and 1,3,5-tri-t-butylbenzene) chromium tricarbonyl were each interpreted in terms of a single conformation that was dominated by steric constraints. Also, the spectrum of m-xylene chromium tricarbonyl was concluded to be indicative of a single conformation preferred for electronic reasons.

A quantitative treatment was also derived (194) based on the assumption that the signal separation between equivalent proton positions in the two possible conformers at a given temperature was related to the relative population of these conformers.

The derived expression being:

$$P_I = \frac{\Theta_{max} - \Theta}{2\Theta_{max}}$$

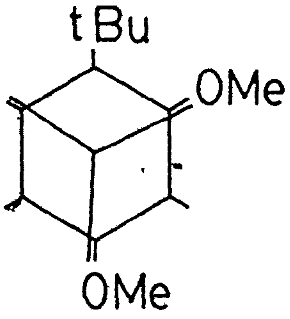
where P_I is the proportion of conformer I, Θ_{max} the signal separation for the single conformer I at -273°C and Θ the observed signal separation.

Barbieri and Taddei (197) investigated the p-methoxy derivatives of t-butyl and isopropylbenzene complexes and their conclusions led them to disagree with the aforementioned implication of there being a rotation that was slow on the n.m.r. time scale.

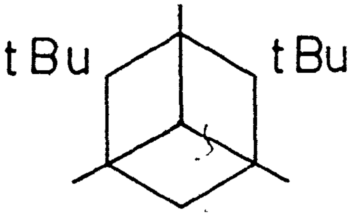
A further n.m.r. study of alkylbenzene chromium tricarbonyl complexes showed n-propyl, n-butyl and isobutylbenzene complexes to have a preferred eclipsed configuration (P_I = 70 - 76%) (190) despite the adverse steric relationship.

Further support was given to the hypothesis that the rotation in t-butylbenzene chromium tricarbonyl is severely restricted (190), the n.m.r. spectrum being essentially unchanged between -60°C and +35°C.

This latter point is also concluded from a ^{13}C n.m.r. study (180) which shows an invariance in ring carbon ^{13}C shifts with temperature changes. A more complete ^{13}C study, which included di- and tri- alkyl substituted arenes was conducted (181) and attempts made to rationalize the data in terms of steric and electronic effects. Also, an attempt was made to stabilize one conformation with the objective of causing kinetically restricted rotation about the ring-metal bond which would be slow on the n.m.r. time scale. The 1-t-butyl-2,4-dimethoxybenzene chromium tricarbonyl was chosen for such a purpose with the t-butyl group affording steric constraints and the methoxy substituents providing their complimentary electronic influences.



However, the carbonyl resonances were not seen to broaden even at -60°. Similarly, for 1,3-di-t-butylbenzene chromium tricarbonyl, no broadening was observed.



As an extension to the above a series of alkyl benzene chromium complexes were investigated where one of the carbonyl groups was replaced by PPH_3 or $AsPh_3$ (182). The objective of observing hindered rotation by introducing the additional steric constraint of the triphenyl groups was not met, thus dicarbonyl(1,3,5-tri-t-butylbenzene) triphenylphosphine chromium at -60°C showed no sign of this phenomenon.

Further evidence exists to indicate that the barrier to this rotation is very low. Electron diffraction has established that benzene-chromium tricarbonyl, in the gas phase, is a "nearly unhindered rotor" (199). Broad line n.m.r. experiments on crystalline benzene chromium tricarbonyl have shown a phase change at -165° which was attributed to this rotation (200).

A ^1H n.m.r. study of a comprehensive series of alkyl substituted chromium tricarbonyl benzenes attempted to quantify the conformer population distribution for the different substituents (192) based on the method of Jackson (194). The value of Θ_{max} is however based on the assumption that (1'-t-butyl-2',2'-dimethylpropyl)-π-tricarbonyl chromium benzene is in a completely staggered conformation. Whilst the slow rotation of the ring - C_α bond has been well established both in the free (201) and complexed system (202,203) the aforementioned assumption is less clear.

Thus, whilst many have sought to observe rotation about the arene-chromium bond which is slow on the n.m.r. time scale there exists no definitive evidence for such a finding.

In the measurement of the anisotropic shielding tensors for hexaethylbenzene chromium tricarbonyl two non-equivalent ring carbon evironments were found. Also, two components of equal intensity were seen for both the methylene and methyl resonances. It became of interest to see if these observations would manifest themselves, under appropriate conditions, in the corresponding solution spectra.

5.2 RESULTS AND DISCUSSION

Low temperature ^{13}C n.m.r. spectra of (HEB)chromium tricarbonyl in CD_2Cl_2 were run (Figure 5.1). Two environments for each of the ring, methylene and methyl carbons are seen at -72°C which on warming are caused to coalesce. The activation energies (204) for the interconversion of the two environments are, respectively, 53.1 ± 2.5, 44.8 ± 2.1 and 46.9 ± 1.7 kJ mol^{-1}.

These results are rationalizable on the basis of an internally eclipsed conformation whereby the carbonyl groups impose a three-fold symmetry on the molecule. Furthermore, it would seem that the conformation in question has a lifetime (at -72°C) which is long on the n.m.r. time scale.

