A Thesis

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"FLUOROCARBON COMPLEXES
OF THE
TRANSITION METALS"

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degree of

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by

JOHN L. DAVIDSON, B.Sc.

Department of Chemistry,
University of Glasgow,
GLASGOW, W2

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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ABSTRACT

Reactions of transition metal carbonyl and cyclopentadienyl complexes with disulphides and acetylenes bearing fluorocarbon substituents have been investigated.

Photolytic reactions of disulphides RSSR, R = CF_3, C_6F_5 are considered to proceed via RS·radicals and with dimeric complexes monomers have been obtained e.g.

$$[\mathrm{CpMo(CO)_3}]_2 \xrightarrow{\mathrm{RS\cdot}} \mathrm{CpMo(CO)_3SR}$$

Use of closed reaction systems has enabled the identification of thermally unstable compounds such as $Mn(CO)_5SCF_3$ and CpNi(CO)SR which decarbonylate readily in an open system to di-or polymeric mercapto bridged complexes e.g.

$$2\mathrm{Mn(CO)_5SCF_3} \longrightarrow [\mathrm{Mn(CO)_4SCF_3}]_2 + 2\mathrm{CO}$$

The dimers in many cases exhibit isomerism due to inversion at sulphur and this has been studied by i.r. and n.m.r. spectroscopy.

The photolytic reactions of disulphides and monomeric carbonyls e.g. $Fe(CO)_5$, $Mo(CO)_6$, gave dimeric mercapto-bridged compounds directly, e.g. $[Fe(CO)_3SCF_3]_2$, $[Mo(CO)_4SCF_3]_2$, but in the absence of u.v. light $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$ gave $CpCo(CO)(SC_6F_5)_2$ which can be decarbonylated to $[CpCoSC_6F_5]_2$, illustrating that monomeric carbonyls can react with disulphides to give sulphur bridged dimers via an oxidative addition reaction. Possible mechanisms of these reactions and steric and electronic effects of the substituent on sulphur are discussed.

Reactions of these organothio derivatives with acetylenes $CF_3C\equiv CCF_3$ and $CF_3C\equiv CH$ gave a variety of novel complexes. Complexes $CpMo(CO)_3SCF_3$, M = Mo, W, were observed to undergo CO substitution by

$CF_3C_2CF_3$ to give $CpM(CO)_2(CF_3C_2CF_3)SCF_3$, the variable temperature n.m.r. spectra of which have been interpreted in terms of restricted rotation of the SCF_3 ligand. Similar complexes were obtained with $CH_3C{\equiv}CCH_3$ and $PhC{\equiv}CPh$. In contrast $CpMo(CO)_3SCF_3$ and $CF_3C{\equiv}CH$ gave the cyclopentadienone derivative $CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$ which was photochemically decarbonylated to $[CpMo[(CF_3C_2H)_2CO]SCF_3]_2$.

Insertion of $CF_3C{\equiv}CCF_3$ into the Mn-S bond of $[Mn(CO)_4SC_6F_5]_2$ gave $Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$ while $CF_3C{\equiv}CH$ gave $Mn(CO)_4(CF_3C_2H)_2SC_6F_5$. With excess acetylene the former yielded $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ which has been shown by X-ray studies to contain a non-planar heterocyclic sulphonium ion $[C_4(CF_3)_4\overset{+}{S}C_6F_5]$ bonded to an $\overset{-}{Mn}(CO)_3$ species. Several other examples of acetylene insertion into M-S bonds were observed but with $[Fe(CO)_3SR]_2$ insertion into the Fe-Fe bond gave complexes $[Fe(CO)_3SR]_2CF_3C_2R'$, $R' = CF_3$, H. X-ray studies of $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ have revealed that this results in a significant change in the Fe_2S_2 ring geometry which allows the formation of the syn (axial, axial) isomer not observed in the parent complexes. $[CpCoSR]_2$ and $CF_3C{\equiv}CCF_3$ in contrast gave $CpCoC_6(CF_3)_6$ containing a tetrahapto hexakis(trifluoromethyl)benzene ligand.

Attempts have been made to rationalise the various reaction types in terms of the properties of possible reaction intermediates.

Reactions of certain cyclopentadienyl-nickel complexes with hexafluorobut-2-yne gave products resulting from condensation of the acetylene and a cyclopentadienyl ligand, e.g.

$$Cp_2Ni \;+\; CF_3C{\equiv}CCF_3 \longrightarrow CpNi[(C_5H_5)C_4(CF_3)_4]$$

while in other cases cyclooligomerisation of the acetylene was observed. These reactions have been rationalised in terms of acetylene coordination promoting a $\pi-\sigma$ rearrangement of a cyclopentadienyl ligand.

Several complexes were isolated in which a π-cyclopentadienyl ligand appears to have been replaced by a nickelacyclopentadiene ring, $CpNiC_4(CF_3)_4$, e.g. $Cp_2Ni_3C_6(CF_3)_6$, $CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$ and $[C_5H_5NiC_2(CF_3)_2]_4$. The crystal structure of the last has been solved and suggests that the molecule is formed by a Diels-Alder addition of the nickelacyclopentadiene ring of a dinuclear intermediate $[CpNiC_2(CF_3)_2]_2$ to the 1,2 positions of a cyclopentadienyl ring of a second dimeric species.

The reactions of $CpMo(CO)_3X$, X = Cl, Br, I, with acetylenes $RC{\equiv}CR$, $R = CF_3$, CH_3, have been found to give sixteen electron molybdenum complexes $CpMo(RC_2R)_2X$ and with $R = CH_3$ tetramethylquinone was also obtained. Variable temperature n.m.r. studies suggest that the coordinated acetylenes undergo an intramolecular exchange reaction at temperatures above $-25^{\circ}C$, $R = CF_3$, $+15^{\circ}C$, $R = CH_3$.

$CpMo(CO)_3X$ and $PhC{\equiv}CPh$ gave sixteen electron complexes $CpMo(CO)(PhC_2Ph)X$ at low temperatures ($< 50^{\circ}C$) or on photolysis in pentane. At higher temperatures the tetraphenylcyclobutadiene derivatives $CpMo(CO)(PhC)_4X$ were obtained.

Brief studies of reactions of acetylenes with transition metal trifluorophosphine complexes suggest that in certain cases the latter react in a similar manner to analogous carbonyl derivatives. $CpCo(PF_3)_2$ and $CF_3C{\equiv}CCF_3$ gave $CpCo[C_4(CF_3)_4PF_3]$ according to mass spectral evidence and this undergoes stepwise hydrolysis to $[CpCoC_4(CF_3)_4PO_2H]$ _via_ $CpCo[C_4(CF_3)_4POF]$. An X-ray study of the terminal hydrolysis product has revealed a structure containing a heterocyclic P(V) ring π-bonded to a cyclopentadienyl-cobalt moiety. This is analogous to $CpCo[C_4(CF_3)_4CO]$ obtained from the reaction of $CpCo(CO)_2$ and $CF_3C{\equiv}CCF_3$.

CONTENTS

INTRODUCTION

The emergence of organo-transition metal chemistry over the past twenty years has led to a new understanding of the principles which govern structure and bonding in all classes of chemical compounds. The development of coordination chemistry has now reached the point where modern theory can give a convincing explanation for many of the new classes of compounds which have been synthesised during the period of intense activity which followed the discovery of ferrocene in 1951.

Research into organo-transition-metal chemistry has necessarily been an interdisciplinary endeavour and consequently studies into the reactivity of coordinated ligands have led to organic synthesis via organo-transition-metal complexes. Many of the compounds produced by synthetic transition metal chemists have proved to be of immense use, not only in homogeneous catalysis, but to offer new routes to organic compounds, employing the principle of carbon skeleton assembly during complex formation. The many unsaturated compounds capable of forming π-bonds with transition metals frequently re-arrange to form new ligands, sometimes organic moieties being produced which are not capable of separate existence (cyclobutadiene), while in other cases entirely new organic compounds are formed.

Two areas of coordination chemistry which have attracted much attention in the past twenty years are those involving sulphide and acetylene complexes and it is with the organometallic chemistry of mercapto and acetylene ligands bearing fluorocarbon substituents, that this thesis is concerned.

INTRODUCTION

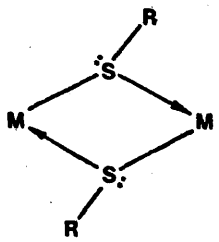
TRANSITION METAL SULPHUR CHEMISTRY

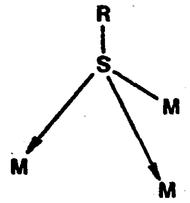
Transition-metal Mercapto Complexes

Since the early 1960's a rapid expansion of the literature on sulphur derivatives of the transition metals has occurred resulting in a comprehensive review in 1968.[1] The following introduction is not intended to be extensive in view of this situation and is limited to the chemistry of organo-transition metal mercaptides with emphasis on their stability, since this is of relevance to the contents of Chapter I. Two basic types of mercapto complex can be described, (i) those containing terminal RS ligands (R = organic group, e.g. CH_3, C_6H_5, CF_3, C_6F_5,) which function as one electron donors to a transition-metal (ii) those containing bridging RS ligands donating three or five electrons to two or three transition-metals respectively.

Structure and Bonding

In valence bond terms the metal sulphur bond in terminal mercapto complexes is formed by overlap of a tetrahedral sp^3 hybrid orbital on sulphur with a σ type orbital on the metal. In bridging mercapto derivatives one or two of the sulphur sp^3 hybrids containing a lone pair of electrons donates these to other metals to form a coordinate bond, e.g.



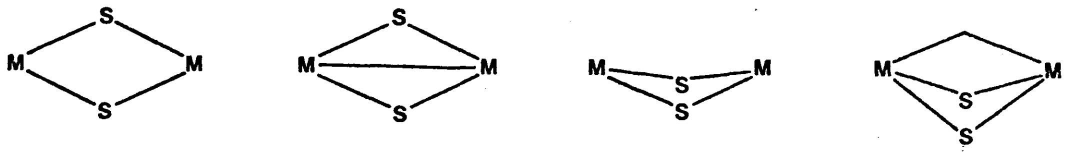


Like phosphorus, sulphur has empty d orbitals which, if energetically accessible, could accept excess electron density from filled d orbitals on the metal to form a metal-sulphur π-bond. However, little reliable information about the extent to which π-bonding contributes to the metal-sulphur linkage is at present available.[2]

An increase in CO stretching frequencies in mercapto derivatives of transition metal carbonyls is observed as the electron withdrawing ability of the organic group R in the mercapto ligand RS increases.[3,4,5,6] Since this greater electronegativity would possibly enhance the π acceptor ability of sulphur the implication is that the M-SR bond has significant π character. However, electron withdrawing substitution will also reduce the σ donor ability of sulphur producing a similar shift in CO stretching frequencies to high energy. It is therefore probable that shifts in carbonyl stretching frequencies reflect overall changes in σ and π components of the metal-sulphur bond[7] and not, as suggested by some workers,[4,5,6] modification to the π acceptor component alone.

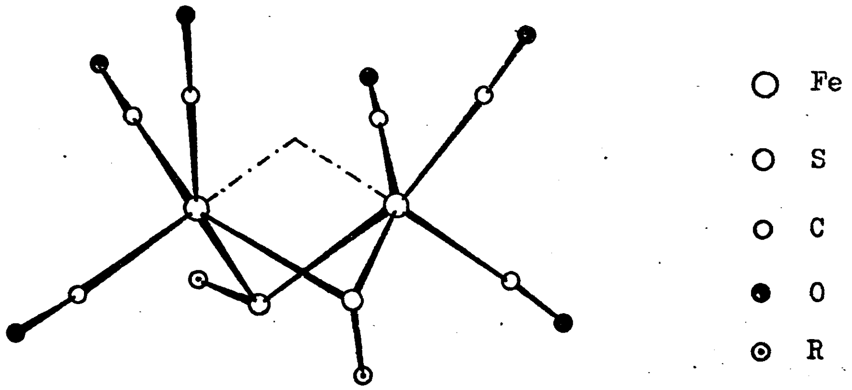
Attempts have been made to relate metal-sulphur and metal-phosphorus σ and π-bonding in $[Fe(CO)_3X]_2$ X = PR_2, SR to the ionisation potential of the ligand, and average Fe-CO ionic bond dissociation energies respectively, these being obtained from mass spectral data.[8] The results suggest that sulphur ligands are less efficient σ donors and surprisingly more efficient π acceptors than phosphorus ligands. However, Greenwood[46] and Dessy[9] have studied similar complexes using Mossbauer spectroscopy and suggest that transmission of negative charge in the sulphur complexes occurs mainly via σ rather than π orbitals.

Perhaps the most conclusive method of estimating π-bonding effects is by measuring the metal-sulphur bond length as revealed by X-ray diffraction studies. No crystal structures of terminal mercapto complexes have yet been reported but several studies of complexes containing bridging RS-ligands have been published in which various types of four membered M_2S_2 rings have been found. The four basic types of ring are shown here :



Planar Non Planar

From the X-ray data available[10] it can be concluded that the metal attempts to achieve either four or six coordination depending on the number and type of ligands coordinated to the metal. Thus the stereochemistry of the iron atoms in $[Fe(CO)_3SR]_2$ is pseudo-octahedral as a result of the grossly non-planar ring system.[11] With a planar



ring the metal atoms would be pentacoordinate with trigonal bipyramidal stereochemistry which is rarely found in transition metal chemistry.[12]

Unlike sulphur and phosphorus, nitrogen does not have energetically available d orbitals to from multiple bonds. Thus, from X-ray studies of transition metal complexes containing $M-NR_2$, $M-PR_2$ and M-SR linkages, it is possible, taking into account the different covalent radii of the bridging atoms, to estimate π-bond character in metal-sulphur and metal-phosphorus bonds. Comparison of M-X bond lengths $X = R_2N$, R_2P, RS, leads to the conclusion that transition-metal sulphur bonds do exhibit a slight shortening indicative of a small amount of dπ-dπ bonding. Thus the single bond covalent radius of sulphur is 1.04 Å so that a chromium-sulphur single bond distance should be close to 2.52 Å. In $[CpCr(NO)SPh]_2$† the average Cr-S bond length is 2.316 Å and the contraction of 0.2 Å therefore suggests some multiple-bond character.[13] Comparison of this metal-sulphur distance with the analogous metal-nitrogen distance in $[CpCr(NO)NMe_2]_2$ 1.99 Å confirms this conclusion.[14] Dahl and co-workers have reached similar conclusions from a comparison of Fe-X bond lengths in $[Fe(CO)_3X]_2$ X = NMe_2, SEt_2.[10] In the related complex $[CpCoPPh_2]_2$,[15] despite the fact that the estimated covalent radius of phosphorus is 0.06 Å greater than that of sulphur, the doubly-bridged Co-PPh_2 distances are significantly shorter than the comparable Fe-SEt distances in $[Fe(CO)_3SEt]_2$ suggesting that metal-phosphorus bonds have substantially greater multiple bond character than metal-sulphur bonds.

In planar or near planar M_2X_2 rings, in the absence of a metal-metal bond, the M-X-M angles are in the region of 100°. However, the presence of a metal-metal interaction produces a reduction in the M-M distance leading to very acute M-X-M angles in the region of 70°, a similar situation also being found in highly puckered rings with a metal-metal bond.[10] The strong M-M interaction which must exist in order to maintain such a distorted geometry has raised unanswered questions concerning the nature of the hybridisation and orbitals employed by the metal in these complexes. In $[Fe(CO)_3SEt]_2$ the octahedral valence model of Dahl[11] considers the Fe-S bond to result from overlap of an sp^3 orbital on the sulphur with a d^2sp^3 orbital

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† (Cp denotes a π-bonded cyclopentadienyl ligand, π-C_5H_5)

on the metal. However, the acute Fe-S-Fe bridge angle of 68.3° necessarily requires bent Fe-S bonds, since each bridging sulphur atom must use two equivalent orbitals to form normal electron-pair bonds to the two metal atoms, and equivalent orthogonal hybrids which point at an angle less than 90° from each other cannot be constructed from s and p orbitals. The situation seems less clear with $[Fe(CO)_3S]_2$ but the octahedral valence model is also favoured by Dahl[16] for this complex. It does however seem contradictory that the Fe-S distance in $[Fe(CO)_3S]_2$ is shorter than in $[Fe(CO)_3SEt]_2$ where because of the angular component the amount of orbital overlap is greater.

It has been pointed out that in the isostructural complexes $[Fe(CO)_3S]_2$, $[Fe(CO)_3SEt]_2$ $[Fe(CO)_3SC(C_6H_5)]_2$[17] the largest Fe-Fe distance is associated with the shortest Fe-S linkage suggesting that the sum of the bond energies of the orbital overlaps in Fe-Fe and Fe-S remains fairly constant. However, Dahl and co-workers have noted[15] in a structural comparison of $[CpNiPPh_2]_2$ and $[CpCoPPh_2]_2$, the latter of which has a metal-metal bond, that the metal phosphorus bond lengths are not affected by the immense structural alteration resulting from this bond.

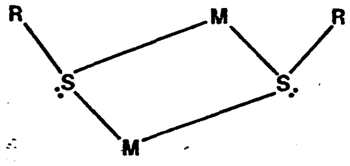
It therefore appears that the stability of the four types of M_2S_2 ring depends on a variety of factors. In the absence of a metal-metal bond maximum overlap of metal and sulphur orbitals can occur when the rings are planar[13] and it is notable that no great distortions from planarity have been observed in such rings. When metal-metal bonds are formed, despite the resulting apparent incomplete orbital overlap within the ring, no significant decrease in stabilty is noticeable. It seems probable that in M-M bonded rings the stability is a function of both M-S and M-M overlap but in view of the rather contradictory bond lengths in $[CpNiPPh_2]_2$ and $[CpCoPPh_2]_2$ and $[Fe(CO)_3S]_2$ the situation remains far from clear.

A consequence of the octahedral valence model presented by Dahl for highly distorted M_2X_2 rings is that the metal-metal bond arises through the non-colinear overlap of a pair of the apical orbitals, one from each metal. This results in the formation of a so called bent metal-metal bond which has aroused some controversy. The results of a single-crystal broad line ^{59}Co N.M.R. study of $Co_2(CO)_8$[18] which, according to Dahl's theory, would also contain a bent bond, do not support this conclusion but suggest the cobalt-cobalt interaction is direct. This is in agreement with the M.O. treatment of $Co_2(CO)_6PhC{\equiv}CPh$ presented by Brown[19] which predicts a direct metal-metal interaction, possibly through the 4pz orbitals.

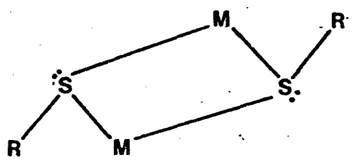
A recent qualitative symmetry-based molecular-orbital theory of the stereochemistry of di- and polynuclear complexes of the main group and transition metals containing bridging RS-, R_2P- and related ligands, has been presented by Mason.[20] This approach adequately explains the range of metal-metal distances found in these complexes and the linear relationship observed between this distance and the M-S-M angle in the sulphur derivatives. The size of the bridging ligand X in M_2X_2 rings is considered to be relatively unimportant in agreement with the conclusions of Dahl[10] and it is also suggested that S-S and M-S bond lengths should be independent of metal configuration. It is concluded, perhaps significantly, that M-M bond lengths, which are decided to a large extent by the electronic configuration of the metal, play the decisive role in determining the M-X-M bridge angles in M_2X_2 ring systems.

As a result of the X-ray studies described it is now well established that in di- and polynuclear complexes the sulphur, being divalent, has a pyramidal configuration. As a result, isomerism is possible due to the relative configurations of the organo groups R about the bridging sulphur atoms.[21,22]

With planar rings two isomers are usually possible, the syn and anti forms illustrated.



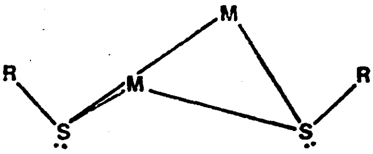
Syn



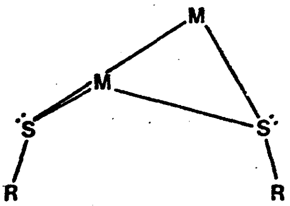
Anti

It can be seen that if for example R = CF_3 both isomers would each exhibit a single resonance in the ^{19}F N.M.R. spectrum. In many cases only one signal is observed at ambient temperature and this can be reconciled with the presence of only one isomer. Alternatively the inversion at sulphur could have a very low activation energy resulting in rapid flipping of the organic groups R above and below the plane of the M_2S_2 ring[22] to give only a single time averaged resonance. At low temperatures it has proved possible to identify both isomers of $[CpNiSCH_3]_2$[23] whereas the syn and anti forms of $Cp_2Ti(SMe)_2Mo(CO)_4$ can be detected at 34°C.[24] These results suggest that the barrier to inversion depends largely on steric interaction between the organic substituent on the sulphur and other ligands coordinated to the metal.

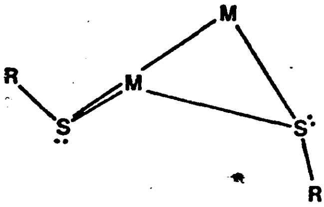
With non-planar M_2S_2 rings, as in e.g. $[Fe(CO)_3SR]_2$, three isomers are possible[11] now. In general when R is small e.g. CH_3,[25] CF_3,[26] two isomers can be detected, the syn (e,e) and anti (e,a) forms (e - equatorial, a - axial) but with bulky R groups only the anti



Syn (e,e)



Syn (a,a)



Anti (e,a)

isomer is observed.[27] In this type of complex the barrier to inversion appears to be relatively high compared with that in planar rings, since it has been possible to isolate both syn and anti forms of $[Fe(CO)_3SMe]_2$ by chromatography.[25] Studies of isomerism in a variety of similar complexes have been made by Bor and factors affecting isomer equilibria subsequently identified.[27]

Mononuclear Mercapto Complexes

The reactions of sulphur and sulphur derivatives with transition metal carbonyls and cyclopentadienyls have produced a wide variety of unusual organometallic complexes.[1] Considering the fairly extensive range of transition-metal mercaptides which also contain a π-bonded ligand it is perhaps surprising that it is only as recent as 1963[28] that a mononuclear derivative was first reported although at the time it was not recognised as such.

Dimethyldisulphide and $CpW(CO)_3H$ react to give a product originally formulated as $[CpW(CO)_2SMe]_2$[28] but which was later shown to be $CpW(CO)_3SMe$ by Knox and Havlin. These workers also prepared a range of similar complexes $CpM(CO)_3SR$, M = Mo, W, R = Me, Ph, C_6F_5 but $CpMo(CO)_3SMe$, could not be isolated, since it apparently decomposed under the conditions of formation to give $[CpMo(CO)_2SMe]_2$[29,30]. The C_6F_5S derivative on the other hand showed exceptional thermal stability and could not be decarbonylated to $[CpM(CO)_2SC_6F_5]_2$ M = Mo, W under any conditions. Later work by Stone showed that unstable monomers $M(CO)_5SC_6F_5$ M = Mn, Re, could be isolated from the reactions of $M(CO)_5H$ and C_6F_5SH under mild conditions, in contrast to similar reactions which gave dimeric, and even tetrameric complexes, with less electronegative groups attached to the sulphur. $Re(CO)_5SCF_3$ has since been isolated[3] but all attempts to obtain $Mn(CO)_5SCF_3$ have met with failure,[3,32] only dimeric $[Mn(CO)_4SCF_3]_2$ being isolated.

Monomeric complexes $CpFe(CO)_2SR$ have been reported with a wide variety of R groups [4] and it is notable that even the CH_3S derivative is fairly stable, thermal decarbonylation to $[CpFe(CO)SMe]_2$ being effected only above 70°C.[33] The C_6F_5S derivative could not be dimerised thermally or photochemically, even under severe conditions.[34,52]

It can be deduced from the results described that the thermal stability of mohomeric carbonyl mercapto complexes depends on several factors, in particular, (a) the metal, (b) other ligands coordinated to the metal, (c) the electron withdrawing ability of the organic substituent R on the sulphur. The last factor was originally recognised by Hayter[35,36] who prepared several monomeric $(CF_3)_2As$ complexes which exhibited unusually high thermal stability. In several cases monomeric selenium and tellurium derivatives have been isolated and their thermal stabilities found to decrease in the order RTe > RSe > RS.[37] Monomeric R_2P- complexes are known,[38] but are less common, since more drastic conditions are frequently required to prepare such derivatives, and dimerisation usually results. This will be discussed more fully in Chapter I with relevance to the mechanism of formation of RS- and R_2E-, E = P, As, complexes.

Di- and Polynuclear Mercapto Complexes

The fact that the mercaptide ligand could be used to bridge two metal atoms in a binuclear complex was realised many years ago and a large variety of such complexes are now known.

In addition to the doubly bridged complexes $[CpM(CO)_2SR]_2$ mentioned earlier[29,30] quadruply bridged $[CpMo(SMe)_2]_2$ is also known.[39,40] However, $[CpCr(CO)_3]_2$ and MeSSMe are reported to yield an unstable triply bridged species $(CpCr)_2(SMe)_3$ although the possibility that a bridging hydride ligand is also present cannot be discounted. A large variety of dimeric tetracarbonyl manganese and rhenium thiolates $[M(CO)_4SR]_2$ have been prepared from a variety of synthetic routes.[1]

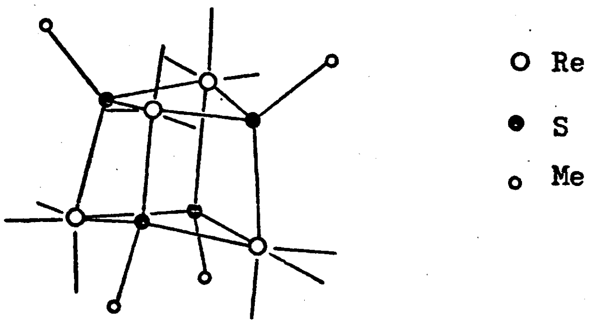
An X-ray study of the related seleno derivative $[\mathrm{Mn(CO)_4SeCF_3}]_2$[41] shows the $\mathrm{Mn_2Se_2}$ ring to be planar with the metal atom effectively octahedrally coordinated. The reaction of alkylthio derivatives of tin with $\mathrm{M(CO)_5X}$ M = Mn, Re, X = halogen results in the high yield formation of oligomeric tricarbonyl complexes.[1,42]

$$\mathrm{Mn(CO)_5Br} + \mathrm{Me_2Sn(SR)_2} \longrightarrow [\mathrm{Mn(CO)_3SR}]_n$$

These derivatives are also obtained in low yield by thermal or photochemical decarbonylation of the dimers $[\mathrm{M(CO)_4SR}]_2$.[1]

Although the alkylthio-tricarbonyls of Mn and Re were originally formulated as trimers on the basis of molecular weight studies in benzene,[31,42] mass spectral studies indicated that the manganese compounds exist as tetramers in the vapour state.[43] A similar situation exists in the crystal state of $[\mathrm{Re(CO)_3SMe}]_4$, an X-ray study[44] of which has revealed an almost regular tetrahedron of rhenium atoms with each sulphur atom equidistant from the three nearest metal atoms and the $\mathrm{CH_3}$-S bonds normal to the triangular planes of the tetrahedron. Thus each rhenium atom achieves the favoured eighteen electron configuration without the formation of formal metal-metal bonds.

(CO groups omitted)



$[\mathrm{Fe(CO)_3SEt}]_2$ the first known carbonyl mercaptide was prepared as long ago as 1928[45] and many similar derivatives are now known.[1]

Substitution of carbonyl groups in these complexes by phosphines arsines and stibenes has been studied extensively and a variety of complex behaviour found.[46,47] In the reactions of $[Fe(CO)_3SPh]_2$ and PR_3, R = Et, OMe, in addition to CO substitution, bridge cleavage was also observed to give $Fe(CO)_3(PR_3)_2$. Mononuclear intermediates were postulated to account for some of the isomeric products obtained and it was concluded that the reactivity of $[Fe(CO)_3SR]_2$ towards group V donor ligands is related to the ease of cleavage of the bridging sulphido ligands, this being more facile with R = Ph than when R = Me, Et.[47] This is in agreement with the stability of monomeric complexes containing terminal RS ligands described earlier.

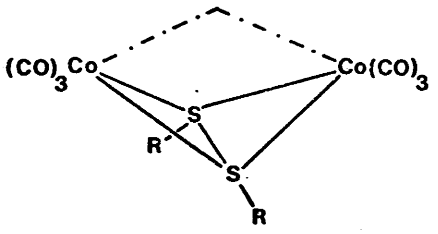
In addition to the dimeric tricarbonyl complexes just described, various derivatives of a polymeric nature are frequently obtained from the reaction of the iron group carbonyls with disulphides, but little is known about their structures.[48] $Fe(CO)_2(NO)_2$ reacts with organosulphur compounds RSX, X = H, RS to give dimeric complexes $[Fe(NO)_2SR]_2$[49] but unlike the tricarbonyl derivatives the Fe_2S_2 ring is planar and the metal atoms tetrahedrally coordinated.[50]

Decarbonylation of the dicarbonyls $CpFe(CO)_2SR$ described earlier gives the dimers $[CpFe(CO)SR]_2$ which exist in two isomeric forms, one of which is thermodynamically more stable than the other. Extensive studies of the stability of the monomers and dimers and isomers of the latter have been carried out by Knox[4,51,52] and this is discussed in greater detail in Chapter I.

Cobalt carbonyl was originally reported to react with mercaptans to yield complexes of empirical formula $[Co(CO)_3SR]_2$[53] R = Ph, Et but subsequent workers have been unable to reproduce these results.[54] Instead, complex reactions have been found which give a variety of complexes depending on reaction conditions, e.g. $Co_4(CO)_5SEt)_7$

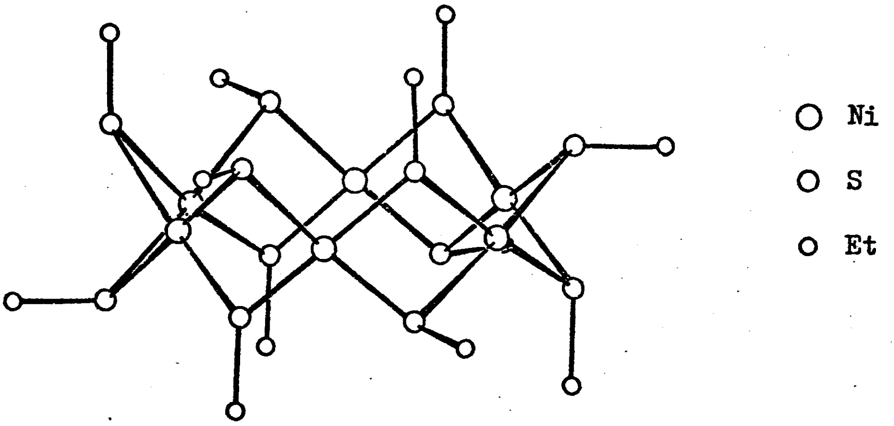
$Co_4(CO)_7(SEt)_3$,$Co_3(CO)_9SPh$[55] etc. and in some cases $Co_3(CO)_9S$, $Co_3(CO)_7S_2$ and $[Co_2(CO)_5S]_n$ are found indicating C-S bond scission. X-ray structures of several of these complexes have been reported by Dahl.[1,56]

However, the observation that electron withdrawing substituents attached to sulphur tend to inhibit formation of polynuclear complexes led Bor and co-workers to investigate the reactions of $Co_2(CO)_8$ with disulphides RSSR, R = C_6F_5.C_6Cl_5, which gave dinuclear complexes $[Co(CO)_3SR]_2$.[57] The number and intensity of CO stretching modes in the i.r. spectra of these derivatives according to Bor suggest the presence of a metal-metal bond, which is only possible if the S-S bond is retained and the sulphur atoms are tetravalent. An X-ray diffraction study of these derivatives would be desirable in view of this unusual and unexpected bonding situation,particularly since the phosphido complexes $[Co(CO)_3PR_2]_2$ R = Ph,[58] CF_3,[59] are also known which give similar infra red spectra.



$CpCo(CO)_2$ and dimethyldisulphide react with complete CO expulsion to give $[CpCoSMe]_2$ for which a puckered ring structure similar to $[Fe(CO)_3SEt]_2$ is proposed.[60] However, $[CpNiSR]_2$, R = Me, Et, Ph obtained from the reaction of nickelocene and RSH,[61] probably have planar M_2S_2 ring systems. Interestingly, the reaction of nickelocene and C_6F_5SH gives black polymeric $[CpNiSC_6F_5]_n$.[34]

High polymer mercaptides were originally obtained from the reaction of $Ni(CO)_4$ and disulphides[62] but soluble hexamers were also obtained by later workers. An X-ray study of one of these $[NiSEt]_6$[63] has revealed an interesting 'crown' structure.



CHAPTER I

PREPARATION AND REACTIONS

OF

TRIFLUOROMETHYLTHIO AND

PENTAFLUOROPHENYLTHIO-METALLATES

INTRODUCTION

Recently several trifluoromethylthio derivatives of transition-metal carbonyls and cyclopentadienyls were prepared (1) from the metathetical reaction between $AgSCF_3$ and carbonyl halides,[3,64] and (2) from the thermal cleavage of CF_3SX, X = SCF_3, SCH_3, Cl, $P(CF_3)_2$, in the presence of metal carbonyls.[32,65] Early attempts to prepare CF_3S derivatives using the disulphide CF_3SSCF_3 were unsuccessful[66] but an alternative method of synthesis was suggested by recent work in these laboratories. On photolysis in pyrex apparatus CF_3SSCF_3 gives adducts and telomers with olefins and perfluoro-olefins in reactions which may be explained in terms of the presence of trifluoromethylthio radicals.[67] On irradiation CF_3SSCF_3 has been reported to give $(CF_3S)_2Hg$[68] in the presence of mercury, CF_3SNF_2[69] in the presence of F_2NNF_2 and CF_3SCl[70] in the presence of $(COCl)_2$. All of these reactions are postulated to proceed through CF_3S radicals produced by homolytic cleavage of the disulphide. These radicals are also postulated as intermediates in the formation of $(CF_3)_2S$ on irradiation of CF_3SSCF_3 in quartz reaction vessels, small quantities of elemental sulphur also being formed[68] indicating C-S as well as S-S bond fission. However, no reaction was observed in pyrex reactors and it is noteworthy that irradiation of CF_3SSCF_3 and olefins in quartz vessels does not give clean products.[67] It appears that the filtering action of the pyrex towards high energy radiation inhibits C-S bond cleavage thus facilitating the formation of CF_3S radicals.

It was therefore decided to study the photolytic reactions of CF_3SSCF_3 and transition metal carbonyls and cyclopentadienyls in pyrex reaction vessels with a view to the preparation of new complexes containing the CF_3S ligand(s). These studies were subsequently found to be successful[71] and the photolytic method extended to the preparation of C_6F_5S derivatives from $C_6F_5SSC_6F_5$.[71b]

General Experimental Methods

Manipulation of non-volatile materials was carried out in a dry oxygen-free, nitrogen atmosphere in a Lintott inert atmosphere box. Volatile materials were transferred using standard vacuum-line techniques. Hydrocarbon solvents were dried over sodium and deaerated before use. Unless stated otherwise, photolytic reactions were carried out in pyrex reaction flasks irradiated by a Hanovia medium pressure mercury lamp, the reaction mixtures being stirred magnetically. Molecular weights were determined by mass spectrometry. Melting points (uncorrected) of air stable compounds were determined on a Reichert hot-stage apparatus and those of air sensitive compounds in sealed capillaries under nitrogen.

Elemental analysis are by Alfred Bernhardt, Mikroanalytisches Laboratorium, West Germany.

Infra-red (i.r.) spectra were recorded as solutions (solvents indicated in Tables 1.1. and 1.2.) in 0.1 mm cells with KBr windows, obtained from R.I.I.C.. Spectra were recorded on Perkin Elmer 225 or 457 spectrophotometers calibrated against carbon monoxide, water vapour, methane and ammonia from Tables of Wavenumbers for the Calibration of Infra-red Spectrometers, I.U.P.A.C. monograph, London, Butterworths 1961. The following abbreviations have been used in the text : s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very; ν, stretch.

Mass spectra were recorded at 70 eV using an A.E.I. M.S. 12 spectrometer with source temperature as stated in the text. Samples were introduced into the ionisation temperature by means of the probe inlet.

