THE CHEMISTRY OF CHROMIUM
SANDWICH COMPLEXES

by

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ABSTRACT

A series of complexes $(C_6H_6)Cr(C_6F_5x)$, where x = CHO, $CH(OH)CH_3$, $COCH_3$ or CO_2Et, have been prepared via the lithium reagent $(C_6H_6)Cr(C_6F_5Li)$. The dilithio derivative $(C_6F_4Li_2)Cr(C_6H_6)$ forms a stable di-ester, but the bis(trimethylsilyl) derivative is very labile. Attempts to synthesise chromarenes with alkenyl substituents are described.

The chemistry and air stability of symmetric chromarenes (Ar_2Cr) and the unsymmetric chromarenes of type $ArCr(C_6H_6)$ can be correlated with the sum of the Hammett σ_m parameters of the substituents. It is proposed that the unsymmetrical chromarenes exhibit an internally compensating stabilization effect analogous to that of the chromium tricarbonyl moiety. This postulate is supported by NMR and polargraphic evidence.

Pentafluorochromarenyl diphenyl phosphine has been prepared and its structure determined by X-ray crystallography; its NMR spectra and reaction with $[Rh(CO)_2Cl]_2$ are also discussed.

The cocondensation reaction of nickel vapor and 6,6-dimethylfulvene produces a mixture of 4,4,8,8-tetramethyl-1,4,5,8- (and 1,4,7,8-) tetrahydro-sym-indacenes, which were identified X-ray crystallographically. Although this dimerization is formally achieveable by a (6+6) cycloaddition, it is believe to proceed via ligand coupling on a nickel template.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1.1 AN INTRODUCTION TO THE METAL VAPORISATION TECHNIQUE

The direct synthesis of organic and organometallic compounds by use of high temperature species entrapped in low temperature matrices is a new area of research which is beginning to fulfill its promise. The pioneering work of recent years has now developed to the point where applications to organometallic and especially catalytic processes are feasible.

1.1.1 Pioneering Work

The first synthetic applications of the atom vaporisation technique grew out of the work of Skell and Wescott (1) in 1963 who demonstrated that carbon atoms generated in an electric arc (under a vacuum of 10^{-6} torr) would react with organic substrates when cocondensed at -196° C. The first application to transition metal chemistry occurred in 1969 when Timms vaporised several transition metals and synthesised some sandwich compounds (2). Since then, this technique has been used to produce many organometallic complexes unavailable using more conventional routes (3).

1.1.2 Principles and Method

The evaporation of pure liquid or solid substances can produce high temperature species which are generally more reactive than in their normal form because of both kinetic and thermodynamic factors. Indeed, metal atoms have virtually no kinetic barrier towards ligand addition whereas the bulk metal may be inert due either to a relatively low surface area, inhibition by a thin oxide film, or large lattice energies. Atoms of all elements are endothermic relative to the elements in their standard states and the heats of formation of atoms range from about 60 kJ/g.atom to over 800 kJ/g.atom (4).

Usually, high temperature atomic species are produced by evaporation at 1000-4000° C in a vacuum of 10^{-3} to 10^{-5} torr, thus, these species may travel to the cold walls of the vessel by essentially collision-free paths. The mean free path of species under reaction conditions at pressures of 1, 10^{-3} and 10^{-6} torr are 6.5×10^{-3}, 6.5 and 6.5×10^{3} cm, respectively. Furthermore, the cold surface of the wall acts as an efficient cryopump so that the pressure due to vapor in the vessel is kept very low and thermal decomposition of organic substrates by the hot source is avoided (5).

Most high temperature species are thermodynamically unstable at low temperature towards recombination to form the species in the bulk state; this recombination process usually involves little or no activation energy. Thus, to obtain a high yield process in which reaction with the substrate can be made to compete successfully with recombinations a large excess of substrate is used to increase interaction and inhibit recombination.

Many main group and transition metals have been vaporised from resistance heated spirals of refractory coated molybdenum or tungsten (6). Other more elaborate methods such as electron bombardment or laser beams have been used and the list of metals vaporised by one of these methods includes Li, Mg, Ca, Ti, V, ~~Cr,~~ Mn, Fe, Co, Ni, Cu, Zn, Mo, W, Pd, Pt, Ag, Au, Ge and Sn. Thus, one is not limited in the number of metals which can conveniently be vaporised but rather by the volatility of the potential substrate which should preferentially boil between -80° and

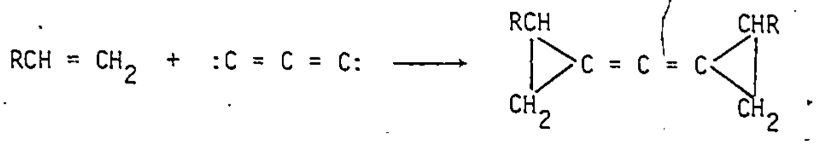
+200° C at atmospheric pressure. More volatile substrates such as N_2, CO, C_2H_4, etc., cause unacceptably high vapor pressures in the reactor and require the use of liquid helium as coolant, while very involatile substrates are difficult to introduce even under high vacuum. Recently however, Green (7) and Timms (4) have designed evaporators in which the substrate, dissolved in an inert solvent, is rotated such that the metal vapor is directed into a constantly renewed thin film of substrate. The static and rotating type metal vapor reactors are shown diagrammatically in Figures 1.1 and 1.2.

The cocondensation technique has allowed the direct synthesis of compounds unstable at ambient temperatures. Thus, the compound $Ni(PF_3)_2(PH_3)_2$ which decomposes above 0° C was prepared by cocondensing nickel vapor and a mixture of the two phosphines at -196° C (8).

1.1.3 Synthetic Applications

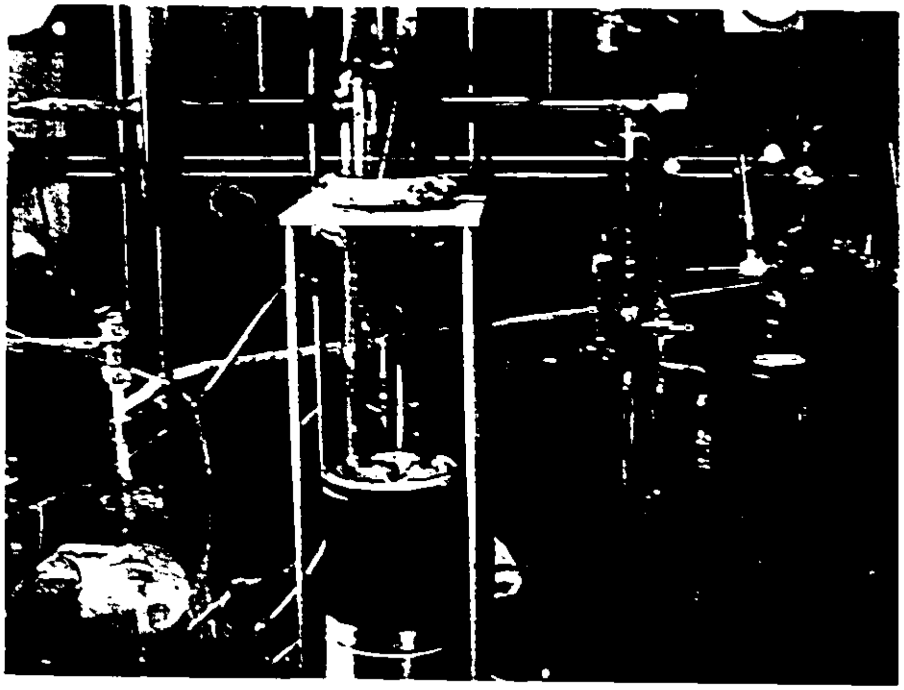
The major portion of this thesis is concerned with the chemistry of products derived from the reactions of chromium atoms with arenes; however, to put this work in perspective a very brief overview of the scope of metal vapor synthesis is presented.

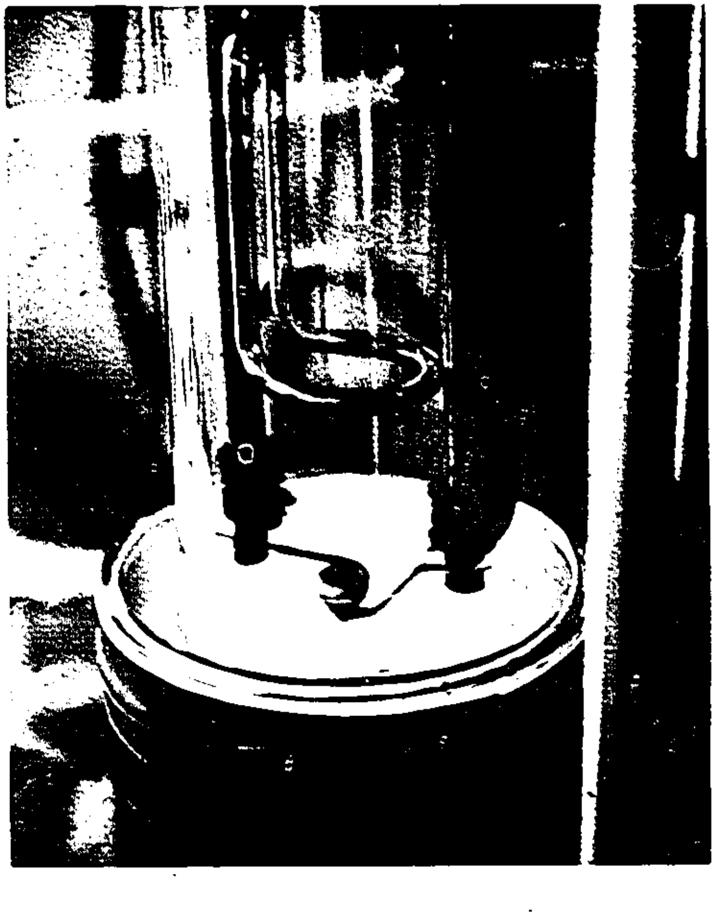
The original work of Skell concerned synthesis using atomic carbon (9) and many previously difficultly synthesisable molecules became available, e.g.



$$CF_2 = CFCl \ + \ :C: \longrightarrow CF_2 = C = CFCl$$

Figure 1.1 Photographs of Vaporization Apparatus.





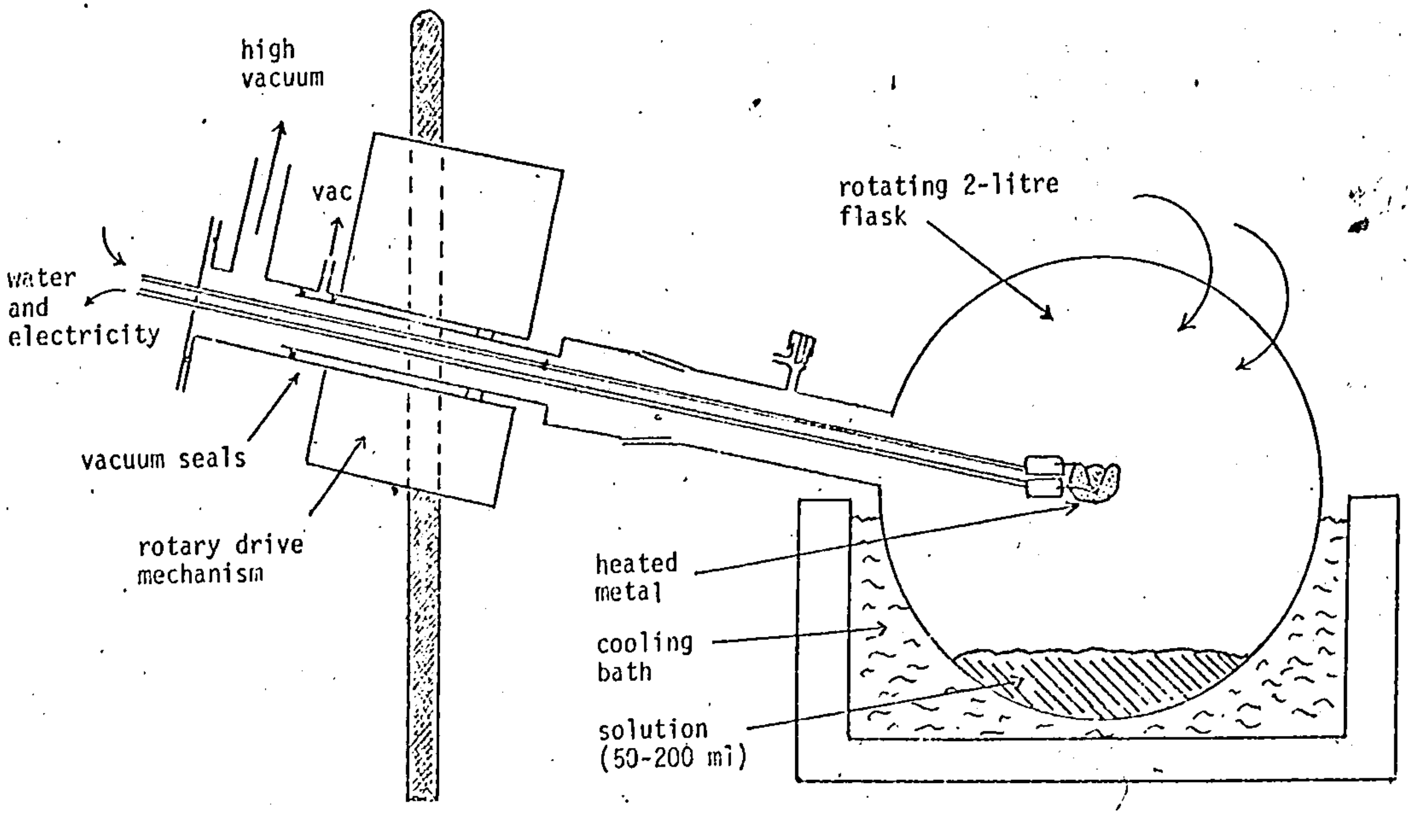


Figure 1.2: Vaporization apparatus with rotating flask.

(courtesy of Dr. P.L. Timms)

$$B_2Cl_4 \quad + \quad :C: \quad \longrightarrow \quad C(BCl_2)_4$$

Other group IV elements, viz., Si and Ge, have also been used as synthetic reagents, e.g.,

$$:Si: \quad + \quad Me_2SiH_2 \quad \longrightarrow \quad (Me_2SiH)_2SiH_2$$

$$:Ge: \quad + \quad CHCl_3 \quad \longrightarrow \quad CHCl_2GeCl_3$$

The chemistry of magnesium vapor has been particularly well studied and the identity of the electronic spin has been determined in some cases (10).

Transition metal vapors have been proven particularly useful for the synthesis of sandwich molecules (see later) and also olefin and phosphine derivatives. Some typical reactions are presented in Table 1.1.

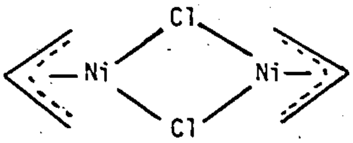
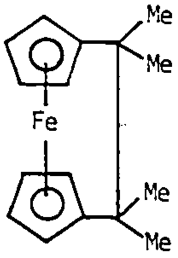
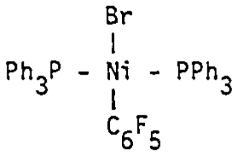
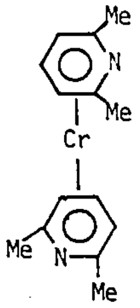
Metal vapors have also been shown to function as catalytic agents in a series of isomerization, hydrogenation and disproportion reactions (3).

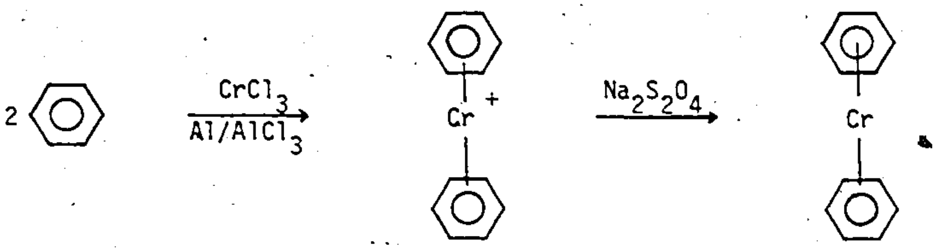
1.2 THE CHEMISTRY OF CHROMARENES

1.2.1. The Reducing Friedel-Crafts Synthesis

The first syntheses of arene- chromium sandwich complexes (chromarenes) were unrecognised as such. Hein, in a series of papers starting in 1919, prepared many derivatives from σ-phenyl chromium compounds (16). The realisation of the sandwich structure and the first logical synthesis must be attributed to Fischer and Hafner in 1955 (17). They used a reducing Friedel-Crafts process with $AlCl_3$ as the catalyst.

TABLE 1.1

Substrate(s)	Metal Vaporised	Product
Allyl chloride	Ni	 (Ref. 11)
6,6-Dimethylfulvene	Fe	 (Ref. 12)
Trifluorophosphine + Nitric Oxide	Mn	$Mn(NO)_3PF_3$ (Ref. 13)
Bromopentafluorobenzene + triphenylphosphine	Ni	 $\mathrm{Ph_3P - \overset{Br}{\underset{C_6F_5}{Ni}} - PPh_3}$ (Ref. 14)
2,6-Dimethylpyridine	Cr	 (Ref. 15)



Unfortunately, due to side reactions with the Lewis acid catalyst ($AlCl_3$), it was not possible to synthesise directly chromarenes containing substituents possessing lone pairs of electrons. Typically, when chlorobenzene was used in Fischer-Hafner process, no chloro-chromarenes were isolable (18); instead π-complexes containing biphenyl were produced. Thus, the chemistry of chromarenes was, for many years, limited to a few low-yield, experimentally difficult metallation reactions (19). The situation was alleviated somewhat by Elschenbroich's use of N,N,N',N'-tetramethylethylenediamine (TMEDA) as solvent and consequent use of alkyl lithiums for metallation processes (20). Russian workers have reported base-catalysed proton-deuteron exchange (21). The known chemistry of chromarenes for the first fifty years after their initial (but unrealised) synthesis by Hein is shown in Figure 1.3.