HEB itself is known to adopt D_{3d} symmetry (118) in which the ethyl groups project alternatively above and below the plane of the ring. It

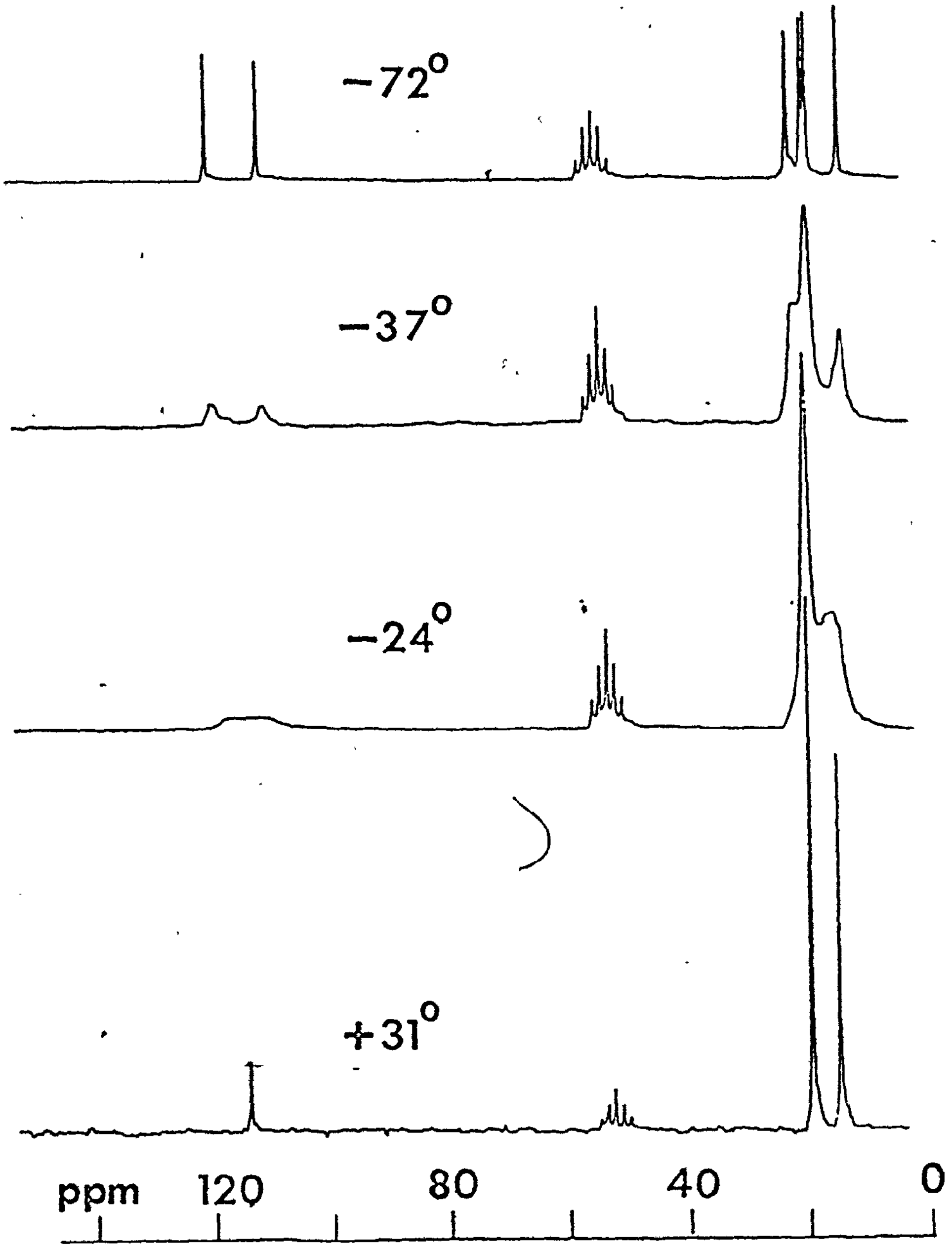


FIGURE 5.1 Variable Temperature ^{13}C N.M.R. Spectra of Hexaethylbenzene Chromium Tricarbonyl in CD_2Cl_2.

is thus not unreasonable to surmise that in the complex the same arrangement for the tentacular ethyl groups exists (Figure 5.2). For steric reasons it is further proposed that the carbonyl groups eclipse the supraplanar substituents.

In an apparently close analogue, viz., hexaethylborazine, $B_3N_3Et_6$, the free ligand has D_{3d} symmetry (205) and the X-ray structure of $Cr(CO)_3$ complex shows it to be eclipsed with the eclipsing ethyl groups projecting above the plane of the ring, i.e., away from the metal (206).

Thus, there are two ring carbon resonances not only because of the different orientations of the ethyl groups to which they are attached (up or down) but also because the chromium-arene rotation would appear to have stopped.

As mentioned previously the conformational preference of the $Cr(CO)_3$ moiety with respect to the complexed ring has been attributed to both steric and electronic effects of the ring substituents. It is noteworthy that in the case of (HEB)chromium tricarbonyl the observed apparent cessation of ring-metal rotation (on the n.m.r. time scale) is purely a steric effect since the metal has no electrically preferred bonding sites on the ring.