N.m.r. spectra were recorded on Perkin Elmer R 10 and Jeol C 60 H.L. spectrometers operating at 60 m.Hz. for ^{1}H and 56.4 m.Hz. for ^{19}F n.m.r. spectra. Probe temperatures were R 10 34°C, C 60 H.L. 20°C. Spectra were recorded in CH_2Cl_2 solution, ^{19}F, and $CDCl_3$, ^{1}H, with CCl_3F and Me_4Si, (T.M.S.) respectively, as internal references.

$$\text{TMS} = 10.0\ \tau$$

$$CCl_3F = 0.0 \text{ ppm}$$

SUMMARY OF REACTIONS

(1) $RSSR + [CpM(CO)_3]_2 \xrightarrow{u.v.} CpM(CO)_3SR$ M = Mo, W

R = CF_3, C_6F_5

(2) $CpMo(CO)_3SCF_3 \xrightarrow{\Delta} [CpMo(CO)_2SCF_3]_2 + [CpMoCOSCF_3]_3$

$CpW(CO)_3SCF_3 \xrightarrow{\Delta} [CpW(CO)_2SCF_3]_2$

(3) $RSSR + Mn_2(CO)_{10} \xrightarrow{h\nu} Mn(CO)_5SR$

(4) $Mn(CO)_5SR \xrightarrow{\Delta} [Mn(CO)_4SR]_2$

(5) $RSSR + [CpFe(CO)_2]_2 \xrightarrow{h\nu} CpFe(CO)_2SR$

$CpFe(CO)_2SCF_3 \xrightarrow{h\nu} [CpFe(CO)SCF_3]_2$

(6) $CF_3SSCF_3 + Co_2(CO)_8 \xrightarrow{h\nu} Co_3(CO)_9CF + [Co_2(CO)_5S]_n$

(7) $C_6F_5SSC_6F_5 + Co_2(CO)_6 \xrightarrow{h\nu} [Co(CO)_3SC_6F_5]_2$

(8) $RSSR + [CpNiCO]_2 \xrightarrow{h\nu} CpNiCOSR$

$CpNiCOSR \xrightarrow{\Delta} [CpNiSR]_n$ R = CF_3, n = 2

R = C_6F_5, n = ?

(9) $[CpNiSCF_3]_2 + PPh_3 \longrightarrow CpNiPPh_3SCF_3$

(10) $CF_3SSCF_3 + M(CO)_6 \xrightarrow{h\nu} [M(CO)_4SCF_3]_2$ M = Mo, W

(11) $\mathrm{CF_3SSCF_3 + Fe(CO)_5 \xrightarrow{h\nu} [Fe(CO)_3SCF_3]_2 + [Fe_2(CO)_6SCF_3]_2S}$

$\mathrm{+ Fe_3(CO)_9S_2 + [Fe(CO)_3S]_2}$

(12) $\mathrm{CF_3SSCF_3 + Fe_2(CO)_9 \xrightarrow{h\nu}}$ " $\mathrm{+ Fe(CO)_5}$

(13) $\mathrm{C_6F_5SSC_6F_5 + Fe_2(CO)_9 \xrightarrow{h\nu} [Fe(CO)_3SC_6F_5]_2}$

(14) $\mathrm{[Fe(CO)_3SCF_3]_2 + PPh_3 \longrightarrow Fe_2(CO)_5(PPh_3)(SCF_3)_2}$

$\mathrm{\longrightarrow [Fe(CO)_2PPh_3SCF_3]_2}$

(15) $\mathrm{[Fe(CO)_3SCF_3]_2 + NO \longrightarrow [Fe(NO)_2SCF_3]_2}$

(16) $\mathrm{CF_3SSCF_3 + CpCo(CO)_2 \xrightarrow{h\nu} [CpCoSCF_3]_2}$

(17) $\mathrm{CF_3SSCF_3 + CpCo(CO)_2 \xrightarrow{\Delta} CpCo(CO)(SCF_3)_2}$? + unidentified products

(18) $\mathrm{C_6F_6SSC_6F_5 + CpCo(CO)_2 \xrightarrow{h\nu} CpCo(CO)(SC_6F_5)_2 + [CpCoSC_6F_5]_2}$

(19) $\mathrm{C_6F_5SSC_6F_5 + CpCo(CO)_2 \xrightarrow{20^\circ C} [CpCoSC_6F_5]}$

(20) $\mathrm{C_6F_5SSC_6F_5 + CpCo(CO)_2 \xrightarrow[pentane]{20^\circ C} CpCo(CO)(SC_6F_5)_2}$

(21) $\mathrm{CpCoCO(SC_6F_5)_2 \xrightarrow{\Delta/h\nu} [CpCoSC_6F_5]_2 + CpCo_2(CO)(SC_6F_5)_3}$?

RESULTS AND DISCUSSION

(A) Reactions of Dinuclear Transition-metal Carbonyls with Disulphides CF_3SSCF_3 and $C_6F_5SSC_6F_5$

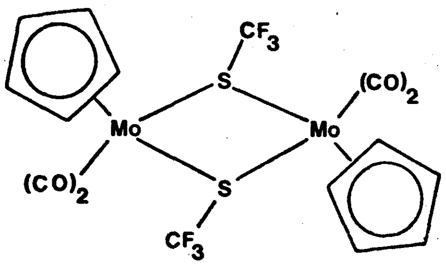
Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $[CpM(CO)_3]_2$, M = Mo, W

The cyclopentadienyl complexes $[CpM(CO)_3]_2$, M = Mo, W, reacted with CF_3SSCF_3 in pentane to give orange-yellow crystalline solids $CpM(CO)_3SCF_3$, M = Mo, Ia, M = W, Ib in 80% yield. Ia was also obtained from $CpMo(CO)_3I$ but in much lower yield. Irradiation of $[CpMo(CO)_3]_2$ and $C_6F_5SSC_6F_5$ in pentane similarly gave $CpMo(CO)_3SC_6F_5$, II, in 70% yield. The CF_3S complexes have similar spectroscopic properties to other mercapto complexes of this type isolated by Knox, who also prepared complex II.[29,30] The mass spectra of Ia and Ib give molecular ions and stepwise loss of carbonyl groups while in the i.r. spectra three CO stretching modes ($2a_1$, a_2) are observed indicating the low symmetry of the molecules (Cs). On this basis a square pyramidal structure is suggested similar to that of $CpMo(CO)_3C_2F_5$ as revealed by X-ray diffraction studies.[72] The ^{19}F n.m.r. spectra in each case gives a sharp singlet at low field in the region (20 ppm - 30 ppm) expected for terminal CF_3S ligands.[3,64]

Due to the CF_3 group reducing the basicity of the lone pairs on the sulphur[3] the thermal stability of these monomers is expected to be greater than that of $CpMo(CO)_3SR$, R = Me, Ph described by Knox[29] and the following decarbonylation temperatures support this contention $CpMo(CO)_3SCF_3$ ~ 40°C, $Cp\text{-}Mo(CO)_3SPh$ ~ 20°C, $CpMo(CO)_3SMe$ ~ 20°C, $CpW(CO)_3SCF_3$ ~ 65°C.

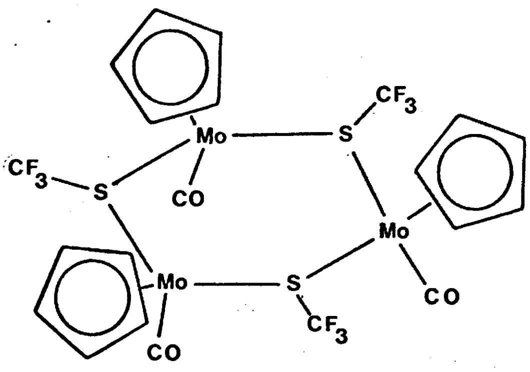
However $CpM(CO)_3SC_6F_5$, M = Mo, W could not be decarbonylated under any conditions.[30]

Thermal decarbonylation of I(a) in refluxing hexane (70°C) gave reasonable yields of the dark brown solid $[CpMo(CO)_2SCF_3]_2$, IIIa which from i.r. and n.m.r. evidence contains bridging CF_3S groups.[3] The mass spectrum does not give a molecular ion, the highest peak corresponding to $[CpMo(CO)SCF_3]_2^+$. In the i.r. spectrum two strong νCO bands are observed suggesting that the carbonyl ligands are <u>trans</u> to each other since the <u>cis</u> isomer would give three terminal CO stretching modes. Two isomers of $[CpM(CO)_2SMe]_2$ exist in solution[28] giving rise to five CO stretching modes, but as with other similar derivatives, e.g. $[CpM(CO)_2SPh]_2$, M = Mo, W,[29] $[CpMo(CO)_2As(CF_3)_2]_2$[35] only the <u>trans</u> isomeric forms are possible for IIa based on <u>cis</u> and <u>trans</u> SCF_3 ligands and the various configurations of the Cp and CO ligands, so it is obviously impossible to identify the isomer isolated from spectral data. A singlet in the ^{19}F n.m.r. spectrum could be reconciled with various possible structures, or alternatively with rapid inversion at sulphur. However, based on the gauche configuration indicated by the i.r. spectrum, steric interactions are probably at a minimum in the <u>trans</u>-gauche isomer indicated below.



Traces of a green solid III were also isolated from the thermal decomposition products of the monomer, but insufficient was obtained for full characterisation. The i.r. spectrum gives a broad band and a shoulder in the terminal CO stretching region and C-F stretching modes near 1100 cm^{-1} characteristic of bridging CF_3S groups. The highest ion in the mass spectrum is observed at m/e 580 = $[CpMo(CO)SCF_3]_2^+$, cf. $[CpMo(CO)_2SCF_3]_2$, but the low solubility of the complex suggests a tri- or tetranuclear species which fragments to the stable dimer in the mass spectrometer.

The reaction of $[CpMo(CO)_3]$ and $(PPh_2)_2$ has been reported by Hayter[73] to give dark green $[CpMo(CO)PPh_2]_3$ which gives a single νCO frequency in the i.r. spectrum. On the basis of its similarity to this phosphido derivative it is tentatively suggested that III is trimeric and has the following structure.



Two isomers are possible (neglecting the disposition of CF_3 groups) but the ^1H and ^{19}F spectrum each give a single resonance in agreement with the postulated structure. The two νCO modes in the i.r. spectrum are also in agreement with this conclusion.

Isolation of the dimeric tungsten complexes $[CpW(CO)_2SCF_3]_2$ IIIb was not achieved but spectral evidence was obtained for its existence as one of the products formed in the thermal decomposition of $CpW(CO)_3SCF_3$. After heating the latter for 4 hr. in vacuo at 85°C an infra-red spectrum of the crude product showed, in addition to weak bands due to the starting material, two strong peaks in the terminal CO stretching region suggesting the trans isomer by analogy with the i.r. spectrum of the molybdenum complex $[CpMo(CO)_2SCF_3]_2$. In the C-F stretching region two sets of two bands were observed characteristic of bridging trifluoromethylthio groups. However, attempted decarbonylation of the remaining $CpW(CO)_3SCF_3$ by further heating resulted in decomposition of both complexes and a pure sample of the dimeric species was not obtained.

Further attempts to obtain $[CpW(CO)_2SCF_3]_2$ by thermal and photochemical decarbonylation of the monomer were unsuccessful and this can probably be attributed to the differences in reactivity of molybdenum and tungsten derivatives noted by other workers.[74] Evidence for the existence of IIIb was obtained from the mass spectrum of $CpW(CO)_3SCF_3$ at 180°C in which a weak ion at m/e 756 and fragments at lower m/e values are observed. This ion corresponds to $[CpW(CO)SCF_3]_2^+$ and by comparison with the mass spectrum of $[CpMo(CO)_2SCF_3]_2$ is considered to result from the thermal decarbonylation of $CpW(CO)_3SCF_3$ to give IIIb in the mass spectrometer.

Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $Mn_2(CO)_{10}$

Irradiation of CF_3SSCF_3 and $Mn_2(CO)_{10}$ in pentane in a closed reaction system gave a pale yellow solution which, according to the i.r. spectrum, contained $Mn(CO)_5SCF_3$, V. It was not possible to isolate a pure sample of the product due to its thermal instability but pale yellow crystals containing 80-90% $Mn(CO)_5SCF_3$, 10-20% $[Mn(CO)_4SCF_3]_2$, VI, could be obtained by careful work up of the product solution. During solvent removal rapid evolution of carbon monoxide occurs to give $[Mn(CO)_4SCF_3]_2$, VI, but this can be minimised by cooling the solution to -10°C prior to this.

A sample of the impure product mixture gives a ^{19}F n.m.r. spectrum containing, in addition to a peak at 34.2 ppm due to VI, a sharp singlet at 25 ppm attributed to the monomer V. On allowing the solution to sit at room temperature in an open n.m.r. tube this signal gradually disappeared as the dimer resonance increased in intensity. This decomposition was also followed by i.r. spectroscopy, the two C-F stretching modes at 1129 cm^{-1} and 1085 cm^{-1} attributed to $Mn(CO)_5SCF_3$ being replaced by the four C-F stretching modes of the dimer VI. The pentacarbonyl gives three strong CO stretching modes characteristic of an $M(CO)_5X$ species of C_{4v} symmetry.[75] However, with strong solutions a fourth weak band at 2090 cm^{-1} was detected and since the very intense band at 2052 cm^{-1} is broadened it appears that the non axial symmetry of the CF_3S ligand is sufficient to activate the B_1 mode and almost split the degeneracy of the E mode.[76] With $Mn(CO)_5SC_6F_5$ this distortion from C_{4v} symmetry is even more pronounced and all five stretching modes of a Cs molecule are clearly resolved.[31]

Grobe,who reacted $NaMn(CO)_5$ and CF_3SCl at 20°C in an attempt to prepare V could only isolate $[Mn(CO)_4SCF_3]_2$, but postulated that this was produced <u>via</u> the monomer. [32] King reacted $Mn(CO)_5Cl$ and $AgSCF_3$ at room temperature and also obtained the dimer.[3] The nature of such metathetical reactions suggests that open reaction systems were employed by these two workers so that carbon monoxide evolution and dimerisation is facilitated, whereas the closed reactions employed in this work inhibits this occurrence. King's method, when employed with $Re(CO)_5Cl$ and $AgSCF_3$, gives a mixture of $Re(CO)_5SCF_3$ and $[Re(CO)_4SCF_3]_2$,[3] thus indicating the rhenium monomer to be more stable than its manganese analogue, as is the case with the C_6F_5S derivatives.[31] The latter were obtained in low yield from the reaction of $M(CO)_5H$ and C_6F_5SH, at room temperature by Stone and co-workers.[31] However, the photolytic reaction of $C_6F_5SSC_6F_5$ and $[Mn(CO)_5]_2$ in pentane, besides being more convenient, gives much higher yields (~90%) of $Mn(CO)_5SC_6F_5$ VII than Stone's method (~ 7%). The thermal stability of VII is measurably greater than that of $Mn(CO)_5SCF_3$ and, since attempts by Stone to obtain $Mn(CO)_5SC_6H_5$ and $Re(CO)_5SC_6H_5$ met with failure,[31] the following order of monomer stability is indicated.

$$M(CO)_5SCF_3 > M(CO)_5SC_6F_5 > M(CO)_5SC_6H_5 \qquad M = Mn, Re$$

$[Mn(CO)_4SCF_3]_2$ and $[Mn(CO)_4SC_6F_5]_2$ which result from thermal decarbonylation of the respective monomeric pentacarbonyls have been reported previously[3,65] but they are accessible in much greater quantities <u>via</u> this photolytic method. The i.r. spectra in the CO stretching region are similar to that of $[Mn(CO)_4SeCF_3]_2$,[77] X-ray studies[41] of which have revealed a planar M_2Se_2 ring and octahedrally coordinated metal atoms.

On photolysing or refluxing $Mn_2(CO)_{10}$ mercaptan mixtures in inert solvents, tetrameric complexes $[Mn(CO)_3SR]_4$ are obtained in low yield.[1] However, attempts to produce a similar CF_3S derivative from $[Mn(CO)_4SCF_3]_2$ by photolytic and thermal degradation were unsuccessful, only insoluble decomposition material and $Mn_2(CO)_{10}$ being formed. Similar unsuccessful results have been reported with $[Re(CO)_4SC_6F_5]_2$[31], and since $[Mn(CO)_3SC_6F_5]_4$[1] obtained <u>via</u> organotin thiolates proved to be unstable, it is probable that $[Mn(CO)_3SCF_3]_2$, although it may be accessible from $R_2Sn(SCF_3)_2$ and $Mn(CO)_5Br$, will also prove to be unstable. The X-ray study[44] of $[Re(CO)_3SCH_3]_4$ revealed that both lone pairs on each sulphur atom are involved in bridge formation and with electron withdrawing substituents CF_3 and C_6F_5 attached, the ability of sulphur to form extended bridge systems must be impaired significantly.

<u>Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $[CpFe(CO)_2]_2$</u>

The thermal reaction of $CpFe(CO)_2I$ and $AgSCF_3$ gave[3] a single monomeric complex $CpFe(CO)_2SCF_3$ VIII in 48% yield and this has now been prepared from the photolytic reaction of $[CpFe(CO)_2]_2$ and CF_3SSCF_3 in 64% yield. Substitution of Cl in $CpFe(CO)_2Cl$ gives VIII in lower yield (37%). Photolysis of $[CpFe(CO)_2]_2$ and $C_6F_5SSC_6F_5$ in pentane similarly gives $CpFe(CO)_2SC_6F_5$ but in much lower yield than the thermal reaction reported by Stone.[34]

$CpFe(CO)_2SCF_3$, like the C_6F_5S complex, is thermally very stable since attempted decarbonylation at 100°C in vacuo, and in hexane solution, was unsuccessful. This compares with the successful decarbonylation of $CpFe(CO)_2SR$, R = Me, Et, Ph, which gives two isomeric forms of the dimer $[CpFe(CO)SR]_2$.[4] However, it was observed that the photochemical reaction, in addition to VIII, gave traces of a soluble green complex, the i.r. spectrum of which exhibits CO and CF stretching modes. Photolytic decarbonylation of the monomer VIII was therefore attempted and the following interesting behaviour found.

Irradiation with unfiltered u/v light of a pentane solution of VIII in an open reactor, under nitrogen, gave a dark green solution containing a mixture of two isomers of the dimer $[CpFe(CO)SCF_3]_2$ IX, A and B. With short irradiation times mainly isomer A was observed but prolonged reaction times resulted in increased quantities of B. Both isomers are olive green, reasonably air stable solids which give similar mass spectra with a molecular ion at m/e 500 confirming the dimeric formulation. Other dimers $[CpFe(CO)SR]_2$, resulting from decarbonylation of the monomers, $CpFe(CO)_2SR$, have been reported by Knox, who found that the isomer first produced is kinetically controlled and this decomposes in solution to the thermodynamically favoured isomer.[4,51] The behaviour of isomers A and B of IX resembles that described by Knox but as can be seen in Fig. 1.1. significant differences are also observed.

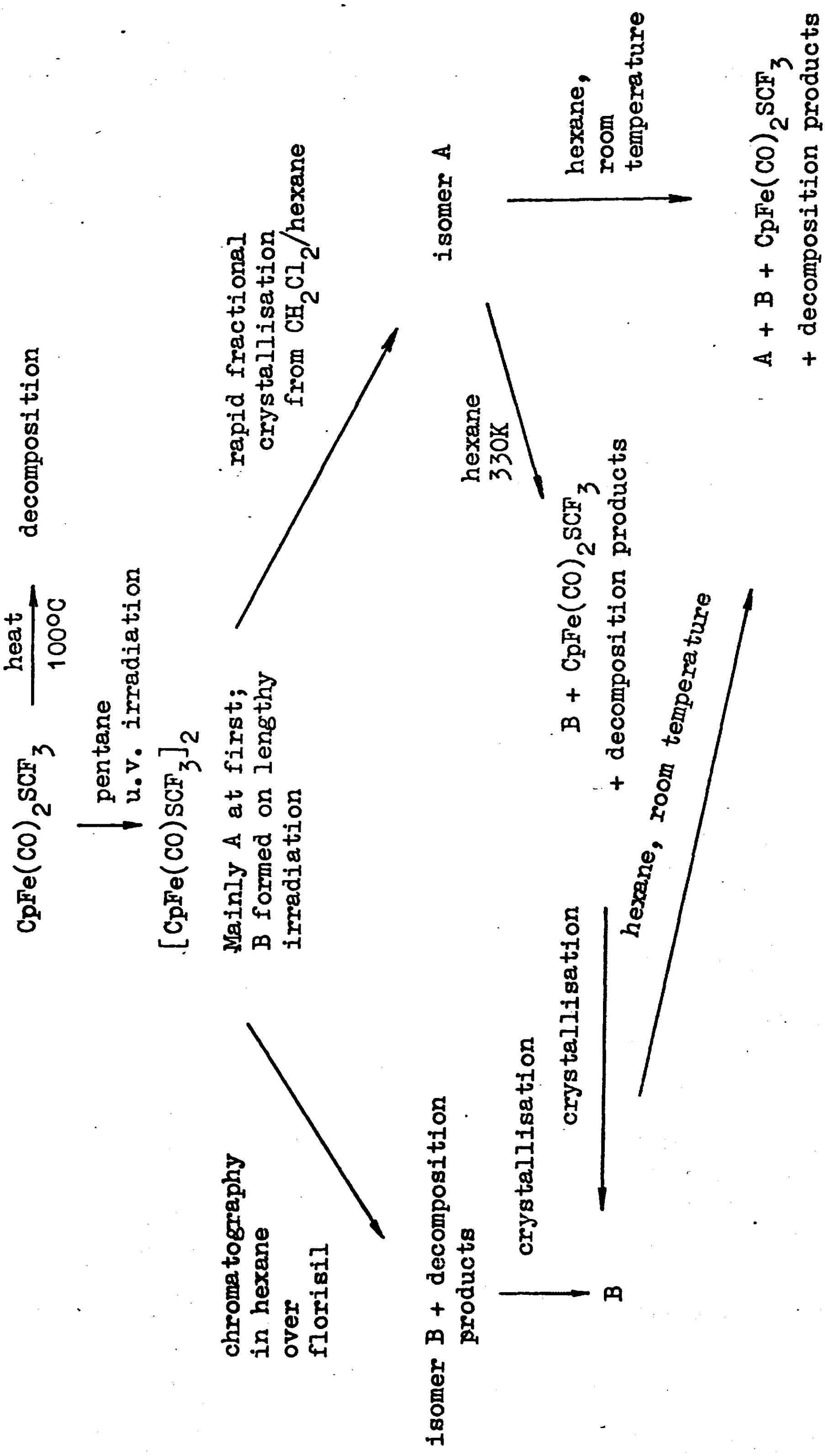

CpFe(CO)$_2$SCF$_3$
heat
100°C
decomposition
pentane
u.v. irradiation
[CpFe(CO)SCF$_3$]$_2$
Mainly A at first;
B formed on lengthy
irradiation
rapid fractional
crystallisation
from CH$_2$Cl$_2$/hexane
isomer A
hexane,
room
temperature
A + B + CpFe(CO)$_2$SCF$_3$
+ decomposition products
hexane
330K
B + CpFe(CO)$_2$SCF$_3$
+ decomposition products
chromatography
in hexane
over
florisil
isomer B + decomposition
products
crystallisation
B
crystallisation
hexane, room temperature

Fig. 1.1.

It was reported that isomer conversion was in no way an equilibrium reaction since the thermodynamically favoured isomer did not revert to the kinetically controlled isomer under any conditions. In contrast, facile interconversions of A and B can be achieved simply by changing the temperature, with B favoured at higher temperatures. A second notable difference is the formation of mononuclear $CpFe(CO)_2SCF_3$ by disproportionation of the dimer, a reaction not observed with the alkyl and aryl mercapto compounds. In addition a strong ion due to $CpFe(CO)_2SCF_3^+$ was observed in the mass spectrum of the dimer IX. These observations would seem to suggest that $CpFe(CO)_2SCF_3$ is thermodynamically more stable than the dimer, thus explaining the original unsuccessful attempts to decarbonylate the former by thermal methods. It appears that the lone pair electrons on sulphur are of sufficiently low basicity to render the dimer thermodynamically unstable and it is significant that $CpFe(CO)_2SC_6F_5$ cannot be decarbonylated by thermal[34] or photochemical[52] means, thus confirming what has already become apparent, that monomeric C_6F_5S derivatives are even more stable with respect to decarbonylation than their CF_3S analogous.

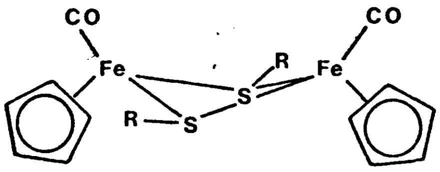
Spectroscopically the two isomers of $[CpFe(CO)SCF_3]_2$ are very similar. In each case both ^1H and ^{19}F n.m.r. spectra give only a single sharp resonance indicating equivalence of the pairs of CF_3 and Cp groups, or an achievement of equivalence through fluxional behaviour. In the terminal CO stretching region isomer A gives two strong bands while isomer B gives only one.

It is apparent from this evidence that unequivocal assignment of structures to these isomers is not possible since a minimum of five geometrical forms can exist depending on the geometry of the Fe_2S_2 ring.[4,51]

An X-ray study[78] of the 'stable' isomer of $[CpFe(CO)SPh]_2$ has revealed a slightly non planar ring with an angle of fold near 17°. The Fe-Fe intramolecular distance 3.39 Å is too long to accommodate a metal-metal bond but this is precluded in any case by consideration of the diamagnetism of the complex. The two cyclopentadienyl and two carbonyl ligands are mutually cis and the phenyl groups have the syn e,e configuration in agreement with the reported ^1H n.m.r. spectrum. However, the i.r.[51] spectrum appears to contradict the cis arrangement of carbonyl ligands since if this geometry is retained in solution two CO stretching frequencies are expected, but only one is observed at 1922 cm^{-1}. The 'stable' isomers of $[CpFe(CO)SR]$ are also reported to give one CO stretching mode. However, the cis isomers of $[CpFe(CO)ER_2]_2$, E = P; R = Me, Ph; E = As; R = Me, which are clearly identifiable by n.m.r. spectroscopy[79] also give only a single band indicating that, in certain cases, coupling between the vibrations of two carbonyl groups is minimal.

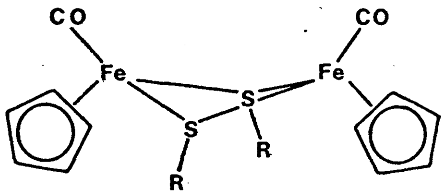
Sim and co-workers have studied the stereochemistry of cis and trans isomers of $[CpCr(NO)NMe_2]_2$[14] by X-ray diffraction methods and have clearly shown that, if the cyclopentadienyl ligands are cis, slight puckering of the M_2X_2 ring occurs as in $[CpFe(CO)SPh]_2$. In the trans isomer of $[CpCrNONMe_2]_2$ and $[CpCr(NO)SPh]_2$[13] however, the ring is rigorously planar. Puckering of the ring in cis isomers is considered to arise from coulombic repulsion between the lone pair on sulphur and the bonding electrons in the M-Cp bond as in $Cp_2Mo(SBu^n)_2FeCl_2$,[80] but since this is not possible in the dimethylamido complex, repulsion between the cyclopentadienyl ligands and the substituents on the bridging atoms must also be important. On the basis of the above observations it is predicted that the all-trans structure of $[CpFe(CO)SCF_3]_2$, if it can exist, probably has a planar Fe_2S_2 ring. Such a structure is in accord with the n.m.r. data for isomer B and would also fit the i.r. spectroscopic data where only one CO stretching mode is required. However, isomer A, which gives two CO modes, on this evidence, must have a cis configuration of carbonyl groups.

Knox, who studied isomerism in complexes $[CpFeCOSR]_2$, R = Me, Et, Ph, has concluded on the basis of the phenylthio complex, that all 'stable' isomers have the cis structure (i) and these are formed via the unstable isomers to which structure (ii) has been assigned from spectroscopic evidence.



(i)

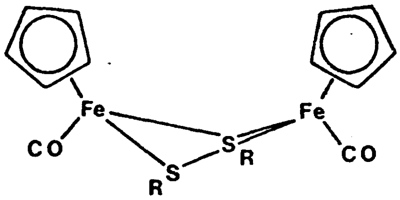
cis syn(e,e)



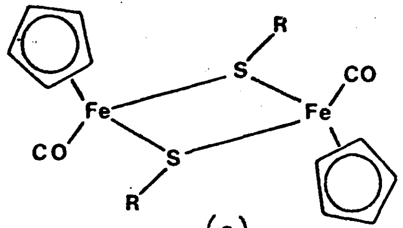
(ii)

cis syn(a,a)

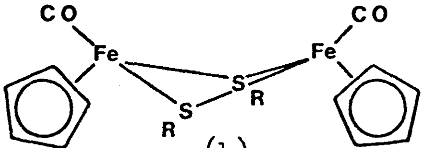
It has been reported recently[81] that $Cp_2Mo(SMe)_2PtCl_2$, which also has a puckered ring and syn configuration of methyl substituents, undergoes a similar syn-syn interconversion process but, due to the symmetry of this molecule, the initial and final configurations are identical and hence this system is not thermodynamically comparable. Schermer and Baddely have, on the basis of spectroscopic and thermodynamic similarities to Knox's mercapto derivatives, assigned appropriate structures to the two isomers of $[CpFe(CO)EPh]_2$, E = Se, Te.[82] While such configurations appear to be the most favoured on spectroscopic evidence, it is probably unwise to categorically assign similar structures to isomers A and B of the trifluoromethylthio derivative particularly since, thermodynamically, they are not directly camparable with the alkylthio and phenylthio complexes, although some similarities do exist. It is therefore concluded that the data available indicate isomer A can have only cis structures (a) or (b) (syn ee or syn aa) while isomer B can have, in addition to any of these configurations, the all trans structure (c).



(a)



(c)



(b)

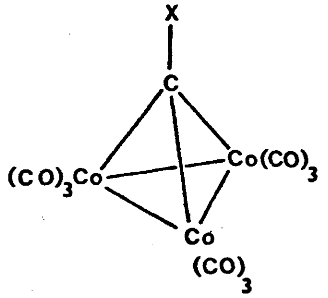
It should be noted that equivalence of the CF_3 groups can also be achieved via rapid inversion at sulphur but since this has not been observed in complexes $[CpFe(CO)SR]_2$ previously or in other puckered ring complexes such as $[Fe(CO)_3SR]_2$ this explanation is less probable.

Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $Co_2(CO)_8$

The high reactivity of cobalt carbonyl towards disulphides and mercaptans leads in many reactions to a large variety of polynuclear products.[1] However, a reduction in the reactivity of mercapto ligands is indicated by the isolation of $[Co(CO)_3SR]_2$ when electronegative substituents, $R = C_6F_5$, C_6Cl_5 are attached to sulphur[57] and a similar phenomenon was expected in the reaction of $Co_2(CO)_8$ and CF_3SSCF_3.

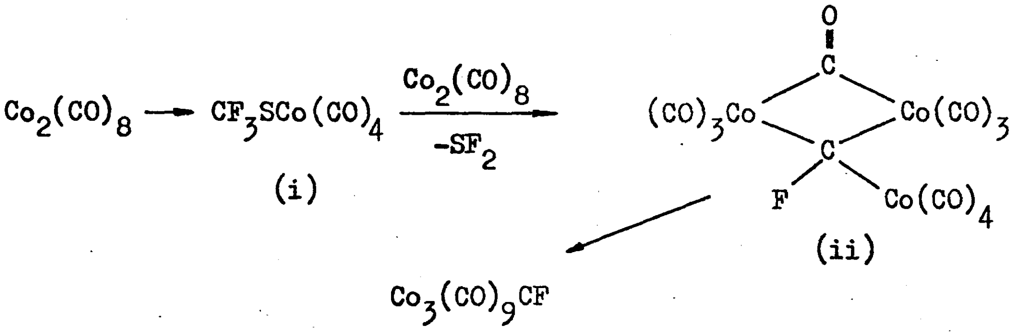
Two products were isolated from this reaction, $Co_3(CO)_9CF$, (X), (23% yield) and $[Co_2(CO)_5S]_n$ in trace quantities. Formation of the latter is not unexpected, but isolation of the methinyltricobalt complex X is surprising since both C-F and C-S bond scission must occur to give this product. $Co_3(CO)_9CF$ has been prepared previously from the reaction of CF_3I[83] or $CFCl_3$[84] and dicobalt octacarbonyl, and the melting point, i.r. and ^{19}F n.m.r. spectra are in agreement with those reported in the literature.[85]

Other methinyltricobalt complexes, $Co_3(CO)_9CX$ are known, and have been prepared by an extensive variety of methods.[85] An X-ray study of $[Co_3(CO)_9C]_2$[86] and other complexes of this type[85] has confirmed the structure originally suggested from spectroscopic[85] and chemical evidence.[87]



The extreme electronic environment of the fluorine atom in X is illustrated by the chemical shift in the ^{19}F n.m.r. spectrum δ = 44.5 ppm downfield from CCl_3F. The only other C-F chemical shifts below CCl_3F are those of CF_2 and CF_3 groups bonded directly to a transition metal.[88]

The formation of $Co_3(CO)_9CF$ from CF_3I and $Co_2(CO)_8$ is considered to proceed via a radical reaction involving $CF_3^{\bullet}$ radical attack on the carbonyl to give $CF_3Co(CO)_4$ which, on further reaction with cobalt carbonyl, gives the product.[83] The isolation of $CF_3Co(CO)_4$ in the photolytic reaction lends support to such a theory. Other workers[89] also considered a radical mechanism to account for the formation of $Co_3(CO)_9CX$ from $Co_2(CO)_8$ and Y_3CX, the initial step being formation of $XCY_2Co(CO)_4$. This reacts further via $XCY[Co(CO)_4]_2$ and $CX[Co(CO)_4]_3$ which loses three carbonyl ligands to give $Co_3(CO)_9CX$. In this context thermal or photochemical decomposition of the known complex $ClSn[Co(CO)_4]_3$[90] might be informative. The reaction of CF_3SSCF_3 and complexes containing metal-metal bonds almost certainly involves initial attack of a CF_3S radical on this bond as will be discussed later. Thus $CF_3SCo(CO)_4$ seems a likely intermediate. Elimination of sulphur would give $CF_3Co(CO)_4$, but since this was not detected, such a reaction is considered unlikely. It would therefore appear that an alternative reaction path is involved in the formation of $Co_3(CO)_9CF$. An interesting speculation is SF_2 elimination from $CF_3SCo(CO)_4$ to give the carbene complex $FCCo(CO)_4$ which reacts with $Co_2(CO)_8$ to give the final product. Isolation of the carbene bridged complex $Co_2(CO)_7$ $CFCF_3$, which reacts with $Co_2(CO)_8$ to give $Co_3(CO)_9CCF_3$ has been reported by Haszeldine et al.[91] and suggests an intermediate of structure (ii) may be involved in the formation of X. The following mechanism is therefore proposed



The formation of large quantities of decomposition material in this reaction can be explained by fluorination of $Co_2(CO)_8$ by SF_2 to give cobalt fluorides. Some of the decomposition material dissolved in water giving coloured solutions supporting this contention. The formation of $[Co_2(CO)_5S]_n$ can be explained similarly. Formation of cobalt fluorides and halides was also observed in the formation of $Co_3(CO)_9CCF_3$ from $[Co_2(CO)_8]_2$ and $CF_2 = CFX$; X = F, Cl, Br, <u>via</u> the carbene intermediate mentioned above.

The reaction of thiophenol and dicobalt octacarbonyl gives, among other products,[55] a complex structurally related to $Co_3(CO)_9CF$ of stoichiometry $Co_3(CO)_9SC_6H_5$. Such a species possibly results from the reaction of $PhSCo(CO)_4$ and $Co_2(CO)_8$ and could lead to $Co_3(CO)_9S$ also formed in this reaction. Attempts were therefore made to prepare $Co_3(CO)_9SC_6F_5$ by reacting dicobalt octacarbonyl and $C_6F_5SSC_6F_5$ in pentane with u.v. irradiation, but only $[Co(CO)_3SC_6F_5]_2$ was formed, which is also obtained in the absence of irradiation.[57]

Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $[CpNi(CO)]_2$

Irradiation of pentane solutions of $[CpNi(CO)]_2$ and a disulphide, RSSR, R = CF_3, C_6F_5, for 15-20 hr. in a closed reactor gave dark red solutions which readily evolved carbon monoxide when the reactor was opened. The reactor was therefore cooled to -20^oC prior to opening to inhibit decarbonylation and a sample of the solution quickly transferred to an infra-red solution cell, which was then sealed. The i.r. spectrum obtained in this way in both cases exhibited a weak band above 2100 cm^{-1} and a strong band near 2045 cm^{-1}. The weak band disappeared more rapidly than the latter on evolution of CO gas indicating that two distinct species were present in solution. On removal of solvent from the product mixture loss of carbon monoxide occurred, and the CO free complexes $[CpNiSCF_3]_2$, XIIa, and $[CpNiSC_6F_5]_n$, XIIb,[34] were obtained in ~80% yield. Insoluble decomposition products were also found. The strong CO stretching mode in the i.r spectrum near 2045 cm^{-1} can be compared with the single band observed in this region with complexes CpNi(CO)R, R = CF_3, C_2F_5 etc. described by Stone.[92] It is proposed that the monocarbonyls CpNi(CO)SR, XIa, R = CF_3, XIb, R = C_6F_5 are formed initially and, like $Mn(CO)_5SCF_3$, are fairly stable in a closed system but decompose rapidly in the absence of a CO atmosphere. A similar phenomenon has also been reported[93] when $[C_6F_5Se]_2$ and $[CpNi(CO)]_2$ are allowed to react. Monomeric $CpNi(CO)SeC_6F_5$ was detected prior to work-up but only $[CpNiSeC_6F_5]_n$ could be isolated. However, the identity of the species responsible for the weak CO stretching frequency in the product mixture from the disulphide remains unknown, since no analogous species was detected in the seleno reaction. The dimer $[CpNiSCF_3]_2$ was also obtained, but in very small quantities, from the photochemical reaction of nickelocene and bistrifluoromethyldisulphide in pentane.