1.2.2 The Metal Atom Synthesis

In 1969 Timms reported the synthesis of ferrocene from iron vapor and cyclopentadiene and also of chromarene from benzene and chromium atoms (2). The first halogenated chromarenes were reported (22) by Skell, McGlinchey and Williams-Smith in 1972 and in the same year 1,2,3,4,5,6-hexafluorochromarene ($C_6F_6CrC_6H_6$) was prepared by Timms (13). This opened up much new chemistry of chromarenes, and many substituted chromium

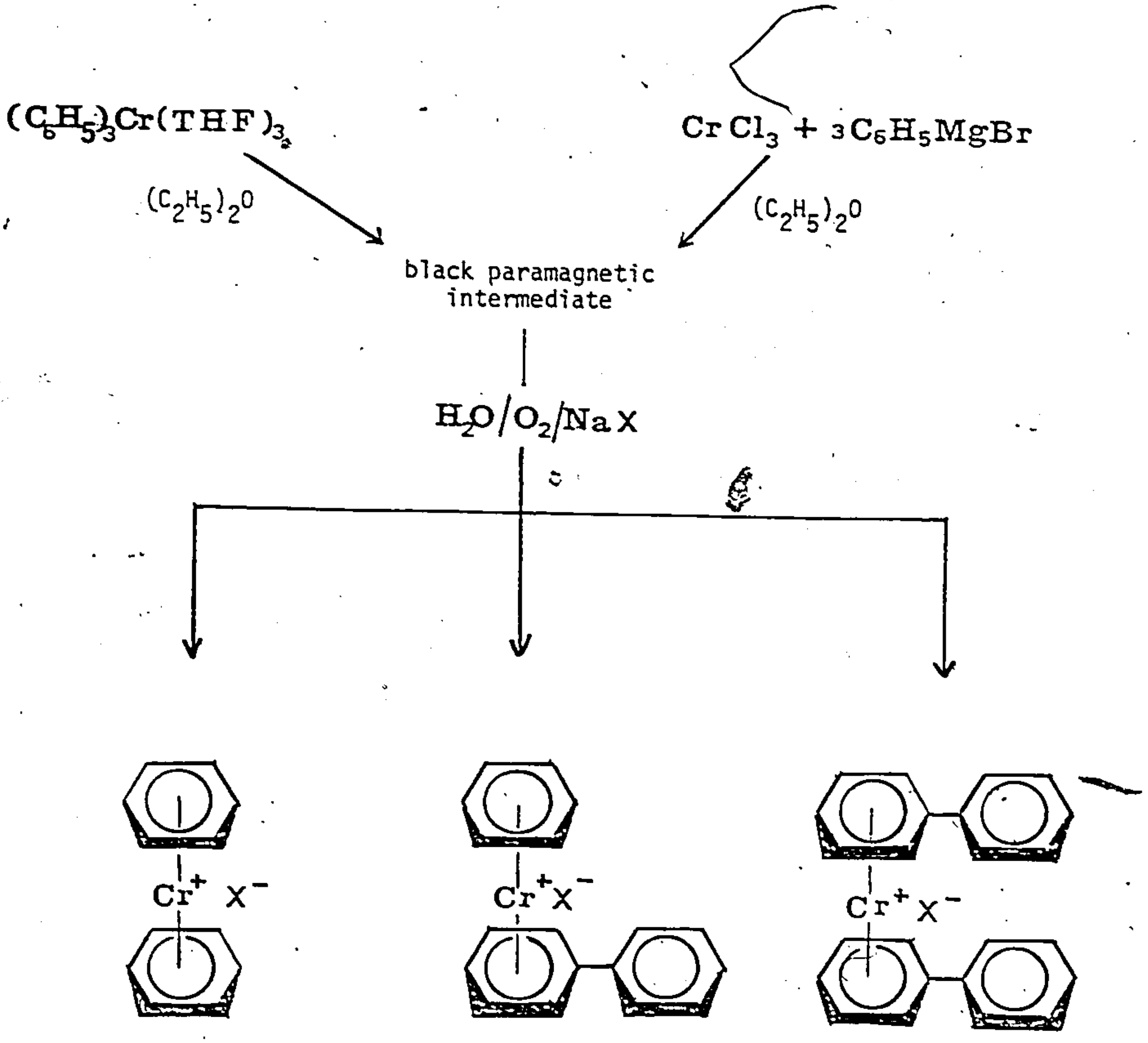


Figure 1.3: Hein synthesis of π-bis(benzene)Cr$^+$; π(benzene)-π(bisphenyl)Cr$^+$ and π-bis(biphenyl)salt.
X = I or B$(C_6H_5)_4$

(and also molybdenum and tungsten) arene sandwich complexes were prepared. An extensive study of the chemistry of fluorinated chromarenes was undertaken by Tan who was the first to predict (23) and observe (24) nucleophilic displacement processes in such systems. Tan also prepared 1,2,3,4,5-pentafluorochromarene ($C_6HF_5CrC_6H_6$) and demonstrated the ease of lithiation in the pentafluorophenyl ring (25). These discoveries led to a rapid extension which is summarised in Figures 1.4 and 1.5.

1.2.3 N.M.R. Spectroscopic Studies in Chromarenes

It had been known for several years prior to the metal atom route to chromarenes that protons in π-complexed arene rings exhibited relatively large (2-3 p.p.m) upfield shifts compared to the free arenes (26). Tan demonstrated that upon complexation ^{19}F nuclei showed upfield shifts of ∿ 50 p.p.m. (23), and a comprehensive study by Graves and Lagowski established some of the major factors influencing ^{13}C shifts in chromarenes (27).

The large upfield shifts of π-bonded nuclei have been attributed to many effects and an appraisal of the situation has been presented by Waugh (28). The utility of n.m.r. chemical shifts as criteria of chemical reactivity will be discussed later.

1.3 AIMS OF THIS PROJECT

The ready availability of polyfluorinated chromarenes most of which are air-stable and easily manipulated, suggests that not only could one extend and develop the organic chemistry of such systems but also use this as an opportunity to study the effect of π-C_6H_6-Cr moiety on arene chemistry. Also structural and spectroscopic studies should allow one to probe the electronic perturbations brought about at the ring by this

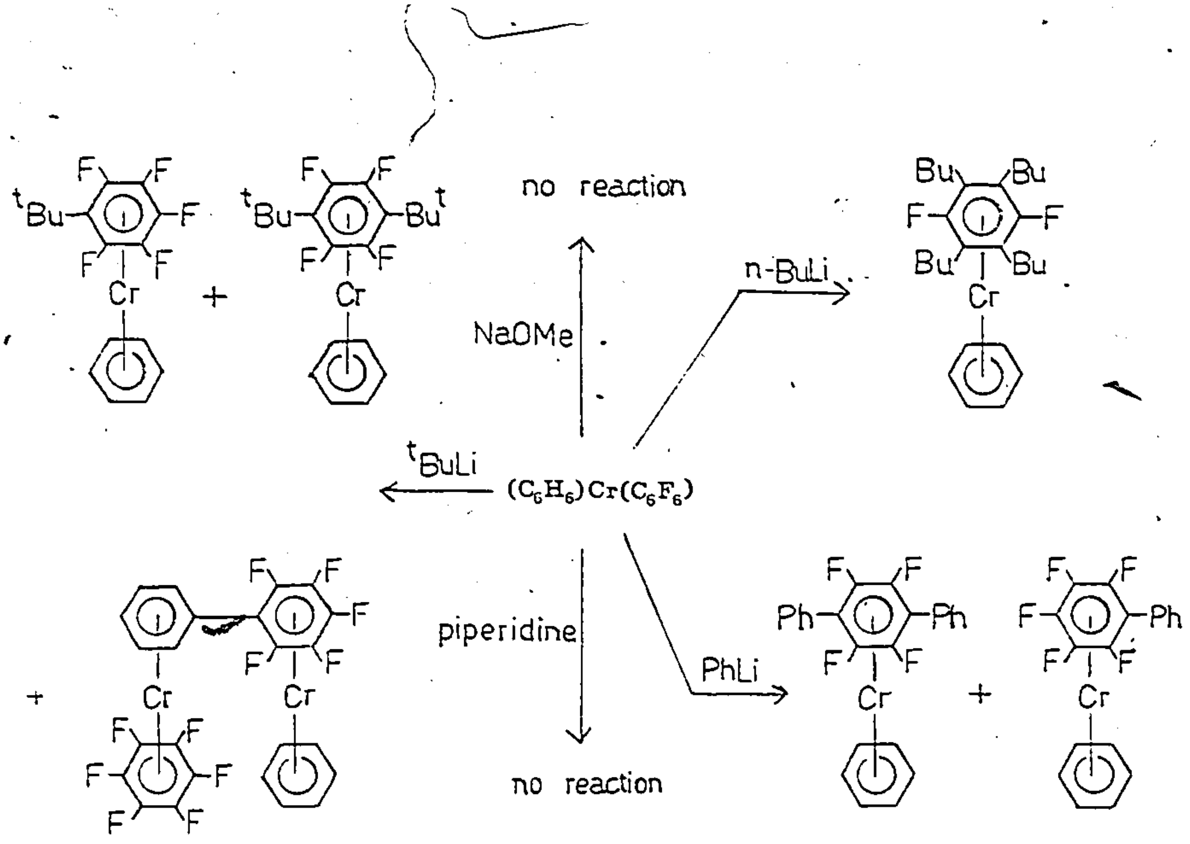


Figure 1.4: Summary of the reactions of $(C_6H_6)Cr(C_6F_6)$ with nucleophiles.

Figure 1.5: Reactions of $(C_6F_5Li)Cr(C_6H_6)$ with

(i) $(C_5H_5)Fe(C_5H_4CHO)$

(ii) $(CH_3)_2CO$

(iii) CO_2

(iv) $(CH_3)_3SiCl$

(v) $(C_5H_5)Fe(CO)_2I$

(vi) $IRe(CO)_5$

(vii) $(CH_3)_3SnCl$

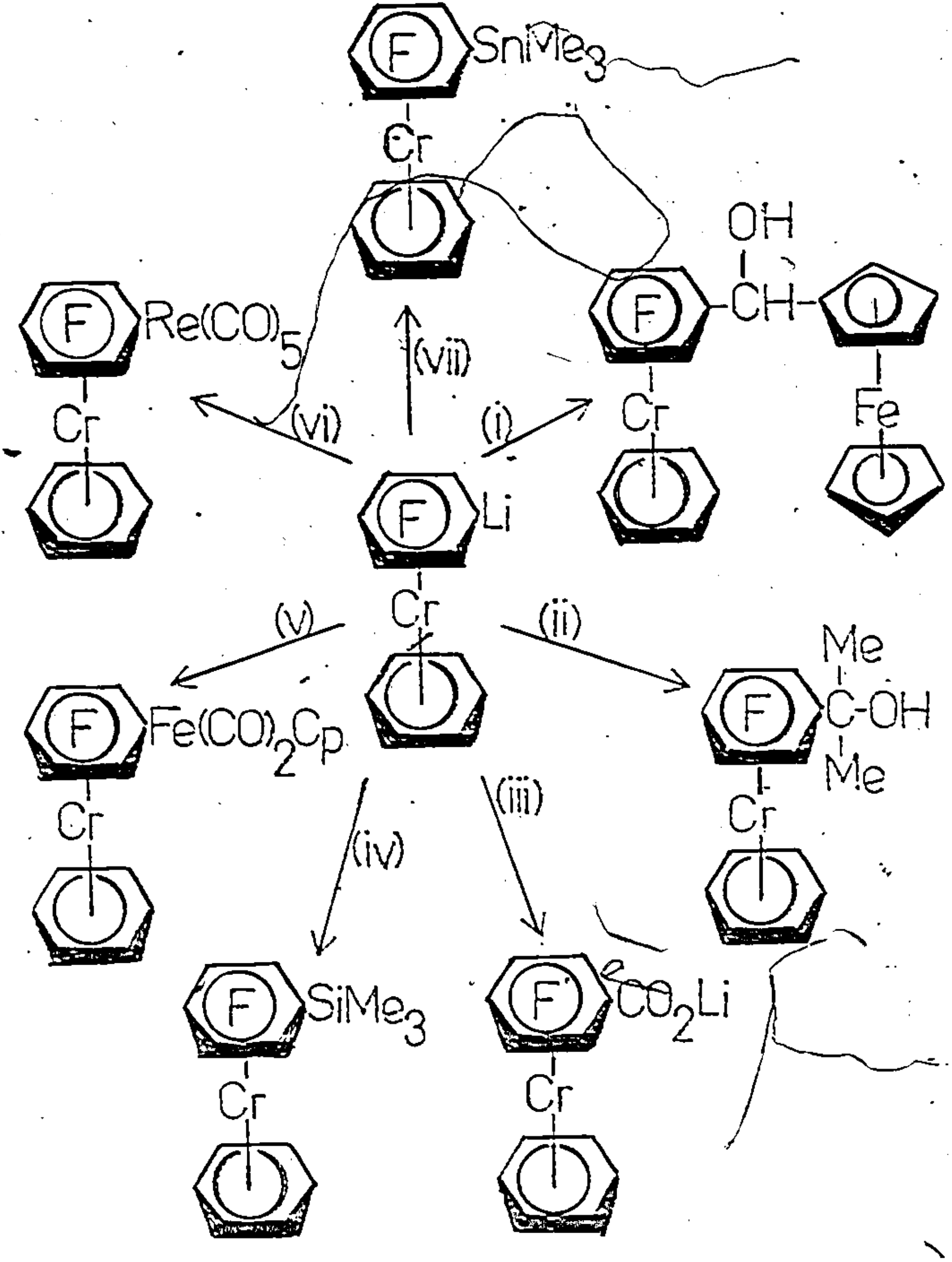

F
SnMe3
Cr
Re(CO)5
(vii)
(vi)
(i)
OH
CH
Fe
Li
(v)
(ii)
Me
C-OH
Me
Fe(CO)2Cp
(iv)
(iii)
SiMe3
CO2Li

Figure 1.5:

π-bonded substituent. Finally, the air and thermal stability of fluorinated chromarenes give hope to the possibility of producing polymers with a metallic back-bone.

CHAPTER II

THE METALLATION OF CHROMARENES

2.1 THE METALLATION OF 1,2,3,4,5-PENTAFLUOROCHROMARENE

Until the development of the metal atom route to chromarenes, the chemistry of $(C_6H_6)_2Cr$ was restricted to metallation reactions (19, 20,21) and base-catalysed hydrogen-deuterium exchange processes (29,30). The known chemistry of this system for the first 50 years after its initial synthesis by Hein (16) is summarised in Figure 1.3.

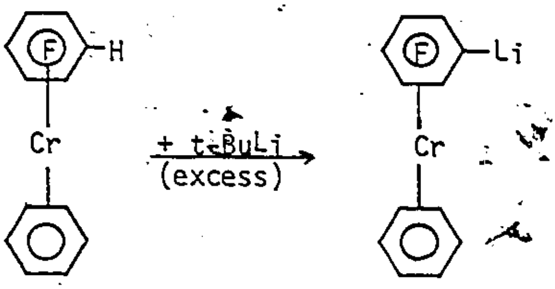
Electrophilic or free radical attack on the complexed arene rings was unlikely owing to the presence of the relatively electron-rich chromium atom which provided a much more attractive target for an incoming electrophile. Conversely, nucleophilic attack on the complexed rings should be enhanced relative to the free arene, and indeed, in the corresponding arene chromium tricarbonyl systems, synthetic schemes have been based on this premise (31).

However, nucleophilic displacement required the presence of suitable leaving group, and such systems could not be synthesised by the route pioneered by Fischer and Hafner (17), since arenes possessing substituents with non-bonded electron pairs reacted with the Lewis acid catalyst ($AlCl_3$) thus preventing the formation of sandwich complexes (18). Fortunately, the recently developed metal atom co-condensation technique (3,4) provided a viable synthetic route by which leaving groups (e.g., halogens) could be incorporated into chromarenes (13,22,23,32).

Early attempts to metallate chromarenes required impeccable experimental technique in order to handle the very air-sensitive products;

furthermore, the scope of this reaction was limited to "relatively acidic" hydrocarbons (33). The use of diamines such as N,N,N',N'-tetramethylethylene diamine (TMEDA) to activate the alkyllithium somewhat alleviated the situation (34), and a few substituted chromarenes have since been reported (20,35).

The known versatility of pentafluorophenyllithium as a synthetic reagent (36), coupled with the thermal and oxidative stability of fluoro-substituted chromarenes (22,23,24,27,37) prompted Tan to attempt the synthesis of 1-lithio-2,3,4,5,6-pentafluorochromarene (25). It was hoped that such a study would allow a comparison of molecules of the type C_6F_5X and $(C_6F_5X)Cr(C_6H_6)$ and a consequent evaluation of the rôle of the π-$Cr(C_6H_6)$ moiety. Indeed, pentafluorochromarene provided an ideal system in which to study the metallation of sandwich compounds for a number of reasons. First, it is much more air-stable than $(C_6H_6CrC_6H_6)$ complex. Second, it contains a relatively highly acidic proton. Thus, the metallation can be performed easily without using an extremely powerful base such as amylsodium, nor does one need to activate the alkyllithium with TMEDA. Third, compared to chromarene itself or ferrocene, the pentafluorochromarene, (I), can be easily lithiated in only one ring, thus avoiding the separation problems associated with mono- and di- lithiated products. Finally, in the $(C_6F_5H\ CrC_6H_6)$ case there was an easily observable colour change when lithiation occurred. Hence, the acidic proton of the π-complexed C_6F_5H ring was lithiated using t-butyllithium at -78°C, without adding any TMEDA, and gave the lithio-derivative (II) in excellent yield.