The majority of previous investigations involved attempts to slow the rotation by increasing the steric requirements of an alkyl group on the ring. This approach required overcoming an inherent electronically preferred conformation that was in opposition to the sterically preferred conformer.

In a previously mentioned ^{13}C study (181) of alkylated arene

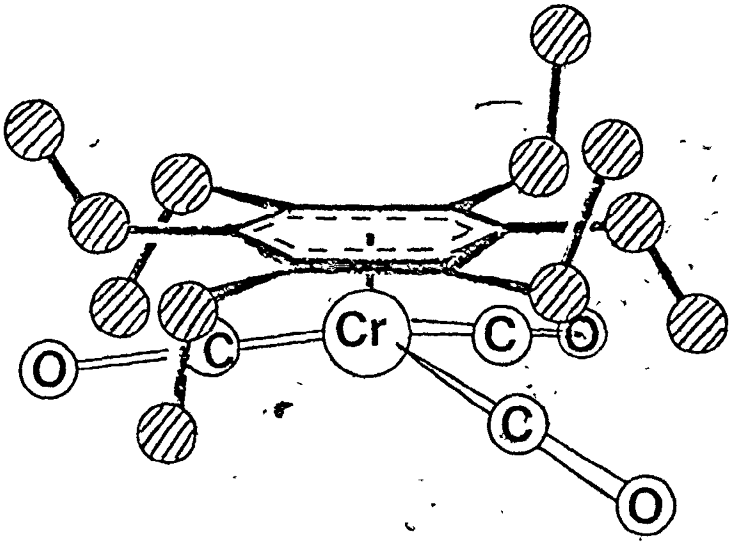


FIGURE 5.2 Hexaethylbenzene tricarbonylchromium(0)

Note: A recent publication (G. Hunter, D.J. Iverson and K. Mislow, J. Amer. Chem. Soc., 102, 5942 (1980)) reports the crystal structure of Hexaethylbenzene chromium tricarbonyl. Gratifyingly, the above structural conclusions and the assumptions cited in Chapter 4 appear to be justified.

complexes where the substituents have a gradation of steric requirements, but little electronic disparity, it was shown that, in cases where the eclipsed rotamer predominates, the eclipsed ring carbons exhibit a smaller complexation shift (δ free - δ complex) than when they do not lie directly above the carbonyl groups. In the case of (HEB)$Cr(CO)_3$ it is thus tempting to assign the ring carbons such that those with the higher field isotropic shift are bonded to the ethyl groups proximate to the $Cr(CO)_3$ moiety. This shift difference (in the limit) between the two ring carbon environments is quite large (8 ppm) and is, gratifyingly, almost identical to that in the solid state where rotation has presumably stopped.

Although the above data are consistent with a cessation of tripodal rotation it does not demand that this be so as it could be argued that the arene ring carbons are magnetically non-equivalent by virtue of the different orientations of the ethyl groups (i.e., proximal or distal with respect to the chromium). To this end, the tungsten analogue was acquired in the hope of detecting two different tungsten-ring carbon coupling constants. Unfortunately, even though the molecule behaved analogously (see Figure 5.3) to the chromium system, the desired coupling constants were not observed. Only J_{W-CO} was seen, with a value of 183 Hz which is typical of such systems (207). This lack of coupling is perhaps not surprising as there are no known reports of such coupling constants between tungsten and carbon atoms of polyhapto ring systems (207). The lower coalescence temperatures for the W complex (~ -40°C) relative to that for (HEB)$Cr(CO)_3$ (~ -25°C) are consistent with the greater size of

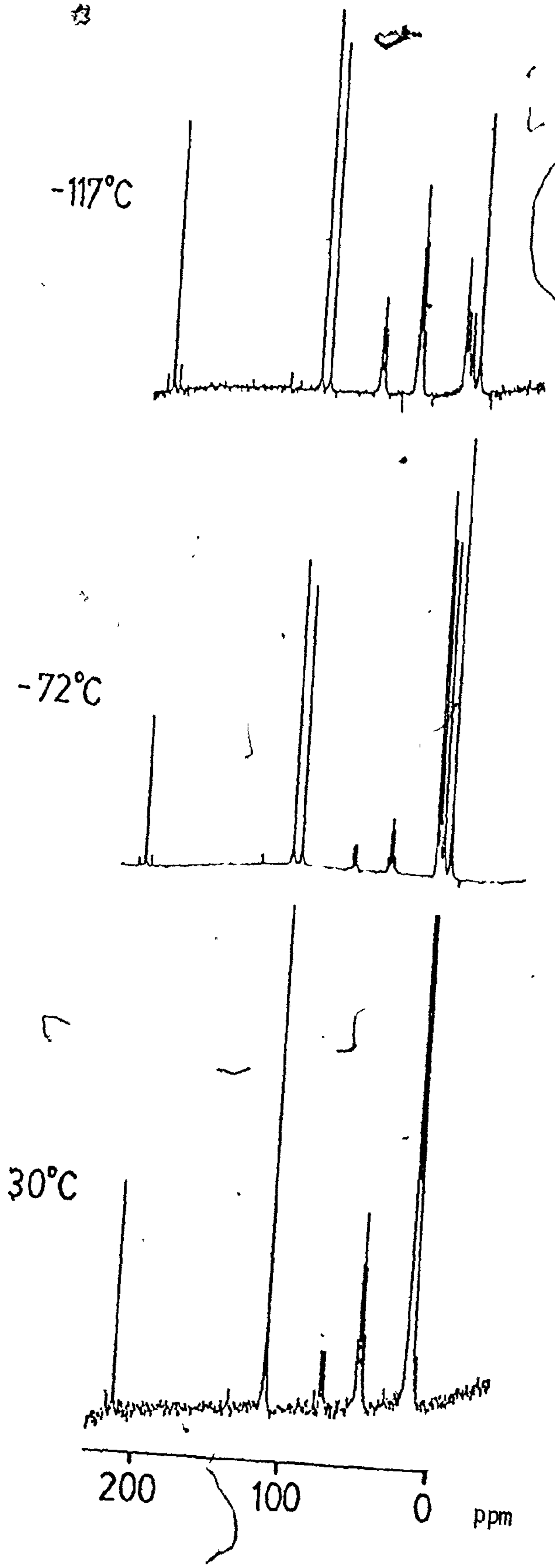
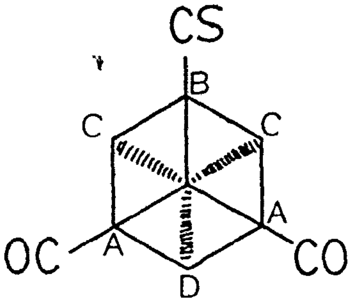