A molecular ion at 448 in the mass spectrum of XIIa and the presence of four C-F stretching modes in the i.r. spectrum indicate a dinuclear, CF_3S bridged complex, and the structure is probably similar to that of $[CpNiPPh_2]_2$,[15] the M_2S_2 ring therefore being planar and, as expected, a singlet is observed in the ^{19}F n.m.r. spectrum at 34°C. Since proton n.m.r. studies revealed two isomers of $[CpNiSMe_3]_2$[23] at low temperatures the ^{19}F n.m.r. spectrum of the trifluoromethylthio complex was studied down to -90°C but no splitting of the sharp singlet was observed. Either the <u>syn</u> and <u>anti</u> isomer resonances are coincident, or a much lower barrier to inversion exists in XII, relative to the methylthio derivative. The latter explanation is preferred since weakening of the Ni-S coordinate bond, as a consequence of replacing CH_3 by CF_3, might be expected to reduce the energy barrier to inversion. This follows from the work of Cross[21] who studied inversion in complexes $(RSC_2H_4SR)MX_2$; M = Pd, Pt. Weakening of the metal sulphur bond when X has a high <u>trans</u> effect was found to lower the temperature of which coalescence of the proton resonances occurs.

The related complex $[CpNiP(CF_3)_2]_2$ has been isolated from the reaction of nickelocene and $P(CF_3)_2H$[94] and, in addition, the interesting organo-phosphorus compound $C_5H_7P(CF_3)_2$ was also obtained. The latter, which appears to result from the addition of $(CF_3)_2P$ and hydrogen to a cyclopentadienyl ring, is also obtained in addition to C_5H_8 and organocobalt complexes from the reaction of $CpCo(CO)_2$ and $P(CF_3)_2H$.[95] No organosulphur products were detected in the reaction of CF_3SSCF_3 and nickelocene and when C_6F_5SH and other mercaptans are allowed to react with Cp_2Ni the only organic compound isolated is dicyclopentadiene. The facile elimination of C_5H_6, which subsequently dimerises, explains why thiols react with nickelocene to give high yields of $[CpNiSR]_2$.[96] However, the reaction of CF_3SSCF_3 and nickelocene is very slow, indicating possibly that only very energetic radicals are sufficiently reactive to promote cleavage of M-Cp bonds to give $[CpNiSCF_3]_2$.

The reaction of XIIa and $P(C_6H_5)_3$ results in cleage of the nickel-sulphur bridge and orange crystalline $CpNiPPh_3SCF_3$, XIII is formed in high yield. A similar product $CpNiPPh_3SC_6F_5$ has been reported previously from the reaction of PPh_3 and $[CpNiSC_6F_5]_n$.[34] The two C-F stretching modes in the i.r. spectrum and the low chemical shift of the CF_3 group in the ^{19}F n.m.r. spectrum (23.1 ppm) are in accord with a monomeric complex containing a terminal CF_3S ligand. The product is thermodynamically more stable than the carbonyl $CpNiCOSCF_3$ which decomposes below room temperature whereas dimerisation of XIII with elimination of triphenylphosphine does not occur below 180°C. At this temperature the mass spectrum reveals ions due to $[CpNiSCF_3]_2$ and PPh_3 but no trace of ions due to $CpNiPPh_3SCF_3$ was found.

(B) Reactions of Monomeric Transition-metal Carbonyls with Disulphides CF_3SSCF_3 and $C_6F_5SSC_6F_5$

Reactions of CF_3SSCF_3 with $M(CO)_6$, M = Cr, Mo, W

Irradiation of group VI metal carbonyls $M(CO)_6$, M = Cr, Mo, W and CF_3SSCF_3 in pentane gave insoluble polymeric material which was not investigated further. The green solid obtained from $Cr(CO)_6$ is similar to $Cr(SMe)_3$ obtained by irradiation of $Cr(CO)_6$ and CH_3SSCH_3[97] suggesting the stoichiometry $Cr(SCF_3)_3$. After several minutes irradiation the reaction mixture of $Cr(CO)_6$ and CF_3SSCF_3 turned purple but on further irradiation this colour disappeared. This suggested formation of an intermediate organometallic complex which undergoes further reaction to $Cr(SCF_3)_3$. The reactions were therefore repeated using a low energy filter and small quantities of the blue solids $[M(CO)_4SCF_3]_2$, M = Mo, XIVa, W, XIVb, were isolated chromatographically on work up of the reaction mixture. It was not possible to isolate the analogous chromium complex although this is considered to be responsible for the transient purple colour mentioned above. The greater reactivity of the latter is not unexpected in view of the significant differences in reactivity of chromium molybdenum and tungsten organo derivatives frequently reported in the literature[74] and encountered earlier in decarbonylation studies of $CpM(CO)_3SCF_3$, M = Mo, W.

The molybdenum and tungsten dimers XIVa, and XIVb are dark blue crystalline solids which dissolve in organic solvents to give green solutions. The i.r. spectra exhibit three strong CO stretching modes instead of the expected four. A similar phenomenon has been reported with complexes $[M(CO)_4ER_2]_2$[98,99] M = Mo, W, E = P, As, and since, in both CF_3S derivatives the low frequency band is very intense and broadened slightly, it would appear that two of the modes are virtually degenerate and are not resolved. The mass spectra are fairly typical of CF_3S bridged carbonyl compounds and lose all the carbonyl groups sequentially. The ^{19}F n.m.r. spectrum in each case gives a single resonance at relatively high field indicating rapid inversion at sulphur.

Both derivatives can be compared with $[Mo(CO)_4PMe_2]_2$[100] which contains a planar Mo_2P_2 ring. The eighteen electron rule requires a metal-metal bond and in the phosphido derivative the resulting M-M distance 3.057 Å produces a strained M-P-M angle of 75.4°. In $[Mn(CO)_4SeCF_3]_2$[41] in the absence of a metal-metal interaction the corresponding M-Se-M angle at 96.9° is much nearer the ideal sp^3 hybrid angle of 109°. Since the overall structure of $[M(CO)_4SCF_3]_2$ probably consists of two distorted octahedra sharing an edge, this metal-metal interaction can occur <u>via</u> dxy orbital overlap.

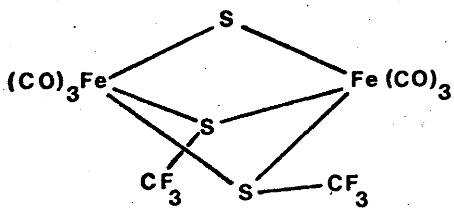
These are the first mercapto derivatives of this stoichiometry to be reported although a large variety of complexes are known with bridging phosphido ligands.[98,99] Anionic monomers $M(CO)_5SR^-$, M = Mo, W, R = CF_3, CH_3, C_6H_5 are known[101] isoelectronic with $Mn(CO)_5SCF_3$ and $Mn(CO)_5SC_6F_5$ described earlier but, unlike the latter derivatives, these do not undergo decarbonylation to dinuclear species or react with $M(CO)_6$ or $M(CO)_5(THF)$, although complex anions $M_2(CO)_{10}SR^-$ are known.[102]

Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $Fe(CO)_5$ and $Fe_2(CO)_9$

The reactions of CF_3SSCF_3 with $Fe_2(CO)_9$ and $Fe(CO)_5$ are virtually identical but the ennea-carbonyl reacted much more quickly and also gave $Fe(CO)_5$ as one of the products. A mixture of four sulphido complexes was obtained in each case, the main product $[Fe(CO)_3SCF_3]_2$ XV being separated by repeated slow recrystallisation from cold pentane. The other products obtained in trace quantities were isolated by chromatography of the residues from crystallisation and identified spectroscopically as the new complex $[Fe_2(CO)_6SCF_3]_2S$ and the known derivatives $Fe_3(CO)_9S_2$ and $[Fe(CO)_3S]_2$. Evidently C-S bond scission occurs in these reactions. Similar products were obtained in identical relative yields, but much more slowly, from the dark reaction of $Fe_2(CO)_9$ and CF_3SSCF_3 in pentane, illustrating that cleavage of C-S bonds is not a photochemical process.

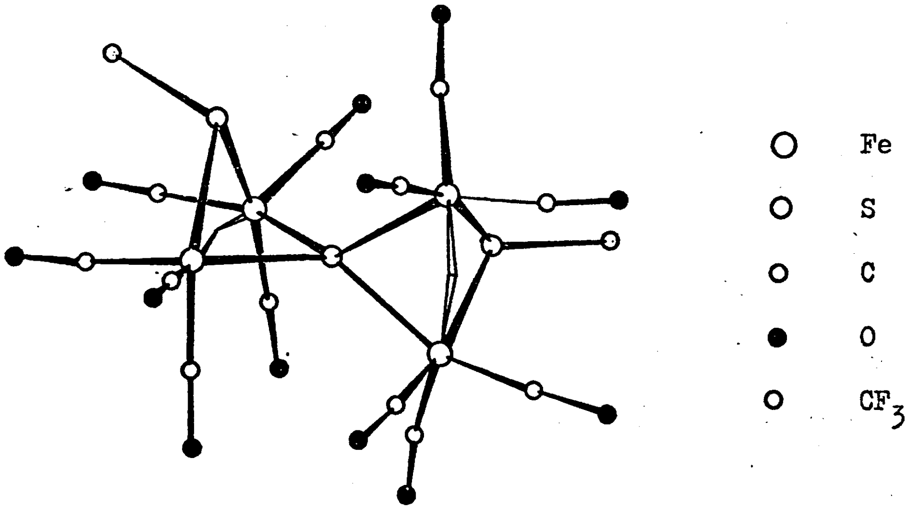
The i.r. spectrum of $[Fe(CO)_3SCF_3]_2$ exhibits four strong terminal CO stretching modes above 2000 cm^{-1} and a weak ^{13}CO mode characteristic of such derivatives.[6,27] A grossly non-planar M_2S_2 ring in $[Fe(CO)_3SEt]_2$ has been revealed by X-ray studies, and as discussed in the introduction indicates that three isomeric forms are possible.[11] However, the <u>syn</u> a,a form has been precluded on steric grounds so that with $[Fe(CO)_3SCH_3]_2$ the two isomers have been separated chromatographically and identified as the <u>syn</u>(e,e) and <u>anti</u> (e,a) forms by proton n.m.r. studies.[25] The ^{19}F n.m.r. spectrum of $[Fe(CO)_3SCF_3]_2$ contains two resonances at 23.7 ppm and 35.7 ppm characteristic of the <u>anti</u> isomer and a third weak resonance at 32.0 ppm attributable to the <u>syn</u>(e,e) isomer. The ratio <u>syn</u>:<u>anti</u> = 1:12 compares with <u>syn</u>:<u>anti</u> = 1:4 in the methylthio derivative. The factors affecting isomer type and equilibria will be discussed in greater detail in Chapter II.

The thermal reaction of $Fe(CO)_5$ and CF_3SSCF_5 has been reported[65] to give $[Fe(CO)_3SCF_3]_2S$ structurally related to $[Fe(CO)_3SCF_3]_2$ but with a sulphur atom having inserted into the Fe-Fe bond of the latter. No analytical data or melting point are reported for this derivative



although brief details of the i.r., n.m.r. and mass spectra are given. This complex, which was not detected in the photolytic reactions, appears to identify closely with XV. In both cases four CO stretching modes are observed in the i.r. spectrum $[Fe(CO)_3SCF_3]_2$: 2086m, 2066vs, 2031s, 2022.5s, $[Fe(CO)_3SCF_3]_2S$: 2090s, 2066s, 2026s, 2019s. Differences could be accounted for by use of different solvents. The position and intensity of the high frequency mode near 2090 cm^{-1} depends on the interaction constant between CO groups trans to the metal-metal bond in $[Fe(CO)_3SCF_3]_2$ and trans to sulphur in $[Fe(CO)_3SCF_3]_2S$.[6,57,103] Since these are comparable in both complexes it seems strange that interaction through a metal-metal bond is as great through a sulphur atom. In the i.r. spectrum of $[Fe(CO)_3SCF_3]_2C_4F_6$, (described in Chapter (II)) where an acetylinic species has inserted into the metal-metal bond of XV, the high frequency band has a very low intensity and, on this evidence, it would appear that $[Fe(CO)_3SCF_3]_2S$ is in fact $[Fe(CO)_3SCF_3]_2$. This is further supported by the molecular ion observed in the mass spectrum of the former at 481 which is strangely identified by the authors as $[Fe(CO)_3SCF_3]_2S^+$ whereas the molecular ion of $[Fe(CO)_3SCF_3]_2$ occurs at 482.

The other new product XVI isolated from the reaction of iron carbonyls and bistrifluoromethyldisulphide was obtained in very low yield and anlalytical data could not be obtained. However, the mass spectrum gives a molecular (?) ion at m/e 798 corresponding to the formula $[Fe_2(CO)_6SCF_3]_2S$ and this loses twelve carbonyl groups in a stepwise manner. The i.r. spectrum in the CO stretching region shows five bands with an intensity and frequency distribution comparable to those of $[Fe_2(CO)_6SR]_2S$, R = Me[104], Bu^t[105] but shifted to higher frequencies. On this evidence complex XVI is formulated as the trifluoromethyl analogue of $[Fe_2(CO)_6SCH_3]_2S$, the structure of which has been elucidated by X-ray crystallography.[104] The structure of XVI shown consists of two $[Fe_2(CO)_6SCF_3]$ fragments bridged by a metal-coordinated tetrahedral-like sulphur atom which donates all six valence electrons to the four iron atoms.



The methyl substituents in the methylthio derivative were found to occupy equatorial positions in the solid state and the appearance of only one proton resonance in the ^1H n.m.r. spectrum indicates that this configuration is retained in solution. A single CF_3 resonance at 32.4 ppm in the ^{19}F n.m.r. of the trifluoromethylthio complex suggests a similer conclusion, which is not surprising, since $[Fe_2(CO)_6SCF_3]_2S$ is formally derived from $[Fe(CO)_3SCF_3]_2$ with $Fe_2(CO)_6SCF_3$ occupying both axial and equatorial positions on the sulphur formerly occupied by CF_3 and a lone pair. Steric interactions would therefore prevent the CF_3 from taking up an axial position.[11]

The other sulphur complexes obtained in this reaction, $[Fe(CO)_3S]_2$ and $Fe_3(CO)_9S_2$, are frequently isolated from reactions involving iron carbonyls and sulphur derivatives[1] and apart from indicating C-S bond scission no special significance is attached to their formation from iron carbonyls and bistrifluoromethyldisulphide. The structures of both complexes[16,106] have been determined by X-ray methods.

The reaction of iron carbonyls with C_6F_5SH appears to be much simpler than with CF_3SSCF_3 only $[Fe(CO)_3SC_6F_5]_2$ being formed.[27] An identical result was obtained on irradiation of pentane mixtures of Fe_2CO_9 and $C_6F_5SSC_6F_5$ and obviously C-S bond scission is not favourable in this case.

Substitution of carbonyl groups in complexes $[Fe(CO)_3SR]_2$, R = CH_3, C_6H_5 etc. by phosphines has been studied extensively by a number of workers and in particular by Haines and Greenwood.[46,47] The results of these studies indicate that the organic substituents on the phosphine and the mercapto ligand are important factors in determining the rate and products of the substitution reactions. The reaction of triphenylphosphine and $[Fe(CO)_3SCF_3]_2$ was therefore studied and the following results obtained.

$[Fe(CO)_3SCF_3]_2$ and PPh_3 (1:1 molar ratio) reacted vigorously in pentane, at room temperature, with rapid evolution of carbon monoxide, to give the deep red oil, $Fe_2(CO)_5PPh_3(SCF_3)_2$ XVII, which could not be crystallised and was characterised only by i.r. and n.m.r. spectroscopy. This complex reacted further with triphenylphosphine (1:1 molar ratio) to give the disubstituted complex $[Fe(CO)_2PPh_3SCF_3]_2$, XVIII, as dark red crystals. Similar results have been obtained by other workers[46] with related alkyl and aryl mercapto complexes and, as with these derivatives, i.r. spectra in the CO stretching region indicate that CO ligands trans to the metal-metal bond have been substituted. This is further supported by the structures of related complexes $As_2\ Co_2(CO)_5PPh_3$[107] and $Rh_2(PF_3)_4(PPh_3)_2PhC{\equiv}CPh$[108] in which triphenylphosphine is in the apical position. The four CO stretching modes of $Fe_2(CO)_5PPh_3(SCF_3)_2$ correspond to isomer I of Greenwood[46] whereas the three carbonyl bands of $[Fe(CO)_2PPh_3SCF_3]_2$ are similar to isomer II. The lability of the apical carbonyl groups is possibly related to the trans-effect of the metal-metal bond, this apparently being greater than for bridging mercapto ligands. However, since no significant difference in the M-CO (apical) M-CO (basal) distances in complexes $[FeCO)_3SR]$[10] was revealed by X-ray studies it must be concluded that steric factors may also influence CO substitution.

It should be noted that the reactions of $[Fe(CO)_3SMe]_2$ and $P(Et)_3$ or PPh_3 in refluxing benzene gave only monosubstituted compounds, disubstitution requiring higher temperatures or u.v. irradiation. This contrasts with the ready formation of both mono and disubstituted derivatives of $[Fe(CO)_3SCF_3]_2$, XVII and XVIII, at room temperature probably as a consequence of weaker M-CO bonding in the latter. This is suggested by the CO stretching modes in the i.r spectra, which are shifted to high frequency in the trifluoromethylthio complex as a result of lower M-CO back donation[7]. The electron withdrawing ability of the organic substituent on the sulphur which produces this effect has also been observed[47] to influence the reactivity of $[Fe(CO)_3SR]_2$, R = Me, Et, Ph towards chelating diphosphines, but in a slightly different context. The difference in reactivity was found to be related to the ease of cleavage of the bridging sulphido groups, which was more facile with the complex containing the more electronegative phenyl substituents.

An interesting consequence of replacing carbonyl ligands with triphenylphosphine is the gradual change in isomer population observed on increased substitution. The isomer ratios, measured by integration of CF_3 ^{19}F n.m.r. signals, are syn:anti $[Fe(CO)_3SCF_3]_2$ 1:12, $Fe_2(CO)_5(PPh_3)(SCF_3)_2$ 1:4, $[Fe(CO)_2(PPh_3)SCF_3]_2$ 1:1, indicating gradual destabilisation of the anti isomer. Since the apical carbonyl ligands trans to the metal-metal bond are replaced by the bulkier triphenylphosphine, increased steric interaction between the apical ligands and the CF_3 group in the axial position must result. This will subsequently destabilise the anti(e,a) isomer with respect to the syn (e,e) isomer accounting for the observed trend in isomer equilibria. A similar trend has been reported by Bor et al.[27] but these workers only studied $[Fe(CO)_3SR]_2$, R = CH_3, C_2H_5, C_6H_5, C_6F_5, and the monosubstituted derivatives, R = CH_3, C_2H_5, although in greater detail than the present work.

However, these results are in contrast to the work of Cullen[109] who reacted the separate isomers of $[Fe(CO)_3SMe]_2$ with triphenylphosphine and obtained monosubstituted products with retention of methyl group configuration. Bor, who reacted the $[Fe(CO)_3SMe]_2$ isomer mixture with PPh_3, attempted to separate the isomers chromatographically but failed due to the very rapid isomer equilbration. It can only be concluded, on the basis of these two completely contradictory reports, that the n.m.r. spectra reported by Cullen were collected immediately on dissolving the isomer samples before significant isomerisation occurred. It should also be noted that Greenwood observed[46] only the syn isomer in $Fe_2(CO)_5SbPh_3(SMe)_2$, $Fe_2(CO)_5L(SR)_2$, $L = Ph_2P\cdot CH_2\cdot PPh_2$, $Ph_2As\cdot CH_2\cdot AsPh_2$, R = Me, Et.

Substitution of carbonyl ligands in $[Fe(CO)_3SCF_3]_2$ was also effected by nitric oxide which reacted to give brown air-sensitive crystals of $[Fe(NO)_2SCF_3]_2$ XIX in high yield. The amido complex $[Fe(CO)_3NH_2]_2$[110] has also been reported to react with NO to give $[Fe(NO)_2NH_2]_2$ but this does not appear to be a general route to such nitrosyl derivatives since no reaction was observed between nitric oxide and $[Fe(CO)_3PMe_2]_2$.[111] However, stronger M-CO bonding in the dimethylphosphido complex is indicated by lower CO stretching frequencies and this may be responsible for the reported lack of reactivity towards NO.

Synthetic routes to both $[Fe(NO)_2SR]_2$ and $[Fe(NO)_2PR_2]_2$ <u>via</u> the readily available mixed nitrosyl carbonyl complex $Fe(CO)_2(NO)_2$ have been reported,[49,112] and are of more general applicability. An X-ray study of $[Fe(NO)_2SEt]_2$[50] has revealed a planar M_2S_2 ring with the tetrahedrally coordinated iron atoms separated by 2.72 Å, implying substantial metal-metal interaction. As with the ethyl mercapto and related derivatives the i.r. spectrum of $[Fe(NO)_2SCF_3]_2$ exhibits two strong NO stretching modes near 1800 cm^{-1} and a similar structure is therefore proposed. The multiplicity of C-F stretching frequencies in the i.r. spectrum and the sharp singlet in the ^{19}F n.m.r. spectrum of XIX are also in accord with a structure of this type.

Reactions of CF_3SSCF_3 and $C_6F_5SSC_6F_5$ with $CpCo(CO)_2$

The reaction of $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$ depends to a great extent on the conditions employed. Thus a 1:1 molar ratio of reactants in the absence of solvent gave the dark green, air sensitive solid, $[CpCoSC_6F_5]_2$, XX, characterised by elemental analysis, i.r., n.m.r. and mass spectroscopy. In pentane solution no reaction was observed up to -10°C when black crystals of $CpCo(CO)(SC_6F_5)_2$, XXI, formed slowly and the solution turned green due to formation of small quantities of $[CpCoSC_6F_5]_2$. The same result was obtained on irradiation of the reactants in pentane at 20°C whereas the thermal reaction in pentane at 20°C or above, in the dark, gave $CpCo(CO)(SC_6F_5)_2$ exclusively. In the last reaction the red solution turned green at first but this colour disappeared as crystals of $CpCo(CO)(SC_6F_5)_2$ were deposited. Solutions of XXI when heated above 50°C gave mixtures of XX and a green solid XXII which analyses as $CpCo_2(CO)(SC_6F_5)_3$ (oxygen content by difference). As the reaction temperature was raised, increased amounts of the dimer XX were obtained. Separation of $[CpCoSC_6F_5]_2$ from $CpCo(CO)(SC_6F_5)_2$ and $CpCo_2(CO)(SC_6F_5)_3$ in these reactions was achieved by extraction with pentane and slow recrystallisation at -78°C.

The dark reaction of $CpCo(CO)_2$ and CF_3SSCF_3, with or without a solvent, gave an ill defined purple-black solid which could not be obtained pure. Traces of a dark red solid were also detected which gave a single CO stretching frequency in the i.r. spectrum at 2095 cm^{-1} and C-F stretching modes near 1100 cm^{-1}, suggesting the formula $CpCoCO(SCF_3)_2$ by analogy with $CpCo(CO)(SC_6F_5)_2$. Unfortunately, the low yield and instability of this complex prevented further characterisation.

The photolytic reaction of $CpCo(CO)_2$ and CF_3SSCF_3 in pentane gave good yields of the air-sensitive, green-black solid $[CpCoSCF_3]_2$, XXIII, analogous to $[CpCoSC_6F_5]_2$ and the previously reported methylthio derivative $[CpCoSMe]_2$.[60] These three derivatives probably have a similar structure to $[CpCoPPh_2]_2$ which has been shown[15] to have a puckered M_2X_2 ring like $[Fe(CO)_3SEt]_2$ and, as with the latter and $[Fe(CO)_3SCF_3]_2$ described earlier, two isomers are expected. However, the ^{19}F n.m.r. spectrum gives a sharp singlet for the CF_3S derivative and three multiplets, integrated ratio 2:1:2, for the C_6F_5S complex, suggesting that in both complexes the perfluoroorgano substituents are in identical environments. Similarly, the ^1H n.m.r. of $[CpCoSMe]_2$ gives only a sharp singlet in the methyl group region. These spectra would suggest that either the syn (a,a) or syn (e,e) isomer only is present in each case, although the former is probably unstable as a result of steric interactions. In $[Fe(CO)_2SR]_2$ the syn:anti equlibria usually favours the anti isomer particularly when the substituents on sulphur are bulky,[27] making the presence of only the syn(e,e) isomer also difficult to explain. Alternatively, the barrier to inversion may be very low in $[CpCoSR]_2$ as a result of minimal steric interaction between the cyclopentadienyl ligand and the organic group R. It is generally considered that a cyclopentadienyl ligand is sterically much less demanding than three carbonyl ligands so that fluxional behaviour, involving inversion at sulphur, could effectively explain the n.m.r. data obtained.

The monocarbonyl $CpCo(CO)(SC_6F_5)_2$ also exhibits unexpected spectral features, although the stoichiometry and method of preparation suggest a similar structure to complexes $CpCo(CO)X_2$,[113] X = Cl, Br, I and $CpCo(CO)R_FI$,[114] $R_F = CF_3$, C_2F_5 formed by oxidative addition of X_2 and R_FI to $CpCo(CO)_2$. A single CO stretching mode near 2100 cm^{-1} and a weak C-H stretching frequency at 3120 cm^{-1} characteristic of a π-cyclopentadienyl ligand are observed in the i.r. spectrum. No molecular ion is detected in the mass spectrum due to decomposition in the spectrometer to $[CpCoSC_6F_5]_2$ which gave a molecular ion at m/e 646 but molecular weight studies in chloroform solution confirm the monomeric formulation. The ^{19}F n.m.r. spectrum gives three multiplets of ratio 2:1:2 as expected for two C_6F_5 groups in identical environments, but the proton n.m.r. does not give a spectrum characteristic of a π-bonded cyclopentadienyl ligand. Instead, a flat, extremely broad band, centred at 4.55τ and extending over 2.5τ units, is observed at 34°C, but as the temperature is lowered this changes considerably and at -80°C a sharp singlet is obtained,

It has been observed[115] that rotation of the substituted cyclopentadienyl ring in $[\pi\text{-}C_5H_4C(CF_3)_2OH]Ru(PPh_3)[C_2(COOMe)_2H]$ does not occur as a result of hydrogen bonding between the ring substituent $C(CF_3)_2OH$ and the ligand $C_2(COOMe)_2H$. This suggests the possibility of steric interaction between the C_6F_5 groups and the cyclopentadienyl ring in $CpCo(CO)(SC_6F_5)_2$ sufficient to slow rotation of the Cp ring to the point where a sharp n.m.r. singlet is no longer observed for the ring protons at ambient temperature. At -80°C the C_6F_5 groups are probably pointing away from the cyclopentadienyl ligand but as the temperature is raised the barrier to free rotation about sulphur is overcome, but at the expense of completely free rotation of the cyclopentadienyl ligand as a result of steric interaction between these two groups. Since a more suitable explanation is not immediately apparent an X-ray diffraction study would seem desirable.

The exact constitution of $CpCo_2(CO)(SC_6F_5)_3$ is not known with certainty but this formulation is based on two separate analyses for C, H, S, F and Co. Possible oxygen content is indicated only by difference and the high error inherent in elemental analysis of organometallic complexes containing fluorine makes this uncertain. The i.r. spectrum gives bands characteristic of cyclopentadienyl and C_6F_5 groups but no indication of terminal, bridging or ketonic carbonyl groups is given. A molecular ion is not found in the mass spectrum, but ions assigned to $(C_6F_5S)_2^+$, $CpCoF^+$ and $CpCo^+$ are observed, while the

^{1}H n.m.r. spectrum confirms that a π cyclopentadienyl ligand is present with a single peak at 5.5τ. However, the single multiplet observed in the ^{19}F n.m.r. spectrum at 153.3 ppm is unexpected for a complex containing C_6F_5 groups. Since the analytical and spectral data are inconclusive it is obviously impossible to assign a structure to this complex.

Spectroscopic Properties of the Complexes

The i.r., n.m.r. and mass spectral properties of transition-metal trifluoromethylthio derivatives have been discussed briefly by King.[3] No new spectral features have emerged from the studies described herein (see tables 1.1 and 1.2) so that further discussion is considered unnecessary.

Mechanisms of the Reactions

The chemical and physical properties of mercapto complexes of the transition metals have been studied by many workers as described in the introduction. Isolation and study of these trifluoromethylthio and pentafluorophenylthio complexes now allows a more complete appraisal of the properties of transition metal mercaptides particularly from the aspect of thermal stability. Interest in the mechanism of formation of monomeric and dimeric complexes[1,36] also prompts a discussion of reaction mechanisms at this point.

Monmeric Mercapto Complexes

Evidence for the formation of CF_3S radicals on photolysis of CF_3SSCF_3 has already been discussed and the high yield formation of monomeric CF_3S derivatives, described in this work, provides support for this theory. Ready formation of C_6F_5S complexes in a similar manner suggests that photolysis of $C_6F_5SSC_6F_5$ may also result in S-S bond scission. Thus C_6F_5S radicals may be involved although such reactions were generally found to be somewhat slower than those of CF_3SSCF_3. On photolysis, dimethyl disulphide CH_3SSCH_3 is also considered to produce radicals CH_3S.[116]

Table 1.1. Infra-red and n.m.r. spectra of CF_3S complexes

	Infra-red spectrum $(cm^{-1})^{\dagger}$		N.m.r. spectrum	
Compound	ν C–O	ν C–F	^{19}F (ppm)	^{1}H τ
$CpMo(CO)_3SCF_3$	2048s, 1981vs, 1966vs	1111m, 1087s, 1059w	+26.2	
$CpW(CO)_3SCF_3$	2041vsm 1991vs, 1966vs	1113m, 1079s, 1060w	+27.0	
$[CpMo(CO)_2SCF_3]_2$	1958s, 1896s	1142m, 1131m, 1098m, 1087s	+40.6	
$[CpMo(CO)SCF_3]_3$	1945msh, 1910s	1144m, 1130m, 1086s	+41.6	4.49
$[CpW(CO)_2SCF_3]_2$	1941s, 1891s	1147m, 1133m, 1093msh, 1085s		
$[Mo(CO)_4SCF_3]_2$	2059s, 2019s, 199vsb	1155m, 1151msh, 1091msh, 1055m	+40.5	
$[W(CO)_4SCF_3]_2$	2049s, 2004s, 1995vsb	1162m, 1157msh, 1092msh, 1083m	+43.1	
$Mn(CO)_5SCF_3$	2134wm, 2052vsb, 2012s	1129m, 1085	+25.3	
$[CpFe(CO)SCF_3]_2A$	1991vs, 1972s	1130wmsh, 1119m, 1994msh, 1087vs	+34.0	5.39
$[CpFe(CO)SCF_3]_2B$	2000vs	1133wm, 1121m, 1101wsh, 1089s	+37.4	5.39
$[Fe(CO)_3SCF_3]_2$	2096m, 2066vs, 2031s, 2024s	1153wmb, 1092, 1079wm	+23.7, +35.7(anti) +32.0(syn)	
$[Fe_2(CO)_6SCF_3]_2S$	2099m, 2072s, 2057vs, 2023s, 2014s	1159m, 1152m, 1091s, 1064w	+32.4	
$Fe_2(CO)_5(PPh_3)(SCF_3)_2$	2064vs, 2016vs, 2000ms, 1968m	1121m, 1090msh, 1084m	+26.3, +36.3(anti) +32.9(syn)	
$[Fe(CO)_2PPh_3SCF_3]_2$	2067vw, 2017vs, 1979m, 1962s	1140msh, 1133m, 1098m, 1080	+25.3, +35.0(anti) +32.1(syn)	

Table 1.1. (cont'd)

$[Fe(NO)_2SCF_3]_2$	νNO 1823vs, 1720vs	1157s, 1123vw, 1100w, 1091m, 1081s	+32.0*
$[CpCoSCF_3]_2$		1138m, 1131m, 1099m, 1089s	+33.1
$CpNi(CO)SCF_3$	2047vs, 2012vw		
$CpNi(PPh_3)SCF_3$		1095s, 1083s, 1075ssh	+22.4
$[CpNiSCF_3]_2$		1129m, 1122m, 1090msh, 1083s	+32.0

† hexane solution

* ^{19}F n.m.r.

Table 1.2. Infra-red and n.m.r. of C_6F_5S complexes

		Infra-red spectrum $(cm^{-1})^e$			N.m.r. spectrum	
Compound	Solvent^e	ν C-O	C_6F_5 skeletal modes		^{19}F (ppm)	^1H τ
$CpCo(CO)(SC_6F_5)_2$	a	2079m	1506s, 1476s	1084m	162.2, 157.0, 128.2	4.7
$CpCo_2(CO)(SC_6F_5)_3$	b		1512s, 1476s	1085m	153.3	5.5
$\lfloor CpCoSC_6F_5\rfloor_2$	c		1510s, 1486s	1081m	163.6, 158.0, 129.6	5.15
$CpNi(CO)SC_6F_5$	d	2040vs				

a) CCl_4

b) $CHCl_3$

c) cyclohexane

d) hexane

It has been suggested previously that more electronegative groups attached to sulphur facilitate S-S bond scission in disulphides.[36] A mass spectrometric investigation[117] of CF_3SSCF_3 and CH_3SSCH_3 has produced the following bond energy data.

Table 1.3. C-S and S-S bond energies (k.cals./mole)

Compound	C-S	S-S
CH_3SSCH_3	68.5	83.7
CF_3SSCF_3	45.5	89.8

These results however, indicate that the S-S bond is stronger when electronegative groups are attached and also that preferential bond rupture would possibly occur at the weaker C-S bond. Haszeldine[68] showed that S-S bond cleavage in CF_3SSCF_3 is the primary result of irradiation and C-S bond cleavage is a secondary process. Thus bond energy data cannot be used with certainty to predict ease of cleavage of S-S bonds in disulphides. It therefore seems possible that photolytic reactions involving metal complexes and $C_6F_5SSC_6F_5$ are less facile as a result of less efficient uptake of radiation by the disulphide relative to CF_3SSCF_3 and not because of a significant change in the S-S bond strength.

Photolysis of metal carbonyls also leads to bond cleavage and in most cases carbonyl groups are expelled.[118] However, photolysis of $Mn_2(CO)_{10}$ does not result in CO loss[119] but evidence has been found for cleavage of the metal-metal bond to give $Mn(CO)_5\cdot$ radicals.[120] Thus formation of $Mn(CO)_5SR$, R = CF_3, C_6F_5, probably proceeds via radical combination

$$Mn(CO)_5\cdot + RS\cdot \longrightarrow Mn(CO)_5SR$$

However, the same product can also be obtained by radical attack of RS· at the metal or the metal-metal bond of uncleaved $Mn_2(CO)_{10}$. Formation of $CpM(CO)_3SR$, M = Mo, W, $CpFe(CO)_2SR$, $Co_3(CO)_9CF$ and CpNiCOSR can also be explained in this way although no evidence has yet been reported for cleavage of the parent dicarbonyls to give radicals. In fact, with carbonyl bridged dimers $[CpFe(CO)_2]_2$, $Co_2(CO)_8$ and $[CpNiCO]_2$ this is less probable and exclusive attack of RS radicals on the dinuclear species is more likely.