(I) (II)

The reactions reported by Tan (25)are shown in Figure 1.5

2.2 THE ORGANIC CHEMISTRY OF 1,2,3,4,5-PENTAFLUOROCHROMARENE

The known chemistry of ($C_6F_6CrC_6H_6$) can be summarised as follows:

(i) Although nucleophilic substitution occurs in the fluorinated ring it is, however, more difficult than in C_6F_6 itself.

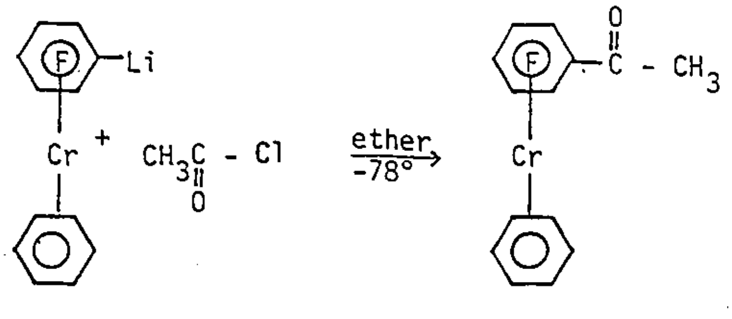
(ii) The acidity of the π-complexed C_6H_6 ring is enhanced relative to that of free C_6H_6.

(iii) The air stability of the hexafluorochromarene is quite remarkable relative to that of $(C_6H_6)_2Cr$.

A hypothesis (24) to account for this behavior is that the hexafluorochromarene molecule is "internally oxidised", i.e., electron transfer has occurred from the chromium atom to the C_6F_6 ring. Thus, the formal +1 oxidation state of the chromium would enhance the acidity of the C_6H_6 ring and prevent aerial oxidation of the central metal. Concommitantly, the increased electron density in the hexafluorobenzene ring would reduce the susceptibility towards nucleophilic substitution. A satisfactory test for such a hypothesis would be a comparison of the pK_a values of pentafluorobenzoic acid and the corresponding pentafluorochromarenoic acid, viz., $(C_6F_5CO_2H)Cr(C_6H_6)$.

The pK_a values of substituted benzoic acid chromium tricarbonyls (38) and of ferrocene carboxylic acids (39) have been extremely useful indicators of the type of reactivity to be expected for these now almost ubiquitous systems. However, these data are not yet available for the chromarene series and, although a chromarenoic acid has not yet been obtained, one can now report (40) the incorporation of a variety of substituents which may eventually lead to the target.

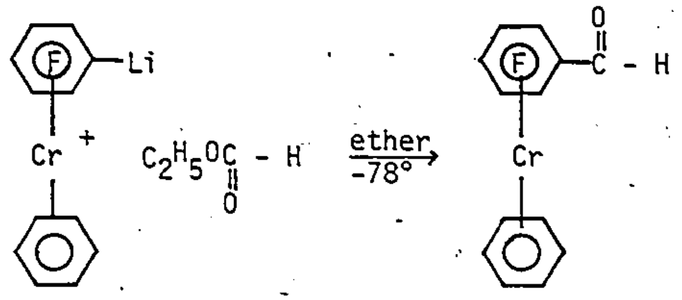
Previous attempts to prepare 2,3,4,5,6-pentafluorochromarenoic acid via the carbonation of the analogous lithiochromarene, (II), were unsuccessful (25). Some of the more obvious alternate routes which might be viable include, (a) the haloform reaction on the methyl ketone, (III), (b) oxidation of the corresponding aldehyde, (IV), or (c) hydrolysis of an appropriate ester, (V). Reaction of acetyl chloride with (II) might have been expected to give respectable yields of methyl ketone,(III), but in fact the desired product was obtained only in small quantities. (The analogous furoyl compound is,however, readily prepared by this route and is discussed below).



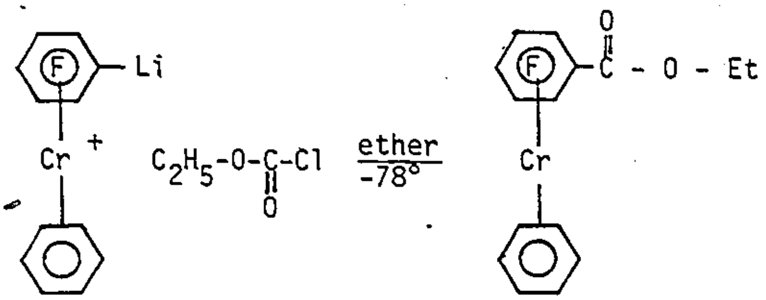
(II) (III)

small quantities

The reaction of (II) with ethyl formate gave the corresponding aldehyde, (IV), while treatment with ethyl chloroformate led to a good yield of ethyl pentafluorochromarenoate (V).



(II) (IV)



(II) (V)

Since the ester,(V), was obtained in such good yield it was decided to attempt a hydrolysis to produce the acid. Thus, the ethyl ester was refluxed in methanol solution containing potassium hydroxide and then neutralised. The products, however, were rather surprising in that, while no pentafluorochromarenoic acid was obtained, the major product was pentafluorochromarene together with traces of methoxytetra-

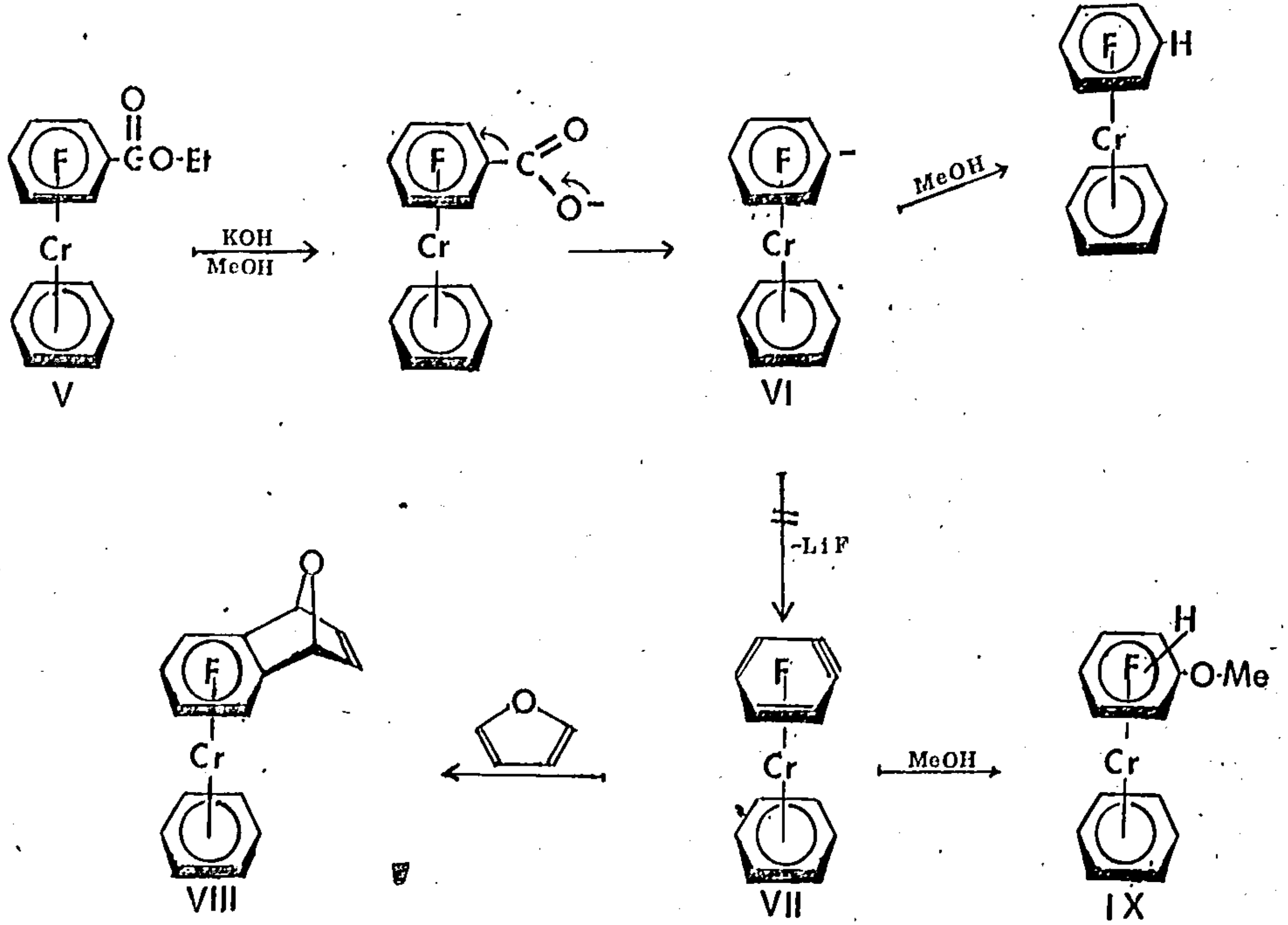
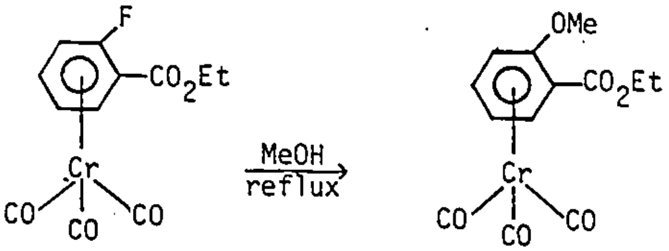


Figure 2.1: Reaction of ethylpentafluorochromarenoate with MeOH and KOH

fluorochromarene, (IX).

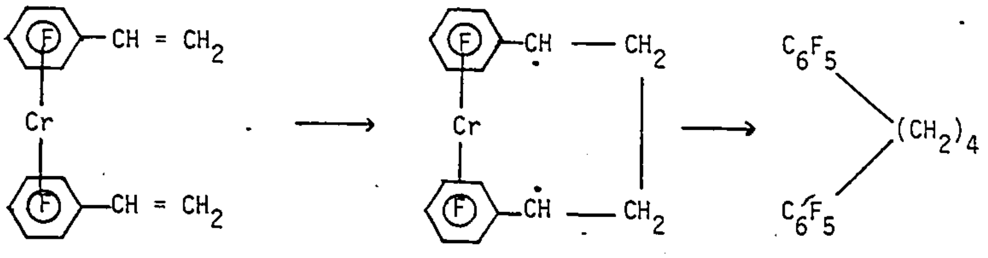
A number of mechanistic possibilities may be considered to account for this curious result. One could visualise, first of all, hydrolysis of the ester to give the carboxylate which then eliminated CO_2 to produce the anion (VI). This anion could now either abstract a proton giving pentafluorochromarene or eliminate a fluoride ion to produce a benzyne; subsequent addition of methanol to the π-complexed benzyne (VII) could then produce the methoxy-tetrafluorochromarene as in Figure 2.1. However, repeated attempts to trap the presumed π-complexed benzyne intermediate with furan - an excellent Diels-Alder trap for tetrafluorobenzyne - were unsuccessful, suggesting that the benzyne mechanism is not viable.

Another possibility, as yet unproven, is that a small percentage of nucleophilic attack by methanol occurred to give a methoxy substituted ethyl tetrafluorochromarenoate which, after hydrolysis and elimination of CO_2, produced the observed molecule. Such a possibility has a related precedent in that (ethyl fluorobenzoate)$Cr(CO)_3$ yields (ethyl methoxybenzoate)$Cr(CO)_3$ when refluxed in methanol (41).



Despite the failure to isolate 2,3,4,5,6-pentafluorochromarenoic acid from the ester hydrolysis reaction, it is to be hoped that, given mild enough conditions, the acid may be obtained from one of the previous precursors.

With a view to incorporating unsaturated moieties in the side-chains of chromarenes, a mixture of benzene and pentafluorostyrene was cocondensed with chromium vapour. The only volatile product isolated after removal of the starting materials was identified by mass and n.m.r. spectroscopy as 1,4-bis(pentafluorophenyl)butane, (XI). Pentafluorostyrene is known to polymerise (42), albeit less readily than styrene itself, but the product isolated from the cocondensation reaction has not apparently been reported previously. Blank reactions, using normal cocondensation conditions, but with no metal in the crucible gave no (XI); likewise, (XI) was not produced when Ni vapour was used. A possible rationale involves the initial formation of an unstable bis(pentafluoro-styrene) chromium complex, (X), which then undergoes ligand coupling (see Figure 2.2) in an analogous manner to that observed for iron vapour and dimethylfulvene (12). Subsequent hydrogen abstraction from the excess unreacted arenes could then lead to the observed product.

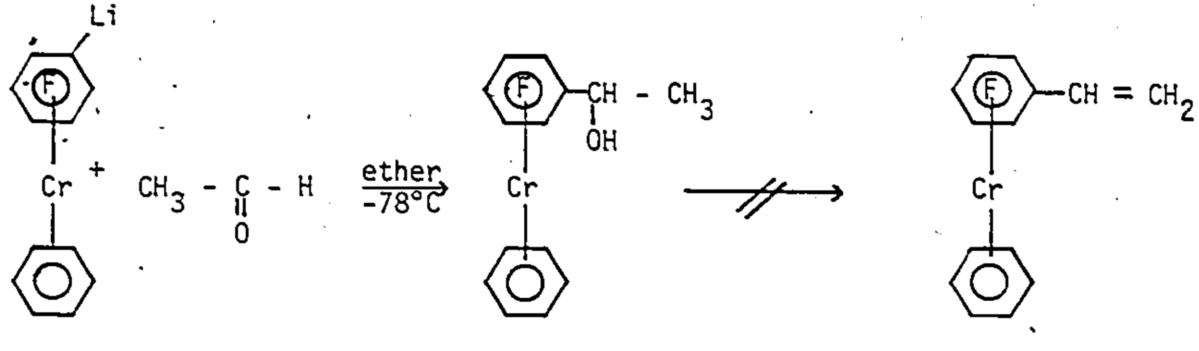


(X)

(XI)

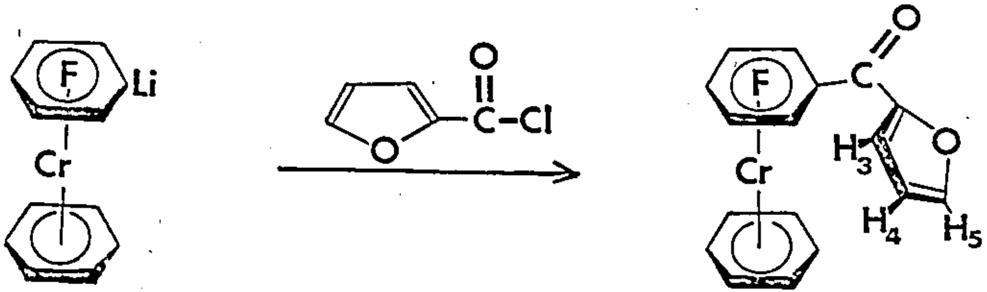
Figure 2.2: Coupling reaction of pentafluoro-styrene.

An alternative route to 1-vinyl-2,3,4,5,6-pentafluorochromarene (XIII) which appeared viable was the dehydration of appropriate alcohol (XII). Indeed, reaction of lithiochromarene, (II), with acetaldehyde gave the desired alcohol, (XII), in good yield, but attempts to dehydrate the sidechain without thereby destroying the complex have so far been unsuccessful. Furthermore, reaction of (II) with allyl bromide did not yield a chromarene with an unsaturated side chain but instead gave a number of products which are still under investigation.