FIGURE 5.3 Variable Temperature ^{13}C N.M.R. Spectra of Hexaethyl-

the third row element and the accompanying decreased steric interactions between the pendant ethyl groups and the $M(CO)_3$ moiety.

To further investigate the hypothesis of a "fixed" tripod which is preferentially bonded to three of the ring carbon atoms, low temperature ^{13}C spectra of $(HEB)Cr(CO)_2CS$ were run and the crystal structure determined (Figure 5.4). This latter molecule was shown to behave analogously to that of $(HEB)Cr(CO)_3$ down to approximately -50°C at which point the ring-carbon resonances did not sharpen up but rather broadened out to give, at -144°C, four clearly resolved peaks in the ratios of 2:1:2:1 (see Figure 5.5). This can only be consistent with a lowering of the symmetry from pseudo-C_{3v} to C_S.



III

It would seem that although tripod rotation has ceased, thus rendering the two types of ring carbon non-equivalent, there can still be low amplitude oscillations of the tripod which only become slow at very low temperature and thus splits out each environment into two with ratio 2:1 as demanded by the ratio of carbonyl to thiocarbonyl.

It is suggested that the low frequency (more shielded) peaks, C

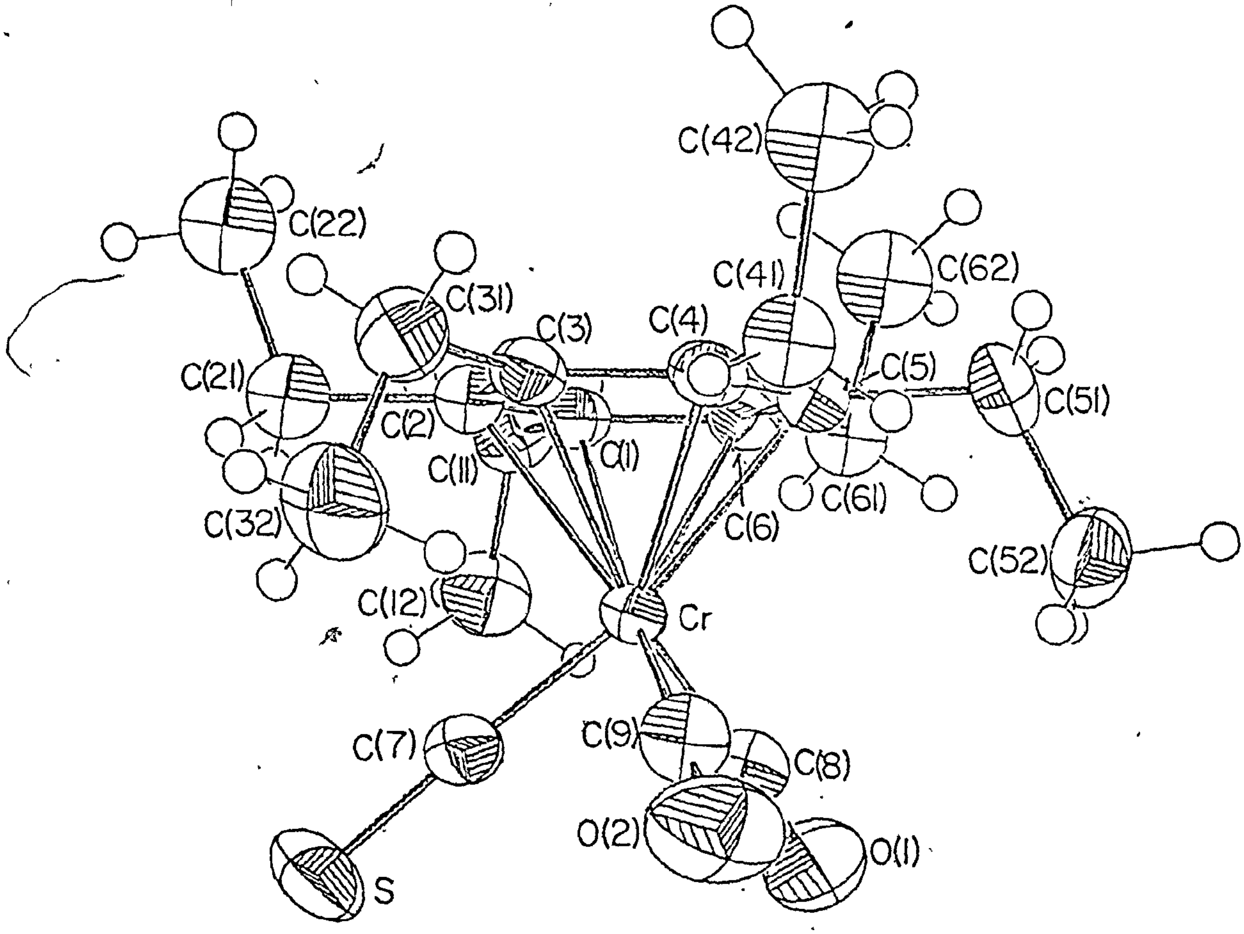


FIGURE 5.4 ORTEP Diagram of dicarbonyl(hexaethylbenzene)-(thiocarbonyl)chromium(0)

(This crystal structure was kindly provided by Dr. C.J.L. Lock and Mr. R. Faggiani).

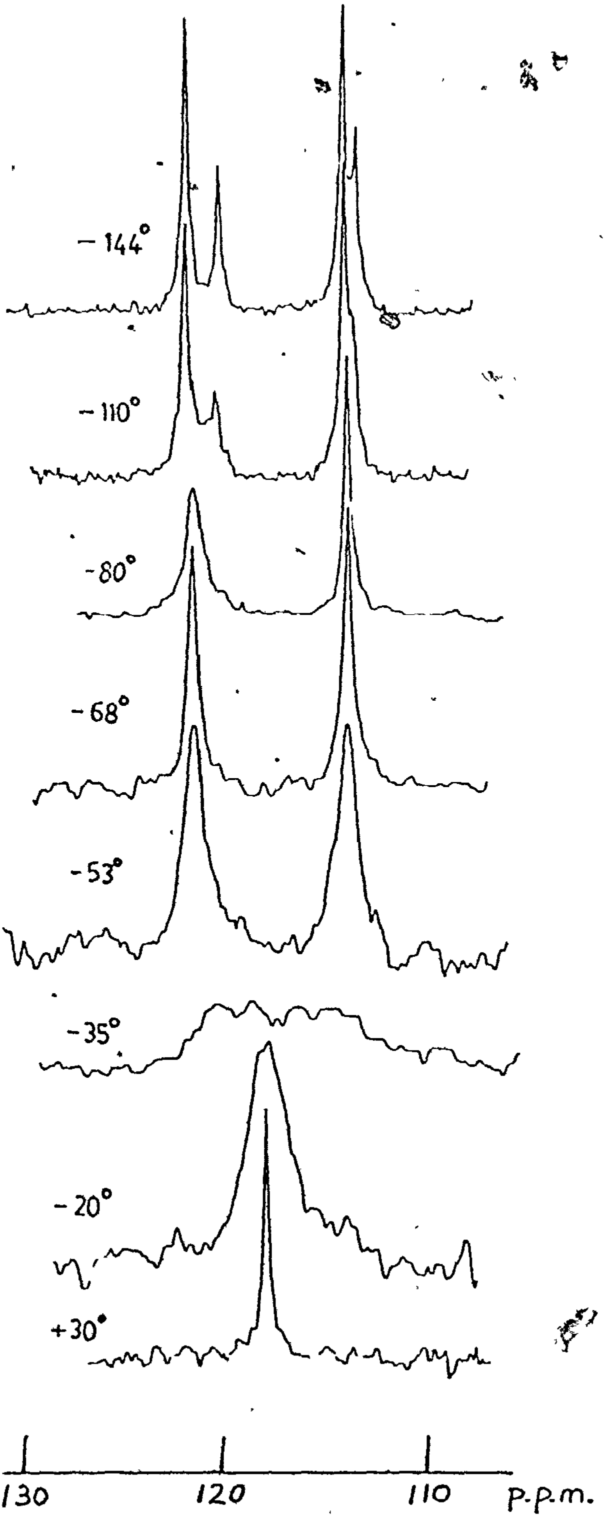


Figure 5.5 Ring carbon resonances of ^{13}C spectrum of (hexaethylbenzene) dicarbonyl thiocarbonyl chromium (0).