Thermal Stability of Monomers

Comparison of the C-O stretching frequencies of transition metal carbonyl mercaptides indicates that with the trifluoromethylthio derivatives carbon-oxygen π bonding is at a maximum since, in these compounds, the C-O stretching modes are at higher frequency.[7]

Table 1.4. CO stretching frequencies of $CpFe(CO)_2SR$

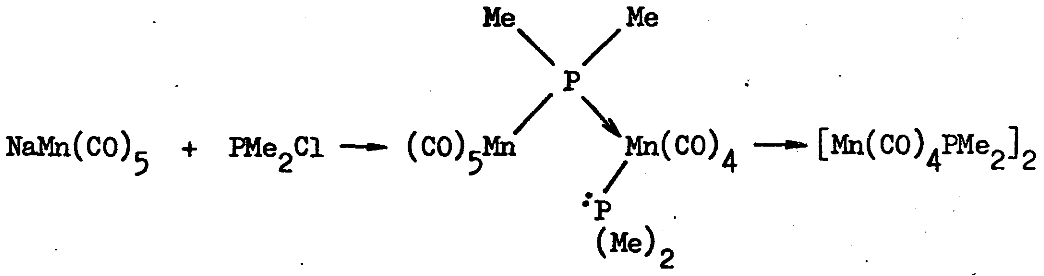
R	Frequency cm^{-1}		Solvent	Ref.
CF_3	2044	2000	cyclohexane	3
C_6F_5	2040	1997	cyclohexane	34
C_6H_5	2030	1987	CCl_4	4
CH_3	2029	1981	CCl_4	4
C_2H_5	2028	1983	$CHCl_3$	4

This further implies that the CF_3 group has greater electron withdrawing ability than C_6F_5, Ph and Me and subsequently M-CO bonds will be weaker in complexes containing the CF_3S ligand. Since decarbonylation of terminal CF_3S and C_6F_5S carbonyl complexes is more difficult than with

Table 1.5. CO stretching frequencies of $[Fe(CO)_3SR]_2$

R	Frequency cm^{-1}				Solvent	Ref.
CF_3	2096	2066	2031	2024	cyclohexane	table 1.1
C_6F_5	2089	2062	2027	2013	hexane	27
C_6Cl_5	2080	2051	2015	2007	hexane	27
C_6H_5	2075	2039	2007	1998	hexane	27
CH_3	2073	2037	2002	1992	hexane	27

comparable PhS and MeS derivatives, dimerisation by loss of carbon monoxide is not predominantly dependent on the M-CO bond strength. Thus the dimerisation reaction probably involves nucleophilic attack of a lone pair at the sulphur on the metal centre of a second molecule of monomer.[31] Evidence for such a bimolecular mechanism is provided by isolation of $Mn_2(CO)_9(PMe_2)_2$ as an intermediate in the following reaction[58]



This suggests that dimerisation is controlled by the availability of the lone pair-electrons on sulphur for attack at the positive metal centre of another molecule of monomer.[1,31] Therefore, the electron withdrawing CF_3 and C_6F_5 substituents must by electrostatic attraction contract the sulphur orbitals containing the lone pairs of electrons and thus impair the ability of sulphur to attack a second molecule. This electronic control of the dimerisation process and hence of monomer stability has been noted by many workers previously.[1,3,4,5,31,36]

Having studied the thermal stabilities of monomeric CF_3S and C_6F_5S derivatives comparison with C_6H_5S and CH_3S compounds suggests the following order of stability for complexes $M(CO)_mSR$ and $CpM(CO)_nSR$

$$C_6F_5S > CF_3S > C_6H_5S > CH_3S$$

Since, from comparison of C-O stretching frequencies the CF_3 group appears to be more electronegative than C_6F_5, their relative positions in this series are anomalous. It is therefore proposed that decarbonylation and dimerisation of monomeric carbonyl mercapto complexes is controlled not only by the electron withdrawing ability of the substituent on sulphur but also by the size of this substituent. Nucleophilic attack by the sulphur will be affected by steric interaction between the substituent on the sulphur atom and other ligands coordinated to the metal, thus making the monomeric C_6F_5S complexes more stable than their CF_3S analogues. Support for this theory is derived from the observation that the difference in thermal stability of $Mn(CO)_5SC_6F_5$ and $Mn(CO)_5SCF_3$ is greater than between $CpNiCOSC_6F_5$ and $CpNiCOSCF_3$. Thus steric inhibition of the dimerisation is more pronounced in six coordinate $Mn(CO)_5SR$ than in CpNiCOSR in which the nickel atoms are effectively less than five coordinate and hence more vulnerable to nucleophilic attack.

Since M-S bonds have little π character the effect of electron withdrawing groups will be to destabilise mercapto bridged di- and polynuclear complexes by weakening the M-S coordinate bonds. Destabilisation will also be effected by bulky groups on the sulphur and so the thermodynamic instability of $[CpFeCOSCF_3]_2$ and $[Mn(CO)_3SC_6F_5]_4$[1] relative to analogous alkylthio complexes is effectively explained.

Where π-bonding effects are considerable, as in metal phosphorus bonds, the electronegativity of CF_3 groups tend to stabilise dimeric complexes so that $[Fe(CO)_3P(CF_3)_2]_2$[95,112] and $[CpCoP(CF_3)_2]_2$[95] are more stable than the dimethylphosphido derivatives.

It is therefore concluded that these observations suggest that the electronegativity of the substituent R attached to sulphur in $M(CO)_mSR$ and $CpM(CO)_nSR$ influences the stability of these monomeric complexes in a uniform manner. Steric effects are also an important factor but their contribution depends on the stereochemistry of the metal and the steric requirements of the other coordinated ligands. The strengths of the M-CO bond also help determine relative monomer stability as can be seen from table 1.6.

Table 1.6.

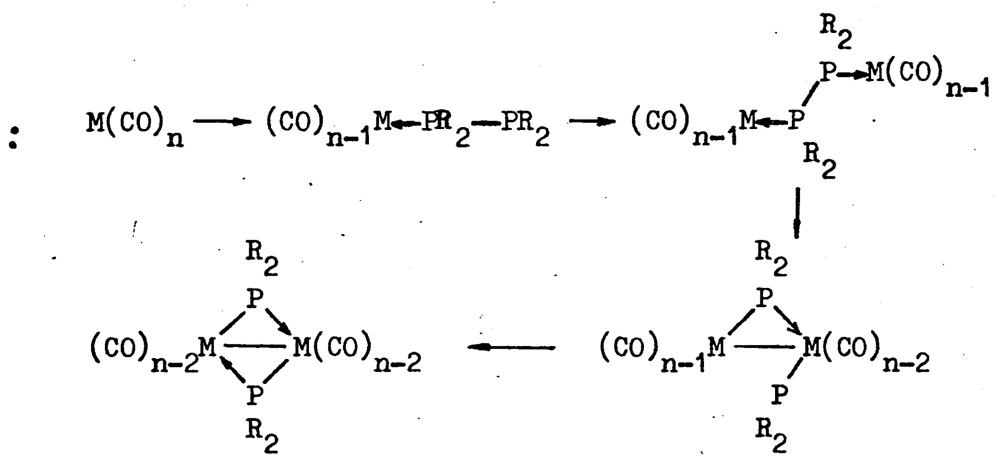
← Increasing stability of monomers

$CpNiCOSC_6F_5$	$CpNiCOSCF_3$	CpNiCOSPh	CpNiCOSMe
$Mn(CO)_5SC_6F_5$	$Mn(CO)_5SCF_3$	$Mn(CO)_5SPh$	$Mn(CO)_5SMe$
$Re(CO)_5SC_6F_5$	$Re(CO)_5SCF_3$	$Re(CO)_5SPh$	$Re(CO)_5SMe$
$CpMo(CO)_3SC_6F_5$	$CpMo(CO)_3SCF_3$	$CpMo(CO)_3SPh$	$CpMo(CO)_3SMe$
$CpW(CO)_3SC_6F_5$	$CpW(CO)_3SCF_3$	$CpW(CO)_3SPh$	$CpW(CO)_3SMe$
$CpFe(CO)_2SC_6F_5$	$CpFe(CO)_2SCF_3$	$CpFe(CO)_2SPh$	$CpFe(CO)_2SMe$

A similar table was originally complied by Abel and Crosse[1] but this modified version takes into account the results of the work described herein.

Dimeric Mercapto Complexes

The reactions of disulphides with a) dimeric carbonyls $[M(CO)_m]_2$ and $[CpM(CO)_n]_2$ and b) monomeric carbonyls $M(CO)_m$, $CpM(CO)_n$, possibly proceed via different reaction pathways since the latter do not possess a metal-metal bond which functions as a reactive centre for radical attack, or reduction of uncleaved disulphide.[36] On the basis of isolable intermediates the reaction of monomeric carbonyls with diphosphines R_2P-PR_2 can be considered to involve the following steps.[36,121]



However, no evidence has yet been found for possible mechanism (s) involved in the formation of $[M(CO)_4SR]_4$, M = Mo, W, $[Fe(CO)_3SR]_2$, $[CpCoSR]_2$ from the reactions of iron carbonyls and $CpCo(CO)_2$ with disulphides. Oxidative addition of RSSR to these carbonyls is a possibility in view of the ready formation of $Fe(CO)_4X_2$[122] and $CpCo(CO)X_2$.[113] X = Cl, Br, I, but attempted isolation of $Fe(CO)_4(SR)_2$,[123] R = C_6H_5, C_6F_5, from the reaction of $Fe(CO)_4H_2$ and RSH at 20°C was unsuccessful, only the dimers $[Fe(CO)_3SR]_2$ being detected. Similarly the reaction of $C_3F_7Fe(CO)_4I$ and $AgSCF_3$ gave only $[C_3F_7Fe(CO)_3SCF_3]_2$.[66] However, on the basis of studies involving the reaction of $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$ and analogies with the reaction of diphosphines with mononuclear metal carbonyls the following mechanism is proposed, Fig. 1.3.

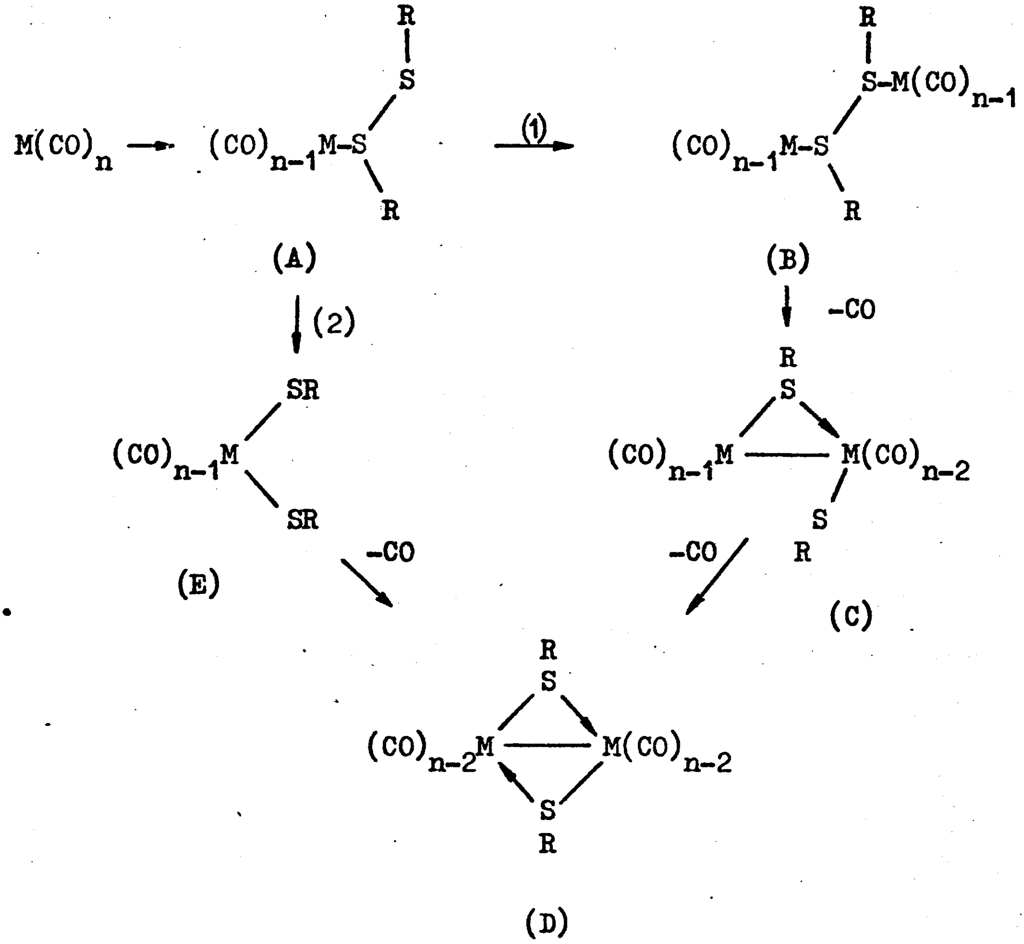
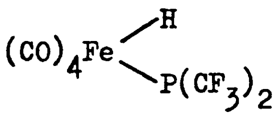


Fig. 1.3.

Thus preliminary coordination of the disulphide with CO expulsion gives A which has two alternatives depending on the reaction conditions. By analogy with the diphosphine mechanism, reaction of A with another molecule of $M(CO)_n$ occurs to give B which decarbonylates *via* C to give the dimeric product D. This explains the formation of $[CpCoSC_6F_5]_2$ in good yield when $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$ react in the absence of solvent since A probably exists long enough to collide with a molecule of $CpCo(CO)_2$ to give B. Alternatively, since S-S bond scission is much more facile than P-P bond cleavage,[36] A can undergo internal oxidative addition to compound E which, depending on the thermal stability of such an intermediate, can either be isolated, e.g. $CpCoCO(SC_6F_5)_2$, or decompose to the dimer D. The latter mechanism effectively explains the formation of $CpCoCO(SC_6F_5)_2$ exclusively from the reaction of $CpCo(CO)_2$ and the disulphide in pentane above 20°C. The presence of a solvent decreases the chance of A reacting with $CpCo(CO)_2$ before oxidative addition can occur, so that formation of $[CpCoSC_6F_5]_2$ via mechanism (1) is not observed. Attempts were made to detect intermediate A by carrying out the reaction in pentane at low temperature but no reaction was observed up to -10°C when crystals of $Co(CO)(SC_6F_5)_2$ began to form. Keeping the reaction mixture at this temperature also gave $[CpCoSC_6F_5]_2$ in addition to the monocarbonyl complex. This suggests that at -10°C A is formed initially as before but S-S bond scission and the resulting oxidative addition reaction is sufficiently slow to allow A to react with $CpCo(CO)_2$ and hence form the dimer in low yield.

It should be noted that the reaction of $Fe(CO)_5$ and $P(CF_3)_2H$ is considered to proceed via the monosubstituted derivative $Fe(CO)_4P(CF_3)_2H$.[95,112] The latter has been isolated from the reaction of $Fe_2(CO)_9$ and $P(CF_3)_2H$ under mild conditions and decomposes thermally to the dimer in accord with the above suggestion. This reaction is considered[95] to proceed via an oxidative addition reaction giving



$$(CO)_4Fe\begin{cases}H\\P(CF_3)_2\end{cases}$$

which dimerises with loss of carbon monoxide. Although not isolated, formation of this intermediate hydride complex is indicated by the isolation of the dimeric hydride $[HFe(CO)_3P(CF_3)_2]$ as one of products of thermal decomposition of the tetracarbonyl. Thus reaction mechanism (2) accounts for such products and can therefore be adapted to explain the reaction of mercaptans, RSH with iron carbonyls which yields $[Fe(CO)_3SR]_2$, and $Fe(CO)_2(NO)_2$ which yields $[Fe(NO)_2SR]_2$.[1] Oxidative addition of perfluoroalkyl iodides and iodine to carbonyl and nitrosyl complexes has also been reported, e.g.

$$CpMo(CO)_2NO \longrightarrow CpMoCONOI_2 \longrightarrow [CpMoNOI_2]_2{}^{124a}$$

$$CpCo(CO)_2 \longrightarrow CpCoCOI_2 \longrightarrow [CpCoI_2]_n{}^{124b}$$

$$Fe(CO)_5 + R_FI \longrightarrow Fe(CO)_4R_FI \longrightarrow [Fe(CO)_3R_FI]_2{}^{124c}$$

Decarbonylation of the intermediate monomer in each case gives iodine bridged dimers or poylmers.

The photolytic reactions of monomeric carbonyls will also involve reactions between RS radicals and reactive organometallic species eg. $Mo(CO)_5^*$, $W(CO)_5^*$, $Fe(CO)_4^*$ and $CpCoCO^*$. Photolysis of metal carbonyls in hydrocarbon glasses and helium matrices at low temperatures has been shown by i.r. spectroscopy to give such reactive species.[125] Thus radical intermediates such as $\cdot M(CO)_5SR$, $\cdot Fe(CO)_4SR$ may be involved in photolytic reactions and these can react with other radicals and/or reactive organometallic species to give the final products. It is interesting to note that the photolytic reaction of $CpCo(CO)_2$ and CF_3SSCF_3 gives high yields of $[CpCoSCF_3]_2$ which was not observed in dark reactions. The photochemical reaction of $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$ at 20°C gives mainly $CpCoCO(SC_6F_5)_2$ which probably results from a thermal reaction involving the uncleaved disulphide. This is indicated by simultaneous control reaction carried out in the absence of u.v. irradiation. However, crystals of $[CpCoSC_6F_5]_2$ (not produced in the control reaction) which formed on the side of the reaction vessel adjacent to the u.v. source are indicative of a radical reaction. In addition, clusters of $CpCoCO(SC_6F_5)_2$ crystals also formed in the same place indicating that formation of the latter may also occur via a photochemically initiated radical reaction in addition to a thermal reaction.

Conclusions

The high yields of mercapto complexes obtained in the majority of the reactions described indicate that the photolytic method is generally superior to thermal methods where, it is possible to draw direct comparisons. This is particularly true when unstable species such as $Mn(CO)_5SR$ are involved and are not accessible in quantity by thermal methods. Also the reagents required for photolytic reactions are usually more accessible than those frequently required for alternative synthetic routes, but in the reaction of $C_6F_5SSC_6F_5$ and $[CpFe(CO)_2]_2$ the much faster thermal reaction suggests that, in certain cases, the photolytic route is not the most efficient.

It is not immediately apparent how general photochemical reactions of this type might be, although they have been used occasionally by some workers.[1] It is recalled that photolysis of CH_3SSCH_3 probably gives CH_3S radicals[116] so that methylthio complexes may be readily accessible. However, the photochemical reaction of PhSSPh and $Fe(CO)_5$ in pentane gives $[Fe(CO)_2(PhS)_2]_2$[126] containing coordinated disulphide ligands, whereas thermal reactions yield the dimer $[Fe(CO)_3SPh]_2$.[1] Extension of the photolytic method to other systems such as diphosphines does not appear to be feasible[121] even with $(CF_3)_2PP(CF_3)_2$[127] due to the difficulty with which the P-P bond is cleaved. It may be that in cases where photolytic scission of the S-S (or P-P) bond is not possible, the required products of the cleaved disulphide (or diphosphine) may be accessible from mercapto RSH (or phosphines PR_2H) which possibly give RS• (or R_2P) radicals more easily.

INTRODUCTION

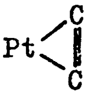
TRANSITION METAL ACETYLENE CHEMISTRY

During the last war the discovery by Reppe that alkaline solutions of iron carbonyl hydride gave hydroquinone when reacted with acetylene[128], opened up an exciting new field of research. The coordination of an acetylene molecule to a transition metal is frequently the initial step in extremely complex reactions from which can be isolated organo-transition metal complexes containing cyclic organic ligands formed by condensation of two or more acetylenes. In many cases incorporation of other coordinated ligands into the organic moiety occurs and with carbonyl complexes cyclopentadienone, tropone and quinone derivatives have been isolated.

The first step in the cyclooligomerisation process is usually coordination of an acetylene molecule to the metal[129], but in most reactions leading to cyclisation it is not possible to isolate this complex, except when the acetylene has very bulky substituents such as CMe_3 or $SiMe_3$.[129] The type of reaction(s) undergone by this intermediate π complex depends, among other things, on the nature of the bond between the metal and the acetylene and this is determined by a variety of factors as will be described later. The metal-acetylene bond is, in most respects, similar to metal-olefin bonds except that the latter can only involve one π orbital on the organic molecule.

Relatively few complexes are known in which an acetylene molecule is coordinated to a metal other than the noble metals rhodium, iridium, palladium and platinum and it is not surprising that most of the theories of metal-acetylene bonding are based on studies of such complexes, particularly of platinum-acetylene compounds.[130]

Metal-Acetylene Bonding

The platinum-acetylene (and olefin) bond is usually described in molecular orbital terms using the theory of Dewar,[131] Chatt and Duncanson.[132] The bonding essentially involves a σ bond from a filled pπ-orbital of the acetylene to an empty hybrid-orbital on the metal, complemented by a π back-bond from a filled hybrid orbital on the metal to an empty pπ^* (antibonding) orbital of the acetylene. In this bonding scheme the acetylene is formally neutral and the platinum in the +2 oxidation state. An alternative description of the bonding has been put forward within the framework of valence-bond theory[133] which involves two platinum-carbon σ bonds, giving a three membered  ring, and the acetylene carries a formal charge of 2- with the metal in the +4 oxidation state.

From a study of the i.r. spectra of divalent platinum complexes $(RC_2R)PtCl_2L$, (L = Cl$^-$, amine), Chatt et al. deduced that the metal-acetylene interaction was relatively slight , their criterion being $\Delta\nu C{\equiv}C$ = [$\nu C{\equiv}C$(free acetylene)-$\nu C{\equiv}C$ (coordinated acetylene)]cm^{-1}.[134] The decrease in frequency observed, about 200 cm^{-1}, and the low intensity of the $\nu C{\equiv}C$ band of symmetrical acetylenes, appeared to indicate rather weak bonding to the metal with only a small distortion of the acetylene from its uncomplexed geometry.

The second type of complex, $(Ph_3P)_2Pt(RC_2R^1)$, investigated by Chatt showed a strong band near 1800 cm^{-1} in the i.r. spectrum assigned to the C≡C stretching mode of the coordinated acetylene. $\Delta\nu C{\equiv}C$ was much larger in these complexes and it was suggested that the bonding of the acetylene to the metal, (formally Pt(0)), was much stronger than in the PtII complexes.[134] Thus, in the zero valent complexes the metal acetylene bonding is described more accurately by the valence-bond model involving Pt-C σ bonds.

In a later paper[135] Chatt pointed out that the possibility existed of a series of complexes in which a gradual transition occurred between the two bonding types. He also pointed out that the essential difference between the two types was due to the electron-releasing or withdrawing character of the group R on the acetylene. Subsequently, metal-acetylene bonding became rather a controversial issue and Collman and Kang summarised the position in 1967[136]. "At the present time it is an unsettled question whether the two bond types represent energy minima and could be found in valence tautomerism or whether these are extreme descriptions of a gradual transformation". These authors inclined towards the second viewpoint as have subsequent workers who recently attempted to present a unified description of the metal-acetylene linkage involving a single bonding scheme embracing PtII and Pt0 complexes.[130,137]

Platinum II Olefin and Acetylene Complexes

The success of a theory depends on its ability to explain experimental observations and, in PtII-acetylene complexes, one of these has already been mentioned viz. the reduction of νC≡C by 200-250 cm^{-1} from that of the free acetylene. Among other experimental observations the more important are the slight lengthening of the multiple bond and bending of the substituents R away from the metal to give a cis bent configuration. In addition the energy barrier to free rotation of the acetylene is probably very low since in analogous olefin complexes it is in the region 10-15 K.cal/mole. X-ray studies have revealed that, as a result, crystal packing forces are sometimes sufficient to distort the square planar arrangement from 90°.[130]

Description of Bonding

The original molecular orbital treatment of Dewar, Chatt and

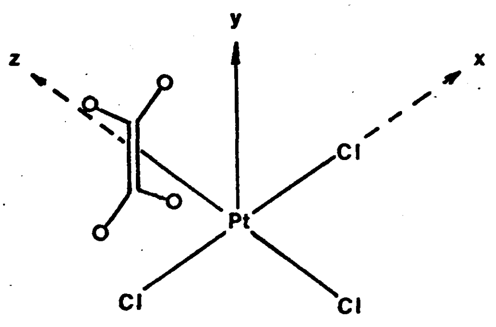


Fig. (i) PtII olefin complex

Duncanson, when applied to PtII complexes, Fig. (i), envisaged the acetylene (or olefin) platinum bond being formed by donation of charge from a full $p\pi$ orbital on the acetylene to the empty $5d_z 2 5d_{x^2-y^2} 6s6p_z$ hybrid orbital on platinum, and the π-backdonation occurring from the $5d_{yz}$ $6p_y$ hybrid orbital on the metal to an empty $p\pi^*$ orbital on the acetylene. This bonding scheme requires the acetylene to be perpendicular to the square plane surrounding the platinum and, to account for the low energy barrier to rotation, it is also necessary to allow back donation to occur from the $5d_{xz}$ orbital on platinum. Calculations have shown[138] that $d\pi$-$p\pi$ hybridisation involving an unoccupied p orbital leads to a stronger metal-ligand π-bond so that the $5d_{yz}$ orbital will give a weaker bond than the $5d_{yz}$ $6p_y$ hybrid orbital and this explains why the perpendicular arrangement of the C-C bond is the most stable. This argument has recently been put on a semi-quantitative basis by calculation of the total energy of trans-$Pt(NH_3)Cl_2(C_2H_4)$ as a function of the angle between the C-C axis and the $PtNCl_2$ plane.[139] The results show a deep energy minimum when this angle is 90° which corresponds to the position necessary for maximum π back-donation from the $5d_{yz}$ $6p_y$ orbital of the platinum, and a shallow minimum when the angle is 0°, at which back-donation from the

$5d_{xz}$ orbital reaches a maximum.

Platinum (0) Olefin and Acetylene Complexes

With complexes of the type $(Ph_3P)_2PtRCCR^1$ in which large values of $\Delta\nu C\equiv C$ ($\sim$ 500 cm^{-1}) are found, X-ray studies have revealed that the axis of the multiple bond lies close to the plane containing the metal and phosphine ligands (Fig. ii). The dihedral angle α usually lies in the range $8-12^{\circ}$ while the multiple bond subtends an angle β at the platinum atom close to 40°, and again the substituents bound to the multiple bond have the <u>cis</u> bent configuration. In general, the C-C bond is weakened to a greater extent upon coordination than in PtII complexes and this effect is particularly prominent with olefin and acetylenes bearing electron withdrawing substituents. This indication of stronger M-acetylene (olefin) interaction is also reflected in the stabilities of these complexes which are usually greater than those of unsaturated molecules containing electron releasing substituents.

Description of Bonding

The last two observations, and the fact that percyano olefin and acetylenes, which are very poor σ donors but very good π acceptor ligands, form stable complexes with Pt(0), suggest that the bonding can be described in terms of the Dewar-Chatt-Duncanson model. In

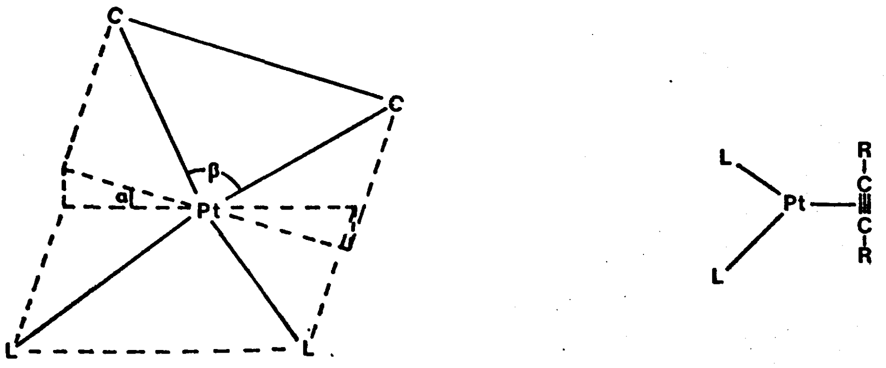
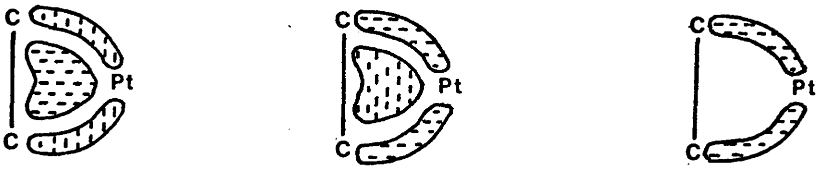


Fig. (ii)

these complexes, however, back-donation to the π^* orbitals of the acetylene (olefin) is much greater than in PtII compounds, thus accounting for the greater weakening of the multiple bond on coordination and the change in hybridisation of the sp^2 carbon atoms towards sp^3. Calculations,[139] similar to those for PtII complexes, have shown that for $(PH_3)_2Pt(CH_3C{\equiv}CCH_3)$ the total energy of the system has a single minimum when the multiple bond lies in the $Pt(P)_2$ plane, thus accounting for the absence of free rotation of the acetylene or olefin in Pt(0) compounds.

If the carbon atoms of the C-C bond were to be completely rehybridised to sp^3 the olefin or acetylene would be a dicarbanion forming two σ bonds to the metal as in the valence bond model of Gelman. Although superficially this appears to be very different from the Dewar-Chatt-Duncanson approach, in reality the two models merge as shown by Maitlis et al[137] and Hartley.[130] By considering changes in the relative importance of the σ and π contributions to the Pt-acetylene bond, these workers suggest that the two classes of complex observed, PtII and Pt(0), are in fact extreme types. In the former σ donation predominates and such complexes are stabilised by electron releasing substituents on the acetylene, while in the latter the predominant π back-donation is facilitated by electron withdrawing substituents. This is illustrated by the following diagram which shows the effect on the distribution of electron density as the σ and π components are altered.

Recent molecular calculations[140] have reinforced the conclusion that electron withdrawing substituents on the C-C multiple bond stabilise Pt(0) complexes by showing that the strength of the metal-acetylene bond is strongly dependent on the amount of π-back-donation.

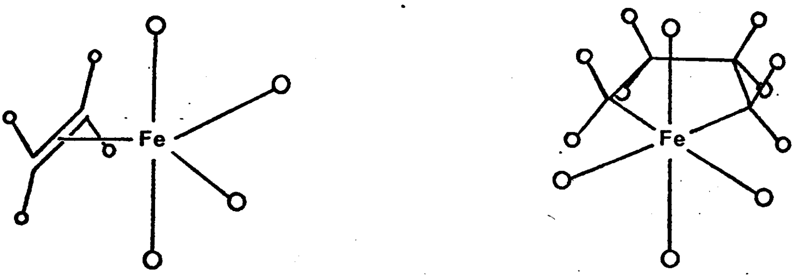


▨ Region of high electron density

▥ Region of low electron density

This appears to be a fairly general conclusion since Kramer, who has studied olefin rotation in $CpRhL_2$ and acac RhL_2, L = olefin, acac = acetylacetonato, found that rotation of coordinated ethylene and monofluoroethylene occurs readily but coordinated tetrafluoroethylene remains in a fixed orientation, even at 100°C.[141] This indicates a greater barrier to rotation of coordinated $CF_2{=}CF_2$, and possibly stronger metal-olefin bonding. The latter conclusion was subsequently confirmed by X-ray diffraction studies of $LRh(C_2H_4)(C_2F_4)$, L = acetylacetonato,[142] Cp.[143] In both compounds the metal-olefin bond is much shorter with $CF_2{=}CF_2$ and the increase in C=C distance on coordination is much greater with the fluoroolefin. These results imply that complexes such as $CpRh(C_2F_4)_2$ have metal-olefin bonds intermediate between those in PtII and Pt(0) complexes. $CpMn(CO)_2CF_3C_2CF_3$[144] which shows an acetylenic C-C stretching mode at 1919 cm^{-1} in the i.r. spectrum ($\Delta\nu = 381\ cm^{-1}$), also appears to be intermediate between the two extremes. Olefin and acetylene complexes of transition metals other than platinum are also known which appear to fall into the more extreme classes[130], but Chatt's original postulate of the existence of a series of complexes in which a gradual transition occurs between the two types, has now become an experimental reality.

It has become apparent that the presence of electron-withdrawing substituents on acetylenes (or olefins) influences the nature of the metal-acetylene (olefin) bond significantly and, as suggested earlier, this in turn influences the reactivity of complexes containing coordinated acetylenes[145] or olefins. An interesting example of this is the type of product obtained when iron carbonyls react with ethylene or perfluoroethylene. Thus CH_2=CH_2 gives $Fe(CO)_4C_2H_4$ [146a] containing a coordinated olefin, while CF_2=CF_2 gives $Fe(CO)_4(CF_2)_4$ [146b] with the structure illustrated. The ethylene complex contains a



○ CO ◦ F ∘ H

simple metal-olefin bond, whereas in the fluoro-carbon compound condensation of two C_2F_4 units has occurred, and these are linked to the iron by Fe-C σ bonds. This tendency to form transition metal complexes containing M-C σ bonds is a characteristic feature of fluoro-olefins and fluoro-acetylenes and must be due to the stability of such linkages when compared with those in which the carbon has hydrogen or alkyl substituents attached.[145]

The strength of M-C σ bonds has attracted much interest over the past twenty years and recent developments[147] suggest that transition metal-carbon bonds are not, as was originally thought, thermodynamically unstable, but owe their lability to kinetic factors, suitable pathways being available for facile M-C bond-cleavage. The stability of transition-metal-perfluoroalkyl linkage was originally suggested to result from π-back-bonding between filled d orbitals on the metal and

π^* orbitals on the ligand.[148] Evidence from i.r. spectroscopy and short M-C bond lengths, combined with large M-C-F angles in crystal-structures of perfluoroalkyl derivatives, seemed to support this.[148] However, an alternative explanation for the i.r. data has been given,[149] Graham's interpretation of CO force-constants[150] suggest that π-bonding in M-C σ bonds is negligible, and recent calculations by Fenske[151] can account for the short M-C distances. It is important to note that these conclusions relate only to M-C σ bonds and not to metal-acetylene and olefin linkages which, in many cases, have predominantly π character. However, in addition to accounting for the instability of transition-metal-alkyl bonds, it is now apparent that new theories of M-C bonding must also be required to explain the greater stability of transition-metal-perfluoroalkyl bonds.

In addition to their stabilising influence on M-C σ bonds, the presence of electronegative substituents on carbon substantially affects the reactivity of unsaturated molecules as already illustrated in reactions of iron carbonyls and olefins. This effect is particularly marked in the reactions of transition-metal complexes with acetylenes[145] and has led to an increase in the study of reactions involving hexafluorobut-2-yne $CF_3C{\equiv}CCF_3$ and, to a lesser extent, $CF_3C{\equiv}CH$, $C_6F_5C{\equiv}CC_6F_5$ and $C_6F_5C{\equiv}CH$ over the past decade.

Several reviews covering various aspects of transition metal acetylene chemistry have been published recently,[129,152,153] one of which covers the chemistry of fluoroacetylenes exclusively.[154] Three basic types of product can be identified from the studies reported : (1) complexes in which RC≡CR units are present, (2) complexes resulting from insertion of an acetylene into a metal ligand bond, (3) complexes resulting from condensation of RCCR groups. The following text describes briefly some of the chemistry of such derivatives and, in view of the reactions described in chapters II-V, is confined mainly to complexes derived from fluoroacetylenes.

Complexes in which RCCR units are Present

A number of complexes have been isolated in which one or more acetylenes coordinate to a transition metal other than platinum and still retain their identity.

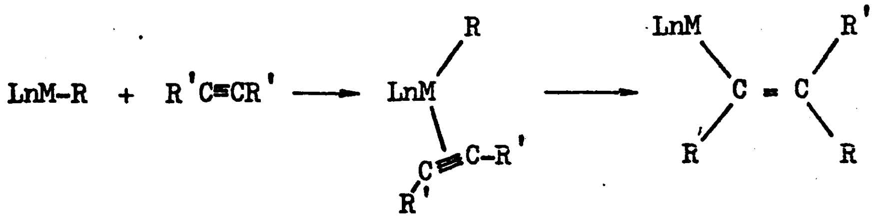
Group VI metal acetylene complexes of stoichiometry $M(RCCR)_3X$, $M = W$, $R = Ph$, $X = CO$, $M = Mo, W$, $R = CF_3$, $X = CH_3CN$, are known[155,156] in which each of the three coordinated acetylenes is considered to donate four electrons to the metal. This gives a formal twenty electron configuration but a qualitative M.O. treatment[156] suggests the two 'extra' electrons are situated in a non-bonding orbital. This theory is in agreement with the geometry of the coordinated acetylenes as revealed by a recent X-ray study of $W(CO)(PhCCPh)_3$.[157] Photochemical substitution of one carbonyl group in $CpMn(CO)_3$ by acetylenes gives $CpMn(CO)_2RCCR$, $R = CF_3$,[144] Ph.[158] A weak band at 1919 cm^{-1} in the i.r. spectrum of the hexafluorobut-2-yne complex, according to Wilkinson, indicates that the acetylene functions as a simple electron-donor, but, as suggested earlier, a small degree of π acceptance in this complex is also probable.