(II) (XII) (XIII)

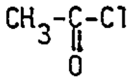
A more successful approach was the synthesis of furoyl chromarene (XIV), from lithio derivative (II), and furoyl chloride. Interestingly, the ^1H n.m.r. spectrum of the complex, (XIV), showed the absorption of the furan ring protons to be displaced considerably upfield of their normal resonance positions. This is interpreted to mean that the furan



II XIV

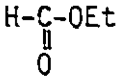
Figure 2.3: Reactions of $(C_6F_5Li)Cr(C_6H_5)$ with

(i)



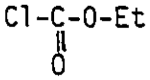
$CH_3-\underset{\overset{\|}{O}}{C}-Cl$

(ii)



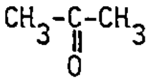
$H-\underset{\overset{\|}{O}}{C}-OEt$

(iii)



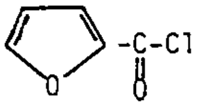
$Cl-\underset{\overset{\|}{O}}{C}-O-Et$

(iv)



$CH_3-\underset{\overset{\|}{O}}{C}-CH_3$

(v)



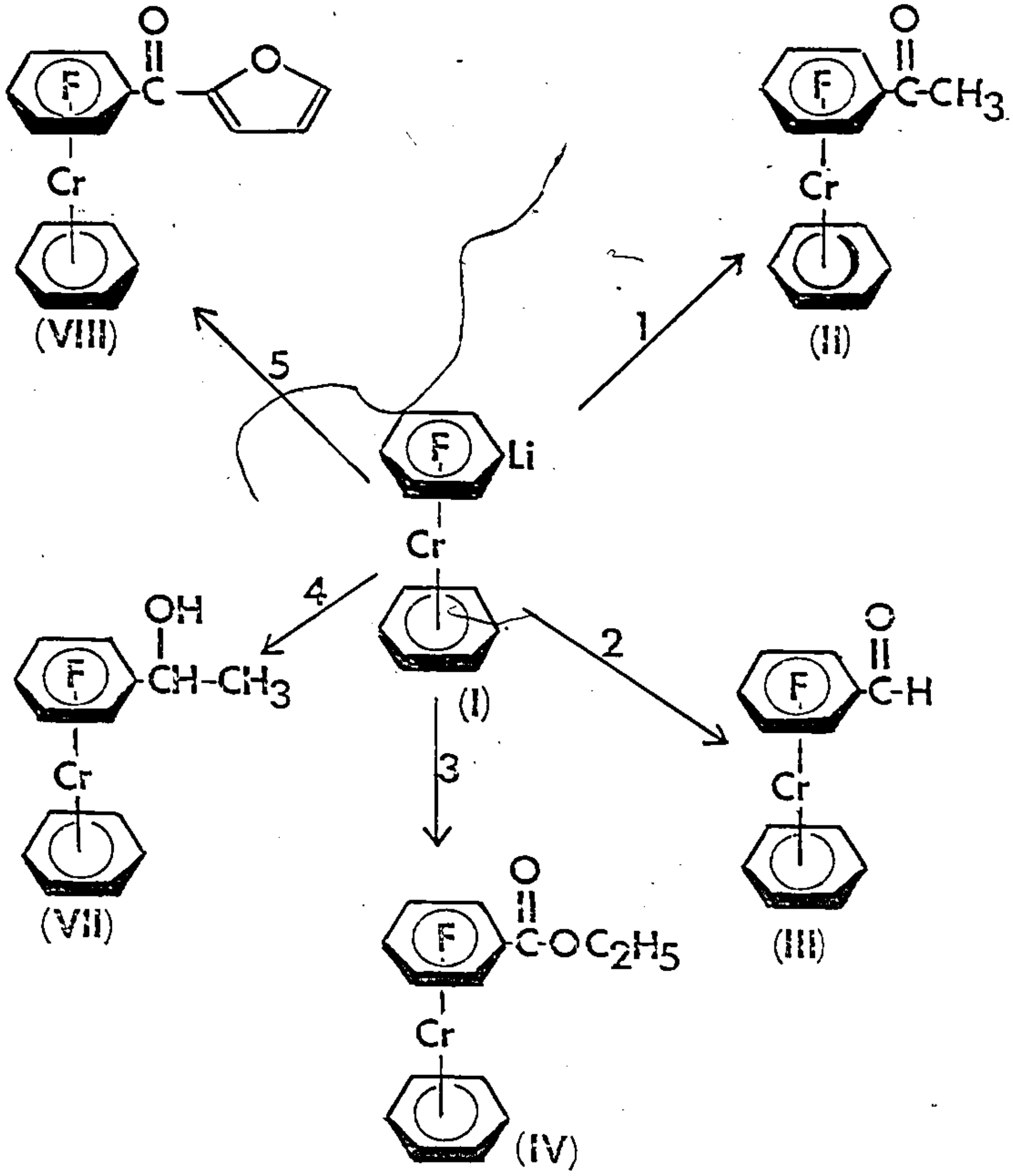
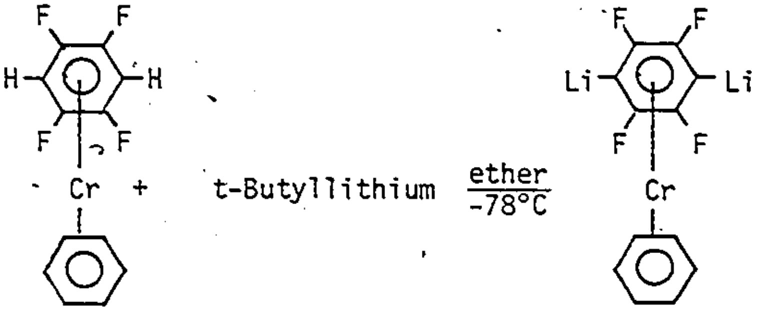


Figure 2.3:

is positioned proximate to the chromium atom whose magnetic anisotropy leads to a marked shielding of the furan protons.

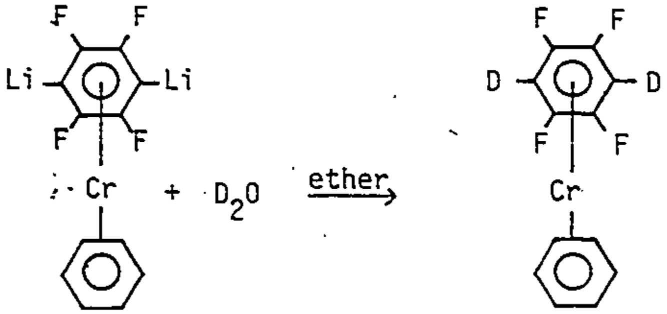
2.3 ORGANIC CHEMISTRY OF 1,2,4,5-TETRAFLUOROCHROMARENE

The recent synthesis (25) of 1,2,4,5-tetrafluorochromarene opened up the possibility of incorporating two functionalities into the same ring of sandwich compound. This would require that both protons in the fluorinated ring be readily lithiated as in (XV).



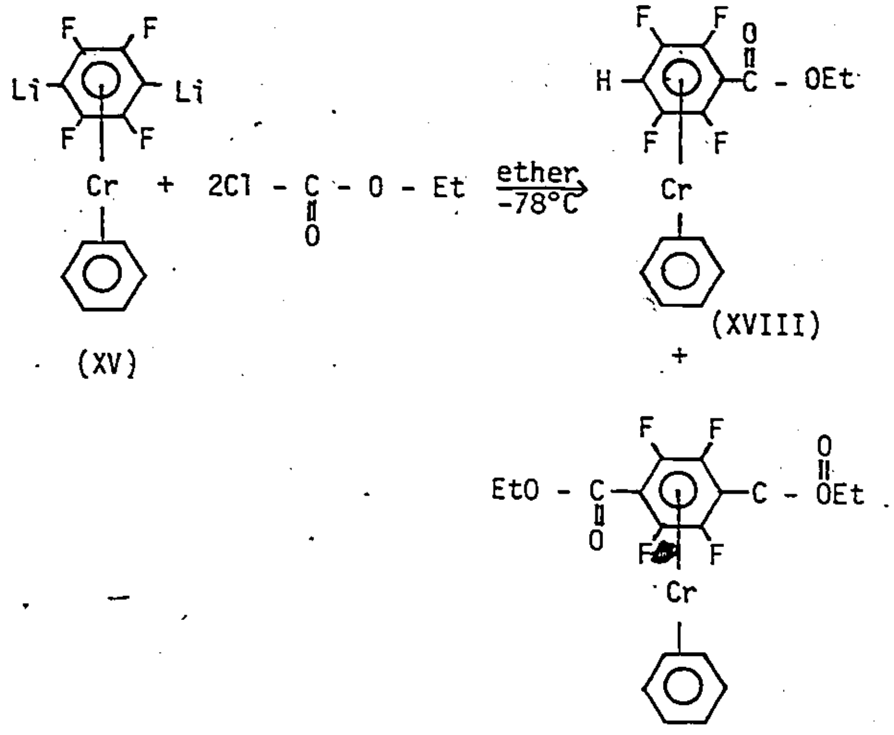
(XV) (XVI)

We find that a four-fold excess of t-butyllithium is required to ensure di-lithiation of 1,2,4,5-tetrafluorochromarene and this is readily confirmed mass-spectrometrically after quenching with D_2O, giving compound (XVII).



(XV) (XVII)

Analogously, reaction of excess ethyl chloroformate with (XV) gave a mixture of mono (25% yield) and chromarene diester (65% yield). The monoester is 1-(carbethoxy)-2,3,5,6-tetrafluorochromarene, (XVIII), which decomposes in air in about 2-3 days, the diester, (XIX), 1-4-bis-(carbethoxy)-2,3,5,6-tetrafluorochromarene is remarkably stable.

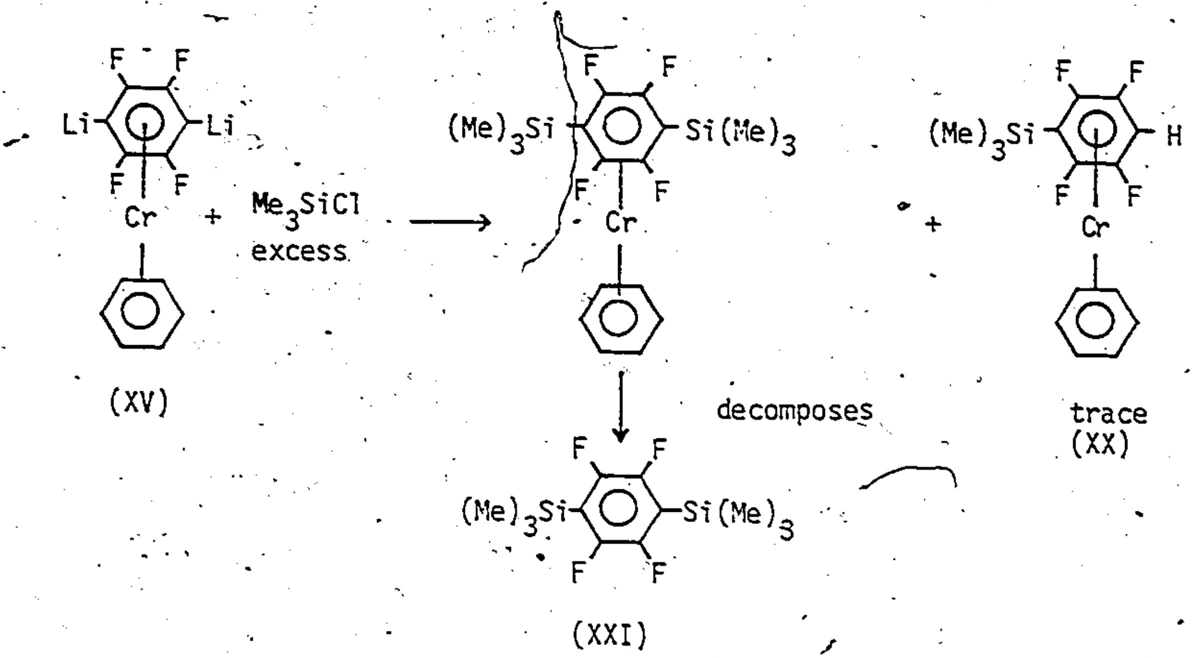


(XV)

(XVIII)

(XIX)

In contrast, chlorotrimethylsilane gave only a trace of the mono-silylated chromarene, (XX), while the major product was 1,4-bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene, (XXI), which was readily identified by comparison with the literature data (43). Apparently, the 1,4-bis(trimethylsilyl)tetrafluorochromarene must have dissociated and liberated the parent arene.



2.4 CONCLUSIONS

It has been noted by Tan and McGlinchey (22-25) and others (13,37, 27) that the oxidative stability of halogenated chromarenes is highly dependent on the electronic properties of the arene substituent. In particular, electronegative substituents which reduce the π-basicity of the arene concomitantly retard the oxidation of the formally zero-valent chromium and thus enhance its kinetic rather than its thermodynamic stability. Consequently, the introduction of two electron-releasing trimethylsilyl moieties is apparently not compatible with a kinetically stable fluorochromarene.

Clearly, to produce a stable chromarene, one requires a rather delicate balance of these electronic factors and pragmatically, one can use Hammett substituent parameters as a guide to the probable stability of a given chromarene.

CHAPTER III

THE STABILITY OF CHROMARENES

3.1 INTRODUCTION

The widespread use of metal vapors as synthetic reagents (3,6,44,45) has led, among other things, to a resurgence of interest in the chromium-arene sandwich complexes (chromarenes) (25). The ready incorporation of a wide variety of substituents into this hitherto almost unexplored system has revealed much fascinating new chemistry. Over the past five years, more than 60 substituted chromarenes have been prepared, and some general chemical trends within the system are now becoming apparent.

3.2 SUBSTITUENT EFFECTS AND STABILITY OF SYMMETRIC CHROMARENES, Ar_2Cr

The existence of this series of compounds depends upon the subtle interplay of two effects, viz., (a) the thermodynamic stability of the molecule, which is a reflection of the strength of the arene-chromium bond, and (b) the kinetic barrier to decomposition via the one-electron oxidation of the chromium atom.

The thermodynamic stability could in principle be investigated experimentally by methods such as calorimetry (46), or by a comparison of bond lengths obtained from crystallographic studies (47). Unfortunately, few data are currently available although the situation will undoubtedly change - indeed some workers have already announced this as a long-range goal (48). Valuable predictions are clearly possible with molecular orbital calculations, but again few molecules have actually been studied (49). Perhaps the most readily available technique is that of vibrational spectroscopy, and Klabunde (37) has demonstrated that the incorporation of electron -

withdrawing substituents in symmetrical chromarenes of the type $(C_6H_4X_2)_2Cr$ leads to smaller complexation shifts of the aryl in-plane stretching vibrations than is observed for benzene itself. He was thus able to conclude that the chromium to arene back-donation was less pronounced in the case of chromarenes with electronegative substituents, and consequently that the arene-chromium bond was weaker than in $(C_6H_6)_2Cr$ itself. This view is supported by the enhanced thermal stability of chromarenes with increasing alkyl substitution (50) and by the failure to isolate complexes of the type $(C_6F_nH_{6-n})_2Cr$ when n exceeds 2. In essence, the π-basicity of arenes with a multitude of electron-withdrawing substituents is apparently too low to lead to isolable sandwich compounds of the type Ar_2Cr.

In contrast, the presence of electronegative substituents in the arene rings should retard the one-electron oxidation to Ar_2Cr^+ and the activation energy barrier should correlate well with the oxidation potential which is perhaps best measured polarographically (37). Russian workers have shown that the incorporation of alkyl groups into the arene rings leads to a shift of the half-wave potential ($\varepsilon_{1/2}$) towards negative values of the potentials. The change in $\varepsilon_{1/2}$ was found to be directly proportional to the number of alkyl groups introduced and was 0.3V per alkyl group (51).

Another physical technique which might give some information as to the distribution of electron density within the molecule is NMR spectroscopy and ^1H (22,52) and ^{19}F (23) spectra have been reported. In this vein, the most comprehensive study is that of Graves and Lagowski (27) who carefully examined the factors influencing the ^{13}C chemical shifts in a large number of symmetrical chromarenes. They showed that the transmission of substituents effects to the C-4 ring carbon was drastically reduced, that the π-electron density was considerably modified from that of the free arene and that enhanced susceptibility to nucleophilic substitution on the ring was to be expected. This prediction, which was also in agreement with an analysis of the ^{19}F NMR shifts (23), was subsequently realised experimentally (24).

Thus there emerges from these facts a picture of the symmetrical chromarenes in which thermodynamically stable and kinetically inert complexes will only be formed for a somewhat limited range of substituents. The kinetic inertness of the chromarenes is reflected in their resistance to aerial oxidation and these data have been well documented by a number of laboratories (13,22,23,25,37). It appears that it is the identity of the substituents which is crucial and that positional isomerism is less important. Thus 1,1',3,3'-tetrakis(trifluoromethyl)-chromarene is remarkably air-stable but so also is the 1,1',4,4'-isomer (37); in like manner, the oxidative stabilities of the ortho, meta and parafluorotoluene complexes are comparable (23,27). It therefore seems reasonable to attempt to correlate the oxidative stability of the chromarenes with the sum of the inductive parameters of the substituents. For this purpose we chose the Hammett σ_m values (53) (but the Swain-Lupton (54) F values also work well). As can be seen from Figure 3.1, the sum of the Hammett parameters - $\Sigma\sigma_m$ - is an excellent indicator of the oxidative stability of the given chromarene. Using this simple concept, one can now place realistic limits on the substituents one can incorporate and still maintain the desired stability of the complex. It is not an unreasonable prediction that the

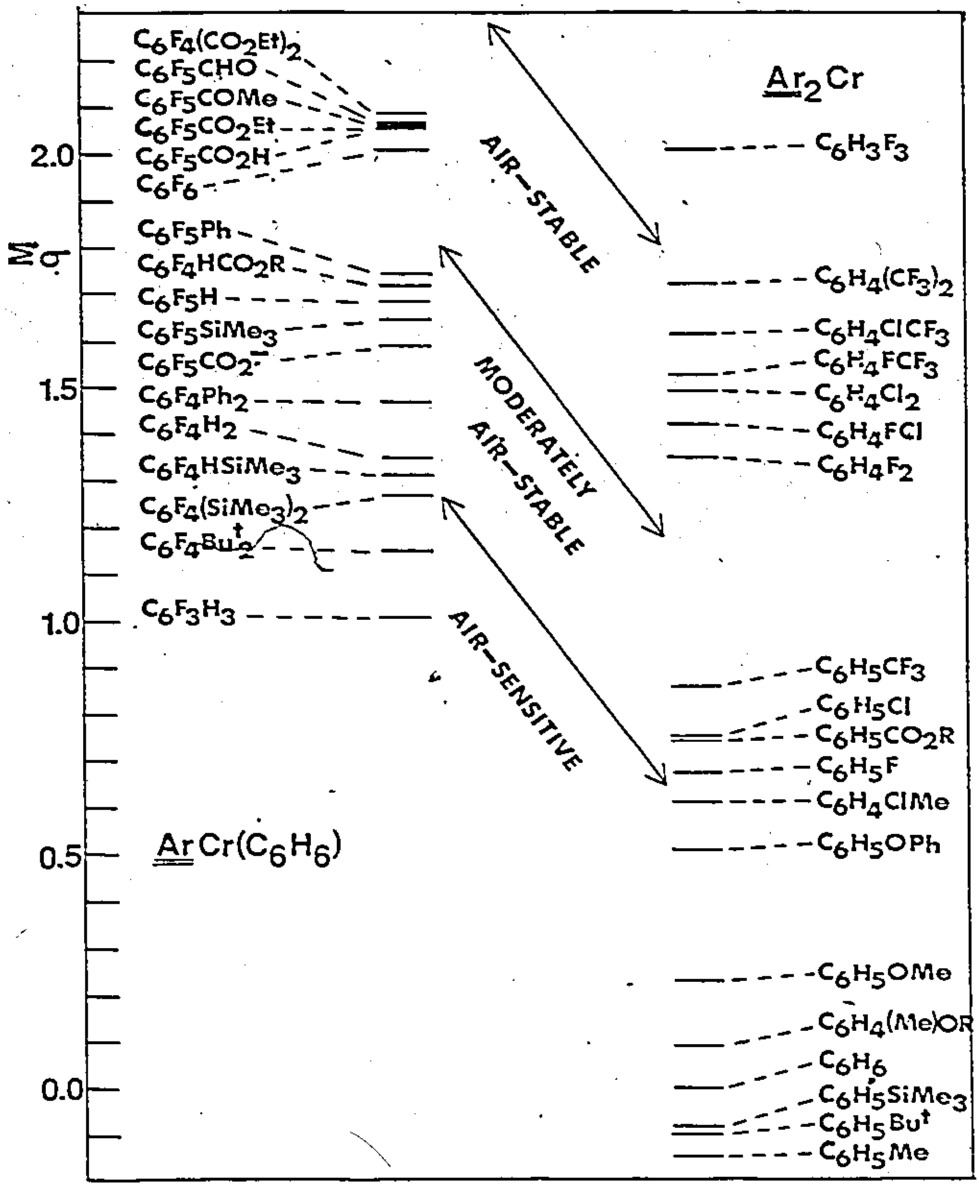


Figure 3.1 The sum of the σ_m values of a series of symmetrical and unsymmetrical chromarenes.