and D (in III), be assigned to the directly bonded ring carbon atoms trans to the carbonyl and thiocarbonyl groups. In the absence of direct coupling constants (such as had been hoped for in (HEB)W$(CO)_3$) unequivocal assignments cannot be made, but the following arguments are presented to support the aforementioned contentions. Firstly, it is well established that complexation to a chromium atom greatly shields the arene carbons and one might thus naively have expected the more shielded absorptions to correspond to those interacting most strongly with the metal. Secondly, and more subtly, one can examine the changes in the tensor elements of the arene carbons of HEB upon complexation with a Cr$(CO)_3$ unit. It is known that (HEB)Cr$(CO)_3$ exhibits two different isotropic shifts and that these are separated by 9 ppm. This separation is almost entirely attributable to a difference in the tangential tensor element which is the one most readily visualizable as being dependent on interaction of a chromium 3d orbital with the carbon $2p_z$ orbital. Now comparing the six tensor elements observed in (HEB)Cr$(CO)_3$ with the three of HEB itself it is seen that the only noticable changes are to the radial elements (which both change by 50 ppm) and to only one of the tangential elements. It is therefore suggested that it is to this carbon that the chromium is attached, i.e., the more shielded signal corresponds to the directly bonded carbon.

Note that this requires a greater chemical shift difference between the ring carbons which lie above the carbonyl and thiocarbonyl groups than those which are directly bonded to chromium and are thus trans to the CO and CS ligands. However, the anisotropic deshielding experienced by nuclei sited equatorially to triple bonds can be very different depending on the identity of the atoms involved. Thus χ, the diamagnetic anisotropy of the molybdenum-molybdenum triple bond (208) is only about half that of the alkyne linkage (209). For the present situation χ for the thiocarbonyl linkage apparently exceeds that for the carbonyl moiety.

Irrespective of the validity of the foregoing arguments it is clear that the ring carbon trans to and directly above the thiocarbonyl group are to high field of the respective ring carbons associated with the carbonyls. Thus, although the overall effect of substituting a CO by a CS is to deshield the ring carbons, the isolated effect of a thiocarbonyl is to shield the carbon trans to it relative to the corresponding carbon trans to a carbonyl. Presumably, the strong π-accepting ability of CS relative to CO (which is reflected in the increase in ν_{CO} and the deshielding of $\delta_{^{13}CO}$) (210) has the effect of deshielding the ring-carbons trans to the remaining carbonyls and so the global effect upon introducing a thiocarbonyl in place of a carbonyl is to increase the mean resonance frequency of the ring carbons.

The fact that the activation energies for the interchange of proximal and distal ethyl groups are very sensitive to the steric requirements of the tripodal groups shows that this is not merely a case of the metal affecting magnetically different environments. Thus, the activation energies are not just a measure of the barrier to the rotation of an ethyl group past its ortho partners. The rotation of the $Cr(CO)_3$ moiety with respect to the arene is apparently highly correlated (211) with the motion of the ethyl groups, perhaps somewhat analogous to the action of a bevel gear. However, such speculation must await the results of molecular orbital calculations (212) on the various conformations of the molecule. Interestingly, it has been shown that, in the case of hexaphenylbenzene, the fluxional mechanism probably involves the rotation of only one peripheral ring at a time (213).

CHAPTER 6

EXPERIMENTAL

6.1 GENERAL TECHNIQUES

Fluorine-19 nuclear magnetic resonance spectra, for the data found in Chapter 2, were recorded on a Varian DP-60 spectrometer using trichlorofluoromethane as internal reference. Infrared spectra were run as Nujol mulls between NaCl plates on a Perkin-Elmer 337 grating spectrometer. Mass spectra were recorded on a C.E.C. 21-110-B spectrometer operating at 70 eV.

The proton spectra for [10]-paracyclophane and its chromium tricarbonyl complex were obtained on a Varian HR-220 spectrometer operating at 220 mHZ and 18°C in $CDCl_3$ with tetramethylsilane as internal reference. Proton homonuclear decoupled spectra were obtained on a Varian HA-100 spectrometer operating at 100 MHz at 35°C using standard techniques with TMS as internal reference. Concentrations of 0.1 - 0.2 M were used in $CDCl_3$ as solvent, and the peak positions were extrapolated to infinite dilution.

Carbon-13 n.m.r. spectra were obtained on a Bruker WH-90 spectrometer operating at 22.62 MHz at 35°C using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Field/frequency stabilization was achieved by locking to the deuterium of the solvent. Proton noise decoupled spectra were obtained with the decoupler frequency centred at 4 ppm downfield from TMS.

Melting points are uncorrected.

Most of the fluoroarenes were supplied by Penninsular Chem. Research, Gainesville, Florida; chromium hexacarbonyl was obtained from Strem

Chemicals Inc., di-butyl ether and tetrahydrofuran from Fisher Chemicals. Hexaethyl- and hexamethyl- benzene were also supplied by Fisher and used as received. All solvents were dried over sodium pellets for 2-3 days and thoroughly purged with dry nitrogen before use. The sample of [10]-paracyclophane was kindly supplied by Prof. N. L. Allinger (University of Georgia).

Preparation of the arene chromium tricarbonyl complexes followed the general approach of Strohmeier (214). The following is typical of the method used.

6.2 PREPARATION OF FLUOROBENZENE CHROMIUM TRICARBONYL

In a typical preparation 10 g (0.1 mol) of fluorobenzene and 2.2 g (10 mM) of $Cr(CO)_6$ were heated under reflux in dibutyl ether (25 ml) and tetrahydrofuran (7 ml) for 60 h under a nitrogen atmosphere. The reaction vessel consisted of a two-neck, 250 ml, round bottom flask. One neck was fitted with a water cooled condenser whilst the other neck was constructed so as to include a stopcock which later on in the work-up was used for ensuring a positive nitrogen flow during all procedures.