A variety of acetylenes react with $Co_4(CO)_{12}$ displacing two carbonyl ligands to give complexes $Co_4(CO)_{10}RC_2R$ in which the acetylene bridges all four metal atoms.[129,152] With dicobalt octacarbonyl at room temperature, complexes $Co_2(CO)_6RC_2R$ have been obtained[129,152] and an X-ray study of the diphenylacetylene derivative[159] has shown that the bridging acetylene functions as a two electron donor to each metal atom. A similar structure has been found[160] in the complex $Co_2(CO)_6C_6F_6$ which results from partial defluorination of of octafluorocyclohexa-1,3-diene in the presence of $Co_2(CO)_8$. The bridging acetylene is hexafluorocyclohex-1-yne-3-ene.

Products containing a coordinated tetrafluorobenzyne molecule have been isolated from the reactions of $Co_4(CO)_{12}$ and $Fe_2(CO)_9$ with C_6F_5MgBr.[161] The cobalt complex gives $Co_4(CO)_{10}C_6F_4$, analogous to $Co_4(CO)_{10}RC_2R$, while the iron carbonyl gives a dimetallated benzyne derivative $Fe_2(CO)_8C_6F_4$. Recently benzyne derivatives were reported to be formed in the reaction of triphenylphosphine with osmium carbonyl under certain conditions and the X-ray structures of some of them have been solved.[162] These apparently result from metallation of phenyl groups on the phosphines and, in some cases, cleavage of the P-C bond has also occurred.

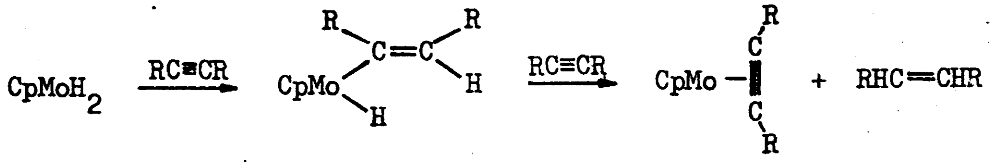
Insertion Reactions

A type of ligand combination reaction undergone by acetylenes (and olefins) is that involving insertion into a metal-ligand bond to give a σ bonded olefinic or alkyl ligand. In certain cases preliminary coordination of the unsaturated organic compound has been shown to precede the insertion reaction and it is possible that many, if not all insertion reactions, proceed through this pathway. The



transition metal catalysed polymerisation of unsaturated organic molecules is believed to involve multiple insertion reactions of this type, although intermediates have not often been isolated, and the exact mechanisms remain obscure. However, evidence is now beginning to accrue which suggests that reactions of this type, at least with alkynes bearing electron withdrawing substituents, may proceed by different routes in certain circumstances.[163]

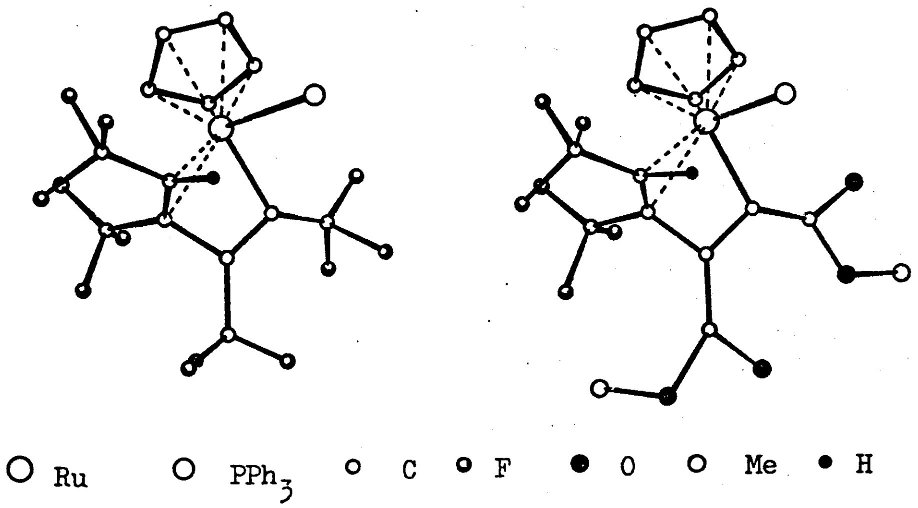
The reactions of acetylenes PhC≡CPh, COOMeC≡CCOOMe and $CF_3C{\equiv}CCF_3$ with the dihydride Cp_2MoH_2[164] give products which illustrate the effect of electronegative substituents on the reactivity of M-C σ bonds. With $CF_3C{\equiv}CCF_3$,insertion into one of the Mo-H bonds was observed and the trans olefinic isomer of $Cp_2MoH[C(CF_3){=}C(CF_3)H]$ was isolated. In contrast, insertion of dimethylacetylenedicarboxylate at 20°C gave the cis olefinic isomer of $Cp_2MoH[C(COOMe){=}C(COOMe)H]$, but this could be converted to the trans isomer at 110°C. However, with Cp_2MoH_2 and diphenylacetylene,the π-bonded substitution product Cp_2MoPhC_2Ph was obtained, although an intermediate insertion product was suggested by the isolation of stilbene from this reaction. To account for these observations the following mechanism was proposed .



The stability of the intermediate complexes appears to depend on the electron-withdrawing ability of R and hence on the stability of the M-C σ bond.

Insertion of hexafluorobut-2-yne and 3,3,3-trifluoropropyne into metal-hydrogen bonds of the hydrides $Mn(CO)_5H$ and $Re(CO)_5H$ has also been studied[165,189] and in each case trans addition observed. Trans addition of acetylenes RC≡CR, R = CF_3, COOMe,[166] CN,[167] to iridium-hydrogen bonds has also been observed and an X-ray study of the dicyanoacetylene complex, $Ir(PPh_3)_2(CNC_2CN)[C(CN)=C(CN)H]$,[168] has revealed a structure containing both the vinyl ligand and a coordinated acetylene molecule. It was therefore suggested that similar complexes may be involved in the linear polymerisation of acetylenes.

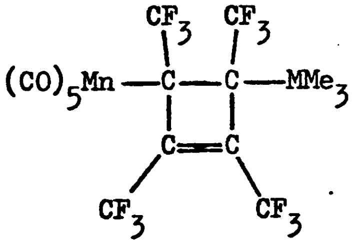
In contrast, insertion of electrophilic acetylenes into Re-H,[169] Rh-H[170] and Pt-H[171] bonds, has been observed to give *cis* vinyl complexes suggesting perhaps, a different reaction mechanism may be involved relative to reactions which give *trans* products. *Cis* vinyl complexes $CpRu(PPh_3)_2(CR=CRH)$ have also been isolated from the reactions of $CpRu(PPh_3)_2H$ and RC≡CR, R = CF_3, COOMe,[163] and these react with $CF_3C{\equiv}CCF_3$ to give $CpRuPPh_3[C_4(CF_3)_4H]$ and $CpRuPPh_3[C_2(COOMe)_2C_2(CF_3)_2H]$ respectively. The crystal structure of the former has been solved and would appear to indicate insertion of an acetylene into the M-C bond of the vinyl complex. However, the structure of the dimethyl acetylenedicarboxylate complex suggests otherwise and an ionic mechanism was therefore proposed to account for the apparent insertion of $CF_3C{\equiv}CCF_3$ into a carbon-hydrogen bond.



Formation of $\overline{Co(CO)_3C_4(CF_3)_4CH_2CMe}{=}CH_2$ from $CF_3C{\equiv}CCF_3$ and tricarbonyl (π-2-methylallyl)cobalt[172] can be explained by a similar mechanism.

Insertion of hexafluorobut-2-yne into the platinum-carbon bond in $L_2PtClCH_3$, L = tertiary phosphine, arsine, has been shown to proceed via five coordinate complexes containing a π bonded acetylene ligand.[173,174] The stability of these intermediates and the ease with which they formed insertion products $L_2PtCl[C(CF_3){=}C(CF_3)CH_3]$ was found to follow the trans effect of the ligands L. It was concluded on this basis that the reactivity of methyl-platinum compounds towards insertion depends on the stability of the intermediate π-complex.

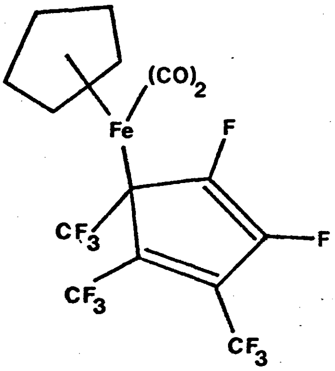
Insertion of hexafluorobut-2-yne and 3,3,3-trifluoropropyne into the M-M bonds of $CpFe(CO)_2MMe_3$ and $Mn(CO)_5MMe_3$, M = Si, Ge, Sn, has been studied by Clark.[175,176] Several products of simple insertion were found, e.g. $CpFe(CO)_2[C(CF_3){=}C(CF_3)SnMe_3]$, but frequently compounds were obtained, possibly due to reaction of mono-insertion derivatives with another molecule of acetylene e.g.



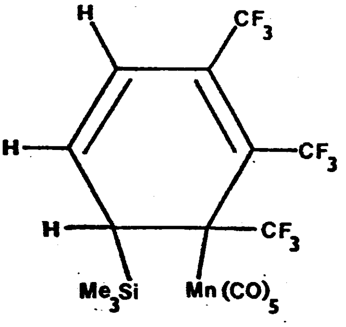
M = Si, Ge, Sn

However, under conditions which produced $Mn(CO)_5[C_4(CF_3)_4MMe_3]$, $CpFe(CO)_2SnMe_3$ and $CF_3C{\equiv}CCF_3$ gave $CpFe(CO)_2C_8F_{11}$ which has been assigned the following structure.

It was therefore proposed that $CpFe(CO)_2[C_4(CF_3)_4SnMe_3]$ is formed initially, but eliminates Me_3SnF to give $CpFe(CO)_2C_8F_{11}$. Me_3SnF was detected in the above reaction and in other reactions which gave products resulting from insertion and subsequent elimination.



With $CF_3C\equiv CH$ several cases of mono-insertion into M-M bonds were observed but this acetylene generally proved to be less reactive than $CF_3C\equiv CCF_3$. However, with $Mn(CO)_5SiMe_3$ a product assigned the structure



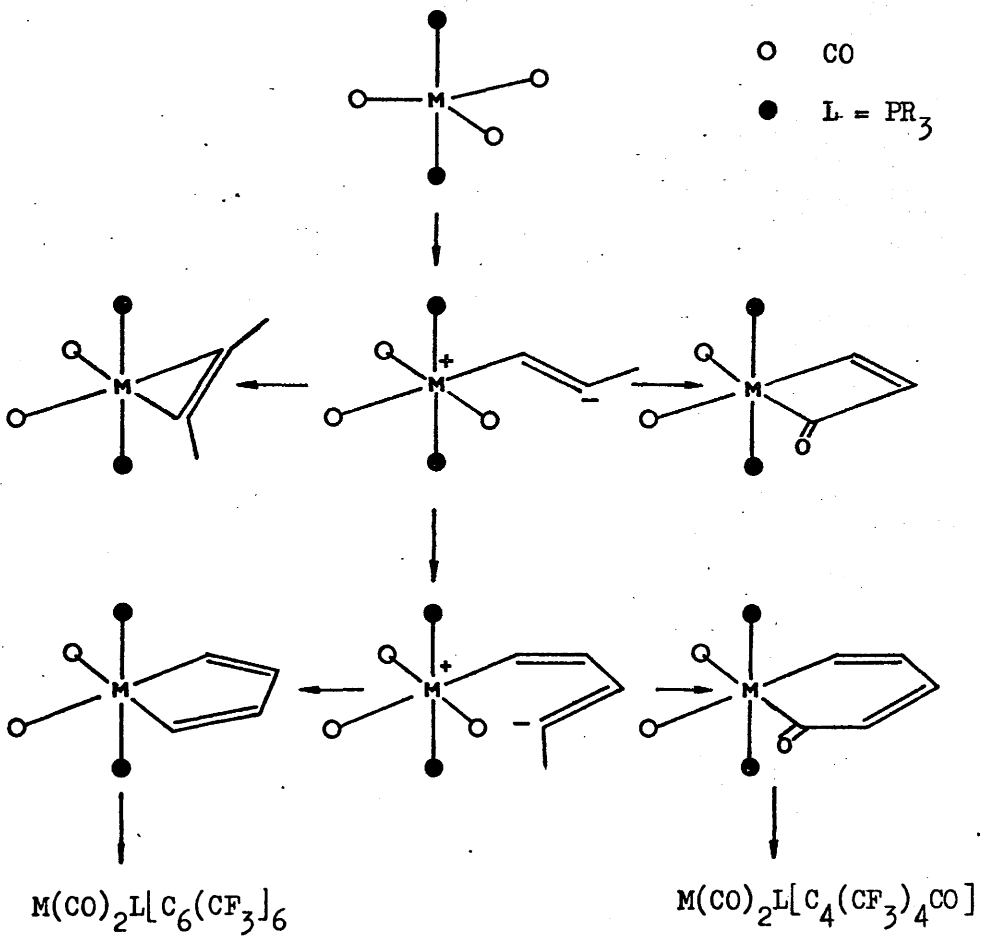
was isolated. The formulation of such a structure would imply bond-cleavage within the acetylene and proton, or CF_3, migration. Although this is not impossible, an X-ray study of this compound would seem desirable to clarify the situation.

Reactions involving Cyclooligomerisation of the Acetylene

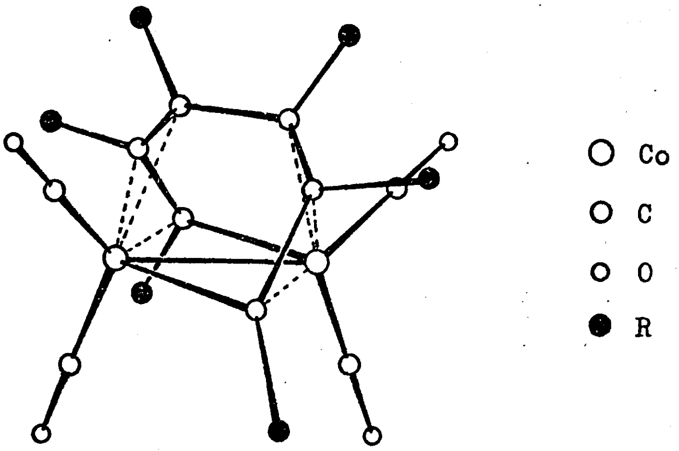
Although the reactions of a wide variety of low-valent transition metal complexes with fluorinated acetylenes have been investigated, comparatively few studies involving the early transition metals have been reported. Moreover, indications are that only substitution reactions occur, in contrast to the reactions of diphenylacetylene with $CpM(CO)_4$, M = V, Nb, Ta,[177,176] $Mo(CO)_6$ and $Mo(CO)_3(diglyme)$,[179] which give a wide range of unusual products containing coordinated acetylene molecules, substituted cyclobutadiene and cyclopentadienone ligands. However, fluoroacetylenes have been observed to undergo cyclisation in reactions with complexes of the Group VIII metals, with which extensive studies have been carried out. It should be noted however, that complexes of the iron, cobalt and nickel subgroups also appear to be more reactive towards diphenylacetylene and other related acetylenes.[129,152]

The reaction of acetylenes $CF_3C{\equiv}CCF_3$,[180] $CF_3C{\equiv}CH$[181] and $C_6F_5C{\equiv}CH$[182] with iron carbonyls gives, in all cases, a cyclopentadienone iron tricarbonyl complex $Fe(CO)_3[C_4R_4CO]$. However, the reaction of with $C_6F_5C{\equiv}CC_6F_5$ gives $Fe_2(CO)_6(C_6F_5C_2\ C_6F_5)_2$ which, according to spectroscopic data, contains a ferracyclopentadiene ring.[183] This is in contrast to the reactions of iron carbonyls with acetylenes bearing alkyl and aryl groups which yield a large variety of products.[129,152] However, these products were usually isolated in low yield from large scale reactions whereas the fluoro-acetylene reactions have been carried out on a small scale, due to the relative inaccessibility of the acetylenes, so that a direct comparison is perhaps not valid. This suggestion appears to be substantiated by the recent report[184] that $PhC{\equiv}CC_6F_4Cl$ reacts with $Fe_3(CO)_{12}$ to give a complex mixture containing at least twelve products. Only three of these could be isolated in sufficient quantity for characterisation, $Fe_2(CO)_6(PhC_2C_6F_4Cl)_2$, $Fe_2(CO)_2[(PhC_2C_6F_4Cl)_2CO]$ and $Fe(CO)_3(PhC_2C_6F_4Cl)_2$, all of which have analogues produced from dialkyl and diaryl acetylenes.

A wide variety of transition metal complexes act as catalysts for the cyclotrimerisation of acetylenes to benzene derivatives and several mechanisms have been proposed to account for this reaction.[129] Recently attention has been focussed on the intermediacy of metalocyclopentadiene complexes, the stepwise building up of an arene ring being clearly demonstrated.[185] This led Green and co-workers to investigate the reaction of hexafluorobut-2-yne with phosphine substituted carbonyls of the iron group metals, and from the intermediates isolated, the following ionic mechanism was proposed[186] Fig. (iii).



The simple substitution products $Co_2(CO)_6RC_2R$, described earlier, react at high temperatures with excess acetylene to give complexes $Co_2(CO)_4(RCCR)_3$[129,152] and substituted benzenes $(CR)_6$. X-ray studies of $Co_2(CO)_4[C_2H_2)(Bu^tC_2H)_2]$[187] and $Co_2(CO)_4(CF_3C_2H)_3$[188] revealed an interesting flyover structure which may indicate how the substituted benzenes are produced in this reaction.

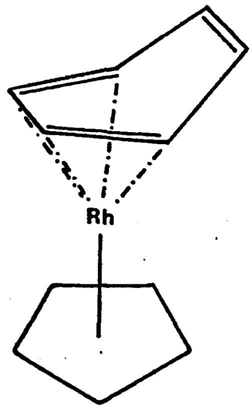


3,3,3-Trifluoropropyne reacts with cobalt carbonyl to give, in addition to $Co_2(CO)_6CF_3C_2H$ and $Co_2(CO)_4(CF_3C_2H)_3$,a methinyltricobalt enneacarbonyl complex $Co_3(CO)_9CCH_2CF_3$,similar in structure to $Co_3(CO)_9CF$ described in Chapter I.[181,189] A related complex,$Co_3(CO)_9CCH_2C_6F_5$, was subsequently reported to result from the reaction of $Co_2(CO)_8$ and $C_6F_5C{\equiv}CH$.[182]

The substituted cyclopentadienone complex $CpCo[PhC)_4CO]$ was formed in 80% yield on irradiation of $CpCo(CO)_2$ and PhCCPh in benzene while in refluxing xylene an additional complex $CpCo(PhC)_4$ was isolated which contains a tetraphenylcyclobutadiene ligand. However, acetylenes with fluorocarbon substituents usually give only the cyclopentadienone derivatives,[190] although the use of compounds CpCoL, L = C_5H_5, 1,5-cyclooctadiene, as a source of the CpCo moiety enabled the cyclobutadiene complex $CpCo(PhC_2CF_3)_2$ to be obtained from $PhC{\equiv}CCF_3$.[191] Originally it was suggested that the presence of a phenyl substituent on the acetylene promoted the formation of cyclobutadiene complexes, perhaps as a result of conjugation between the phenyl ring and the acetylene triple bond,[191] but recent work does not support this contention.[192] Formation of cyclobutadiene derivatives has been shown to occur <u>via</u> complexes of stoichiometry $(CpCo)_2(RC_2R)(CO)$ containing bridging acetylene and carbonyl groups[193] and also <u>via</u> metalocyclopentadiene intermediates $CpCoL(RC)_4$.[194] With fluorocarbon substituents the stability of Co–C σ bonds in such intermediates might explain why cyclobutadiene derivatives have never been obtained from $CF_3C{\equiv}CCF_3$ and other fluoroacetylenes.

The reaction of acetylenes with $CpRh(CO)_2$ as with $CpCo(CO)_2$ also gives cyclopentadienone complexes but in some cases the reactions are much more complicated and, in addition, give large amounts of hexa-substituted benzenes $(RC)_6$ formed by cyclotrimerisation of the acetylene. Thus with $C_6F_5C{\equiv}CC_6F_5$ Rausch obtained,[195] in addition to the cyclopentadienone derivative and $(C_6F_5C)_6$, $(CpRh)_3(C_6F_5C_2C_6F_5)CO$ and $(CpRh)_2[C_4(C_6F_5)_4]$. Similar complexes were also obtained with diphenylacetylene. The reaction of $CpRh(CO)_2$ and hexafluorobut-2-yne was originally reported to give a cyclopentadienone complex and $CpRhC_6(CF_3)_6$[196] an X-ray study of the latter revealing a non-planar tetrahapto hexakis(trifluoromethyl)benzene ring π-bonded to a CpRh residue.[197] This reaction was later found to be very sensitive to

(CF_3 groups omitted)



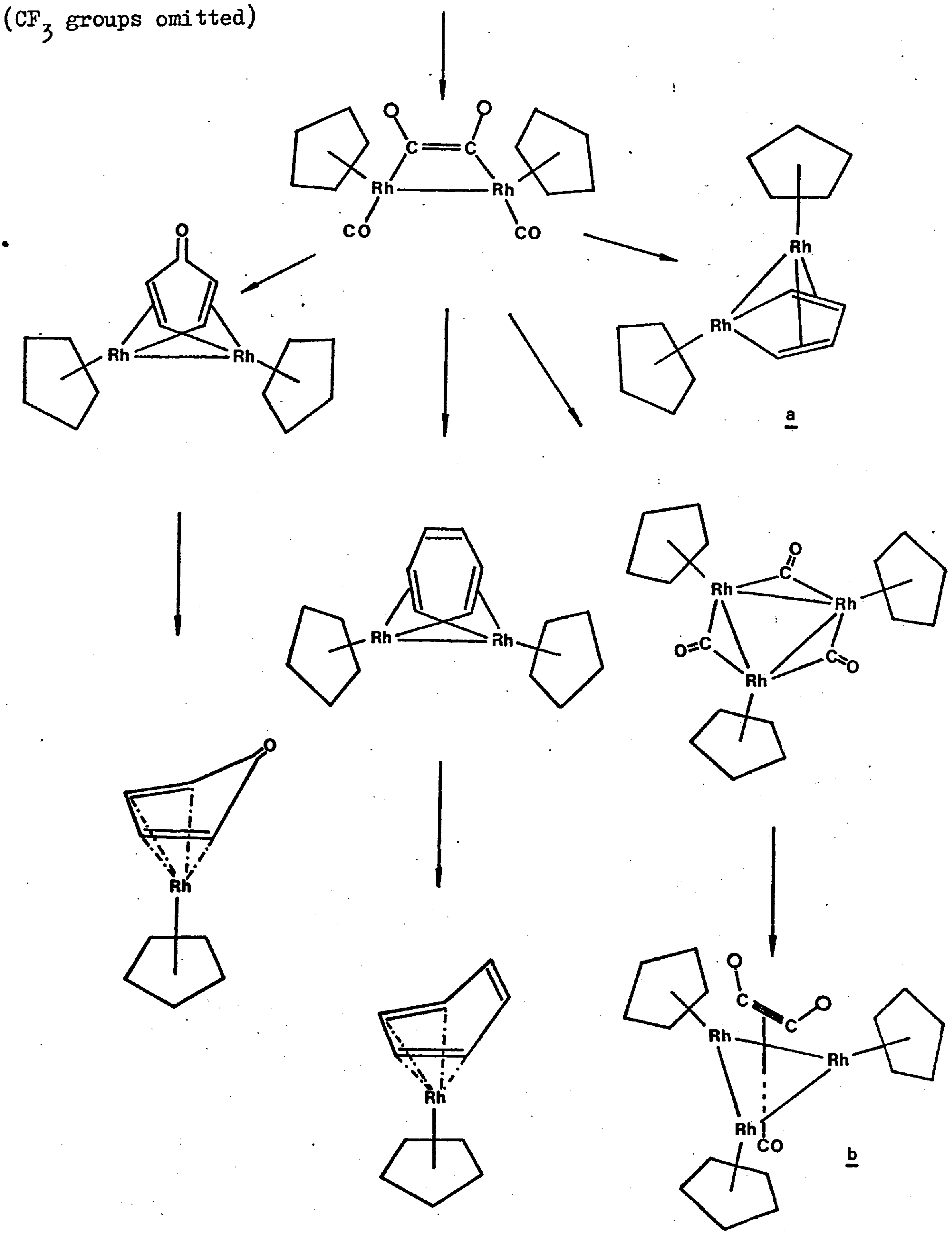
temperature and the following reaction scheme was therefore postulated to account for the products obtained under a variety of conditions[198] Fig. (iv).

The stoichiometries of (a) and (b) are equivalent to products obtained from $C_6F_5C{\equiv}CC_6F_5$ and $CpRh(CO)_2$.[195] It is notable that the metalocyclopentadiene complex $(CpRh)_2C_4(CF_3)_4$ does not react with excess acetylene to give a benzene derivative in contrast to the work of Green.[186]

Fig. (iv)

$\underline{CpRh(CO)_2 + CF_3C{\equiv}CCF_3}$

(CF_3 groups omitted)



CHAPTER II

REACTIONS OF ACETYLENES WITH SOME TRIFLUOROMETHYLTHIO- AND PENTAFLUOROPHENYLTHIO METALLATES

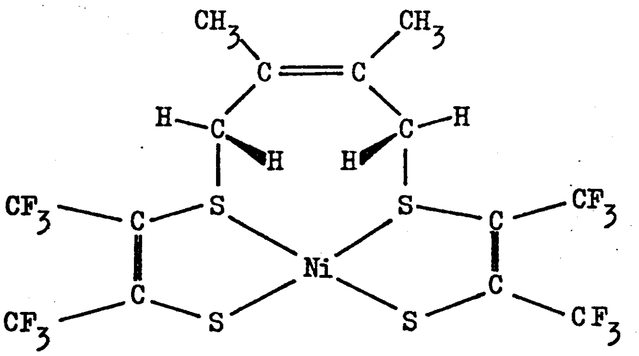
INTRODUCTION

It is apparent from the reactions described that one of the most interesting aspects of transition metal-acetylene chemistry is the reactivity of coordinated acetylenes towards other coordinated ligands. Until recently most studies involving ligand synthesis have involved simple insertion or cyclisation reactions, but, in some cases involving fluroacetylenes, cyclo-addition reactions with unsaturated organic ligands have also been observed.[199,200,201] The increased reactivity of unsaturated organic molecules when coordinated to a transition metal is well known and, although not so well documented, the same appears to be true of inorganic ligands.[129,202,203,204] However, the ready availability of trifluoromethylthio and pentafluorophenylthio complexes provided an opportunity to study the potentially interesting reactions of these sulphido derivatives towards acetylenes, in particular hexafluorobut-2-yne.

An extensive chemistry of organo-sulphur derivatives is known,[205] no doubt as a result of the importance of such compounds in biological systems, and this is also the reason behind recent interest in some aspects of transition metal sulphur chemistry.[206] Due to the unavailability of perfluoroorgano compounds their reactions with sulphur and its derivatives have not been so well documented until recently.[207]

Hexafluorobut-2-yne and elemental sulphur give a variety of products depending on reaction conditions, two of the most interesting being bis(trifluoromethyl)dithietene, $(CF_3C)_2S_2$, and tetrakis(trifluoromethyl)thiophene, $[C_4(CF_3)_4S]$.[207] The former, which has a reactive S-S bond, has proved to be an extremely interesting ligand towards transition metals.[208] The ligand properties of the latter have not been investigated as yet, although the variety of reactions undergone by thiophene and thiophene derivatives with transition metal complexes[1] should provide impetus for such studies, particularly in view of the well known ability of CF_3 substituents to change the coordinating properties of unsaturated organic molecules.[145]

Few reactions of acetylenes and other unsaturated organic compounds with sulphido complexes have yet been reported. Nickel sulphide and diphenylacetylene react to give the dithiobenzil complex $[(PhC)_2S_2]_2Ni$[209] which reacts with excess alkyne at higher temperatures to give tetraphenylthiophene. Oxidative cyclo-addition of norbornadiene and butadiene derivatives to related nickel and platinum ditholene complexes have been reported and an X-ray study of the adduct produced from 2,3-dimethylbutadiene and $[(CF_3C)_2S_2]_2Ni$ has given the following structure.[210]



The stereochemistry of this and other butadiene derivativ^s cannot be explained by direct application of Woodward-Hoffmann rules, but a simple orbital correlation model, proposed by Wing and co-workers, can account for the observed products.

These results, although rather meagre, are sufficient to suggest purposeful research into the reactivity of organosulphur derivatives of the transition metals towards other unsaturated organic molecules such as acetylenes with a view to discovering new chemistry of the coordinated sulphido ligand.

The following text describes the results of studies into the reactivity of hexafluorobut-2-yne, $CF_3C{\equiv}CCF_3$, and 3,3,3-trifluoropropyne, $CF_3C{\equiv}CH$, towards some of the trifluoromethylthio and pentafluorophenylthio metallates described in Chapter I. A variety of reaction types have been observed and isolation of reaction intermediates in several instances has enabled discussion of possible reaction mechanisms. Where appropriate, these have been compared and contrasted with those proposed recently on the basis of contemporary theories of fluoroacetylene reactivity in the presence of transition metal derivatives.[163,186] Brief attempts have also been made to rationalise the various reaction types in terms of these reaction mechanisms, and the reactivity of both the organosulphur complexes and the acetylenes.

General Experimental Methods

Reactions were carried out in dry pentane as solvent (~ 20 ml.), in thick-glass reaction vessels (~ 100 ml. capacity), sealed by teflon stopcocks (Ace Glass Inc.).

I.R. spectra were recorded on a Perkin-Elmer 225 spectrophotometer. N.m.r. spectra were recorded on a Jeol C 60 H.L. spectrometer and on a Varian Associate H.A. 100 spectrometer (at 100 M.Hz (^1H) and 94.1 M.Hz (^{19}F).) All other experimental details are as described in Chapter I, page 16.

SUMMARY OF REACTIONS

(1) $\mathrm{RC{\equiv}CR + CpM(CO)_3SCF_3 \longrightarrow CpM(CO)_2(RC_2R)SCF_3}$

$\mathrm{M = Mo;\ R = CF_3,\ CH_3,\ C_6H_5;\ M = W;\ R = CF_3,\ CH_3}$

(2) $\mathrm{CF_3C{\equiv}CH + CpMo(CO)_3SCF_3 \xrightarrow{30^\circ C} CpMo(CO)[(CF_3C_2H)_2CO]SCF_3}$

(3) $\mathrm{CpMo(CO)[(CF_3C_2H)_2CO]SCF_3 \xrightarrow{h\nu} [CpMo[(CF_3C_2H)CO]SCF_3]_2}$

(4) $\mathrm{CF_3C{\equiv}CCF_3 + [Mn(CO)_4SC_6F_5]_2 \xrightarrow{20^\circ C} Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5}$

(5) $\mathrm{CF_3C{\equiv}CCF_3 + [Mn(CO)_4SR]_2 \xrightarrow{80^\circ C} Mn(CO)_3[C_4(CF_3)_4SR]}$

$\mathrm{R = CF_3,\ C_6F_5}$

(6) $\mathrm{CF_3C{\equiv}CH + [Mn(CO)_4SC_6F_5]_2 \xrightarrow{20^\circ C} Mn(CO)_4(CF_3C_2H)_2SC_6F_5}$

(7) $\mathrm{Mn(CO)_4(CF_3C_2H)_2SC_6F_5 \xrightarrow{80^\circ C} Mn(CO)_3[(CF_3C_2H)_2SC_6F_5]}$

(8) $\mathrm{CF_3C{\equiv}CCF_3 + CpFe(CO)_2SR \xrightarrow{70^\circ C} CpFe(CO)_2[C(CF_3){=}C(CF_3)SCF_3]}$

$\mathrm{R = CF_3,\ C_6F_5}$

(9) $\mathrm{CpFe(CO)_2C(CF_3){=}C(CF_3)SR \xrightarrow{h\nu} CpFe(CO)C(CF_3){=}C(CF_3)SR}$

$\mathrm{R = CF_3,\ C_6F_5}$

(10) $\mathrm{CF_3C{\equiv}CCF_3 + CpFe(CO)C(CF_3){=}C(CF_3)SC_6F_5 \xrightarrow{h\nu} CpFe[C_4(CF_3)_4SC_6F_5]}$

(11) $\mathrm{CF_3C{\equiv}CR' + [Fe(CO)_3SR]_2 \xrightarrow{h\nu} [Fe(CO)_3SR]_2CF_3C_2R}$

$\mathrm{R' = CF_3,\ H;\ R = CF_3,\ C_6F_5}$

(12) $$CF_3C{\equiv}CCF_3 + [Fe(CO)_3SR]_2CF_3C_2CF_3 \xrightarrow{70^\circ C} Fe(CO)_3[C_4(CF_3)_4CO]$$

$$R = CF_3,\ C_6F_5$$

(13) $$CF_3C{\equiv}CCF_3 + [CpCoSR]_2 \xrightarrow{80^\circ C} CpCoC_6(CF_3)_6$$

(14) $$CF_3C{\equiv}CCF_3 + CpCo(CO)(SC_6F_5)_2 \xrightarrow{40^\circ C} CpCo[C_4(CF_3)_4CO]$$

(15) $$CF_3C{\equiv}CCF_3 + [Co(CO)_3SC_6F_5]_2 \xrightarrow{40^\circ C} Co_2(CO)_6[C_4(CF_3)_4S] +$$

$$Co_2(CO)_6CF_3C_2CF_3 + Co_2(CO)_4C_6(CF_3)_6$$

RESULTS AND DISCUSSION

Reactions of RC≡CR, R = CF_3, CH_3, C_6H_5 and $CpM(CO)_3SCF_3$, M = Mo, W

The reactions of $CpM(CO)_3SCF_3$, M = Mo, W with acetylenes $CH_3C{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$ in pentane proceed slowly at 30°C,(M = Mo), 60°C, M = W, to give monosubstituted complexes $CpM(CO)_2RC_2RSCF_3$, M = Mo, R = CF_3, I, CH_3, II; M = W, R = CF_3, III, CH_3, IV. Above these temperatures decarbonylation of the tricarbonyls becomes significant, reducing the yield of the acetylene derivatives so that the temperature must be controlled accurately. It was noticed that, in addition to giving higher yields of products, but-2-yne reacted more quickly than the fluoroacetylene and it was subsequently found that diphenylacetylene and $CpMo(CO)_3SCF_3$ reacted readily,under similar conditions,to give a high yield of $CpMo(CO)_2PhC_2PhSCF_3$, V. Attempts were made to react $[CpMo(CO)_2SCF_3]_2$ with hexafluorobut-2-yne but,after 70 hrs. at 90-100°C,no reaction was observed.

The complexes are dark red, II, IV, purple,III,and blue solids,I and V,soluble in all common organic solvents. They are air and light sensitive to varying degrees, the following approximate order of stability being observed. $CpW(CO)_2(CF_3C_2\ CF_3)SCF_3$ > $CpMo(CO)_2(PhC_2Ph)SCF_3$ > $CpMo(CO)_2(CH_3C_2CH_3)SCF_3$ ~ $CpW(CO)_2(CH_3C_2CH_3)SCF_3$ > $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$. The i.r. spectrum in each case indicates a terminal CF_3S ligand and two strong bands near 2000 cm^{-1} are assigned to the symmetric and asymmetric stretching modes of the two carbonyl groups. Two acetylenic C≡C stretching modes are observed in the i.r. spectrum of $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ at 1735 cm^{-1} and 1830 cm^{-1}, but only one band at 1714 cm^{-1} is observed with $CpW(CO)_2(CF_3C_2CF_3)SCF_3$. This can be explained by the presence of two isomers of the former but only one of the latter, as will be discussed later. These reductions in frequency from 2300 cm^{-1} in the free acetylene are among the largest so far observed,[130,137] indicating a significant contribution from a σ bonded structure[133] due to increased population of the π^* orbitals of the acetylene. This would imply that hexafluorobut-2-yne tends to occupy two coordination positions about the metal[130] although, in view of the high coordination number in $CpM(CO)_2LX$ complexes, it is perhaps unwise to take this interpretation too literally.

In contrast to the complexes of hexafluorobut-2-yne the C≡C stretching modes of the acetylene in the but-2-yne and diphenylacetylene complexes are too weak to be observed so that it is not possible to estimate the bond type. Since the intensity of this stretching mode will depend on the non-linearity of the coordinated acetylene,[144] these differences in intensity are not surprising. The increased back-donation to coordinated hexafluoro-2-butyne as a result of the electron withdrawing ability of the CF_3 groups will lead to a significant departure of this acetylene from linearity, producing an increase in intensity of the carbon-carbon stretching mode.

The mass spectra of the complexes are all very similar, the highest ion in each case being $[CpM(CO)(RC_2R)SCF_3]^+$. Primary fragmentation processes include loss of CO, RC≡CR, R, CF_3 and CF_2S as might be expected.[3] The n.m.r. spectra also show regular features but interesting differences also exist as will now be described.