$E_{1/2}$ values obtained polarographically should correlate well with $\Sigma\sigma_m$, and we trust that the appropriate data will soon be available (37).

3.3 SUBSTITUENT EFFECTS AND STABILITY OF UNSYMMETRICAL CHROMARENES, ArCrAr'

While it is clear that the role of the substituents is crucial to the behaviour of a given chromarene, it is also noticable that in the unsymmetrical systems of the type $ArCr(C_6H_6)$, it is possible to incorporate more electronegative groups (see Figure 3.1) than is possible in the Ar_2Cr sandwich molecules. Thus, although $(C_6H_3F_3)_2Cr$ has not so far been synthesised, $(C_6F_nH_{6-n})Cr(C_6H_6)$, when n = 4, 5 or 6, are readily available (13,24,25,55) and their chemistry has been extensively studied (25,40). It seems that, in the unsymmetrical chromarenes, there exists a self-compensating mechanism whereby the full effect of the arene substituents need not be tolerated solely by the chromium (as is presumably the case for Ar_2Cr) but can be, to some extent, electronically buffered by the π-C_6H_6 ring. There is clearly electronic interaction between the two rings as is evidenced by the surprisingly large inter-ring J_{HF} coupling constants in the molecules $(C_6F_nH_{6-n})Cr(C_6H_6)$, where n = 4, 5 or 6 (24,25). Furthermore in $(C_6F_6)Cr(C_6H_6)$, the C_6H_6 ring is readily deprotonated by strong bases (24). It has also been shown by a comparison of corresponding ν_{CO} bands in the infrared spectra of the molecules $C_6F_5M(CO)_x$ and $(C_6F_5M(CO)_x)$-$Cr(C_6H_6)$ the the π-$(C_6H_6)Cr$ moiety pushes electron density into the fluorinated ring (25); this is also consistent with the somewhat reduced susceptibility to nucleophilic attack of $(C_6F_6)Cr(C_6H_6)$ relative to free C_6F_6 (24).

Thus, the π-C_6H_6 ring must be comparable to three PF_3 ligands which can also stabilise the π-$(C_6F_6)Cr$ moiety (13), whereas the analogous molecule $(C_6F_6)Cr(CO)_3$ is currently unknown. Indeed, the subtle interplay of thermodynamic and kinetic effects is nicely exemplified by the cocondensation reaction of Cr vapor, PF_3 and the equimolar mixture of arenes $C_6F_nH_{6-n}$, where n = 0 through 6, which showed that the difluorobenzene complex was the favored product. One must, however, recall the point made by Timms (13) that the cocondensation method may not always work even when a more conventional route has been successful; $Cr(NO)_4$ provides a nice example of this phenomenon (13,56).

If the π-C_6H_6 group has the capacity to donate electron density on demand to satisfy the relative electron deficiency of its arene partner which is heavily substituted with electronegative groups, this should be reflected in the NMR spectroscopic properties of the π-C_6H_6 ring. Thus, increasing the withdrawal of electron density from the C_6H_6 ring might be expected to deshield the aromatic protons and this is in fact the case (see Table 3.1 and Figure 3.1). Such effects have been noticed previously (57) in a series of ethyl-substituted chromarenes in which the introduction of extra alkyl groups in one ring shields the ring protons in the other. However, the shifts are quite small and it is essential that all the spectra are recorded under identical conditions. Of course, a complicating factor here is that changes in the C_6H_6 to chromium bonding could also alter the ring current and the local anisotropic contributions to the shifts of directly bonded protons (58). In particular, although a withdrawal of electron density should deshield the protons, a diminution of the ring current would lead to an apparent shielding and so these two effects tend to nullify each other to some extent leading to a less than unequivocal result (59).

A much clearer picture emerges from the ^{13}C NMR shifts of the C_6H_6 moiety in the series $(C_6F_nH_{6-n})Cr(C_6H_6)$ in which the correlation (see Figure 3.2) between the ^{13}C shifts and the number of fluorine atoms in the other ring is remarkably good, ($\bar{r} = 0.9997$). Although it is true that the use of ^{13}C NMR spectroscopy to interpret changes in bonding in organometallic systems must be treated with some caution, nevertheless, with the reservations discussed by Lagowski (16), it can be an excellent probe for a series of closely related molecules. Table 3.1 lists the ^{1}H and ^{13}C NMR chemical shifts for a series of molecules $ArCr(C_6H_6)$ and it is noticable that the shifts, in general, correlate with $\Sigma\sigma_m$ and with the oxidative stability of the complex (see Figure 3.1).

It is thus apparent that ^{13}C NMR spectroscopy provides a measure of the electronic buffering effect of the unsubstituted ring as it tries to compensate for the electronic effects of the substituents in the other ring of the chromarene. In many ways, this effect parallels the well-known correlation of inductive parameters with ν_{CO} in arene chromium tricarbonyl systems.

3.4 CONCLUSIONS

These relatively simple ideas using substituent parameters to correlate molecular reactivity not only provide a rationale for the ease or difficulty of obtaining certain compounds but may also have some predictive value. Thus it is now apparent that in the difunctionalisation of 1,2,4,5-tetrafluorochromarene (40), with a view to producing air-stable

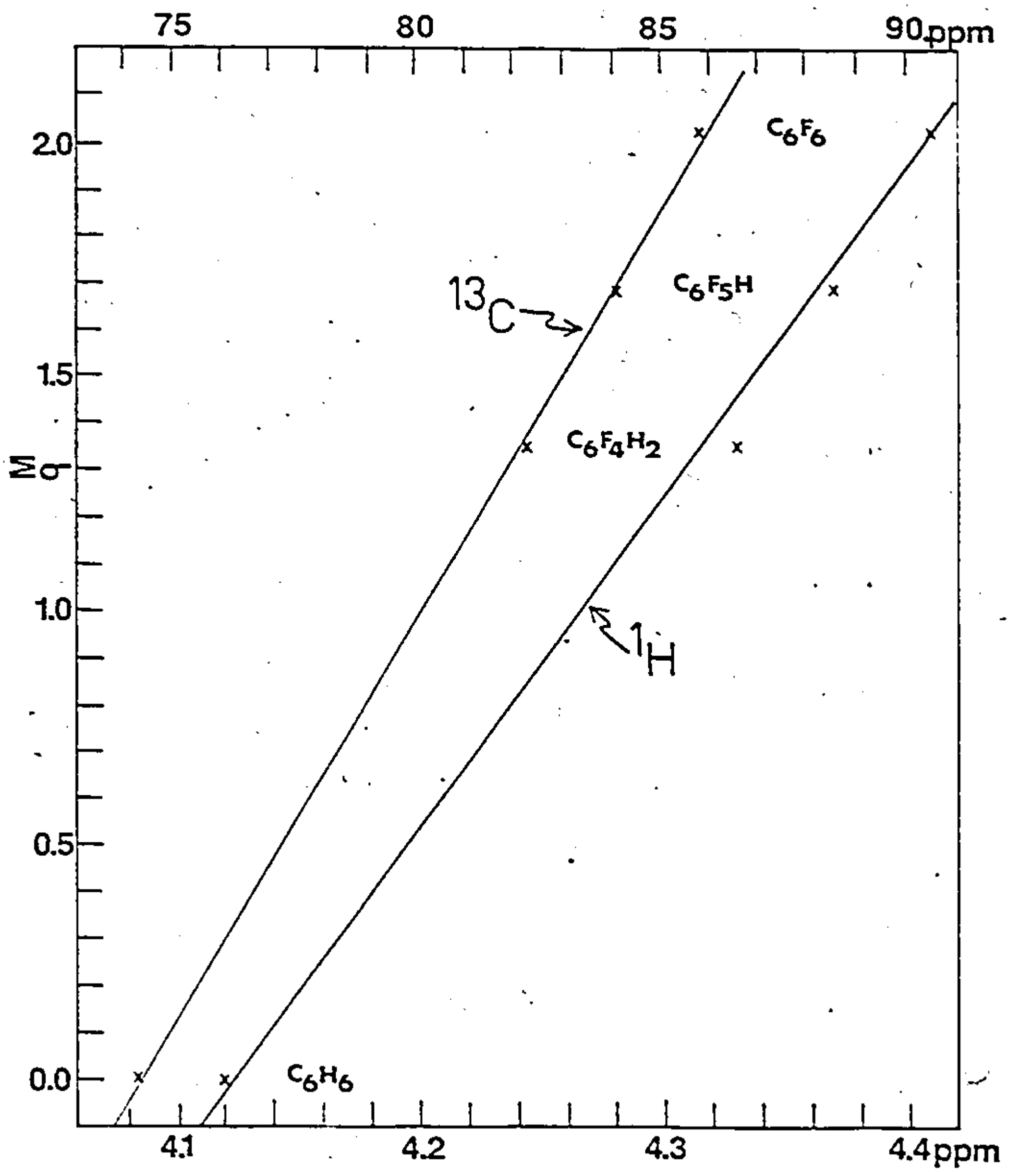


Figure 3.2 Plots of the sum of the σ_m values of the substituents of ArCr(C_6H_6) versus ^{1}H and ^{13}C NMR chemical shifts of the C_6H_6 ring.

Table 3.1 NMR Chemical Shifts[a] for the C_6H_6 ring of $ArCr(C_6H_6)$

Ar	^1H	^{13}C
$C_6F_4(CO_2Et)_2$	4.64	88.6
C_6F_5CO-furyl	4.71	87.6
$C_6F_5CO_2Et$	4.54	87.0
C_6F_6	4.41	85.5
C_6F_5H	4.37	84.0
$C_6F_4H_2$	4.33	82.2
C_6H_6 [b]	4.12	74.2

[a] All spectra recorded on a Bruker WH-90 spectrometer; all samples run as 5% solutions in C_6D_6 containing TMS as the internal standard and quoted in ppm downfield of this standard.

[b] Data taken from Refs. (27) and (52).

organometallic copolymers using a fluorochromarene as one of the monomers, the substituents must be chosen with some forethought. Hence, to prepare a polyamide, the electron-withdrawing acyl linkages, rather than the electron-donating amino groups, would be incorporated in the chromarene-containing monomer. Likewise for polyesters, the chromarene-containing monomer should possess the acid or ester but not the hydroxyl substituents.

We can also make predictions about the stabilities of as yet unsynthesised chromarenes. Thus, for several years it has been our aim to obtain 2,3,4,5,6-pentafluorochromarenoic acid with the intent of measuring its pK_a value. The $\Sigma\sigma_m$ value of this molecule, 2.055, would indicate it to be of comparable stability to the known $(C_6F_5CO_2Et)Cr(C_6H_6)$ (40) and hence readily isolable. However, although the desired molecule is probably stable enough, routes to it involving the strongly electron-releasing carboxylate functionality would not be favored. Indeed base hydrolysis of the ethyl ester of pentafluorochromarenoic acid yields not the carboxylate but products conceivably derivable from the π-complexed tetrafluorobenzyne (see p. 21). This latter intermediate could arise by elimination of CO_2 and fluoride ion from the initially produced carboxylate. Thus, other routes to the acid need to be explored and these are discussed elsewhere (22).

In conclusion, substituent parameters provide a useful probe as to the stability and chemistry of chromarenes.

CHAPTER IV

A CHROMARENYL PHOSPHINE

4.1 INTRODUCTION

The ready availability of functionalised chromarenes via the metal vapor co-condensation procedure has stimulated much recent activity in this area,(13,22,23,27,37,40,62,63). The known ability of the chromarene system to catalyse polymerisation (64) or hydrogenation processes (65) suggested that molecules containing both a chromarene moiety and another catalytic centre, such as a sixteen-electron square planar rhodium atom, would be attractive targets for synthesis. To this end, we have prepared a pentafluorochromarenylphosphine and discuss its structure, n.m.r spectra and reaction with $[Rh(CO)_2Cl]_2$.

4.2 SYNTHESIS AND N.M.R. SPECTRA

The 1,2,3,4,5-pentafluorochromarene (I) preparable by co-condensing benzene, pentafluorobenzene and chromium vapor at -196°C (55), is known to possess a relatively acidic proton in the fluorinated ring (25). Lithiation and reaction with chlorodiphenylphosphine gave a 30% yield of 1,2,3,4,5-pentafluoro-6-diphenylphosphinochromarene, (XXII), as cherry-red, airstable crystals which are readily soluble in benzene, but somewhat unstable when left in chloroform or methylene chloride for a few hours. Treatment of a benzene solution of $[Rh(CO)_2Cl]_2$ with (XXII) at room temperature gave a 90% yield of trans-chlorocarbonyl-bis(chromarenylphosphine)rhodium(+I), (XXIII), as brown air stable microcrystals (Fig. 4.1).

The ^{19}F n.m.r. spectra of the molecules (XXII), and (XXIII), proved to be particularly interesting when compared to those of the corresponding

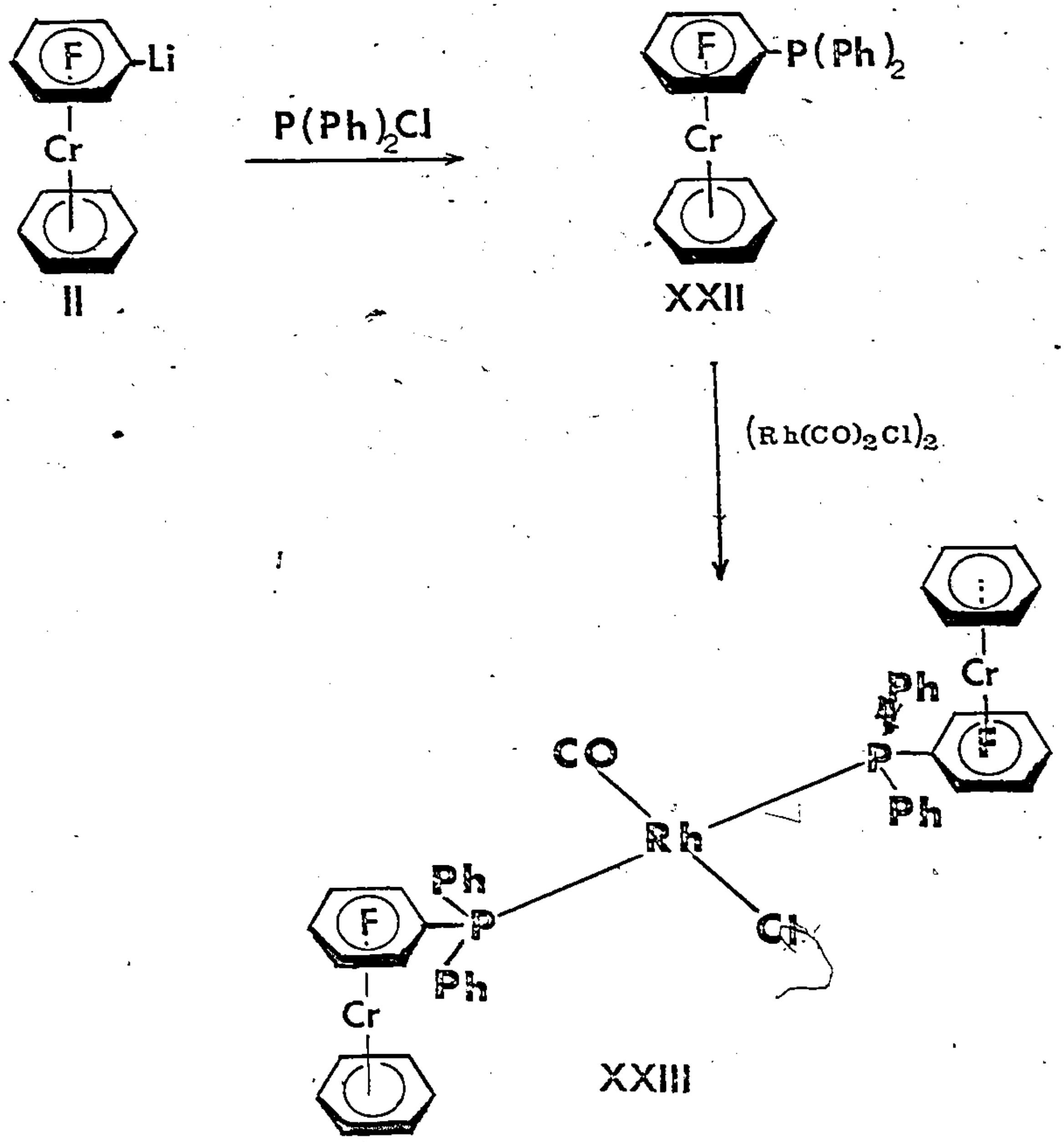


Figure 4.1: Preparation of pentafluorochromarenylphosphine and its reaction with $[Rh(CO)_2Cl]_2$.

free arenes, viz., $C_6F_5PPh_2$ and its Rh complex (66). The ^{19}F nuclei in fluorochromarene are known (23) to exhibit upfield shifts of 40 - 50 ppm relative to the shifts of the free arenes and this effect obtains in (XXII) and (XXIII). However,an analysis of the six-spin C_6F_5P systems in the chromium complexes show very markedly different coupling constants to those of their non-π-complexed analogues (see Table 4.1), of special interest are the enormous $^3J_{FF}$ and $^4J_{FF}$ values compared to those in all other C_6F_5X systems (67). It is well established that ortho fluorine-fluorine coupling constants in aromatic systems are ∿ 20 Hz and all negative (68). These very large increases in $^3J_{FF}$ values in the chromarenes are not amenable to a simple explanation but calculations are currently underway to examine the factors involved. To our knowledge, the only reported instances of such anomalously large coupling constants between aromatic fluorines were those reported by Olah (69) on the fluorobenzenium ions, e.g., $C_6H_5F_2^+$ where J_{FF} = 80 Hz.