When the reaction vessel had cooled unreacted arene (if a liquid) and solvents were removed under vacuum. To the remaining material in the flask was added diethyl ether. The inorganic salts were filtered off by use of a positive nitrogen pressure. The ether was then removed on a rotovap and the resulting bright yellow product dried under vacuum. The solid which remained was sublimed onto a water-cooled sublimer.

All fluorinated arene complexes were prepared similarly as were benzene, hexamethylbenzene and hexaethylbenzene chromium tricarbonyls. The [10]-paracyclophane complex was purified by recrystallization from a 1:1 mixture of chloroform:cyclohexane.

Table 6.1 lists physical and mass spectral data for a number of the complexes.

Table 6.1: Physical and Mass Spectral Data of some Arene Chromium Tricarbonyl Complexes

Complex	Colour	m.p.(°C)	Mass Spectral Data
p-$(FC_6H_4F)Cr(CO)_3$	Bright yellow	124-126	250, $C_9H_4O_3F_2Cr^+$ (81.7); 222, $C_8H_4O_2F_2Cr^+$ (2.1); 194, $C_7H_4OF_2Cr^+$ (16.8); 166, $C_6H_4F_2Cr^+$ (59.2); 114, $C_6H_4F_2^+$ (40.1); 52, Cr^+ (100).
p-$(CH_3C_6H_4F)Cr(CO)_3$	Bright yellow	58-60	246, $C_{10}H_7O_3FCr^+$ (54.4); 227, $C_{10}H_7O_3Cr^+$ (1.9); 218, $C_9H_7O_2FCr^+$ (2.1); 190, $C_8H_7OFCr^+$ (30.1); 162, $C_7H_7FCr^+$ (100); 110, $C_7H_7F^+$ (34.5); 91, $C_7H_7^+$ (10.6); 52, Cr^+ (8.1).
p-$(ClC_6H_4F)Cr(CO)_3$	Bright yellow	47-49	266, $C_9H_4O_3ClFCr^+$ (6.1); 231, $C_9H_4O_3FCr^+$ (2.4); 210, $C_7H_4OClFCr^+$ (2.9); 182, $C_6H_4ClFCr^+$ (8.3); 130, $C_6H_4ClF^+$ (15.0); 95, $C_6H_4F^+$ (13.9); 52, Cr^+ (100).
p-$(NH_2C_6H_4F)Cr(CO)_3$	Bright yellow	102-104	247, $C_9H_6O_3FNCr^+$ (12.4): 191, $C_7H_6OFNCr^+$ (5.3); 163, $C_6H_6FNCr^+$ (18.3); 111, $C_6H_6FN^+$ (17.7); 52, Cr^+ (100).
p-$(CF_3C_6H_4F)Cr(CO)_3$	Bright yellow	59-61	300, $C_{10}H_4O_3F_4Cr^+$ (51.0); 272, $C_9H_4O_2F_4Cr^+$ (0.4); 244, $C_8H_4OF_4Cr^+$ (12.3); 216, $C_7H_4F_4Cr^+$ (53.0); 164, $C_7H_4F_4^+$ (31.7); 145, $C_7H_4F_3^+$ (73.3); 126, $C_7H_4F_2^+$ (45.3); 107, $C_7H_4F^+$ (62.6); 95, $C_6H_4F^+$ (16.0); 52, Cr^+ (100).
p-$(CH_3OC_6H_4F)Cr(CO)_3$	Bright yellow	69-71	262, $C_{10}H_7O_4FCr^+$ (6.0); 206, $C_8H_7O_2FCr^+$ (16.3); 178, $C_7H_7OFCr^+$ (14.3); 126, $C_7H_7OF^+$ (100); 111, $C_6H_4OF^+$ (63.3); 95, $C_6H_4F^+$ (12.0); 52, Cr^+ (16.0).
$(C_6H_5F)Cr(CO)_3$	Bright yellow	121-123	232, $C_9H_5O_3FCr^+$ (10.2); 204, $C_8H_5O_2FCr^+$ (0.8); 176, $C_7H_5OFCr^+$ (16.1); 148, $C_6H_5FCr^+$ (100); 96, $C_6H_5F^+$ (54.7); 52, Cr^+ (64.0).

Table 6.1: (contd.) Physical and Mass Spectral Data of some Arene Chromium Tricarbonyl Complexes