The coordination geometry about the metal atom in these and similar molecules may be conveniently described as a square pyramid with the cyclopentadienyl moiety at the apex and the remaining ligands at the corners of a square base. The possible geometric arrangements of the CF_3S, acetylene and carbonyl groups about the corners of the square allows for one <u>trans</u> and two enantiomeric <u>cis</u> isomers. Interconversion of such isomers in other monosubstituted complexes $CpMo(CO)_2LX$ has been studied extensively and, on the n.m.r. time scale, two distinct processes, cis-trans isomerisation and cis-cis racemisation, may be observed.[211]

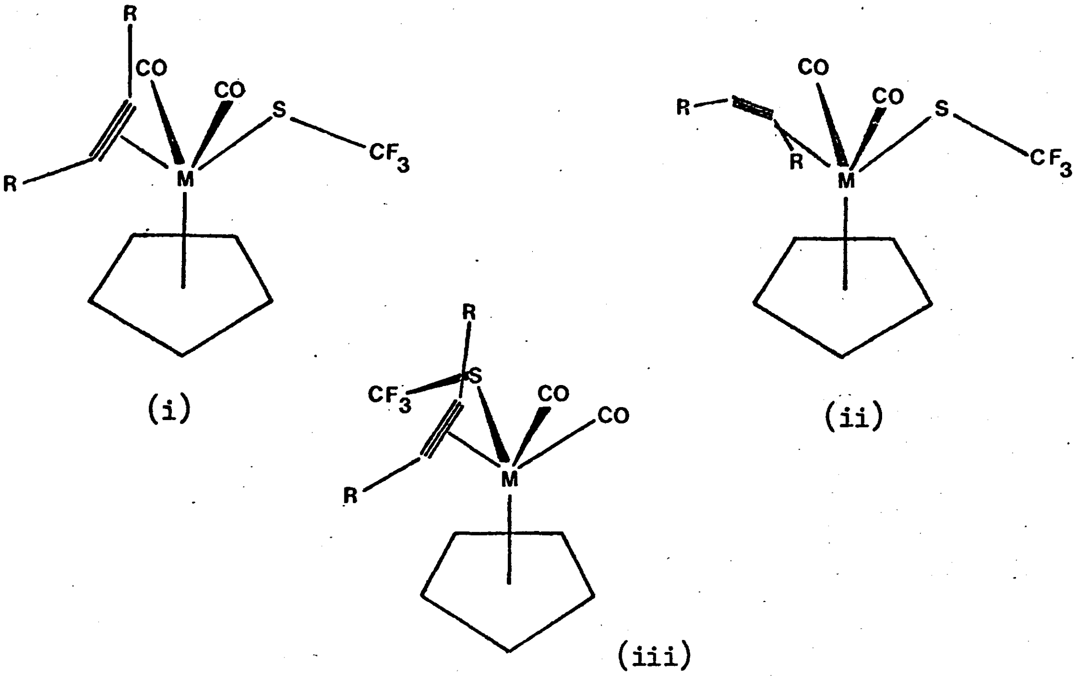
The ^{19}F n.m.r. spectrum of $CpW(CO)_2(CF_3C_2CF_3)SCF_3$ is shown in Fig. 2.1. Since CF_3 groups attached to divalent sulphur usually resonate in the range 20-45 ppm the low field signal is assigned to the CF_3S group. The presence of two coupled acetylene CF_3 resonances at room temperature suggests that the two extremities of the acetylene are in different environments and it appears that only one isomer is present.

Calculation of the angle between the carbonyl ligands in cis and trans isomers of $CpM(CO)_2LX$ and other complexes is possible[212] since this angle, (θ), is related to the intensities of the symmetric (Is) and asymmetric (Ia) C-O stretching modes by the following expression

$$Ia/Is = \tan^2(\theta/2)$$

This formula, deduced from the theory of localised oscillating dipoles, has been criticised but appears to be sufficiently rigorous to yield meaningful results.[213] In general the angle calculated for trans isomers is in the range 100°-120°C while for cis isomers this reduces to 75°-95°.[212] The angle calculated for $CpW(CO)_2(CF_3C_2CF_3)SCF_3$, $\theta = 112^\circ$, suggests that in this complex the carbonyl groups have a trans configuration. It is proposed therefore that the trans isomer has structure (i) since the alternative (ii) would give rise to only a single sharp acetylenic CF_3 resonance. On steric grounds this result is not surprising.

The ^1H spectra of $CpM(CO)_2(CH_3C_2CH_3)SCF_3$, M = Mo, W, suggest a similar structure for these complexes, the acetylenic methyl resonance



(i)

(ii)

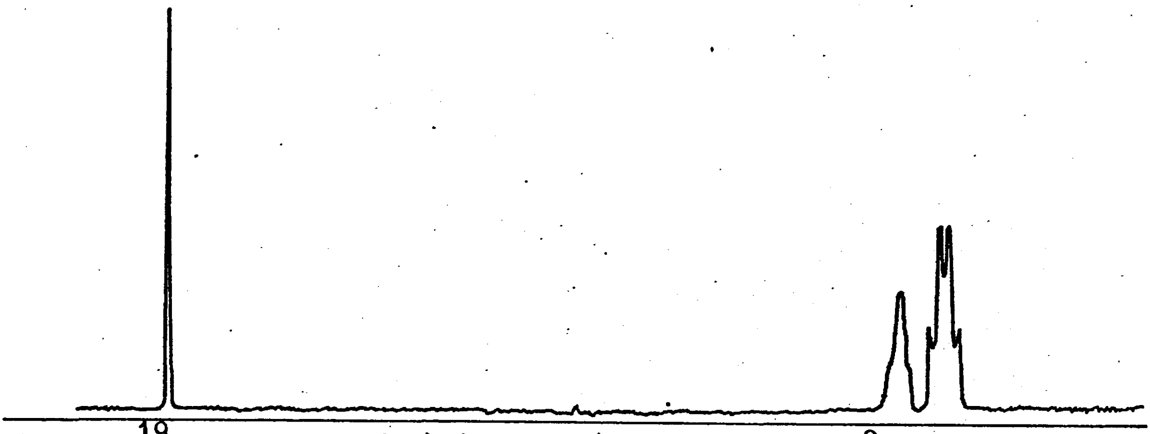
(iii)

near 7τ being split like that of the CF_3 groups in the hexafluoro-2-butyne complex. Although it is not possible to ascertain the stereochemistry of the diphenylacetylene ligand in $CpMo(CO)_2PhCCPhSCF_3$ due to the breadth of the aromatic proton resonance, there is no reason to suggest the structure of this complex is different from (i).

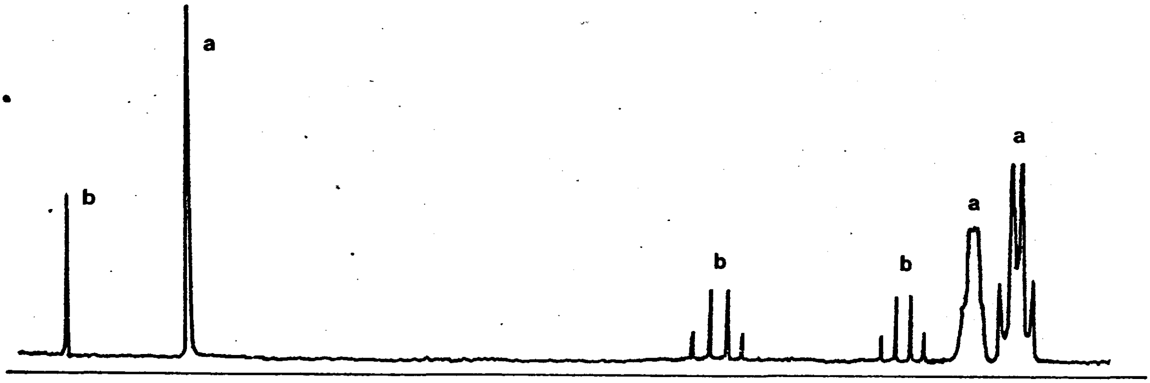
The variable temperature ^{19}F n.m.r. spectra of $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ are shown in Fig. 2.1. and at 34°C two isomers are indicated. The signals (a) are assigned to the trans isomer by comparison with the spectrum of the tungsten complex. The weaker signals (b) are considered to be due to a second isomer (probably cis) in which the two CF_3 substituents of the acetylene are again in different environments, (iii).

The variable temperature spectra indicate that no structural changes occur in this isomer down to -105°C but, at this temperature, the trans isomer exists in two different forms, I(x), I(y). As the temperature is raised the separation of the peaks due to I(x) and I(y) decreases and at -45°C coalescence occurs. The variable temperature spectra of $CpW(CO)_2(CF_3C_2CF_3)SCF_3$ are similar but coalescence occurs at -30°C. It is notable that no change in the high field acetylenic CF_3 resonance occurs in either case and it must be concluded that in the two low

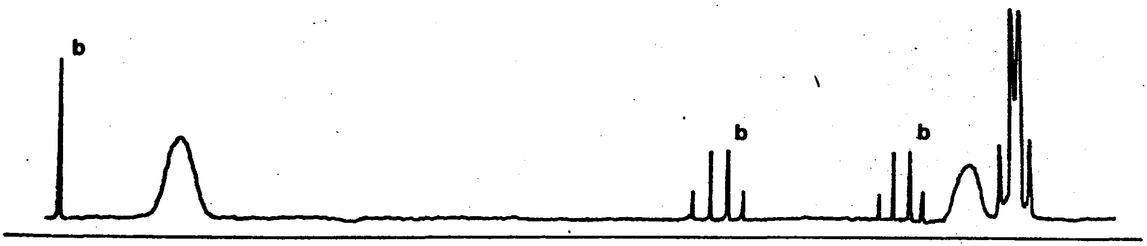
Fig. 2.1.



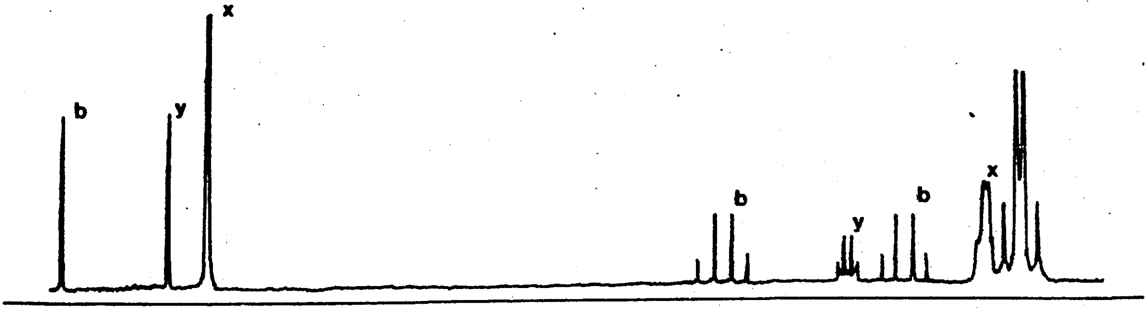
^{19}F n.m.r. $CpW(CO)_2(CF_3C_2CF_3)SCF_3$ T = 34°C



^{19}F n.m.r. $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ T = 34°C



$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ T = -45°C



$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ T = -105°C

Table 2.1.

N.m.r. spectral parameters for the complexes $CpMo(CO)_2(RC_2R)SCF_3$ and $CpW(CO)_2(RC_2R)SCF_3$

	^{19}F				^{1}H			
Compound	$\delta_1(CF_3S)$	$\delta_2(CF_3C)$	$\delta_3(CF_3C)$	J_{2-3}	$\delta_1'(C_5H_5)$	$\delta_2'(CH_3)$	$\delta_3'(CH_3)$	$J_{2'-3'}$
$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ (trans)	39.0	59.1	59.7	2.5	4.31	-	-	-
(cis)	32.5	54.7	57.9	3.6	3.62	-	-	-
$CpW(CO)_2(CF_3C_2CF_3)SCF_3$	40.5	59.3	59.9	2.7	4.22	-	-	-
$CpMo(CO)_2(CH_3C_2CH_3)SCF_3$	35.03	-	-	-	4.45	6.88	6.95	0.67
$CpW(CO)_2(CH_3C_2CH_3)SCF_3$	38.0	-	-	-	4.47	6.93*	-	-
$CpMo(CO)_2(PhC_2Ph)SCF_3$	33.0	-	-	-	4.44	2.53*	-	-

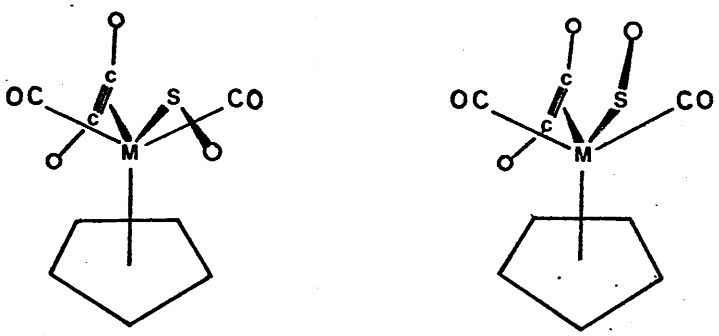
* Broad signal; no splitting observed

phenyl proton resonance

temperature forms of the trans isomer , one end of the acetylene is in virtually the same environment in both cases. However, the parallel temperature dependence of the other CF_3 resonance and that of the CF_3 substituent on sulphur indicates that two environments are possible for each of these two groups.

In view of the axial asymmetry of the CF_3S ligand, these observations can be rationalised in terms of the CF_3 group on sulphur having preferred locations at low temperature. At higher temperatures the energy barrier between these positions is overcome and free rotation of the CF_3S group about the M-S bond commences. Fig. 2.2. illustrates the probable preferred conformations of the CF_3S ligand.

Fig. 2.2.



(x')   (y')

On intuitive grounds x' would appear to be preferable to y' which accounts for the isomer ratios at -105°C, I(x) : I(y) = 3 : 1, IIIx : IIIy = 5 : 1.

The proton n.m.r. spectrum of $CpMo(CO)_2(CH_3C_2CH_3)SCF_3$ was taken over the range -90°C to +34°C but virtually no change was observed. If, as may be possible, the acetylene is acting simply as a π donor and effectively occupies only one coordination site,[130] steric interaction between the CF_3S and the but-2-yne ligands will be minimal and the molecule remains fluxional even at -90°C. In I and III, if the acetylene is considered to occupy two coordination sites, one of the CF_3 groups attached to the acetylene will occupy an apical site and thus interaction with the CF_3S ligand increases the barrier to free rotation in the trans isomers. In the cis isomer of $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ the lack of temperature dependence of the n.m.r. spectrum must be reconciled, either with the absence of free rotation and one preferred conformation, or else with the existence of a very low barrier to free rotation.

Restricted rotation about M-X σ bonds has been detected in a variety of compounds and in $CpFe(CO)_2SiCl_2Me$ this has been studied by variable temperature i.r. spectroscopy.[214] Restricted rotation about the Mo-C σ bond in $Cp_2Mo(NO)\sigma Cp$ has been studied by Cotton who found that the σ Cp ligand may have one preferred conformation below -60°C and this is supported by a later X-ray study of this complex.[215] Variable temperature n.m.r. studies of $Cp_2MoH[C(CF_3)C{=}C(CF_3)H]$, which contains a sterically demanding side chain, have also been carried out and indicate that two conformational isomers exist in solution.[164]

It was observed that the cis:trans isomer ratio in $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ changed slowly on cooling to low temperature. When allowed to sit in solution at -60°C for ~24 hrs. the peaks in the ^{19}F n.m.r. spectrum due to the cis isomer increased in intensity relative to those of the trans isomer. However, no trace of the cis isomers of $CpMo(CO)_2(CH_3C_2CH_3)SCF_3$ or $CpW(CO)_2(CF_3C_2CF_3)SCF_3$ were detected on cooling solutions of these derivatives to -60°C for 30 hrs. Despite the extensive studies carried out on cis-trans isomerism in similar complexes $CpM(CO)_2LX$ it has not been possible to rationalise the data obtained so far[211] and no attempt is therefore made to explain the above observations.

The i.r. spectrum of $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$, before and after the isomer changes, shows clear differences as expected. However, no differences in the C-O stretching region, apart from slight variation in the relative intensities of the two C-O modes, is detectable, even under high resolution, indicating that the C-O stretching frequencies of the cis and trans isomers are identical. Changes are observed in the number and intensity of the C-F stretching modes but the most noticeable difference is in the $\nu C\equiv C$ region where a significant decrease occurs in the intensity of the high frequency mode at 1830 cm^{-1}. This identifies this band as being due to the trans isomer which is surprising since it is much higher in frequency than the $\nu C\equiv C$ mode of trans $CpW(CO)_2(CF_3C_2CF_3)SCF_3$ which occurs at 1714 cm^{-1}.

It has been suggested that the stability of cis and trans isomers of complexes $CpM(CO)_2LX$ may, in part, be a function of the trans effects of the ligands CO, L and X,[211] despite the large departure of these complexes from the model system based on platinum II compounds. Trans effects are considered to operate via σ or π-bonding mechanisms depending on the type of ligand involved.[216] Since the CO group has a much greater π acceptor ability and trans effect than the CF_3S ligand,[217] it is strange that in the cis isomer of $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$, with CO trans to the acetylene, the $\nu C\equiv C$ value is lower than in the trans isomer, whereas the opposite is expected. Also the C-O stretching frequencies, which are coincident in cis and trans isomers, are obviously insensitive to the trans effect of the ligand opposite and it must be concluded that, if trans effects are important in this type of complex, they do not occur via a π bonding mechanism. A similar conclusion has recently been reached by Faller and Anderson who studied derivatives of the type $CpMo(CO)_2(PR_3)X$.[211]

Table 2.2.

I.r. spectra of complexes $CpM(CO)_2(RC_2R)SCF_3$* (cm^{-1})

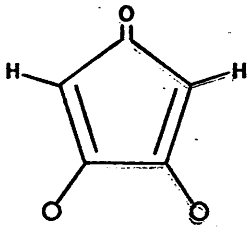
Compound	νCO	νC≡C	νCF
$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$	2034.8ms, 2023.2s, 1976vw	1830wm 1745w	1276msh, 1271m, 1258msh, 1226vs, 1215s, 1174msh, 1158s, 1136s, 1110s, 1089s, 1082s
$CpW(CO)_2(CF_3C_2CF_3)SCF_3$	2024.8ms, 2012.6vs, 1966.5vw	1714wm	1290ms, 1230wsh, 1218vs, 1200wsh, 1155s, 1137s, 1113ms, 1091s, 1067w,
$CpMo(CO)_2(CH_3C_2CH_3)SCF_3$	1964m, 1950vs, 1907vw	-	1111ms, 1090s
$CpW(CO)_2(CH_3C_2CH_3)SCF_3$	1956m, 1941vs, 1899vw	-	1112ms, 1091ms
$CpMo(CO)_2(PhC_2Ph)SCF_3$	1982ms, 1969.7vs, 1924.6vw	-	1116ms, 1089s

* Cyclohexane

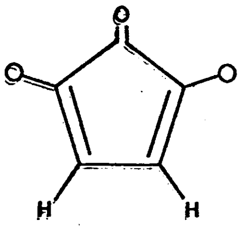
Reaction of $CF_3C{\equiv}CH$ and $CpMo(CO)_3SCF_3$

In contrast to the simple substitution reactions of disubstituted acetylenes with $CpMo(CO)_3SCF_3$, 3,3,3-trifluoropropyne and the latter reacted at 35°C in pentane to give a yellow crystalline solid which analysed as $CpMo(CO)_2(CF_3C_2H)_2SCF_3$(VI). The appearance of a strong band at 1690 cm^{-1} in the i.r. spectrum, characteristic of a ketonic C-O stretching mode, suggests that the complex contains a substituted cyclopentadienone ligand, formed by condensation of two acetylene units and a carbonyl ligand. This formulation is supported by the mass spectrum of the complex where loss of only one CO group from the molecular ion is observed instead of the expected two for a dicarbonyl. An ion due to the cyclopentadienone ligand $[(CF_3C_2H)_2CO]^+$ is also observed which undergoes loss of two hydrogens followed by CO expulsion from the ring.

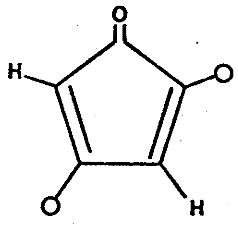
Isomerism in VI is possible due to three different potential arrangements of substituents on the ring, two symmetric and one asymmetric.



(i)



(ii)



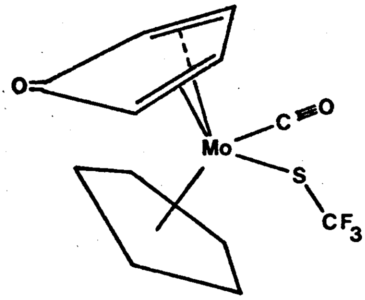
(iii)

Each of these isomers has several other forms depending on the arrangement of the other ligands on the metal, although the i.r. spectrum suggests that only two exist since two C-O stretching modes are present.

The ^{19}F n.m.r. confirms the above conclusion, two sets of three resonances of equal intensity being observed. Integration of the signals gives an isomer ratio of 4:1. The proton n.m.r. only shows peaks due to the predominant isomer because of the low intensity of the signals but the sharp singlet at 4.34τ, attributed to the cyclopentadienyl protons, is slightly asymmetric suggesting the cyclopentadienyl resonance of the second isomer is almost coincident. Two other peaks at 4.06τ and 5.33τ are assigned to the olefinic protons on the cyclopentadienone ring of the predominant isomer and, although broadened due to coupling with adjacent CF_3 groups, the coupling constants J_{F-H} could not be obtained.

It is apparent from the sharpness of the signals in the ^{19}F n.m.r. spectrum that isomer (i) is not present since strong coupling of adjacent CF_3 groups in different environments would be expected. Correlation tables of ^1H resonances data for a variety of compounds, which can formally be classified as 1,3 diene metal complexes, show that the outermost protons, H_α, are shifted to much higher fields relative to H_β upon coordination of the free ligand to a metal.[181] Thus the positions of the single proton resonances of the predominant isomer of $CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$ suggest that one is at an α position and the other at a β position on the ring, (isomer (iii)). This is in contrast to the situation in $Fe(CO)_3[(CF_3C_2H)_2CO]$ which, from n.m.r. data, appears to have a symmetric cyclopentadienone ligand of type (ii).[181]

It is now well established that cyclopentadienone ligands form linkages to metal atoms which result in bending of the ring such that the ketonic carbonyl group lies above the plane of the four other carbon atoms.[218] A structure similar to that of $CpRe(CH_3)_2(C_5H_5CH_3)$[219] is therefore proposed for VI, the four ligands being arranged in a distorted tetrahedral geometry about the metal atom. Steric interactions would appear to be at a minimum with the ketonic C=O group pointing directly away from the CO and CF_3S ligands.



With such a structure it is apparent that four sources of isomerism exist . (1) Arrangement of CF_3 and H substituents on the cyclopentadienone ligand. (2) Restricted rotation of the CF_3S ligand as found in $CpM(CO)_2(CF_3C_2CF_3)SCF_3$. (3) A polytopal rearrangement involving a square planar intermediate,[220] (see Fig. 2.4.). (4) Restricted rotation of the cyclopentadienone group about the metal-ligand axis. The spectroscopic evidence available does not allow unequivocal conclusions to be reached and decarbonylation studies on VI were therefore carried out in an effort to simplify the problem.

It was found that photolysis of the monomer VI proceeded readily in benzene to give reasonable yields of red crystals and small quantities of a white solid. The red crystalline material was separated from the latter (which was not identified) by repeated slow recrystallisation from CH_2Cl_2 and shown to be the expected dimer $[CpMo[(CF_3CCH)_2CO]SCF_3]_2$, VII, by elemental analyses, i.r., n.m.r. and mass spectroscopy. It was also found that ions due to the dimer are observed in the mass spectrum of VI with high source temperatures, indicating that thermal decarbonylation of the latter may also be feasible.

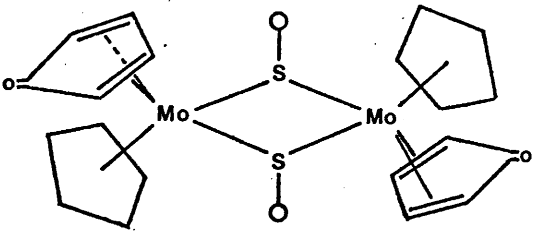
As expected the dimer gives no terminal or bridging C-O stretching modes in the i.r. spectrum but a strong ketonic C-O stretching mode at 1572 cm^{-1} is observed. This frequency is considerably lower than in the monomer and this is attributed to increased polarisation of the ketonic carbonyl group. It has been suggested that back donation of negative charge from the metal to a cyclopentadienone ligand can occur, thus increasing the aromatic character of the organic ring.[129] In VI some of the charge can be removed by the strong π-acceptor carbon-monoxide, whereas in the dimer this is not possible. and excess charge must be removed by the cyclopentadienone ligand, and this results in a decrease in the >C=O stretching frequency. Removal of charge by the cyclopentadienyl and CF_3S ligands is probably minimal in view of their lack of π acceptor ability.[221,222]

Table 2.3.

I.r. spectra (cm^{-1})			
Compound	νCO	ν >C=O	νCF
$CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$*	2065.7s, 2039s	1706s, 1680s	1273m, 1255, 1154s, 1124m, 1090s, 1075s
$[CpMo[(CF_3C_2H)_2CO]SCF_3]_2$†	-	1570s	1258s, 1161m, 1147m, 1129msh, 1076ms

* CCl_4; † $CHCl_3$

The ^{19}F n.m.r. spectrum of VII exhibits three peaks,(integrated ratio 1:1:1),the low field signal at 23.5 ppm being attributed to the CF_3S ligands. This spectrum, coupled with the presence of three resonances in the ^1H spectrum,(ratio 1:5:1), suggests that only one isomer is present and hence that isomerism in the monomer VI does not arise from the arrangement of substituents on the cyclopentadienone ring,nor from restricted rotation of this ligand in the wedge-shaped ground state structure, which is probably retained in the dimer. Isomerism in the dimer can,however,arise from the relative configuration of cyclopentadienyl and cyclopentadienone rings about the metal atoms,and also from the configuration of the CF_3 groups on sulphur. Since several isomers are compatible with the observed spectroscopic data it is impossible to assign a structure unequivocally to this complex,but one of the following two basic forms seems probable.



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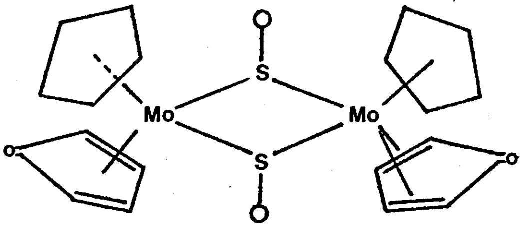


Cis

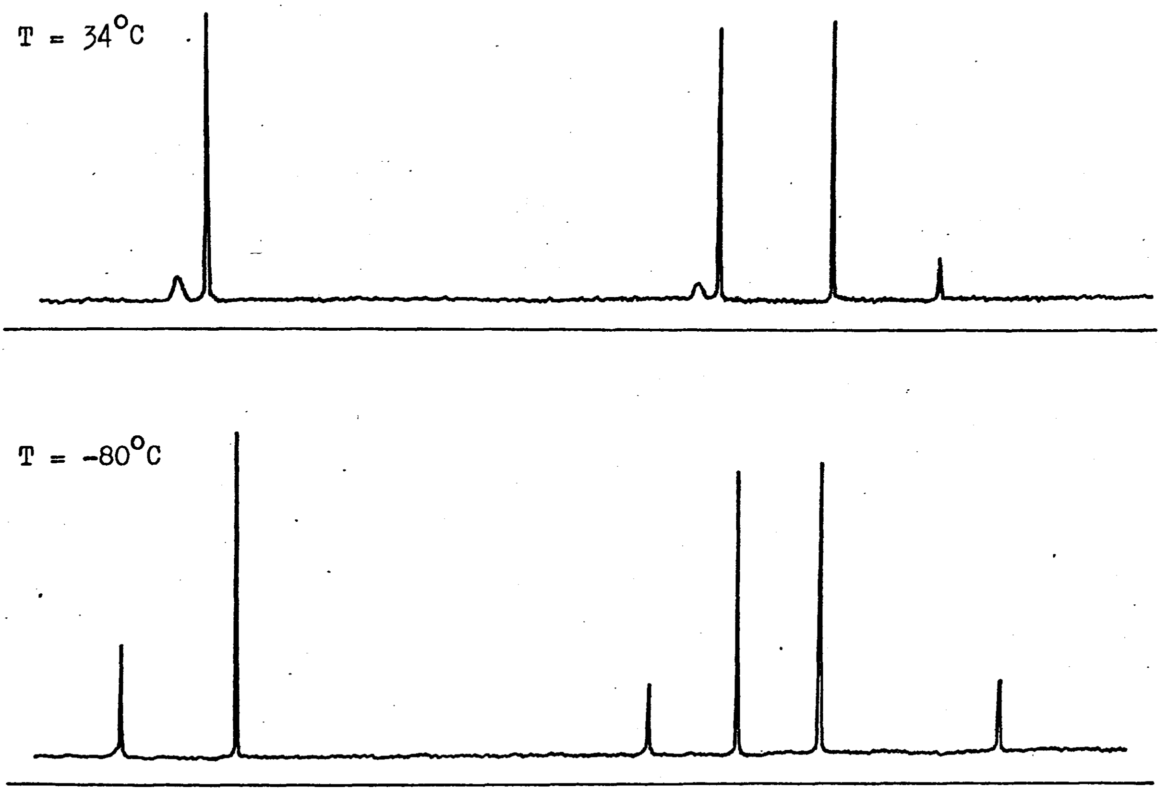
Table 2.4.

N.m.r. spectra						
	^{19}F (ppm)			$^{1}H(\tau)$		
Compound	$\delta_1(CF_3S)$	$\delta_2(CF_3)$	$\delta_3(CF_3)$	$\delta_1'(Cp)$	δ_2'	δ_3'
$CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$ (1)*	29.3	54.2	59.4	4.34	4.06	5.33
(2)	28.0	53.7	57.3	-	-	-
$[CpMo[(CF_3C_2H)_2CO]\ SCF_3]_2$	23.5	57.2	58.5	4.32	4.62	5.03

*Ratio isomer (1) : isomer (2) = 4 : 1

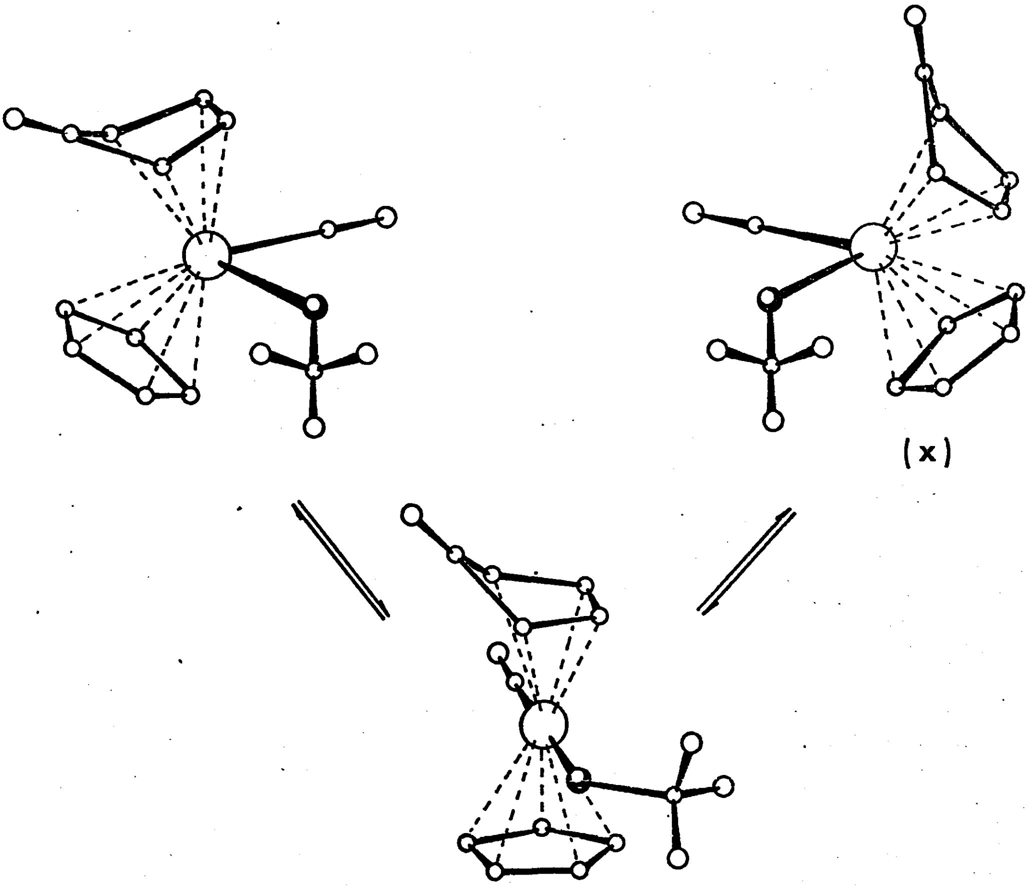
In a further attempt to identify the source of isomerism in the monomer brief low temperature ^{19}F n.m.r. studies were carried out. At -80°C, (Fig. 2.3.), the peaks due to the minor isomer, in addition to being much sharper, shifted considerably from their positions at 34°C. This would seem to suggest that, at some temperature above 34°C, coalescence of signals due to both isomers will occur. It is recalled that in $CpM(CO)_2(CF_3C_2CF_3)SCF_3$, M = Mo, W, relatively low coalescence temperatures were found. In addition, virtually no differences in the chemical

Fig. 2.3. ^{19}F n.m.r. spectra of CpMo(CO)[(CF$_3$C$_2$H)$_2$)CO]SCF$_3$



shifts of the CF$_3$ group remote from the CF$_3$S ligand were observed in the two low temperature conformers. However, in CpMo(CO)[CF$_3$C$_2$H)$_2$CO]SCF$_3$, the observation that all the CF$_3$ resonances shift considerably on lowering the temperature is more compatible with a polytopal interconversion process. It is also notable that the barrier to free rotation of the σC$_5$H$_5$ ligand in the structurally comparable derivative Cp$_2$Mo(NO)σCp is relatively low and fluxional behaviour is only arrested completely at -110°C.[215] An estimated coalescence temperature in the n.m.r. spectrum of CpMo(CO)[(CF$_3$C$_2$H)$_2$CO]SCF$_3$ of ~ 100°C therefore seems inconsistent with restricted rotation of a sterically less demanding CF$_3$S ligand.

Assuming that a polytopal rearrangement is responsible for isomerism in VI, four different structural isomers are possible, each of which, due to the asymmetry of the molecule, has two enantiomeric forms which cannot be distinguished by n.m.r. spectroscopy, (Fig. 2.4.). Even taking into account the fact that only one isomeric form of the dimer VII exists, since it is not possible to assign a structure to this isomer, it is impossible to identify the isomeric forms of the monomer because of the lack of information available. Photolytic dimerisation of the latter probably involves CO expulsion to give a sixteen electron intermediate[118] and possible rearrangements in this transition state also complicate the situation. However, it is interesting to note that all the observed facts can be explained by the existence of one isomer with a stable ground-state structure analogous to CpRe$(CH_3)_2(C_5H_5CH_3)$ which undergoes a polytopal rearrangement to a higher energy form (x).



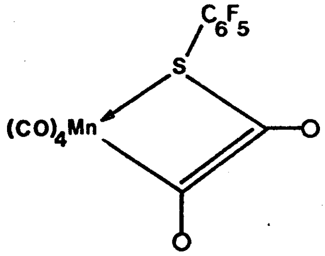
Square-planar intermediate

Fig. 2.4.

Reaction of $CF_3C{\equiv}CCF_3$ and $[Mn(CO)_4SR]_2$, R = CF_3, C_6F_5

The product obtained from the reaction of hexafluorobut-2-yne and $[Mn(CO)_4SR]_2$, R = CF_3, C_6F_5, depends on the reaction temperature and on the substituent R. At 20°C $[Mn(CO)_4SC_6F_5]_2$ reacted in pentane to give a pale yellow solid which analysed as $Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$, VIII. At higher temperatures a yellow crystalline tricarbonyl complex was obtained (VIII acting as an intermediate) which was found to have the stoichiometry $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$, IX(a). No reaction was observed between the acetylene and $[Mn(CO)_4SCF_3]_2$ up to 75°C when the tricarbonyl $Mn(CO)_3[C_4(CF_3)_4SCF_3]$, IX(b), was obtained as oily yellow crystals, no trace of a tetracarbonyl intermediate being detected.

Spectroscopic data on the tetracarbonyl complex VIII are in accord with a structure in which the acetylene has apparently inserted into the Mn-S bonds of $[Mn(CO)_4SC_6F_5]_2$.