It is notable that although it is, as yet, not possible to assign absolute signs of the coupling constants and it is obviously rather risky to argue solely by analogy to the non-complexed C_6F_5X systems, it is clear that $J_{2,3}$ and $J_{3,4}$ are of different sign. Spectral simulations in which the two $^3J_{FF}$ values have the same sign gave rise to peak intensities quite incompatible with the observed spectra. Our initial thoughts that the bulk of the diphenylphosphino group might be causing significant perturbation of the ring geometry were dispelled not only by comparison of the J_{FF} values in less hindered chromarenes, e.g. (I), but also by the crystal structure (see below). Thus, the complexation shifts induced by the in-

Table 4.1: Chemical shifts of ortho, meta and para fluorine nuclei in $(C_6F_5X)Cr(C_6H_6)$, XXII, and $[(C_6H_6)Cr(C_6F_5PPh_2)_2]_2Rh(CO)Cl$, XXIII; All shifts are to high field of $CFCl_3$. All coupling constants are quoted in Hz.

Compound	Ortho	Meta	Para	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$
XXII	-175.1	-192.8	198.8	71	-106	43
XXIII	-165.8	-193.6	199.4	78	101	42

Table 4.2: The complexation shifts induced by incorporation of a π-$Cr(C_6H_6)$ moiety in ^{19}N.M.R.

	$C_6F_5PPh_2$ (a)	XXII	ΔJ	R^c (b)	XXIII	ΔJ
$J_{2,3}$	-24.2	71	+95.2 or 46.8	-23.0	77.6	100.6 or 65.6
$J_{2,4}$	4.0	43	39.0 or -47.0	4.6	42.3	37.7 or -46.9
$J_{3,4}$	-20.4	-106	85.6 or 126.4	20.6	-100.8	80.2 or 121.4
$J_{2,5}$	10.8	-	-	7.7	0	-7.7 or -7.7
$J_{2,6}$	1.6	-	-	0	+12.0	12.0 or -12.0
$J_{3,5}$	-44.0	-	-	- 5.8	- 6.0	-0.2 or +11.8

(a) Values taken from Ref. (71).

(b) Values taken from Ref. (70).

$R^c = [(C_6F_5PPh_2)_2Rh(CO)Cl]$

corporation of a π-Cr(C_6H_6) moiety are those listed in Table 4.2; two sets are given since it is not possible at the moment to be sure of the absolute signs of the J's in the chromarenes.

McGlinchey and Tan have previously suggested (25) that the π-Cr(C_6H_6) moiety behaves as a net donor of electron density to fluoro-arene rings and thus the phosphine (XXII) would be expected to be more basic than $C_6F_5PPh_2$ itself. In accordance with these ideas, the chromium-containing rhodium complex, (XXIII), exhibits ν_{CO} at 1955 cm^{-1} which is 20 cm^{-1} lower than the value for$[(C_6F_5PPh_2)_2Rh(CO)Cl]$(70).

The ^{31}P and ^{19}F n.m.r. spectra of the molecules $(C_6F_5)_nPPh_{3-n}$ have been interpreted (70,71) in terms of a pπ → dπ interaction between the ring and the phosphorus. Complexation of the C_6F_5 ring to chromium in (XXII), results in a deshielding of the phosphorus by 11 ppm and is presumably a consequence of the enhanced pπ-dπ overlap resulting from the electron donation by the π.Cr(C_6H_6) unit. As is typical (70) when the phosphine is complexed to a metal, the pπ-dπ electron flow from the ring to the phosphorus in (XXIII), must compete with dπ-dπ back donation from rhodium to phosphorus. The net result is a small upfield shift of the ^{31}P nucleus and the disappearance of all the P-F coupling constants. The spectrum did not appear to have a rhodium-phosphorus coupling constant.

We have proposed (72) that the air stability of fluorochromarenes can be correlated with the "internal oxidation" of the molecules; thus, the aerial decomposition (which proceeds via one-electron oxidation of the formally zero-valent chromium) is retarded by the presence of electron-withdrawing substituents in the ring. Indeed, it was predicted (72) that

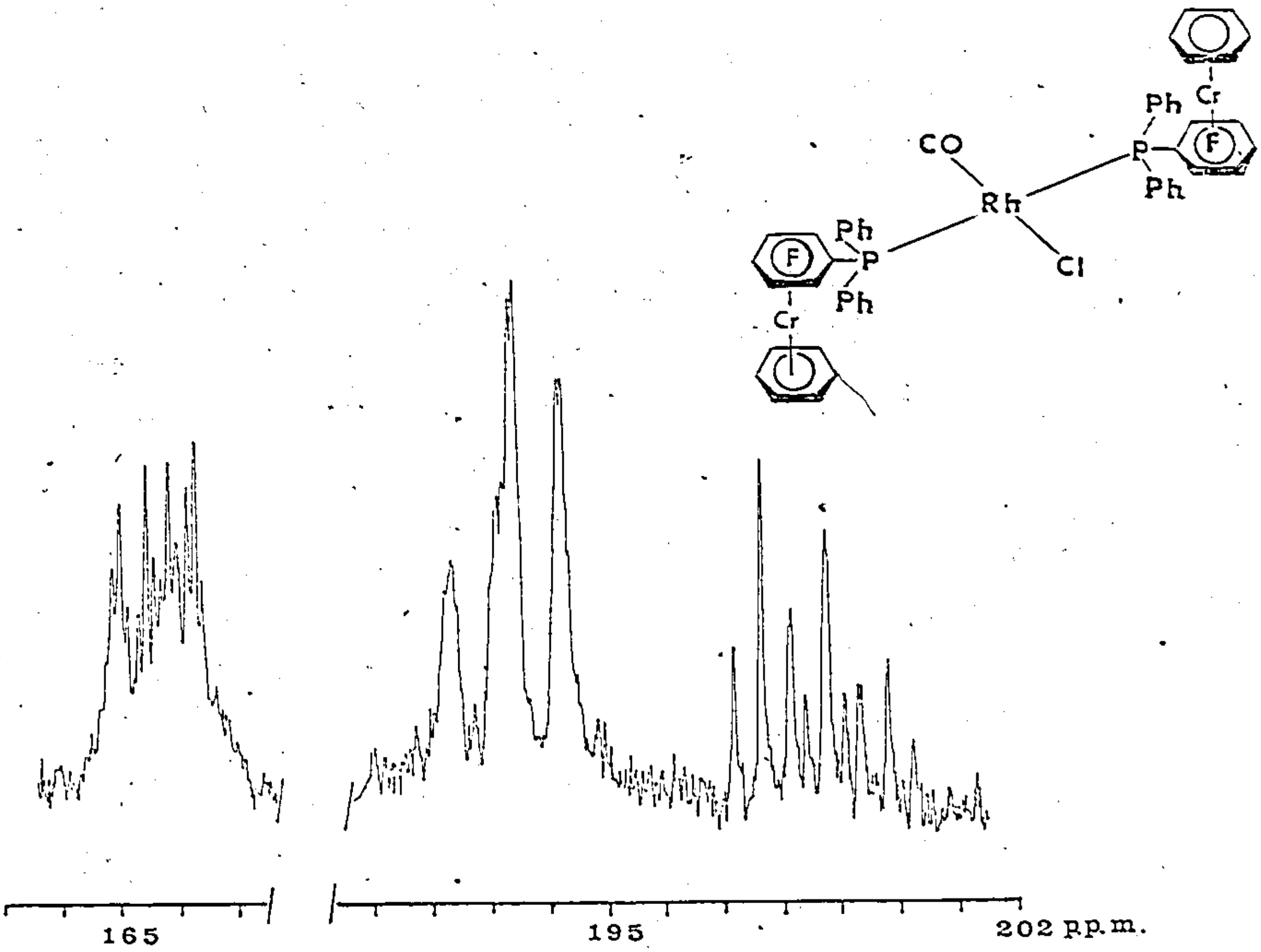


Figure 4.2: The ^{19}F N.M.R. spectrum of trans $[(C_6H_6)Cr(C_6F_5PPh_2)]_2Rh(CO)Cl$.

a correlation should exist between the polarographic half-wave, $\varepsilon^{\frac{1}{2}}$, and the sum of the Hammett meta parameters for the substituents, $\Sigma\sigma_n$; this correlation now has experimental support (73). The remarkable air stability of the molecules $(C_6H_6)Cr(C_6F_5X)$, where X is PPh_2 or SCH_3 (74), is readily rationalised by invoking delocalisation of the excess electron density in the fluoro-arene ring onto the substituent X via $p\pi \rightarrow d\pi$ overlap. This picture is also consistent with ^{31}P n.m.r. spectral data discussed above. A final point to be made in this connection concerns the ^{1}H and ^{13}C n.m.r. chemical shifts of the π-C_6H_6 ring in complex (XV) which occur at δ 4.57 and δ 85.5 respectively. We have previously noted (72) these shifts correlate well with the $\Sigma\sigma_n$ for the substituents in the fluorinated ring and hence with the oxidative stability of the molecules. We note that these shifts suggest that the Ph_2P substituent is behaving electronically somewhere between a fluorine and a carbethoxy group (72) and thus reinforces the idea of electron delocalisation onto the substituent via a $p\pi$-$d\pi$ interaction.

4.3 CRYSTAL STRUCTURE OF $(C_6H_6)Cr(C_6F_5PPh_2)$, XXII

The crystal structure of XXII was solved by Mr. Romolo Faggiani and Dr. C.J.L. Lock of this department. An ORTEP drawing of the structure appears as Figure 4.3. The first point to notice is that the diphenylphosphino moiety is oriented so as to minimise steric interactions with the aromatic fluorines, thus supporting the earlier comment that the large J_{FF} values are not greatly influenced by the steric bulk of the substituent in the C_6F_5X ring. Perhaps the most striking feature of the structure is the proximity of the chromium atom to the fluorinated ring [Cr-C(F),

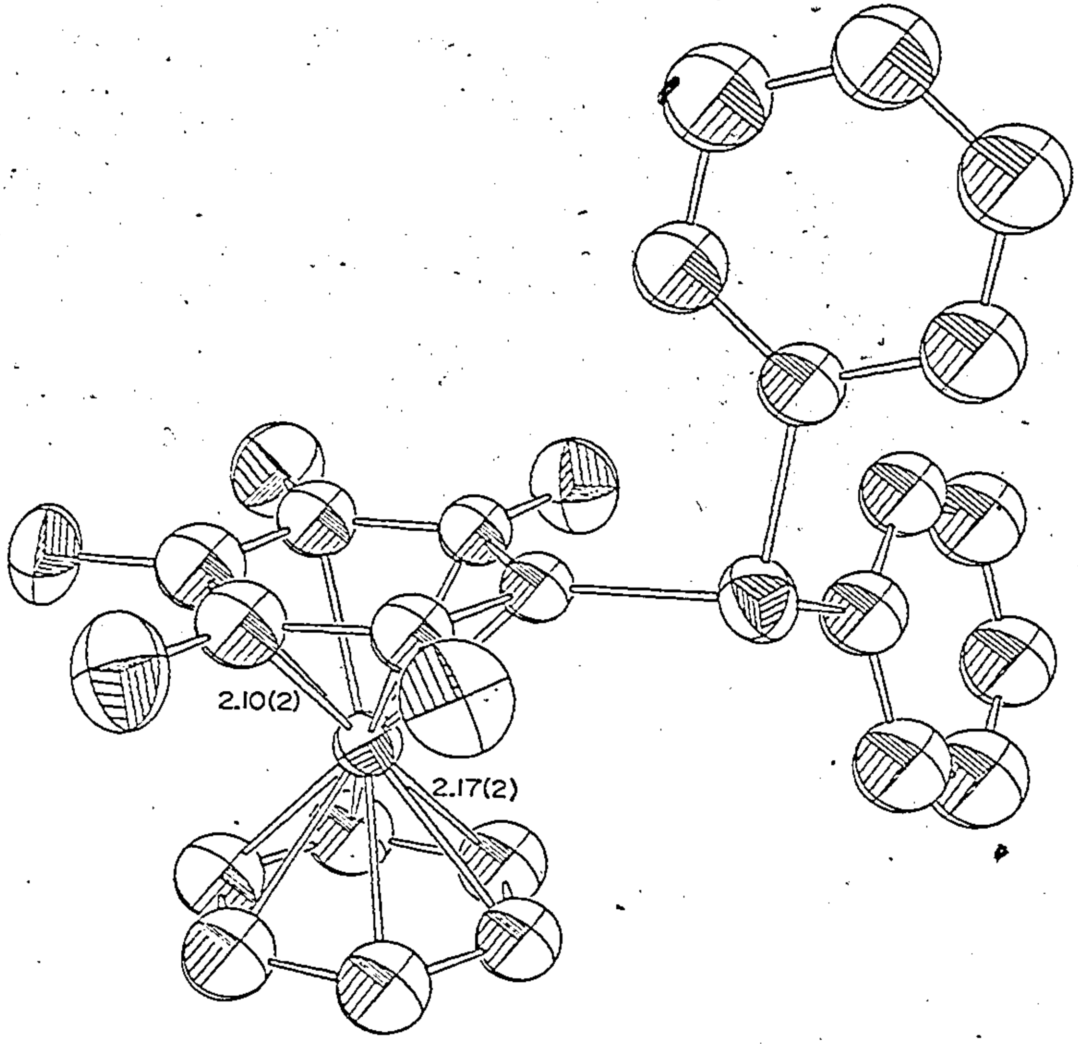


Figure 4.3: Molecular structure of pentafluorochromarenyl phosphine.

2.10(2)Å] relative to the chromium-benzene distance [Cr-C(H), 2.17(2)Å]. The former bond length is noticably shorter than that for $(C_6H_6)_2Cr$ itself where the Cr-C distance is 2.142(2)Å (75). One may interpret (76) this decreased bond length as being symptomatic of greatly increased back-donation by the chromium to the relatively electron-deficient carbons which are bonded to the electronegative fluorine atoms. This enhanced back-donation to the fluorinated ring is in accord with a vibrational study on $(C_6H_6)Cr(C_6F_6)$ in which this point was discussed (77).

CHAPTER V

REACTION OF NICKEL ATOMS WITH FULVENES

5.1 INTRODUCTION

π-Allyl nickel complexes have been proposed as intermediates in a number of nickel-catalyzed reactions for the syntheses of a variety of organic compounds (78). Much effort has been devoted to the study of these processes. Probably the most important catalytic reaction of zero-valent nickel complexes is the cyclotrimerization of 1,3-butadiene to 1,5,9-cyclododecatriene, which is used in the manufacture of Nylon-12 and space vehicle lubricants. The efficacy of nickel to catalyze such dimerization and trimerization processes has been attributed to the ability of this element to alternate between a 16-electron and an 18-electron count (78).

The reaction of nickel vapor with 1,3-butadiene leads to formation of blood-red 2,6,10-dodecatriene-1,12-diyl nickel, and hydrogenation yields n-dodecane. Nickel vapor and norbornadiene yielded no isolable organometallic products, but gave predominantly the exo-trans-exo dimer of norbornadiene (5).

The reaction of 6,6-dimethyl-fulvene with iron vapor had been shown (see Figure 5.1) to give a bridged ferrocene derivative (12),ferrocenophane, and it was thought that an analogous bridged nickelocene derivative might be synthesisable using the same approach. (Figure 5.1).