Complex	Colour	m.p. (°C)	Mass Spectral Data
$(C_6H_5CF_3)Cr(CO)_3$	Bright yellow	44-46	282, $C_{10}H_5O_3F_3Cr^+$ (50.6); 254, $C_9H_5O_2F_3Cr^+$ (0.8); 226, $C_8H_5OF_3Cr^+$ (12.7); 198, $C_7H_5F_3Cr^+$ (62.7); 146, $C_7H_5F_3^+$ (15.3); 127, $C_7H_5F_2^+$ (64.0); 108, $C_7H_5F^+$ (59.0); 89, $C_7H_5^+$ (52.6); 77, $C_6H_5^+$ (46.0); 52, Cr^+ (52.0).
m-$(FC_6H_4F)Cr(CO)_3$	Bright yellow	56-58	250, $C_9H_4O_3F_2Cr^+$ (63.0); 222, $C_8H_4O_2F_2Cr^+$ (0.1); 232, $C_9H_5O_3FCr^+$ (20.0); 194, $C_7H_4OF_2Cr^+$ (12.1); 166, $C_6H_4F_2Cr^+$ (61.8); 148, $C_6H_5FCr^+$ (25.1); 114, $C_6H_4F_2^+$ (43.7); 96, $C_6H_5F^+$ (14.8); 52, Cr^+ (100).
m-$(CH_3OC_6H_4F)Cr(CO)_3$	Bright yellow	48-51	262, $C_{10}H_7O_4FCI^+$ (55.3); 234, $C_9H_7O\,FCr^+$ (1.1); 206, $C_8H_7O_2FCr^+$ (23.4); 178, $C_7H_7OFCr^+$ (100); 126, C_7H_7OF (87.6); 95, $C_6H_4F^+$ (17.3); 52, Cr^+ (95.2).
m-$(CF_3C_6H_4F)Cr(CO)_3$	Bright yellow	138-140	300, $C_{10}H_4O_3F_4Cr^+$ (46.6); 272, $C_9H_4O_2F_4Cr^+$ (1.6); 244, $C_8H_4OF_4Cr^+$ (39.1); 216, $C_7H_4F_4Cr^+$ (72.7); 164, $C_7H_4F_4^+$ (87.1); 145, $C_7H_4F_3^+$ (94.3); 126, $C_7H_4F_2^+$ (89.3); 107, $C_7H_4F^+$ (80.0); 95, $C_6H_4F^+$ (55.1); 52, Cr^+ (100).
m-$(NH_2C_6H_4F)Cr(CO)_3$	Bright yellow	118-120	247, $C_9H_6O_3FNCr^+$ (15.7); 191, $C_7H_6OFNCr^+$ (9.1); 163, $C_6H_6FNCr^+$ (28.2); 111, $C_6H_6FN^+$ (18.8); 52, Cr^+ (100).
m-$(ClC_6H_4F)Cr(CO)_3$	Bright yellow	67-69	266, $C_9H_4O_3ClFCr^+$ (95.1); 238, $C_8H_4O_2ClFCr^+$ (4.0); 231, $C_9H_4O_3FCr^+$ (34.7); 210, $C_7H_4OClFCr^+$ (65.1); 182, $C_6H_4ClFCr^+$ (100); 147, $C_6H_4FCr^+$ (28.7); 130, $C_6H_4FCl^+$ (94.0); 95, $C_6H_4F^+$ (31.8); 52, Cr^+ (52.1).

Table 6.1: (contd.) Physical and Mass Spectral Data of some Arene Chromium Tricarbonyl Complexes

Complex	Colour	m.p.(°C)	Mass Spectral Data*
m-($CH_3C_6H_4F$)Cr(CO)$_3$	Bright yellow	59-61	246, $C_{10}H_7O_3FCr^+$ (100); 227, $C_{10}H_7O_3Cr^+$ (20.1); 218, $C_9H_7O_2FCr^+$ (14.4); 190, $C_8H_7OFCr^+$ (88.7); 162, $C_7H_7FCr^+$ (97.1); 110, $C_7H_7F^+$ (89.8); 52, Cr^+ (76.0).
(C_6H_6)Cr(CO)$_3$	Bright yellow	159-161	214, $C_9H_6O_3Cr^+$ (15.5); 186, $C_8H_6O_2Cr^+$ (1.5); 158, $C_7H_6OCr^+$ (3.0); 130, $C_6H_6Cr^+$ (29.5); 78, $C_6H_6^+$ (26.0); 52, Cr^+ (100).
[10]-paracyclophane-Cr(CO)$_3$	Bright yellow	148-150	352, $C_{19}H_{24}O_3Cr^+$ (19.3); 296, $C_{17}H_{24}OCr^+$ (8.2); 268, $C_{16}H_{24}Cr^+$ (100); 216, $C_{16}H_{24}^+$ (28.1); 52, Cr^+ (85.9).
((CH_3)$_6C_6$)Cr(CO)$_3$	Bright yellow	142-144	298, $C_{15}H_{18}O_3Cr^+$ (22.6); 242, $C_{13}H_{18}OCr^+$ (14.9); 214, $C_{12}H_{18}Cr^+$ (100); 162, $C_{12}H_{18}$ (20.8); 147, $C_{11}H_{15}^+$ (5.4); 117, $C_9H_9^+$ (4.8); 52, Cr^+ (30.9).
((C_2H_5)$_6C_6$)Cr(CO)$_3$	Bright yellow	118-120	382, $C_{21}H_{30}O_3Cr^+$ (14.1); 354, $C_{20}H_{30}O_2Cr^+$ (2.8); 326, $C_{19}H_{30}OCr^+$ (16.3); 298, $C_{18}H_{30}Cr^+$ (100); 246, $C_{18}H_{30}^+$ (32.1); 52, Cr^+ (28.8).

* Values in brackets refer to percentages of the base peak (100%)

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