The mass spectrum gives a molecular ion M and other ions $[M-2CO]^+$, $[M-3CO]^+$, and $[M-4CO]^+$. Prominent ions are also observed due to loss of fluorine and CF_3 groups from the ligand $[C(CF_3)=C(CF_3)SC_6F_5]$ but no peak assignable to the complete ligand ion is present. The i.r. spectrum exhibits the four terminal C-O stretching modes expected for an octahedral <u>cis</u> $M(CO)_4XY$ species[223] and the weak band at 1609 cm^{-1}, although too low in frequency for a coordinated acetylene molecule, is in the region characteristic of uncoordinated olefinic bonds. The ^{19}F n.m.r.

spectrum gives three multiplets of ratio 2:1:2, due to a C_6F_5 group, and two multiplets of equal intensity at 61.0 ppm and 62.8 ppm, assigned to two CF_3 groups in different environments. The low field signal is a quartet, J_{FF} = 8.9 Hz, due to coupling with the other cis CF_3 substituent which gives a complex multiplet due to coupling with both CF_3 and C_6F_5 substituents.

The spectroscopic data of the tricarbonyls IX(a), (b), suggest an interesting structure in which a five-membered heterocyclic ring $[C_4(CF_3)_4SR]$ is π-bonded to a manganese tricarbonyl moiety, particularly significant evidence being obtained from the mass spectra of the complexes. In each case a molecular ion is observed which loses one fluorine atom but no other ions containing both metal and ligands are observed since the complex apparently undergoes extensive fragmentation at this point. Weak ions due to the ligand $[C_4(CF_3)_4SR]$ are observed in both cases, the fragmentation processes of which involve loss of F, CF_3 and C_6F_5 in the appropriate case. The ions $[C_8F_{11}S]^+$ and $[C_8F_{10}S]^+$ are particularly prominent in each spectrum. Interestingly the mass spectrum of IX(b) does not give an ion at m/e 82 assignable to CF_2S^+ and the latter is a characteristic feature of the spectra of complexes containing M-SCF_3 linkages.[3]

The ^{19}F n.m.r. spectra, which show signals due to the substituent on sulphur and two highly coupled resonances of equal intensity near 50 ppm, indicate that two types of CF_3 group are present. The chemical shift of the CF_3 attached to sulphur in IX(b), δ = 68.2 ppm, is extremely unusual since CF_3S groups almost invariably give chemical shifts well below 50 ppm.[3] However, CF_3 attached to S IV gives a chemical shift in the range 50-80 ppm, e.g. CF_3SF_3, δ = 72.8 ppm,[224] and this originally suggested that the sulphur atom in IX(b) is tetravalent. On this evidence a structure (Fig. 2.6.b) was originally

Table 2.5.

N.m.r. Parameters of Manganese Carbonyl Complexes

	^{19}F (ppm)			
Compound	$\delta(1)(CF_3C)$	$\delta(2)(CF_3C)$	$\delta(3)(CF_3S)$	J_{1-2}(Hz)
$Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$	61.0	62.8	-	8.9
$Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$	51.1	52.3	-	-
$Mn(CO)_3[C_4(CF_3)_4SCF_3]$	50.4	52.7	68.2	-

formulated for these derivatives in which a $[C_4(CF_3)_4SR]^{(-)}$ ligand donates six electrons to $Mn(CO)_3^+$ as in $CpMn(CO)_3$.[225] The solution i.r. spectra are in accord with this structure since no bands appear in the region 2000-1500 cm^{-1} which can be attributed to uncoordinated C=C or coordinated C≡C bonds. Three strong C-O stretching modes ($2a_1 + a_2$) are observed above 2000 cm^{-1} due to an $M(CO)_3$ species of Cs or lower symmetry. In the vapour phase the spectrum of IX(b) reveals slight P.Q.R. structure in these modes and, more significantly, a reduction in the separation of the a_1 and a_2 frequencies to 2.2 cm^{-1} which compares with 5.2 cm^{-1} in cyclohexane solution. This would suggest that solvent effects contribute to lowering of symmetry about the three CO ligands and could also explain the presence of a weak band just below the high frequency mode in solution, since this is not observed in the vapour phase spectrum.

In view of the intrinsic novelty of this structure and the potentially interesting $Mn-[C_4(CF_3)_4SR]$ bonding, an X-ray diffraction study of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ was carried out by Professor G.A. Sim, Dr. W. Harrison, and Dr. F.B. Wilson of this department.

Orange yellow, plate like crystals were grown from a saturated solution of the compound in hexane.

X-ray Structure of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$

The complex crystallises in the space group $\underline{P}\bar{1}$, $z = 2$; $D_c = 2.01$. Triclinic $a = 7.889(6)$, $b = 11.737(8)$, $c = 12.195(9)$ Å. $\alpha = 91.45(10)$, $\beta = 69.71(10)$, $\gamma = 81.55(9)^\circ$.

Diffractometer data (Mo-K_α radiation) current $R = 7.1\%$ for 3229 reflections with $I > 3\sigma(I)$.

The structure of the complex is illustrated in Figs. 2.5.(a) and (b) with the structural parameters listed in Table 2.6.

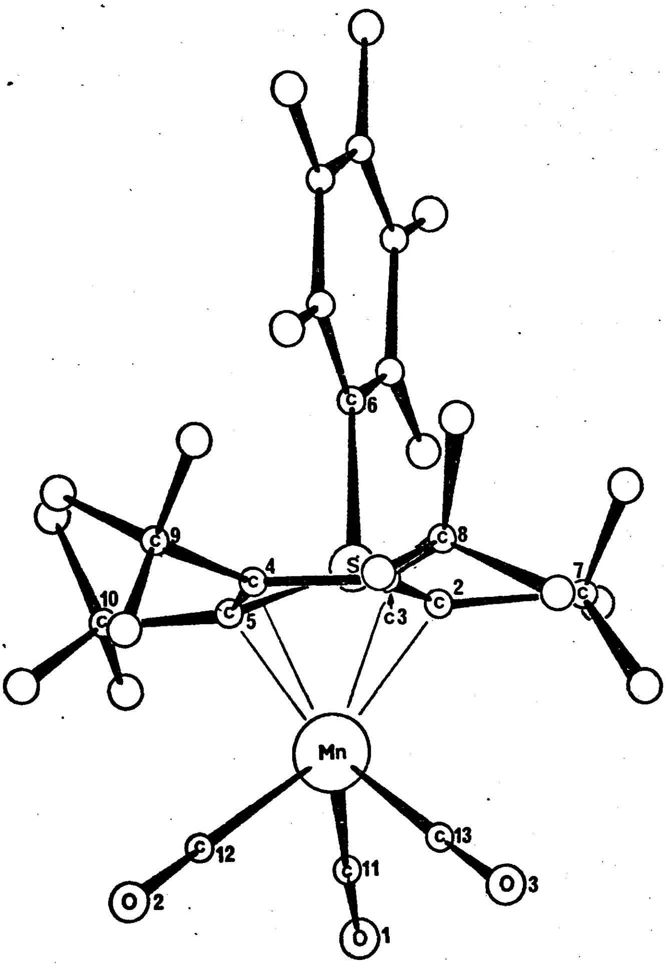


Table 2.6.

Intramolecular Bond Distances and Angles

(A) Bond Distances (Å)

Mn - S	2.793		
Mn - C(2)	2.109	Mn - C(5)	2.103
Mn - C(3)	2.062	Mn - C(4)	2.068
Mn - C(11)	1.814	Mn - C(12)	1.814
Mn - C(13)	1.832		
S - C(2)	1.782	S - C(5)	1.771
S - C(6)	1.815		
C(2) - C(3)	1.425	C(5) - C(4)	1.441
C(3) - C(4)	1.459		
C(2) - C(7)	1.490	C(3) - C(8)	1.488
C(4) - C(9)	1.516	C(5) - C(10)	1.468
C(11) - O(1)	1.131	C(12) - O(2)	1.125
C(13) - O(3)	1.112		

(B) Bond Angles (degrees)

C(4) - C(5) - S	111.36	C(2) - C(3) - S	111.68
C(2) - C(3) - C(4)	109.68	C(3) - C(4) - C(5)	109.31
C(2) - S - C(5)	85.7		
C(6) - S - C(2)	111.9	C(6) - S - C(5)	112.4
C(11) - Mn - C(12)	89.48	C(12) - Mn - C(13)	90.64
C(12) - Mn - C(13)	91.32		

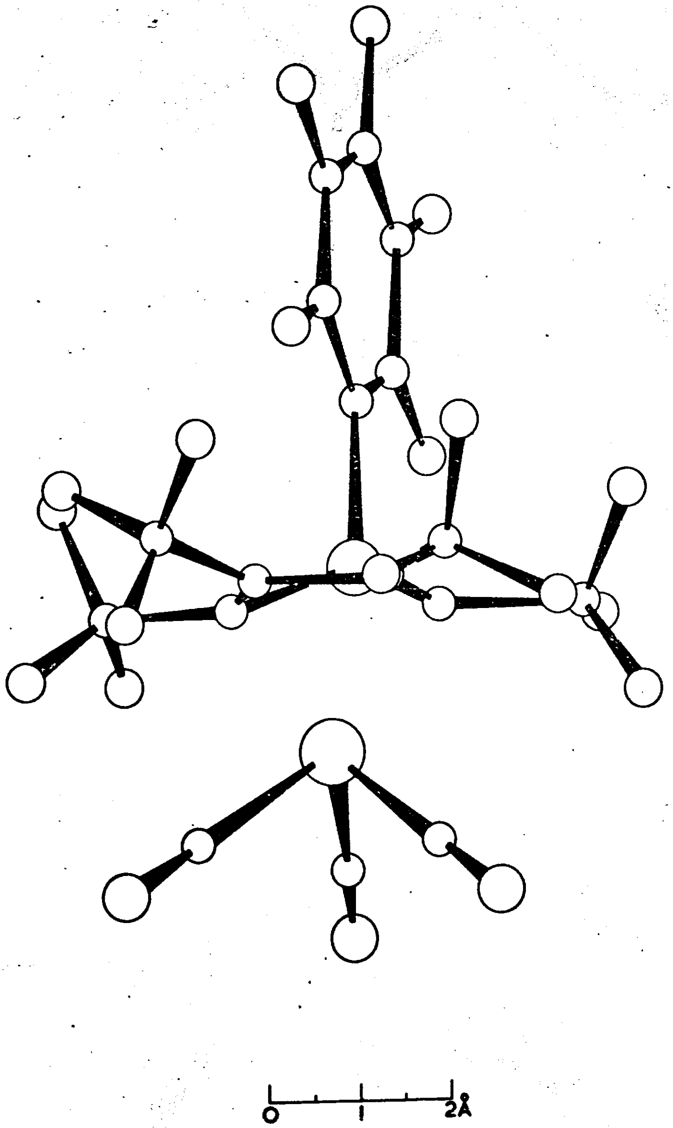


Fig. 2.5 a

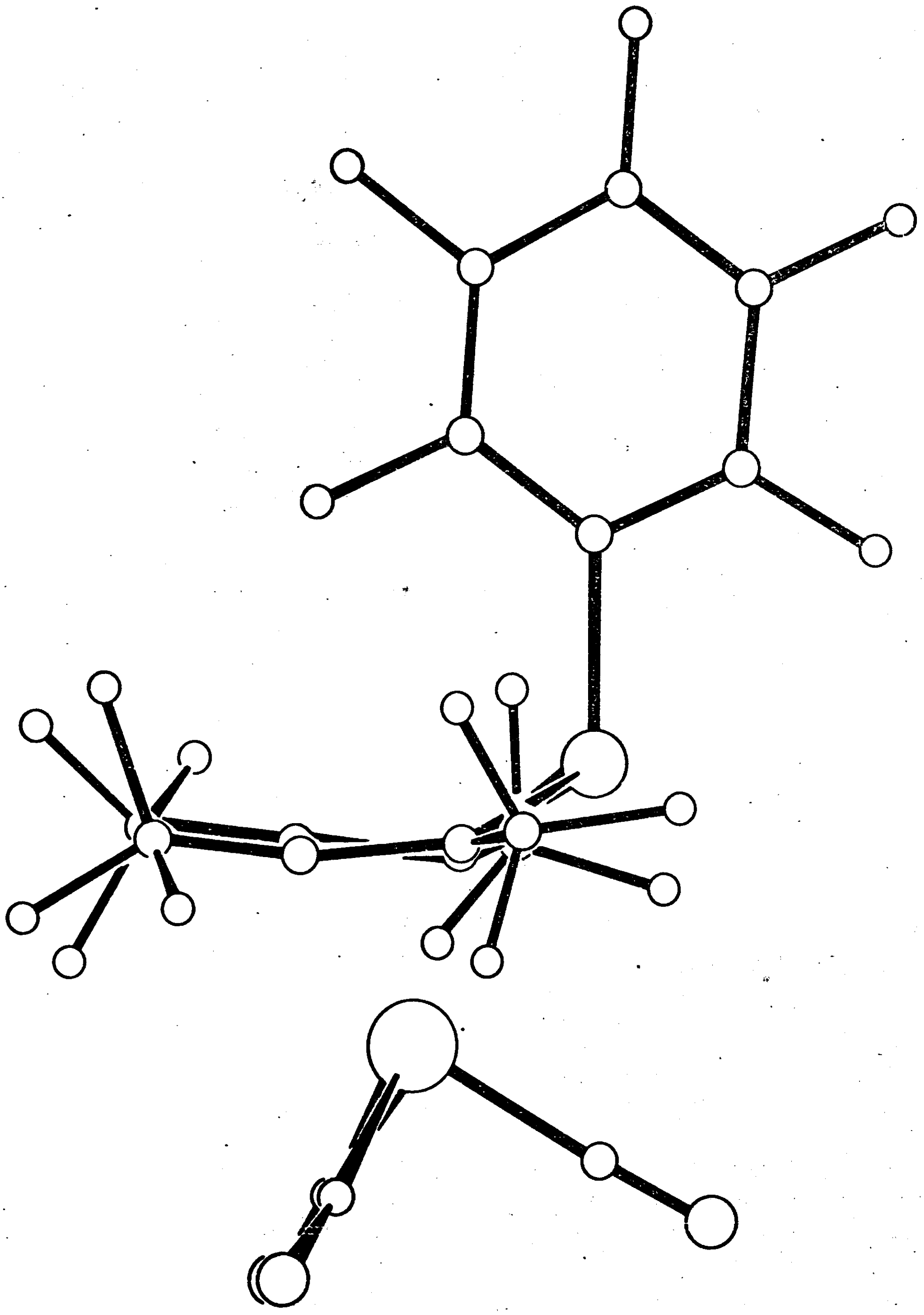
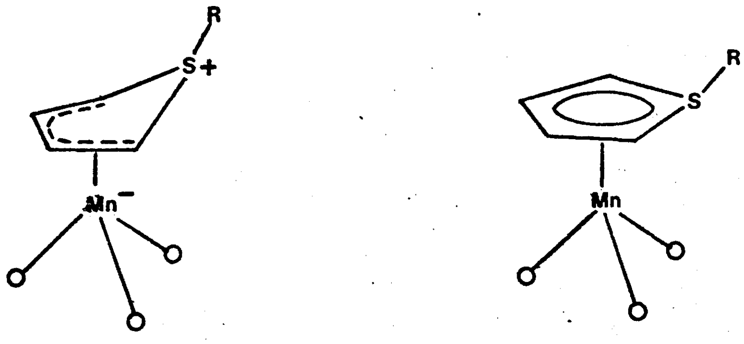


Fig. 2.5 b

The results of this work revealed that, as expected, a heterocyclic ring $[C_4(CF_3)_4 SC_6F_5]$ is bonded to a manganese tricarbonyl residue and IX(a) has the structure illustrated. The most striking feature of the molecule is the non-planarity of the heterocyclic ring which has an envelope configuration with the sulphur atom lying above the plane of the four rigorously coplanar carbon atoms by 0.667 Å. This gives rise to a dihedral angle of 30.81° between the two planes defined by C_2, C_3, C_4, C_5 and C_2, S, C_5. The Mn-C (heterocyclic ring) separations have normal bonded values which vary systematically so that the Mn-C_3 and C_4 contacts are equal and slightly shorter than the Mn-C_2 and C_5 separations. However, the Mn-S distance is appreciably longer than any reasonable sum of the covalent radii of the two atoms and must clearly be considered non-bonding, superficially indicating that the manganese has a seventeen electron configuration. Such a description of the compound is not, however, in accord with the observed diamagnetism, (n.m.r.). Since mass and n.m.r. spectroscopy eliminate the possibility of hydrogens attached to manganese and sulphur it is clear that a significant contribution from a zwitterion structure, Fig. 2.6.(a), must be considered so that the complex is formally that of a heterocyclic sulphonium derivative bonded to a manganese (-1) species. The high chemical shift of the CF_3 group attached to sulphur in IX(b) clearly reflects the cationic nature of the sulphur atom rather than a higher oxidation state as in Fig. 2.6(b).

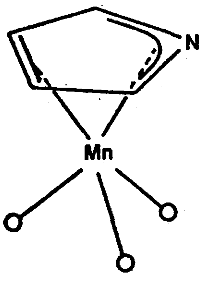
Fig. 2.6.



(a) (b)

It appears on this evidence that a contribution from the aromatic delocalised structure (b) is negligible. Delocalisation of electron density over only the carbon atoms in the ring is indicated by the three C-C distances C_2-C_3 = 1.43 Å, C_3-C_4 = 1.46 Å, C_4-C_5 = 1.44 Å. The C-S distances at 1.78 Å are close to the sum of the covalent radii of sulphur and carbon 1.81 Å,[226] which compares with 1.74 Å in thiophene in which only partial electron delocalisation and sulphur valence shell expansion is considered to occur.[227]

Other complexes containing heterocyclic five-membered rings have been prepared and an X-ray structure of one of them, $[(C_4Ph)_4As]Mn(CO)_3$,[228] has revealed a planar ring in which delocalisation over all five bonds is apparent. However, in the π-pyrrollyl complex $[C_4H_4N]Mn(CO)_3$ disruption of the electron delocalisation in the ring is implied by the results of variable temperature N.Q.R. studies[229] and the authors of this work considered a contribution from the allylic olefin structure illustrated.



More closely related to $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ from the structural aspect is the cyclopentadienone complex $Fe(CO)_3[C_4(CF_3)_4CO]$ in which the carbonyl C atom of the five-membered ring lies above the plane of the other four carbon atoms to give a dihedral angle of 20°.[230] The difference in the dihedral angles of two other cyclopentadienone complexes $CpCo[C_4(CH_3)_4CO]$; 9°,[231] and $CpCo[C_4(CF_3)_4CO)$; 21°,[232] led Mason to suggest[218] that, when electron withdrawing substituents are attached to the ring, the resultant reduction in the energy of the π^* orbitals leads to increased back donation and hence population of the lowest lying anti-bonding orbital of the diene ring. This in turn will be reflected in a greater contribution from an extreme valence bond structure in which the non-planar ring has a large dihedral angle due to sp^3 hybridisation of the carbon atoms C_2 and C_5. It can be concluded from this approach that some form of localised bonding occurs between the metal and the carbon atoms on the 2 and 5 positions of the cyclopentadienone ring. However, a survey of the C-C bond lengths in these complexes often fails to substantiate these conclusions and tends to indicate that all four carbon atoms may still be described as sp^2 hybridised. It is therefore apparent that in these complexes Mason's approach has reached the limits of its applicability. This led Churchill[233] and later Alcock[219] to propose the following alternative explanation for the non-planarity of coordinated cyclopentadienone and other cyclic diene rings. In order for the positive lobes of the butadiene B_2 orbital to maximise their overlap with the metal dyz orbital they will be pulled or twisted inwards, Fig. 2.7. This is consistent with the frequently observed decrease in the distance between C_2 and C_5 and in order to reduce the torsional strain which is produced folding of the ring along the C_2-C_5 axis must occur.

Fig. 2.7.

This approach effectively explains why the diene rings in $CpRe(CH_3)_2(C_5H_5CH_3)$,[219] $CpCo(C_5H_5Ph)$,[234] and $CpCo(C_5H_5COPh)$[233] have large deviations from planarity whereas Mason's theory implicitly requires the presence of electron-withdrawing substituents on the ring. Since the angle of fold depends on the C_2-C_5 separation and the degree of orbital twisting, it must therefore depend on the dimensions of the triangle $\overset{X}{C_2 \text{———} C_5}$ and these will be determined to a significant degree by the size of the non-bonded atom X and its state of hybridisation. With sp^2 hybridisation, $\widehat{C_2-X-C_5}$ will be fairly large, leading to a greater separation of C_2-C_5 and hence a relatively small dihedral angle, e.g. $Fe(CO)_3[C_4(CF_3)_4CO]$, C_2-X-C_5 = 100°, dihedral angle = 20°. However, with an sp^3 hydridised atom X, a reduction in $\widehat{C_2-X-C_5}$ will increase the dehedral angle, e.g. $CpCo[C_5H_5Ph]$, $\widehat{C_2-X-C_5}$ = 93.9°, dihedral angle = 36.5°.[234] It is therefore pleasing to note that in $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ the sulphur is effectively sp^3 hybridised, $\angle \widehat{C_2-S-C_5} = 85.7°$ and the dihedral angle is 30.81°. The slightly low value of the latter relative to $CpCo[C_5H_5Ph]$ can be simply explained in terms of a greater C-X distance allowing greater C_2-C_5 separation and orbital twisting for a similar C_2-X-C_5 angle.

It is also interesting to note that, as in most other cyclic butadiene complexes, the M-C_2, C_5 distances in IX(a) are slightly greater than the M-C_3, C_4 bond lengths. This can be explained by lower M-C_2, C_5 orbital overlap relative to M-C_3, C_4, where little orbital twisting is required as a result of the small C-C distance.

Another consequence of the butadiene orbitals being twisted in towards the metal atom is bending of the substituents on C_2 and C_5 away from their normal butadiene positions (Fig. 2.7.). Alcock pointed out that, in the diene ring of $CpRe(CH_3)_2[C_5H_5CH_3]$, if C_2 and C_5 retained the sp^2 hybridisation of the uncoordinated state, the effect of metal-C_2C_5 orbital overlap would be to bend the substituents on C_2 and C_5 towards the metal atom to make an angle of 29.1° with the C_2, C_3, C_4,

C_5 plane. In $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ the CF_3 groups on C_2 and C_5 are bent towards the metal and make angles of 0.5° and 5.3° with the butadiene plane. The difference in the angles can possibly be explained by CF_3-CF_3 repulsion in the ring as found in $Fe(CO)_3[C_4(CF_3)_4CO]$, although some changes in substituent configuration are to be expected on coordination of the diene as will be discussed in Chapter III.

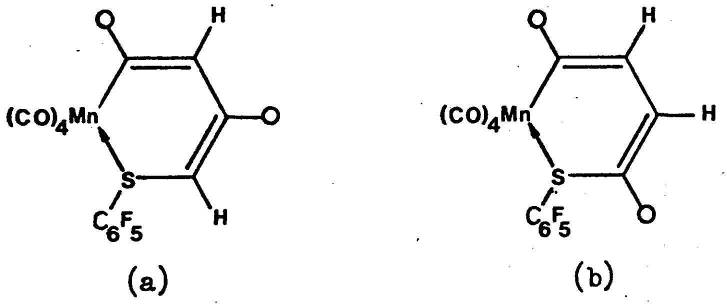
Reactions of $CF_3C{\equiv}CH$ and $[Mn(CO)_4SC_6F_5]_2$

Brief studies of the reaction of 3,3,3-trifluoropropyne and $[Mn(CO)_4SC_6F_5]_2$ have been carried out in an attempt to gain further insight into the mechanism of formation of the heterocyclic ring in IX(a) and IX(b). Although by no means complete, these studies proved to be particularly informative.

The reaction of $[Mn(CO)_4SC_6F_5]_2$ and $CF_3C{\equiv}CH$ at temperatures below 20°C proceeded slowly to give reasonable yields of a pale yellow crystalline material $Mn(CO)_4(CF_3C_2H)_2SC_6F_5$, X, and quantities of a white insoluble polymer which analysed as $(CF_3CCH)_n$. The spectral properties of X are in accord with a σ bonded ring structure,(Fig. 2.8.), rather than a π bonded molecule analogous to IX(a), (b). Thus the i.r. spectrum gives four C-O stretching modes similar to $Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$. Weak bands at 1559 cm^{-1} and 1530 cm^{-1} are attributed to the uncoordinated olefinic bonds of the diene ring while the νC-F region is complex. The mass spectrum gives a molecular ion which undergoes stepwise loss of carbonyl groups, and ions due to $[(CF_3CCH)_2SC_6F_5]^+$ and fragments are clearly identifiable. An ion at m/e 449 corresponding to loss of two fluorines from the latter is, in fact, the strongest ion in the spectrum. Assuming the proposed structure of X is correct, isomerism resulting from different modes of addition of the acetylene is obviously possible, but the ^1H and ^{19}F n.m.r. spectra can be reconciled with the presence of only one isomer. The former gives two resonances of equal intensity, one of which $\delta = 3.66\tau$,is a quartet, $J = 2.2$ Hz, due to coupling with a cis CF_3 group. The other signal, $\delta = 4.12\tau$, does not show distinct fine structure although broadened due to coupling of some description. The ^{19}F n.m.r. spectrum exhibits two CF_3 resonances at 59.3 ppm and 68.3 ppm, both of which are resolved as doublets, $J_{F-H} = 2.2$ Hz and $J_{F-H} = 1.2$ Hz respectively, due to coupling with the protons on the ring. The lack of strong CF_3-CF_3 coupling would therefore seem to rule out the possibility of cis CF_3 substituents.

Comparison of the C-O stretching frequencies of $Mn(CO)_4(CF_3C_2H)_2SC_6F_5$ and $Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$ reveals that in the former these are some 10 cm^{-1} higher and, on this basis, it is proposed that in X one of the CF_3 substituents is likely to be at the α position relative to the $Mn(CO)_5$ group. Thus two structures are possible.

Fig. 2.8.



However, the comparable cis hydrogens have a coupling constant in the region of 6 Hz in the related ring system of $Fe_2(CO)_6C_4H_4Te$[235] and it is therefore concluded that the more probable structure is (a).

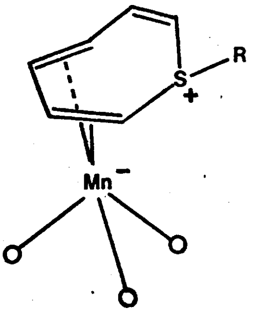
The possible role of a σ bonded intermediate similar to X(a) in the reaction of $[Mn(CO)_4SR]_2$ and $CF_3C{\equiv}CCF_3$ at 80°C prompted thermal decarbonylation studies of X and, at 80°C, a small quantity of a yellow oil (complex XI) was produced in sufficient quantities for i.r. and mass spectroscopic studies only. The i.r. spectrum indicates that XI is a tricarbonyl species of symmetry Cs or lower, with three strong CO stretching modes near 2000 cm^{-1}. The high frequency band has a weak shoulder similar to that of $Mn(CO)_3[C_4(CF_3)_4SR]$. No C=C stretching modes are present, suggesting all olefinic bonds are coordinated, but aromatic skeletal modes of a C_6F_5 group[236] are quite prominent. The mass spectrum of XI gives an ion (M) of highest m/e at 526 corresponding to the stoichiometry $Mn(CO)_3[(CF_3C_2H)_2SC_6F_5]$ but, in contrast with heterocyclic derivatives IX(a), (b), this undergoes stepwise loss of CO to give ions $[M-CO]^+$, $[M-2CO]^+$, $[M-3CO]^+$. Ions due to fragmentation of the ligand $(CF_3C_2H)_2SC_6F_5$, (L), are observed and, as in the spectrum of the tetracarbonyl X, the ion at m/e 349 = L-2F is particularly intense. On this evidence it is considered that XI has a structure analogous to that of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$.

Reactions of $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CH$ with $Mn(CO)_4(CF_3C_2H)_2SC_6F_5$

The reaction of the tetracarbonyl X and hexafluorobut-2-yne, above room temperature, gave a yellow oil, (complex XII(a)), which was not obtained pure. The reaction proved difficult to control and proceeded further to give additional products which could not be separated completely from XII(a) by chromatography or sublimation. A similar complex, XII(b), was obtained from X and $CF_3C{\equiv}CH$ in a complex reaction which gave large quantities of polymer $(CF_3C_2H)_n$. This complex was only obtained in very low yield and, again, could not be obtained pure.

The i.r spectra of XII(a) and XII(b) are similar with three strong CO stretching modes and a weak shoulder near 2000 cm^{-1}, suggesting the presence of an $M(CO)_3$ group and, since strong skeletal modes near 1640 cm^{-1} and 1500 cm^{-1} are observed, the C_6F_5S group appears to have been retained. Extension fragmentation of the complexes occurs in the mass spectrometer and very few ions in the mass spectra of either complex could be identified. However, a strong ion at m/e 350, $[CF_3C_2CF_3(CF_3C_2H)_2]^+$, is observed in the spectrum of XII(a) which undergoes a recognisable fragmentation pattern and this suggests the complex may contain a cyclic ligand, $[CF_3C_2CF_3(CF_3C_2H)_2SC_6F_5]$. Expulsion of C_6F_5S from the ring in the mass spectrometer would be highly favourable in view of the stable arene ring produced. The spectrum of XII(a) was taken under a variety of conditions and one spectrum gave weak ions corresponding to $[CF_3C_2CF_3(CF_3C_2H)_2SC_6F_5]^+$, (L), $[L-H]^+$, $[L-F]^+$, $[L-2F]^+$, but no molecular ion was observed. All spectra recorded gave the ion $[L-2F]^+$ and it is perhaps significant that one of the most intense ions in the spectrum of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ corresponds to loss of two fluorine atoms from the heterocyclic ligand ion.

On this evidence it is tentatively proposed that XII(a) has the stoichiometry $Mn(CO)_3[CF_3C_2CF_3(CF_3C_2H)_2SC_6F_5]$ while XII(b) is $Mn(CO)_3[(CF_3C_2H)_3SC_6F_5]$. The reactions by which they are produced are similar to that of $Mn(CO)_4CCF_3{=}CCF_3SC_6F_5$ and $CF_3C{\equiv}CCF_3$ and so the following general structure is considered possible.



Structurally related tropone[237] and azepine[238] iron tricarbonyl complexes have been studied by X-ray diffraction.

Table 2.7.

I.r. spectra (cm^{-1})* of Manganese Carbonyl Complexes

Compound	νCO	νC=C	νCF
$Mn(CO)_4C(CF_3)=CCF_3SC_6F_5$	2087.5ms, 2086vw, 2021vs, 2015.3vs, 1989.5vs, 1958vw, 1955vw	1609w	1257wm, 1242m, 1172wm, 1160mb, 1149wm, 1137wm
$Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$	2056.2vs, 2046w, 1997.2vs, 1991.5vs, 1960vw, 1956.7vw		1295w, 1246w, 1225ms, 1207m, 1182m, 1156wm, 1142wsh, 1125w, 1099wm
$Mn(CO)_3[C_4(CF_3)_4SCF_3]$	2060.7vw, 2051w, 2002vs, 1996.8vs, 1962.5w		1243m, 1223s, 1210s, 1200ssh, 1180msh, 1165msh, 1150msh, 1126wm
$Mn(CO)_4(CF_3C_2H)_2SC_6F_5$	2099m, 2086vw, 2024.5vs, 2019.6vs, 1977s, 1957.5vw, 1937vw	1559vw, 1530vwsh	1248w, 1229m, 1181wm, 1148m, 1115wm, 1094wm
$Mn(CO)_3[(CF_3C_2H)_2SC_6F_5]$	2049vs, 2044w, 1983.5vs, 1970vs, 1945vw		1251wm, 1205w, 1179wm, 1166wm, 1156wm, 1142m, 1125wm, 1095w
$Mn(CO)_3[(CF_3C_2CF_3)(CF_3C_2H)_2SC_6F_5)]$	2070.3vs, 2060vw, 2021.5vs, 2011.7vs, 1990vw		1267m, 1242wm, 1219w, 1184mb, 1163mb, 1096w
$Mn(CO)_3[(CF_3C_2H)_3SC_6F_5]$	2064vs, 2053vwsh, 2006vs, 1994.2vs, 1960vw		1265mb, 1189msh, 1179m, 1153m, 1143msh, 1095wm

* Cyclohexane

Reactions of $CF_3C{\equiv}CCF_3$ and $CpFe(CO)_2SR$, R = CF_3, C_6F_5

The reactions of hexafluorobut-2-yne and $CpFe(CO)_2SR$ at 80°C, R = CF_3, and 75°C, R = C_6F_5, gave air stable yellow crystals of $CpFe(CO)_2[C(CF_3){=}C(CF_3)SR]$ for which a structure is proposed in which the acetylene has inserted into the Fe-S bond. Insertion reactions of $CpFe(CO)_2X$, X = H, $SiMe_3$, $GeMe_3$, $SnMe_3$, with fluoroacetylenes have already been described so that isolation of the above products is not particularly surprising.

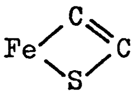
The formulation of the complexes as dicarbonyls is based on elemental analyses and mass spectroscopy. The mass spectra give molecular ions which lose two CO groups in a stepwise manner. The ^{19}F n.m.r. spectrum of $CpFe(CO)_2[C(CF_3){=}C(CF_3)SCF_3]$, XIII(a) consists of two quartets centred at δ_1 = 42.7 ppm, J = 5.17 Hz, δ_2 = 52.0 ppm, J = 15.8 Hz, and a multiplet at δ_3 = 56.6 ppm, which analyses as a quartet of quartets. CF_3 groups attached to divalent sulphur generally have lower chemical shifts than those attached to carbon[239] so that ϕ_1 is assigned to the CF_3S substituent. Since coupling of CF_3S to only one CF_3 group is observed, the CF_3 groups attached to carbon must have a cis configuration in agreement with the coupling constant J_{F-F} = 15.8 Hz, which compares with reported values for $J_{CF_3-CF_3(cis)}$ in the region 11-15 Hz.[163] J_{F-F} values for trans CF_3 groups are usually in the region of 2 Hz[189] while in this case no trans coupling is observed, again supporting the cis configuration. The ^{19}F n.m.r. of the C_6F_5S derivative XIII(b) also indicates that the cis isomer is formed exclusively, the coupling constant of the two CF_3 resonances being 16.0 Hz.

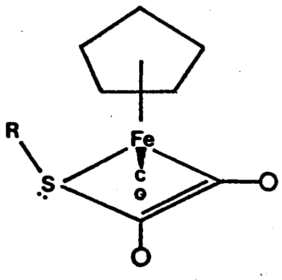
The i.r. spectrum of XIII(b) interestingly exhibits three C-O stretching modes above 2000 cm^{-1} while XIII(a) gives two sets of two bands. This may be due to the presence of rotational isomers, preferred conformations of the $C(CF_3)=C(CF_3)SR$ ligand being possible, as in $CpFe(CO)_2SiCl_2Me$ and $Cp_2MoH[C(CF_3)=C(CF_3)H]$.[164] Since this isomerism was not detected by n.m.r. spectroscopy, the rotation about the iron-carbon σ bond must be fairly rapid and thus the energy barrier to rotation reasonably low. An i.r. spectrum of the SCF_3 derivative taken at -80°C shows significant differences in the relative intensities of the two sets of C=O frequencies, compared to those at room temperature, indicating changes in isomer population. With $CpFe(CO)_2SiCl_2Me$ it was possible to obtain enthalpy and entropy data for the two conformers from similar studies[214] but this was not possible with XIII(a), (b), due to insufficient separation of the isomer frequencies.

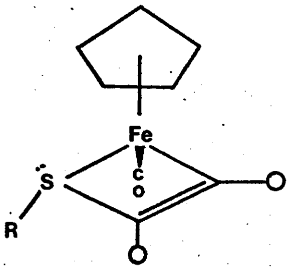
Photochemical decarbonylation of $CpFe(CO)_2[C(CF_3)=C(CF_3)SR]$ in pentane provides further evidence for the <u>cis</u> geometrical configuration of CF_3 groups favoured by n.m.r. spectroscopy. With $R = C_6F_5$, the sole product was a brown oil $CpFe(CO)C(CF_3)=C(CF_3)SC_6F_5$, XIV(b), whereas photolysis of the CF_3S derivative gave, in addition to the monocarbonyl $CpFe(CO)C(CF_3)=C(CF_3)SCF_3$, XIV(a), small quantities of $CpFe(CO)_2SCF_3$, separation of which required chromatography. XIII(a) was also obtained by photolysis of $CpFe(CO)_2SCF_3$ and $CF_3C{\equiv}CCF_3$ in pentane and from the thermal reaction of $[CpFe(CO)SCF_3]_2$ and the acetylene, but these synthetic routes are less useful due to the low yields obtained.