5.2 THE NICKEL ATOM PROMOTED DIMERIZATION OF DIMETHYLFULVENE

In an attempt to produce an alkyl-bridged nickelocene, 6,6-dimethylfulvene and nickel vapor were codeposited at -196° in a metal vapor

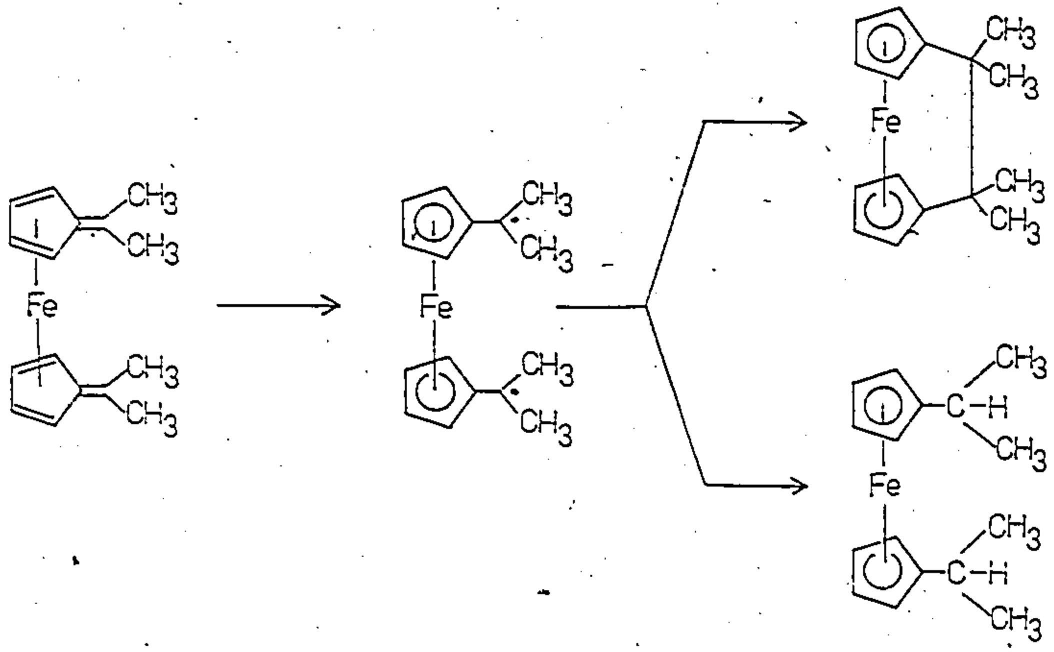


Figure 5.1: Reaction of 6,6-dimethylfulvene with iron vapor.

reactor previously described for the reactions of chromium vapor. However, the only product isolated upon sublimation of the residue was identified by elemental analysis and mass spectrometry as a dimer of dimethylfulvene. This product is not formed via thermolysis or photolysis in the metal vapor reaction (this possibility was eliminated by blank reactions using normal cocondensation conditions but with no metal in the crucible), nor do iron, chromium or palladium vapors bring about this dimerisation. The conventional spectroscopic techniques (see experimental section p. 61), did not permit an unequivocal assignment of the structure but it was identified crystallographically as a mixture of 4,4,8,8-tetramethyl-1,4,5,8-tetrahydro-sym-indacene, (XXVIa) and the 1,4,7,8-isomer, (XXVIb) Figure 5.2. The molecule is formally derivable by a thermally forbidden [6+6] cycloaddition process followed by [1,5]-hydrogen shifts.

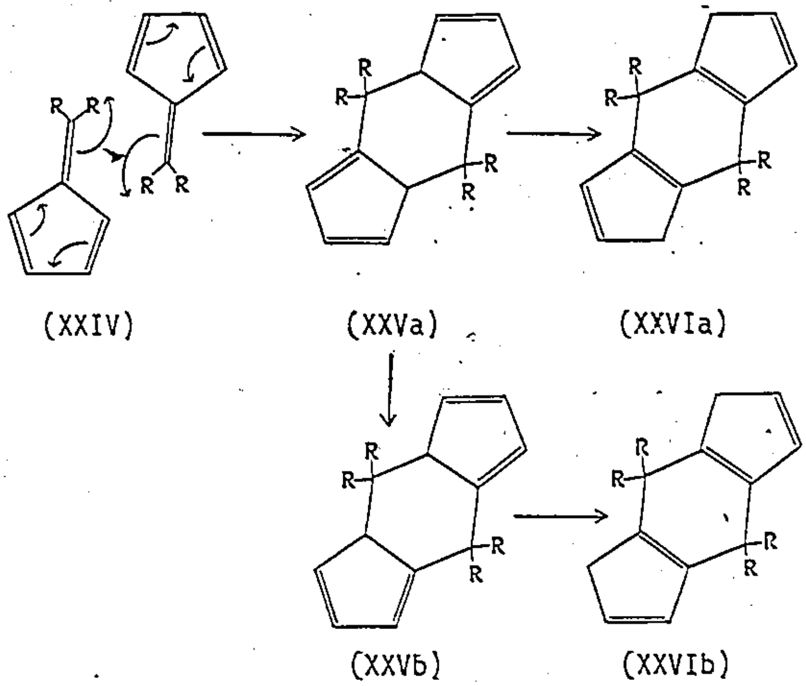


Figure 5.2: Dimerization of 6,6-dimethyl fulvene.

Nevertheless, although the photochemical [6+6] cycloaddition has precedent (79), we suggest that this particular process is a stepwise dimerisation on a nickel atom template. A reasonable initial product is the 18-electron tetrahedral complex, (XXVII) (Figured 5.3) which, unlike bis(cyclopentadiene)nickel (2), cannot form a stable complex simply by hydrogen transfer (3), and so undergoes ligand coupling to give (XXVIII). This would require out-of-plane bending of the exocyclic carbon of the fulvene towards the metal but this phenomenon has been observed previously (80). Subsequently coupling of two π-allyl moieties parallels the now classic work of Wilke's group (81); the requisite hydrogen shifts are well-

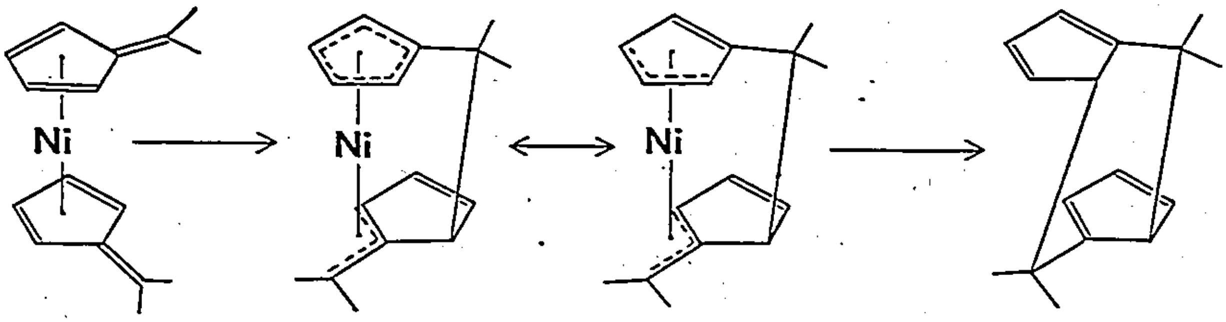

(XXVII) (XXVIII) (XXVIa)

Figure 5.3: A suggested mechanism of dimerisation of 6,6-dimethylfulvene.

documented in nickel vapor reactions (5).
Presumably the tendency to form 20-electron nickelocene systems is low and the dimerisation process is thermodynamically favored.

Interestingly, the product, which is a head-to-tail dimer (in some ways analogous to the nickel promoted isoprene dimer so crucial to Billups' elegant grandisol synthesis), lends support to the ideas of Ehntholt and Kerber (82) with respect to the series of molecules of the type (fulvene)$_2$Fe$_2$(CO)$_x$ prepared in the pioneering investigation of Weiss and Hubel (83). These latter moecules are being investigated in the light of present results.

5.3 X-RAY CRYSTALLOGRAPHY OF TETRAMETHYL TETRAHYDRO-SYM-INDACENE

This crystallographic work was performed by Dr. Jeffery F. Sawyer of this department.

Clear, colorless needle shaped crystals, m.p. 80°, were obtained by vacuum sublimation and were sealed in Lindemann capilliaries. Preliminary X-ray data established the space group as $\underline{P}\ 2_1 2_1 2_1$ (No. 14) with four formula units ($C_{16}H_{20}$) in a cell of dimensions a = 11.928(3), b = 6.746(2) and c = 16.127(5)Å. Three-dimensional data were collected on a Syntex $P2_1$ diffractometer using Mo-K_α radiation to a maximum 2θ of 52°. The structure was solved using the acentric direct methods routines of SHELX, the best E-map revealing all of the non-hydrogen atoms. The hydrogen atoms were located in subsequent difference maps and indicated disorder at the 1,3,5,7 positions. Block diagonal least-squares refinement using 1085 observed reflections ($I/\sigma(I)>2.0$) and with the carbon atoms having anisotropic temperature factors, converged to a final R ($= \Sigma||F_o|-|F_c||/\Sigma|F_o|$) of 0.045 and weighted R ($= [\Sigma\omega||F_o|-|F_c||^2/\Sigma\omega|F_o|]^{\frac{1}{2}}$) of 0.032 where the weights used were $(1/\sigma(F))^2$. The molecule is completely planar in the crystal possessing a non-crystallographic center of symmetry and overall D_{2h} symmetry although this arises from considering the lattice to contain an equal distribution of the dimers (XXVI a and b) with C_{2h} and C_{2v} symmetry respectively. Bond distances and angles are close to accepted values (see Table 5.1).

Table 5.1

Bond distances (Å) and bond angles (°) for Tetramethyl Tetrahydro-s-indancene, with standard deviations in parentheses.

Bond lengths (Å)	
C(1) - C(2)	1.469(4)
C(1) - C(5)	1.341(3)
C(1) - C(12)	1.490(3)
C(2) - C(3)	1.395(5)
C(3) - C(4)	1.403(5)
C(4) - C(5)	1.488(5)
C(5) - C(6)	1.496(4)
C(6) - C(7)	1.496(3)
C(6) - C(15)	1.539(4)
C(6) - C(16)	1.541(4)
C(7) - C(8)	1.481(5)
C(7) - C(11)	1.338(3)
C(8) - C(9)	1.394(5)
C(9) - C(10)	1.403(5)
C(10) - C(11)	1.475(4)
C(11) - C(12)	1.496(4)
C(12) - C(13)	1.544(4)
C(12) - C(14)	1.541(4)

Bond angles (°)	
C(2) - C(1) - C(5)	109.0(2)
C(2) - C(1) - C(12)	125.8(2)
C(5) - C(1) - C(12)	125.3(2)
C(1) - C(2) - C(3)	107.0(3)
C(2) - C(3) - C(4)	109.6(3)
C(3) - C(4) - C(5)	106.2(3)
C(4) - C(5) - C(1)	108.3(3)
C(4) - C(5) - C(6)	125.4(2)
C(1) - C(5) - C(6)	126.3(2)
C(5) - C(6) - C(7)	107.9(2)
C(5) - C(6) - C(15)	109.8(2)
C(5) - C(6) - C(16)	109.9(3)
C(7) - C(6) - C(15)	110.2(3)
C(7) - C(6) - C(16)	110.2(2)
C(15) - C(6) - C(16)	108.9(3)
C(6) - C(7) - C(8)	125.5(2)
C(6) - C(7) - C(11)	126.2(2)
C(8) - C(7) - C(11)	108.3(2)
C(7) - C(8) - C(9)	107.0(3)
C(8) - C(9) - C(10)	109.2(3)
C(9) - C(10) - C(11)	106.7(3)
C(10) - C(11) - C(7)	108.9(2)
C(10) - C(11) - C(12)	125.8(2)
C(7) - C(11) - C(12)	125.3(2)
C(11) - C(12) - C(1)	108.9(2)
C(11) - C(12) - C(13)	109.4(2)
C(11) - C(12) - C(14)	110.3(2)
C(1) - C(12) - C(13)	109.6(2)
C(1) - C(12) - C(14)	110.4(2)
C(13) - C(12) - C(14)	108.2(3)

Figure 5.4

ORTEP view of the molecule showing the numbering scheme used in the structure determination. Temperature ellipsoids are drawn at the 50% probability level. All hydrogen atoms, including those at the disordered positions, are drawn with uniform isotropic thermal parameters.

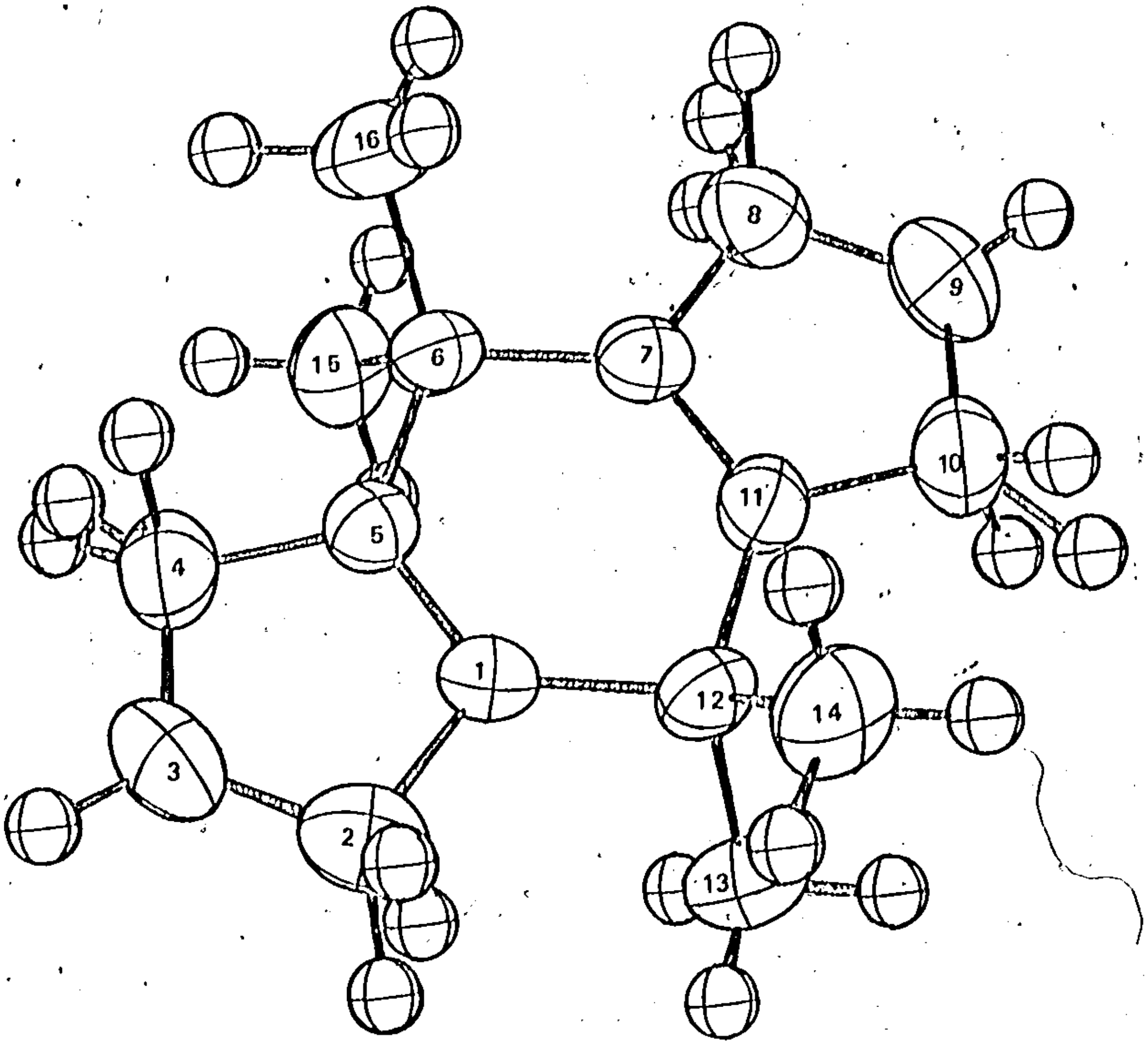


Figure 5.4:

CHAPTER VI

EXPERIMENTAL

6.1 GENERAL TECHNIQUES

Nuclear magnetic resonance spectra were obtained on Bruker WH.90 spectrometer. Concentration of 0.04-0.05 M in benzene-d_6 as solvent were used throughout.

Fluorine-19 spectra were obtained at 84.66 MHz with $CFCl_3$ used as an external reference.

Carbon-13 and proton spectra were obtained at 22.62 MHz and 90 MHz respectively with tetramethylsilane as the internal standard.

Phosphorus-31 spectra were obtained at 36.43 MHz with 85% H_3PO_4.

Mass spectra were recorded on a C.E.C.21-110.B spectrometer.

Elementary analyses were performed by Gygli Microanalysis Laboratory, Toronto.

Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrometer.

Spectral simulation was achieved with Nicolet's E28-7011 iterative program and an 1180 computer.

Most of the arenes were supplied by Peninsular Chem. Research, Grainesville, Florida. Chromium metal chips (purified carbon free fused) were purchased from Fisher Scientific Co. and the crucibles were obtained from Sylvania Emissive Products, Exter, New Hampshire.

The co-condensation apparatus was essentially the same as that used and described in T.S. Tan's thesis and elsewhere (4).

6.2 PREPARATION OF ORGANIC DERIVATIVES OF 2,3,4,5,6-PENTAFLUOROCHROMARENES

6.2.1 1-Lithio-2,3,4,5,6-pentafluorochromarene, I

The $(C_6F_5Li)Cr(C_6H_6)$ was prepared by the lithiation of $(C_6F_5H)Cr(C_6H_6)$ as described previously (25).

6.2.2 Reaction of (I) with Acetyl Chloride

To a solution of I (0.335 mmol) in ether was added a very slight excess of acetyl chloride at -78° under a nitrogen atmosphere. The solution was stirred at -78° for 1 h, by which time the initially red-brown solution had turned yellow. The solution was allowed to warm to room temperature, filtered under nitrogen and the solvent and excess CH_3COCl removed in vacuo. The product was purified by sublimation at $50°/10^{-2}$ mm Hg to give yellow, air-stable 1-acetyl-2,3,4,5,6-pentafluorochromarene, II, (23 mg, 0.068 mmol; 20%), m.p. 92°, whose i.r. spectrum showed ν_{CO} at 1741 cm^{-1}. Mass spectral data: m/e 340, $C_{12}H_9F_5CrO^+$ (12); 325, $C_{13}H_5F_5CrO^+$ (2.5); 298, $C_{12}H_7F_5Cr^+$ (45); 262, $C_8H_3F_5CrO^+$ (14); 168, $C_6F_5H^+$ (23); 149, $C_6F_4H^+$ (40); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (65); 52, Cr^+ (63). Anal. Found: C, 49.5; H, 2.6. $C_{14}H_9F_5CrO$ calcd: C, 49.4; H, 2.6%.

6.2.3 Reaction of (I) with Ethyl Formate

To a solution of I (0.335 mmol) in ether was added ethyl formate (0.40 mmol) in ether at -78° under a nitrogen atmosphere. The red-brown solution gradually became yellow and, after stirring for 1 h at -78°, it was allowed to warm to room temperature and filtered under nitrogen. Ether and excess ethyl formate were removed in vacuo and the residue sublimed at $45°/10^{-2}$ mm Hg to give yellow, air-stable 1-formyl-2,3,4,5,6-pentafluorochromarene, III, (33 mg, 0.101 mmol; 30%), m.p. 85° (decomposes) whose i.r. spectrum showed ν_{CO} at 1680 cm^{-1}. Mass spectral data: m/e 326, $C_{13}H_7F_5CrO^+$ (10); 298, $C_{12}H_7F_5Cr^+$ (35); 248, $C_7HF_5CrO^+$ (8); 168, $C_6F_5^+$ (40); 149, $C_6F_4H^+$ (55); 130, $C_6H_cCr^+$ (70); 78, $C_6H_6^+$ (53); 52, Cr^+ (100). Anal. Found: C, 47.7; H, 2.0. $C_{13}H_7F_5CrO$ calcd: C, 47.8; H, 2.1%.

6.2.4 Reaction of (I) with Ethyl Chloroformate

To a solution of I (0.335 mmol) in ether was added ethyl chloroformate (0.40 mmol) in ether at -78° under a nitrogen atmosphere. The initially red-brown solution was stirred at -78° for 30 min and then slowly allowed to warm to room temperature by which time the solution had become orange-yellow. After filtration under nitrogen and removal of ether and excess ethyl chloroformate in vacuo, the residue was sublimed at 50-60°/10^{-2} mm Hg to give orange, air-stable ethyl 2,3,4,5,6-pentafluorochromarenoate, IV, (99 mg, 0.268 mmol; 80%), m.p. 92-95°, showing ν_{CO} at 1725 cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 exhibited a multiplet at δ 4.63 (6H), a quartet at δ 4.22 (2H) and a triplet at δ 1.10 (3H). Mass spectral data: m/e 370, $C_{15}H_{11}F_5CrO_2^+$ (25); 325, $C_{13}H_6F_5CrO^+$ (3); 298, $C_{12}H_7F_5Cr^+$ (27); 292, $C_9H_5F_5CrO_2^+$ (11); 264, $C_8H_5F_5CrO^+$ (8.5); 168, $C_6F_5H^+$ (14); 149, $C_6F_4H^+$ (58); 130, $C_6H_6Cr^+$ (100); 111, $C_6F_2H^+$ (42); 78, $C_6H_6^+$ (45); 52, Cr^+ (61). Anal. Found: C, 48.8; H, 3.0. $C_{15}H_{11}F_5CrO_2$ calcd: C, 48.6; H, 3.0%.

6.2.5 Reaction of (I) with Furoyl Chloride

To a solution of I (0.335 mmol) in ether was added furoyl chloride (0.40 mmol) in ether at -78° under a nitrogen atmosphere. The red-brown solution turned yellow-brown after stirring at -78° for 45 min and was then allowed to warm to room temperature and was stirred for another 1 h.

After filtering under nitrogen and removal of solvent and excess furoyl chloride in vacuo, the product was sublimed at 55-60°/10^{-2} mm Hg to give yellow-brown, air-stable 1-furoyl-2,3,4,5,6-pentafluorochromarene, VIII, (98 mg, 0.25 mmol; 75%), m.p. 100°, which exhibited ν_{CO} at 1648 cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 showed a doublet (1.7 Hz) of doublets (< 1.0 Hz) at δ 6.92 (H_5), a doublet (3.7 Hz) of doublets (< 1.0 Hz) at δ 6.88 (H_3), a doublet (3.7 Hz) of doublets (1.7 Hz) at δ 5.91 (H_4), and a multiplet at δ 4.80 (6H). Mass spectral data: m/e 392, $C_{17}H_9F_5CrO^+$ (40); 314, $C_{11}H_3F_5CrO_2^+$ (100); 298, $C_{12}H_7F_5Cr^+$ (10); 262, $C_{11}H_3F_5O_2^+$ (27); 244, $C_{11}HF_5O^+$ (8); 196, $C_7HF_5O^+$ (21); 177, $C_7HF_4O^+$ (15); 168, $C_6F_5H^+$ (12); 149, $C_6F_4H^+$ (20); 130, C_6H_6[illegible] (62); 78, $C_6H_6^+$ (57); 52, Cr^+ (61). Anal. Found: C, 52.4; H, 2.6. $C_{17}H_9F_5CrO_2$ calcd: C, 52.0; H,2.3%

6.2.6 .Reaction of (I) with Acetaldehyde

To a solution of I (0.335 mmol) in ether was added acetaldehyde (0.4 mmol) in ether at -78° under a nitrogen atmosphere and the red-brown solution rapidly turned yellow. The solution was stirred at -78° for 1 h, allowed to warm to room temperature and acidified with dil. HCl. After filtration, the solvent and excess acetaldehyde were removed in vacuo and the product sublimed at 30°/10^{-2} mm Hg to give yellow 1-(2,3,4,5,6-pentafluorochromarenyl)ethanol, VII, (91 mg, 0.266 mmol; 80%), m.p. 52-55°. The product is stable in air for about 1-2 days, and shows ν_{OH} at 3400 cm^{-1}. Mass spectral data: m/e 342, $C_{14}H_{11}F_5CrO^+$ (35); 324, $C_{14}H_9F_5Cr^+$ (6); 264, $C_8H_5F_5CrO^+$ (16); 246, $C_8H_3F_5Cr^+$ (3); 212, $C_8H_5F_5O^+$ (2); 196, $C_7HF_5O^+$ (11); 149, $C_6F_4H^+$ (32); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (80); 52, Cr^+ (71). Anal. Found: C, 48.8; H, 3.1. $C_{14}H_{11}F_5CrO^+$ Calcd: C, 49.1; H, 3.2%.

6.3 REACTION OF CHROMIUM VAPOR WITH BENZENE AND PENTAFLUOROSTYRENE

Chromium vapor and 50 ml of a 60/40 v/v mixture of pentafluorostyrene and benzene were co-condensed over a 1 h period in the apparatus previously described (25). Removal of unreacted benzene and pentafluorostyrene and subsequent heating of the residue using a water bath at 60-70° gave a white material, VI, which sublimed onto the water-cooled surface of the reaction apparatus. The air-stable product, m.p. 65°, exhibited two ^1H n.m.r. peaks of equal area at δ 2.73 (triplet) and δ 1.63 (quintet). Mass spectral data: m/e 390, $C_{16}F_{10}H_8^+$ (40); 372, $C_{16}F_9H_9$ (30); 222, $C_{10}F_5H_7^+$ (8); 207, $C_9F_5H_4^+$ (25); 194, $C_8F_5H_3^+$ (60); 181, $C_7F_5H_2^+$ (100); 176, $C_8F_4H_4^+$ (52); 167, $C_6F_5^+$ (25); 162, $C_7F_4H_2^+$ (63); 150, $C_6F_4H_2^+$ (23); 143, $C_7H_2F_3^+$ (45); 131, $C_3F_5^+$ (20).

6.4 PREPARATION OF ORGANIC DERIVATIVES OF 1,2,4,5-TETRAFLUOROCHROMARENE

6.4.1 Lithiation of $(p\text{-}C_6F_4H_2)Cr(C_6H_6)$

The 1,2,4,5-tetrafluorochromarene (100 mg, 0.357 mmol) prepared as described previously (25) was dissolved in 60 ml sodium-dried diethyl ether and 40 ml THF. The solution was flushed with dry nitrogen for 20 min, cooled to -78° and treated with tert-butyllithium(1.80 mmol) in hexane. The initially pale red solution became red-brown, indicative of the formation of the dilithio derivative IX.

6.4.2 Reactions of (XV) with Deuterium Oxide

Addition of excess D_2O to a solution of IX at -78°, followed by stirring for 1 h and gradual warming to room temperature produced a pale orange solution. Removal of solvent and excess D_2O in vacuo followed by sublimation at 35°/10^{-2} mm Hg returned the tetrafluorochromarene essentially quantitatively. Mass spectral data: m/e 282, $C_{12}D_2H_6F_4Cr^+$ (45); 281, $C_{12}DH_7F_4Cr^+$ (35); 263, $C_{12}D_2H_6F_3Cr^+$ (12); 262, $C_{12}DH_7F_3Cr^+$ (8); 152, $C_6F_4D_2{}^+$ (30); 151, $C_{12}F_4HD^+$ (28); 150, $C_6F_4D^+$, $C_6F_4H_2{}^+$ (15); 149, $C_6F_4H^+$ (8); 133, $C_6F_3D_2{}^+$ (20); 132, $C_6F_3DH^+$ (22); 131, $C_6F_3D^+$, $C_6F_3H_2{}^+$ (30); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6{}^+$ (86); 52, Cr^+ (72). An increased ratio of ^{t}BuLi: $(C_6F_4H_2)Cr(C_6H_6)$ gave an increased percentage of the di-deuterated chromarene.

6.4.3 Reaction of (XV) with Ethyl Chloroformate

To a solution of IX (0.357 mmol) in ether was added ethyl chloroformate (0.80 mmol) at -78° under a nitrogen atmosphere. After stirring for 1 h at -78° the red-brown solution had turned brown-yellow. The solution was allowed to warm to room temperature, filtered and the solvent and excess ethyl chloroformate removed in vacuo. The product was sublimed at 90°/10^{-2} mm Hg to give, by mass spectrometry, a mixture of mono- and di-ester which showed ^{1}H n.m.r. peaks in C_6D_6 at δ 4.73 and δ 4.55, in the ratio 2.2:1, and also a quartet at δ 4.27 and a triplet at δ 1.14. The monoester (approxmately 30% yield) decomposed in air in about 2 days while the diester, which was purified by resublimation, is remarkably air-stable. Thus, 1,4-bis(carbethoxy)-2,3,5,6-tetrafluorochromarene, X, m.p. 105°, exhibiting ν_{CO} at 1720 cm^{-1} was obtained in 65% yield. Mass spectral data: m/e 424, $C_{18}H_{16}F_4CrO^+$ (40); 386, $C_{18}H_{16}F_2CrO_4{}^+$ (6); 379, $C_{16}H_{11}F_4CrO_3{}^+$ (10); 351, $C_{15}H_{11}F_4CrO_2{}^+$ (2); 346, $C_{12}H_{10}F_4CrO_4{}^+$ (77); 318, $C_{10}H_6F_4CrO_4{}^+$ (50); 290, $C_9H_6F_4CrO_3{}^+$ (12); 274, $C_9H_6F_4CrO_2{}^+$ (4); 246, $C_7H_2F_4CrO_2{}^+$ (2); 157, $C_7H_3F_2O_2{}^+$ (6); 149, $C_6F_4H^+$ (50); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6{}^+$ (71); 52, Cr^+ (63). Anal. Found: C, 51.0; H, 3.8. $C_{18}H_{16}F_4CrO_4$ calcd: C, 50.9; H, 3.8%.

6.4.4 Reaction of (XV) with Chlorotrimethylsilane

To a solution of IX (0.357 mmol) in ether was added Me_3SiCl (0.80 mmol) at -78° under a nitrogen atmosphere. After stirring at -78° for 30 min and for 1 h at room temperature, the now orange solution was filtered and the solvent and excess chlorotrimethylsilane removed in vacuo. Fractional sublimation gave the known(XXI) 1,4-bis(trimethylsilyl)-2,3,5,6-tetrafluorobenzene and traces of 1,2,4,5-tetrafluoro-3-trimethylsilyl-chromarene, XI, identified mass spectrometrically. Mass spectral data: m/e 352, $C_{15}H_{16}F_4CrSi^+$ (6); 280, $C_{12}F_4H_2Cr^+$ (40); 274, $C_9H_{10}F_4CrSi^+$ (8); 261, $C_{12}H_2F_3Cr^+$ (13); 149, $C_6F_4H^+$ (50); 130, $C_6H_6Cr^+$ (100); 78, $C_6H_6^+$ (80); 73, $C_3H_9Si^+$ (40); 52, Cr^+ (50).

6.5 PREPARATION OF PENTAFLUOROCHROMARENYLPHOSPHINE

To a solution of (IX) (1 mmol) in ether was added a very slight excess of chlorodiphenyl phosphine at -78° under a nitrogen atmosphere. After stirring at -78° for 2 h the initially red-brown solution had turned orange. The solution was allowed to warm to room temperature, stirred a further 3 h, filtered and the ether removed in vacuo. The residue was taken up in benzene and chromatographed on a silica gel column. Elution of a red band with 50% benzene, 40% hexane, 10% ether, gave (XXII) (145 mg, 0.301 mole; 30%). After recrystallisation from benzene, dark cherry-red crystals, m.p. 185° (with decomposition) were obtained. The ^1H n.m.r. spectrum in C_6D_6 exhibited a multiplet at (ppm) 4.57 (6H) benzene ring ; $\delta = 7.68$ (4H othox); $\delta = 7.2$ (6H meta). Mass spectral data: m/e (%) 482, $C_{24}H_{16}CrF_5P^+$ (35); 464, $C_{24}H_{17}CrF_4P^+$ (10); 404, $C_{18}H_{10}CrF_5P^+$ (45); 386, $C_{18}H_{11}CrF_4P^+$ (30); 352, $C_{18}H_{10}F_5P^+$ (15); 334, $C_{18}H_{11}F_4P^+$ (17); 275, $C_{12}H_5F_5P^+$ (14); 219, $C_5F_5Cr^+$ (10); 201, $C_6H_5F_4Cr^+$ (35); 185, $C_{12}H_{10}P^+$ (60); 168, $C_5F_5H^+$ (25);

149, $C_6F_4H^+$ (50); 130, $C_6H_6Cr^+$ (70); 78, $C_6H_6^+$ (100); 52, Cr^+ (90).

6.5.1. Preparation of Trans-chlorocarbonyl-bis(chromarenyl phosphine)-rhodium, (XXIII)

(XXIII) was prepared by stirring (XXII) (0.08 mmol) with $[Rh(CO)_2Cl]_2$ (0.04 mmol) in benzene at room temperature for 4 hrs under N_2 atmosphere. Removal of the solvent gave (XXIII) in 90% yield.

6.6. PREPARATION OF TETRAMETHYL TETRAHYDRO-s-INDANCENE

250 mg of nickel vapor and 6.6-dimethylfulvene were co-deposited at -196°C in a conventional metal atom reactor. 1.30 mg of tetramethyl tetrahydro was obtained after sublimation of the residue. The product is colorless crystals which -

i) I.R. showed strong and medium bands at:

= 3093, 3071, 3060, 3040, 2967(s), 2951(s), 2890(s), 2855, 1647, 1537(s), 1465 and 1208 cm^{-1}

ii) ^1H n.m.r. (in CD_2Cl_2) showed:

- a doublet (5.43 Hz) of triplet (2.50 Hz) at δ 6.51 (2H)
- a doublet (5.43 Hz) of triplet (1.45 Hz) at δ 6.32 (2H)
- a doublet (2.50 Hz) of doublet (1.45 Hz) at δ 3.01 (4H)
- a singlet at δ 1.32 (3H)
- a singlet at δ 1.29 (6H)
- a singlet at δ 1.27 (3H)

iii) ^{13}C n.m.r. (proton coupled) showed:

- a singlet at δ 145.1 ($>C=$)
- a doublet at δ 131.3 ($-CH=$)

- a triplet at δ 38.9 (-CH_2)
- a singlet at δ 34.8 ($\geq CMe_2$)
- three quartets at δ 35.1; 30.1 (double intensity) and 28.7 (CH_3's)

iv) Mass spectral peaks occurred at m/e: 212, 197, 182, 167, 152, 141, 139, 115 and 89.

- mass spectral with high resolution
  - observed mass peak 212.1576515
  - calculated mass peak 212.1564920 with error 0.00116

v) The Raman spectra of the product was essentially identical in CH_2Cl_2 solution and in solid state.

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