Apart from the i.r. spectra the spectroscopic data for the monocarbonyls are very similar to those of the precursors $CpFe(CO)_2SR$. It was noted however, that the <u>cis</u> $CF_3(i) : CF_3(ii)$ coupling constants, $J_{FF} = 8.5$ Hz, (XIV(a), and $J_{FF} = 7.9$ Hz, XIV(b), are much lower than those of the dicarbonyls $J_{FF} = 15.8$ Hz, XIII(a), and $J_{FF} = 16.0$ Hz, XIII(b), but compare favourably with the value $J_{FF} = 8.9$ Hz found for $Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$. Since F-F coupling in these olefinic compounds probably occurs mainly <u>via</u> a through space mechanism[240] this implies that the <u>cis</u> CF_3 groups are further apart in the monocarbonyls.

This is to be expected since distortion of the bond angles about the sp^2 olefinic carbon atoms must occur to form a four membered ring and, as a result, the CF_3 substituents are forced further apart. It was also noticed that the chemical shifts of the CF_3 groups in the monocarbonyls are ~10 ppm higher than in the dicarbonyls. A further effect of ring formation is the shift in the C=C stretching frequency from ~1510 cm^{-1} in the i.r. spectra of the dicarbonyls to ~1600 cm^{-1} in the monocarbonyls possibly as a result of increased electron density in the olefinic bond due to conjugative effects in the ring.

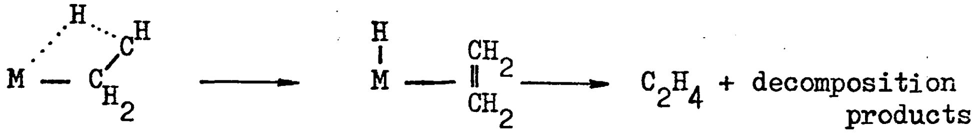
The i.r. spectrum of the CF_3S derivative XIV(a) shows two CO stretching modes near 2000 cm^{-1} instead of the one band expected and this is attributed to the presence of two isomers in which the CF_3 group on sulphur is on the same and on the opposite side of the four membered  ring as the carbonyl group.





There is no reason to expect lack of inversion at sulphur in the C_6F_5S complex so that the appearance of only one CO stretching mode in the i.r. spectrum of XIV(b) is probably due to coincidence of isomer peaks.

In contrast to the small quantities of $CpFe(CO)_2SCF_3$ produced by photolysis of $CpFe(CO)_2C(CF_3)=C(CF_3)SCF_3$, thermal decomposition of the latter at 60°C in hexane gave this complex in significant amounts, suggesting that insertion of hexafluorobut-2-yne into the Fe-S bond may be, to some extent, an equilibrium reaction. In this context it has been found that many other insertion reactions into metal-ligand bonds are reversible.[129] Recent theories concerning the lability of M-C σ bonds, particularly in transition-metal alkyl derivatives,[147] suggest that one of the reasons for the instability of these linkages is the ease with which β hydride transfer can occur, followed by olefin elimination, e.g.



The reverse of this process, insertion of an olefin into a metal-hydrogen bond, yields the alkyl again and the similarity of this system to that involving $CpFe(CO)_2SCF_3$ and $CF_3C{\equiv}CCF_3$ is interesting. Particularly intriguing are the stabilities of the σ alkyl and σ alkenyl complexes (described in the introduction) formed by insertion of fluoroolefins and fluoroacetylenes into transition metal-hydrogen bonds[164] which imply that β hydride elimination is only partly responsible for the lability of M-C σ bonds.

Thermal decomposition of XIII(a) also gave other fluorocarbon compounds which were detected by ^{19}F n.m.r. spectroscopy but not isolated. Thus to some extent this reaction parallels the photochemical decomposition of $CpFe(CO)_2C_2H_4SMe$, which yields $CpFe(CO)_2SMe$, $[CpFe(CO)SMe]_2$, $[CpFe(CO)_2]_2$ and $CpFeCO[(CO)C_2H_4SMe]$,[33] the last of which contains a bidentate sulphur ligand, similar in some respects to $-C(CF_3){=}C(CF_3)SR$. However, at some point in the reaction, migration of C_2H_4SMe onto a coordinated CO ligand must have occurred. It has been observed previously that ligands bearing fluorocarbon substituents (i.e. with strong M-C linkages) do not easily migrate onto coordinated carbon monoxide[186] thus explaining why decarbonylation of $CpFe(CO)_2C(CF_3){=}C(CF_3)SR$ does not result in a CO group being incorporated into the ring.

However, this is not a completely general phenomenon, as the isolation of

$[PhN{:}NC_6H_4.C(CF_3){=}C(CF_3)]COCo(CO)_2$[241] containing a ketonic ligand shows.

The similarity of $CpFe(CO)C(CF_3){=}C(CF_3)SR$ to $Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$, and the reaction of the latter with $CF_3C{\equiv}CCF_3$ to give $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$, suggested that XIV(a) and XIV(b) might react similarly to give $CpFe[C_4(CF_3)_4SR]$. However, the photochemical reaction of CF_3CCCF_3 and the CF_3S complex proved to be unsuccessful and the thermal reaction of the C_6F_5S complex yielded only $CpFe(CO)_2C(CF_3){=}C(CF_3)SC_6F_5$. The latter reaction was subsequently found to occur in the absence of the acetylene and provides further evidence that metal-sulphur coordinate bonds are unstable when electronegative (and bulky) groups are attached to the sulphur.[222] However, the photochemical reaction of $CpFe(CO)C(CF_3){=}C(CF_3)SC_6F_5$ and hexafluorobut-2-yne was subsequently found to proceed slowly in pentane to give yellow brown crystals of the required complex $CpFe[C_4(CF_3)_4SC_6F_5]$, XV. This air sensitive solid decomposes over a period of weeks, even in dry, oxygen-free nitrogen, in contrast with the observed stability of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$, but appears to be fairly stable in solution under a pressure of hexafluoro-2-yne, i.e. under the conditions of its formation.

The i.r. and mass spectroscopic features are almost identical to those of IX(a) so that the presence of a heterocyclic ring $[C_4(CF_3)_4SC_6F_5]$ π bonded to iron is highly probable. A molecular ion at m/e 644 is observed in the mass spectrum which loses one fluorine. A very strong ion at m/e 477 is assigned to $[CpFeC_4(CF_3)_4S]^+$. An ion due to the heterocyclic ring $[(CCF_3)_4SC_6F_5]$ is also present which undergoes a similar fragmentation process to that in the spectrum of IX(a). As with the latter, a peak due to loss of C_6F_6 from this ligand is one of the strongest ions in the spectrum. Interestingly an ion of comparable intensity to the ligand peak (L) is present which may be assigned to

Table 2.8.

N.m.r. Parameters of Cyclopentadienyl-Iron Complexes

	^{19}F (ppm)				^{1}H
Compound	$\delta_1(CF_3C)$	$\delta_2(CF_3C)$	$\delta_3(CF_3S)$	J_{1-2}(Hz)	$\delta(C_5H_5)$
$CpFe(CO)_2C(CF_3)=C(CF_3)SCF_3$	52.0	56.6	42.7	15.8	5.00
$CpFe(CO)_2C(CF_3)=C(CF_3)SC_6F_5$	49.3	53.8	-	16.0	4.90
$CpFe(CO)C(CF_3)=C(CF_3)SCF_3$	59.9	62.6	47.9	8.5	5.15
$CpFe(CO)C(CF_3)=C(CF_3)SC_6F_5$	60.1	62.9	-	7.9	5.33
$CpFeC_4(CF_3)_4SC_6F_5$	51.3	-	-	-	5.25

Table 2.9.

I.r. spectra (cm^{-1})[*] of Cyclopentadienyl-Iron Complexes

Compound	νCO	νC=C	νCF
$CpFe(CO)_2C(CF_3)=C(CF_3)SCF_3$	2046vssh, 2044vs, 2035wsh, 2026vw, 1999vs, 1971w, 1963vw	1525vw, 1508vw	1220m, 1214msh, 1176m, 1156msh 1146m, 1122wm, 1094m
$CpFe(CO)_2C(CF_3)=C(CF_3)SC_6F_5$	2042.8vs, 2033vwsh, 2000.5vs, 1997vs, 1981.5w, 1970w, 1960vw	1530wsh	1230m, 1212m, 1168wm, 1151m, 1136m, 1123wsh, 1092wm
$CpFe(CO)C(CF_3)=C(CF_3)SCF_3$	1994.6vs, 1985.8m, 1949vw	1595wm	1256m, 1238s, 1194msh, 1187ms, 1156ms, 1148msh, 1135msh, 1097msh
$CpFe(CO)C(CF_3)=C(CF_3)SC_6F_5$	1980.8vs, 1934	1598w	1296w, 1256wm, 1241s, 1158m, 1145m, 1135wmsh, 1096wm, 1090wsh
$CpFe[C_4(CF_3)_4SC_6F_5]$	–	–	1287w, 1258w, 1235wmsh, 1219m, 1199m, 1166m, 1150m, 1135ws, 1122w, 1090wm

[*] Cyclohexane

$[L + F]^+$ and possibly results from combination within the spectrometer. The possibility exists of this 'extra' fluorine being attached to sulphur and suggests that SIV heterocycles, $C_4(CF_3)_4SRF$, may be accessible by fluorination of complexes $Mn(CO)_4[C_4(CF_3)_4SR]$ or $CpFe[C_4(CF_3)_4SR]$.

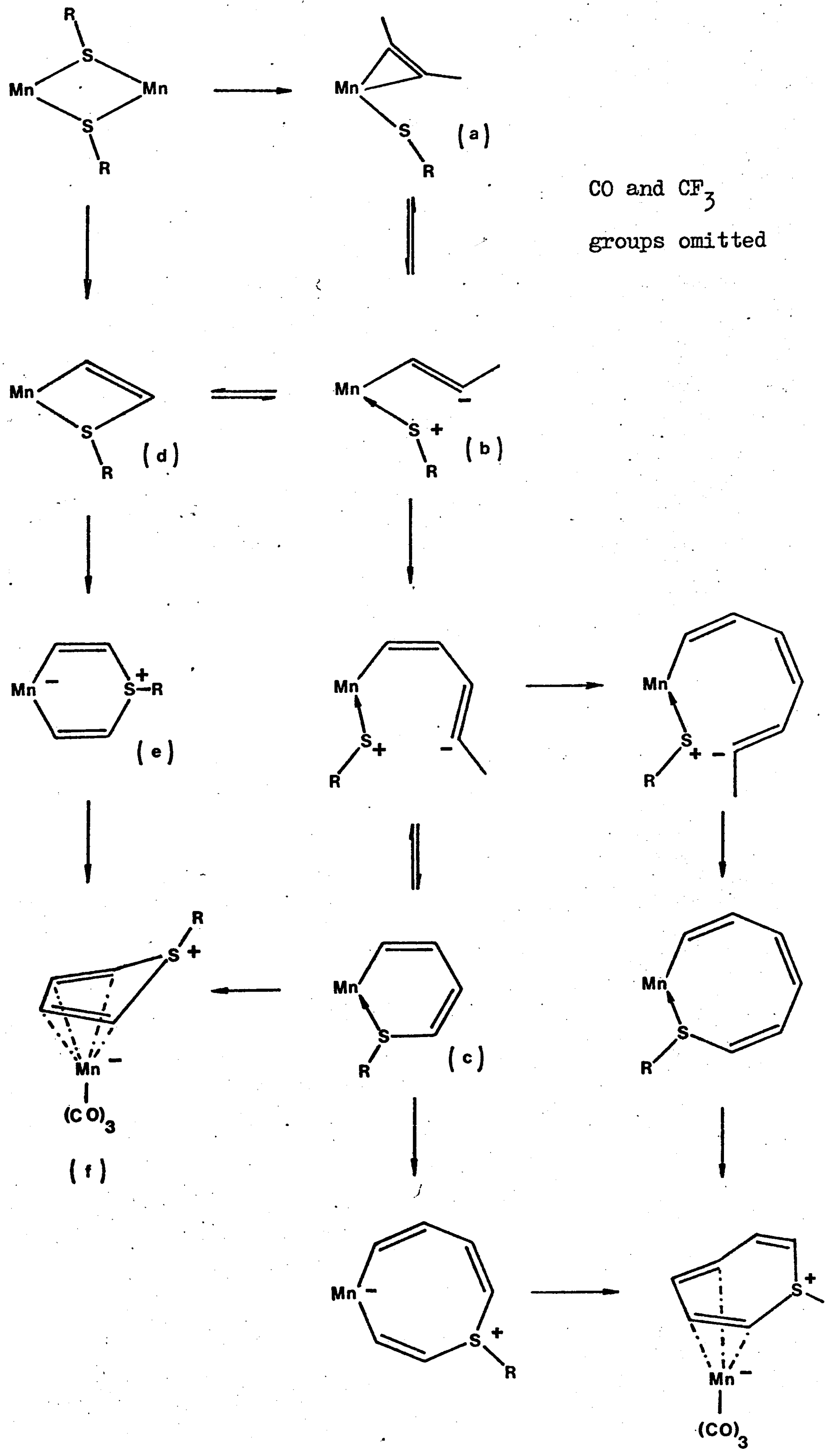
The ^{19}F n.m.r. spectrum shows three multiplets at high field due to the C_6F_5 group but only one CF_3 resonance at 51.3 ppm which, from integration of signals, is due to all four CF_3 substituents on the ring. Since asymmetry and splitting of this signal were revealed by a high resolution spectrum at 94.1 M.Hz it seems likely that the two sets of CF_3 groups have almost identical magnetic environments.

Mechanisms

The reaction of $CpFe(CO)_2SR$ and $CF_3C{\equiv}CCF_3$ to give the cis geometric isomer of $CpFe(CO)_2[CCF_3{=}CCF_3SR]$ is in direct contrast with the work of Stone et al on the carbonyl hydrides of manganese and rhenium which gave the trans isomers of $M(CO)_5C(CF_3){=}C(CF_3)H$, M = Mn, Re, exclusively.[165] However, as already discussed, a variety of insertion reactions of hexafluorobut-2-yne are now known which give only cis isomers. The formation of cis $(PEt_3)_2PtClCCF_3{=}CCF_3H$ rather than the trans product is, according to Clark,[171] explained by either a temperature effect, since cis $Me_2AsCF_3C{=}CCF_3H$ isomerises above 140°C to give the trans isomer, or differences in the reaction mechanism. The latter explanation is favoured by Booth and Lloyd who studied the insertion of a variety of alkynes $RC{\equiv}CR$ into the Rh-H bond of $RhH(CO)(PPh_3)_3$.[170] Only with R = CF_3 was a cis olefinic complex obtained and the ability of hexafluorobut-2-yne to stabilise a five coordinate intermediate π complex was considered to be responsible. It is, however, recalled that insertion of dimethyl acetylenedicarboxylate into an Mo-H bond of Cp_2MoH_2 gives cis $Cp_2MoH(CR{=}CRH)$, R = COOMe, at 0°C but at 110°C this isomerises to the trans isomer.[164] Despite this, a concerted four centre mechanism which gives the cis isomer of $CpFe(CO)_2[C(CF_3){=}C(CF_3)SR]$ directly remains the more attractive explanation, particularly in view of the relatively low reaction temperatures employed.

Although not necessary, it is possible that insertion of the acetylene into the M-S bonds of the dinuclear complexes $[Mn(CO)_4SR]_2$ and $[CpFe(CO)SCF_3]_2$ may involve preliminary bridge cleavage to give an intermediate containing a coordinated acetylene molecule, (a) Fig. 2.9. Intermediates of this type are not generally isolated with complexes of the first row metals, but with certain platinum[173] compounds this has been achieved and the ultimate insertion reaction of the coordinated acetylene subsequently observed. The formation of the cyclic manganese and iron complexes could therefore be explained by the ionic mechanism illustrated in Fig. 2.9. for the reactions of $[Mn(CO)_4SC_6F_5]_2$ and acetylenes hexafluorobut-2-yne and 3,3,3-trifluoropropyne. The formation of $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ from $Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$ could involve initial insertion into the Mn-C bond of the latter to give an intermediate and this, like the 3,3,3-trifluoropropyne complex X, could undergo decarbonylation to the tricarbonyl. However, Stone has pointed out that insertion into M-C bonds in which the carbon has electronegative substituents, i.e. strong M-C bonds, is rather unlikely and no examples of this are yet known with fluoroacetylene reactions[163] although examples of this have been observed with hexafluoroacetone.[242] Despite this, the four to six ring transformation may be possible by ring opening in XIII to give an ionic intermediate (b) which can react with the alkyne to give (c). The reversibility of the reaction of $CpFe(CO)_2SCF_3$ and $CF_3C{\equiv}CCF_3$

Fig. 2.9



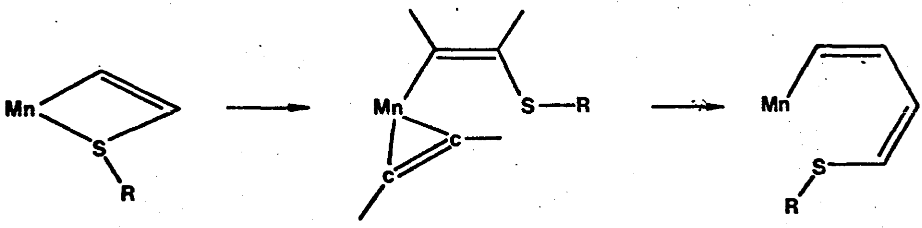
CO and CF_3 groups omitted

provides tentative evidence that a mechanism such as this, involving C-S bond cleavage, is feasible. Stone has proposed a similar mechanism to account for the apparent insertion of hexafluorobut-2-yne into the C-H bond of the vinyl complex $CpRe(PPh_3)_2(CR=CRH)$, R = COOMe.[163]

In the reaction of $[Mn(CO)_4SC_6F_5]_2$ and $CF_3C\equiv CH$ the polar nature of the acetylene may be sufficient to stabilise the intermediate (b) so that the equilibrium between the latter and (d) lies well to the right. Thus $Mn(CO)_4C(CF_3)=C(H)SC_6F_5$ cannot be isolated due to the reaction of the ionic species with another acetylene molecule to give (c), which is sufficiently stable to be isolated.

Alternatively, the reaction of $Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$ and hexafluorobut-2-yne could give the tricarbonyl by a more direct route involving insertion of the alkyne into the Mn-S coordinate bond. The σ bonded zwitterion intermediate (e) thus obtained can undergo a $\sigma - \pi$ transformation with CO expulsion to give the final product (f).

A third possibility is coordination of an acetylene to (d), leading to cleavage of an Mn-S bond. Insertion of the coordinated acetylene into the Mn-C bond is then possible as observed with reactions of hexafluoroacetone and low valent nickel complexes.[242]



The reaction of $CpFe(CO)C(CF_3)=C(CF_3)SC_6F_5$ and $CF_3C\equiv CCF_3$ can obviously proceed by similar pathways but, since u.v. irradiation is required, it is suggested that loss of a carbonyl group is first required to enable coordination of the alkyne to take place. This seems more compatible with the second and third mechanisms proposed above, i.e. insertion into an M-S or M-C bond, but cannot be considered anything more than a tentative indication of such.

In view of the lack of evidence for the nature of complexes XII(a) and XII(b) it is perhaps not wise to postulate a mechanism to account for their formation but, if the structures suggested are correct, the above comments must also apply.

The existence of ionic intermediates such as $\overset{+}{Mn}(CO)_4SRC(CF_3)\overset{-}{C}(CF_3)$ obviously can only be inferred from the limited studies carried out, although similar species are claimed to be stable at low temperatures.[312] As illustrated, these are extreme canonical forms and must be considered as such. Alternative canonical forms could have the positive charge placed on the metal rather than sulphur but, since ring closure involves C-S bond formation, it is considered that some positive charge probably resides on sulphur and hence that the structures illustrated contribute significantly to the overall structures. Consequences of positive charge location in ionic intermediates such as these will be discussed in greater detail in Chapter III.

Reactions of $CF_3C{\equiv}CR'$, $R' = CF_3$, H and $[Fe(CO)_3SR]_2$, $R = CF_3$, C_6F_5

In all cases the above reactions gave adducts of stoichiometry $[Fe(CO)_3SR]_2CF_3C_2R'$ but the reactivity of both complex and acetylene depends significantly on the nature of R and R'. $[Fe(CO)_3SCF_3]_2$ and $CF_3C{\equiv}CCF_3$ reacted below 35°C, in pentane, over a period of several days to give good yields of $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$, XVI(a). Above this temperature the known cyclopentadienone derivative $Fe(CO)_3[C_4(CF_3)_4CO]$[180] was obtained in low yield *via* the 1:1 adduct. No thermal reaction was observed between $[Fe(CO)_3SC_6F_5]_2$ and $CF_3C{\equiv}CCF_3$ up to 60°C, above which,

$Fe(CO)_3[C_4(CF_3)_4CO]$ was produced. In contrast, the photochemical reaction at 20°C gave $[Fe(CO)_3SC_6F_5]_2CF_3C_2CF_3$, XVI(b), in 95% yield after only five hours irradiation, and the 3,3,3-trifluoropropyne derivatives $[Fe(CO)_3SR]_2CF_3C_2H$, XVII(a), (b), were subsequently obtained in low yield by similar photochemical means. Interestingly, irradiating $[Fe(CO)_3SCF_3]_2$ and $CF_3C{\equiv}CF_3$ mixtures in pentane did not accelerate the formation of the 1:1 adduct noticeably.

The complexes are yellow crystalline materials which are reasonably air stable in the solid state but decompose in solution, particularly in acetone. The CF_3S compounds give molecular ions in the mass spectrum which lose the six carbonyl groups in a stepwise manner. Ions $M-(CF_3CCCF_3 + nCO)$, n = 1-6, are also observed indicating that loss of acetylene occurs readily but only in the hexafluorobut-2-yne complex. However, the mass spectra of the C_6F_5S compounds were not obtained due to decomposition in the spectrometer. The i.r. (Table 2.10), and n.m.r. spectra (Table 2.13), of the compounds could be compatible with two different structures, one in which bridge scission has occurred and two $Fe(CO)_3SCF_3$ moieties, each containing a terminal CF_3S ligand, are bridged by a bidentate acetylene. Alternatively, a structure could be envisaged in which the acetylene has inserted into the metal-metal bond of $[Fe(CO)_3SR]_2$. The problem was subsequently solved by a single-crystal X-ray diffraction study of $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ carried out by Professor G.A. Sim and Dr. W. Harrison of this department. Crystals for X-ray studies were prepared by slow crystallisation from hexane under anaerobic conditions.

Table 2.10

I.r. spectra of complexes $[Fe(CO)_3SR]CF_3C_2R'$ (cm^{-1})

Compound	νCO	νC=C	νCF
$[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$*	2120.5w, 2117vw, 2105vs, 2099.8m, 2066.5vs, 2027.6w	1534w	1274s, 1211m, 1180w, 1141sb, 1110sb, 1080ms,
$[Fe(CO)_3SC_6F_5]_2CF_3C_2CF_3$†	2108vw, 2098vs, 2094m 2090wsh, 2061.5s, 2049.6s, 2031w	1525w	1139mb, 1118wm, 1088m, 1083msh
$[Fe(CO)_3SCF_3]_2CF_3C_2H$*	2115w, 2098.2vs, 2097ssh, 2093vwsh, 2060.6sb, 2056.6m, 2047.2m, 2022vw, 2007vw	1520vw	1230wm, 1162w, 1140m 1110m, 1091wm
$[Fe(CO)_3SC_6F_5]CF_3C_2H$†	2106.7w, 2091vs, 2087.5msh, 2055.2m, 2045m, 2026vw, 2013vw	-	1136w, 1106w, 1088w, 1081w
$[Fe(CO)_2(PPh_3)SCF_3]_2CF_3C_2CF_3$‡	2049ms, 2037vs, 1982s	1525w	1261ms, 1186wm, 1148wm, 1120wmb, 1105wm, 1089wm, 1077m

*Cyclohexane †CCl_4 ‡CH_2Cl_2

X-ray Structure of $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$

The complex crystallises in the space group Pnma with a = 10.918(4), b = 12.049(2), c = 15.416(4) Å, z = 4. The analysis employed 1847 independent diffractometer intensities (Mo-K_α radiation), and least squares adjustment of the atomic parameters converged at R = 5.1%. The molecular structure is shown in Fig. 2.10, and some of the principal dimensions in Table 2.11.

The molecule has crystallographically required C_s symmetry which approximates very closely to C_{2v}.

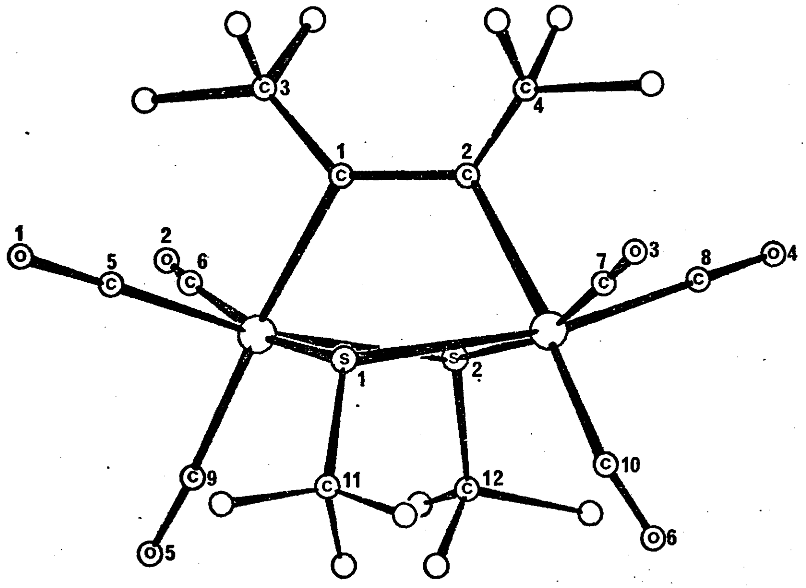


Table 2.11

Intramolecular bond distances and angles

(A) Bond Distances (Å)

Fe(1) - Fe(2)	3.266(1)	S(2) - C(12)	1.81(1)
Fe(1) - S(2)	2.304(1)	Fe(2) - S(2)	2.307(1)
Fe(1) - C(1)	2.048(7)	Fe(2) - C(2)	2.062(7)
Fe(1) - C(6)	1.820(5)	Fe(2) - C(8)	1.811(6)
Fe(1) - C(9)	1.849(8)	Fe(2) - C(10)	1.830(8)
C(1) - C(2)	1.34(1)		
C(1) - C(3)	1.52(1)	C(2) - C(4)	1.51(1)
C(6) - O(2)	1.12(1)	C(8) - O(4)	1.13(1)
C(9) - O(5)	1.13(1)	C(10) - O(6)	1.12(1)

(B) Bond Angles (degrees)

S(1) - Fe(1) - S(2)	87.39	S(1) - Fe(2) - S(2)	87.29
Fe(1) - S(1) - Fe(2)	90.17		
C(2) - C(1) - C(3)	125.06	C(1) - C(2) - C(3)	123.85
Fe(1) - C(1) - C(3)	117.92	Fe(2) - C(2) - C(4)	117.16
Fe(1) - C(1) - C(2)	117.02	Fe(2) - C(2) - C(1)	119.01

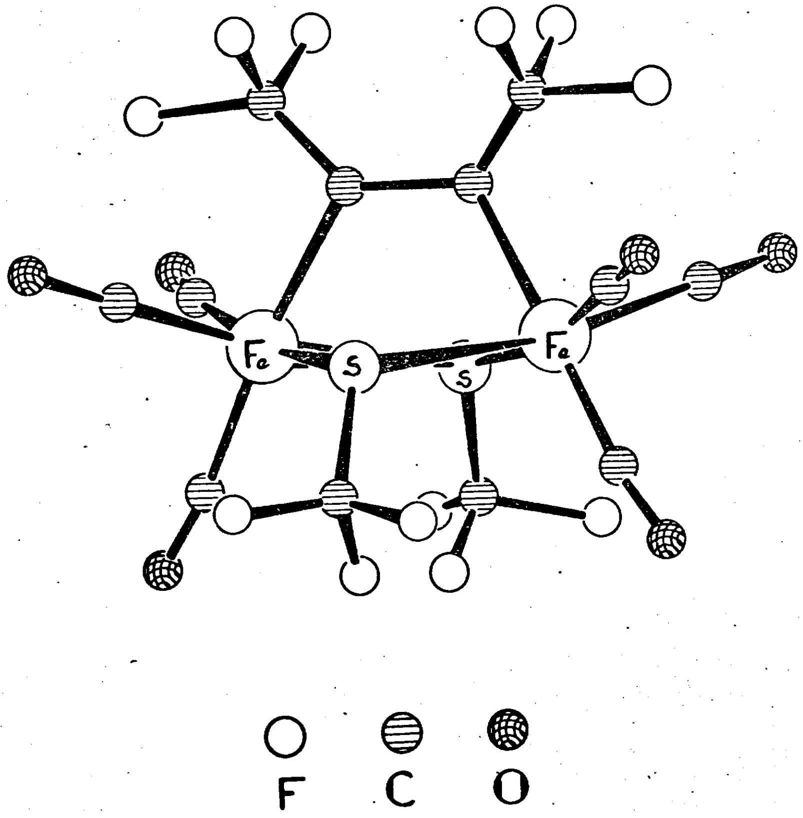


Fig. 2.10

The structure of the complex shows that the acetylene has inserted into the Fe-Fe bond and consequently the fluorocarbon C-C bond is now completely olefinic in character, which explains the C=C stretching mode in the i.r. spectrum of these derivatives near 1525 cm^{-1}. The C=C bond length, 1.34 Å, compares with 1.27 Å in the dimetallated bisolefinic complex $[Ir(NO)(PPh_3)CF_3C_2CF_3]_2$,[243] and with 1.33 Å in ethylene.[226] The bond angles round the olefinic carbon atoms are close to the ideal 120° of sp^2 hybridisation and the slight distortions may be due to CF_3-CF_3 repulsion as found in $Fe(CO)_3[C_4(CF_3)_4CO]$.[230] Alternatively these can be accounted for by the requirements of the Fe-Fe separation which is obviously a function of the angular strain in the five membered Fe, C, C, Fe, S rings.

It has been observed that M-C σ bonds exhibit a degree of shortening when electron releasing groups on the carbon atom are replaced by electron withdrawing substituents e.g. F, CF_3, and this is illustrated by the appropriate distances of 2.40 Å and 2.28 Å in $CpMo(CO)_3C_2H_5$ and $CpMo(CO)_3C_2F_5$ respectively.[218] Until recently this bond shortening has been attributed to greater M-C back-donation in the fluorocarbon compounds,[148,218] but calculations by Fenske[151] suggest that this phenomenon has its origins in the population of the highest filled orbital on carbon. With fluorocarbon substituents this has significant s character which reduces the covalent radius of carbon and hence the metal-carbon distance. In the current period of reaction against an earlier overindulgence in invoking π back-bonding it is worth noting that evidence in support of such conclusions is gradually being collected.[148]

However, when the fluorocarbon ligand has uncoordinated olefinic bonds, conjugative effects sometimes reduce the M-C σ bond distance even further so that in the metalocyclopentene derivative $Fe(CO)_4(CF_2CF)_2$ the average Fe-C bond length is 2.061 Å, whereas in the perfluoroalkyl complex $Fe(CO)_4(CF_2CF_2H)_2$ this has increased to 2.058 Å.[244] The latter distance compares favourably with the average Fe-C σ bond separation in $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ and seems to suggest that conjugative effects are negligible in this complex and hence that little or no π-bonding occurs between Fe(1) and C(1) and Fe(2) and C(2).

As in $[Fe(CO)_3SEt]_2$ and related compounds,[10] only minor differences are observed in the Fe-CO (apical) and Fe-CO (basal) distances of $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$, although significant differences are apparent in $[Fe(CO)_3IPMe_2]_2$.[245] The longer Fe-CO (basal) distances in the latter have been explained by the relatively strong π acceptor phosphorus atoms exerting a weakening trans effect on these bonds. Conversely the absence of π bonding in the Fe-I bonds allows some double bonding in the Fe-CO (apical) bonds trans to iodine. On the basis of these observations, and since the Fe-C (olefin) bonds appear to have little or no multiple-bond character, the small differences in the Fe-CO bond distances in XVI(a) imply that the Fe-S bonds have virtually no double bond character. In agreement with this the Fe-CO distances in $[Fe(CO)_3NH_2]_2$[10] show no significant differences, the nitrogen of course having no d orbitals available for back-bonding.

Comparison of Fe-S distances in $[Fe(CO)_3SEt]_2$, $[Fe(CO)_3SC(C_6H_5)]_2$ and $[Fe_2(CO)_6SMe]_2S$ reveals that all have Fe-S distances near 2.26 Å[10] while in $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ the average is 2.306 Å. The greater Fe-S orbital overlap in the CF_3S derivative, possible because of the unstrained Fe_2S_2 ring, would be expected to produce the opposite effect i.e. shorter Fe-S distances. The implication is that in $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ the Fe-S bonds are weaker than in the other complexes and further substantiates the observations and conclusions of Chapter I, that the presence of electronegative substituents on sulphur reduces the stability of M-SR coordinate bonds. It is however, pointed out that the Fe-S distances may be reduced in complexes containing M-M bonds as a result of the short M-M distance, as revealed by a structural comparison of $[CpCoPPh_2]_2$ and $[CpNiPPh_2]_2$.[15]

The main structural modification resulting from acetylene coordination is in the stereochemistry of the iron atoms, which now have almost undistorted octahedral geometry. Consequently the Fe_2S_2 ring is nearly planar with a dihedral angle of 156° between the two planes S_1-Fe_1-S_2 and S_1-Fe_2-S_2. Combined with a non-bonding Fe-Fe separation of 3.266 Å, this results in average Fe-S-Fe angles of 90.2° and S-Fe-S = 87.4° which are significantly less acute than the corresponding angles of 68.3° and 81° in $[Fe(CO)_3SEt]_2$. Comparison of structural parameters with other complexes which do not contain a metal-metal bond, (Table 2.12), is perhaps more informative and reveals that, as expected, the bridge angles are in all cases less acute.

Table 2.12

Dimensions of dinuclear mercapto-bridged iron complexes

Compound	M-M Å	Fe-S Å	Fe-S-Fe°	S-Fe-S°	Ref.
$[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$	3.266	2.306	90.2	87.4	
$[Fe_2(CO)_6(SMe)_3]^+$	3.062	2.305	83.2	80.7	246
$[CpFe(CO)SPh]_2$	3.39	2.262	98	81	78
$[CpFe(SEt)S]_2$	3.307	2.281	92.95	93.9	248

An interesting consequence of the near planar Fe_2S_2 ring geometry is the greater S-S separation relative to $[Fe(CO)_3SEt]_2$ and hence the change in isomer population relative to $[Fe(CO)_3SCF_3]_2$. In the solid state XVI(a) has the syn(a,a) configuration which is not possible in $[Fe(CO)_3SEt]_2$, and similar complexes with short S-S distances and highly puckered rings.[11] The separation of the two ethyl groups in the hypothetical syn(a,a) isomer of the latter has been calculated to be 2.30 Å[11] and, since the Van der Waals radius of a methyl group is 2.0 Å, this isomer is precluded by steric interactions. On this basis, the syn isomer of $[Fe(CO)_3SR]_2$ observed in solution is considered to have the equatorial-equatorial configuration.[27] However, the existence of the analogous electronically equivalent bis μ-dialkyl and aryl phosphido complexes, $[Fe(CO)_3PRR']_2$ and $[CpCoPRR']_2$, together with various substituted phosphine derivatives, does show that sufficient non-rigidity of the M_2X_2 skeleton exists such that the bridging R_2P groups can replace bridging RS ligands. In these complexes the aryl derivatives appear to be more stable than alkyl complexes, probably due to decreased repulsion in the former.[15] This is possible if the aryl substituents lie with their C_6 planes along the M-M axis as found by the X-ray studies of $[CpCoPPh_2]_2$[15] and syn-$[Fe(CO)_3PMePh]_2$.[247] The latter can, however, exist with the configuration Me(a), Ph(e); Ph(a), Me(e) according to proton n.m.r. studies,[247] but it is not surprising that $[CpCoP(CF_3)_2]_2$, isolated by Dobbie, proves to be very unstable.[95]

With $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$, repulsion between the CF_3 groups on sulphur is obviously minimal and, as a result, the syn(a,a) isomer is the most stable configuration. This also appears to be the case in solution since peaks attributable to syn and anti isomers, ratio 3:1, are observed in the ^{19}F n.m.r. spectrum. No significant structural alteration is expected on dissolution of the crystals so that the syn isomer probably has the axial-axial configuration. In XVII(a) the isomer ratio is syn:anti = 2:1 while it appears that, from the n.m.r. of XVI(b) and XVII(b), only the syn isomers are present.

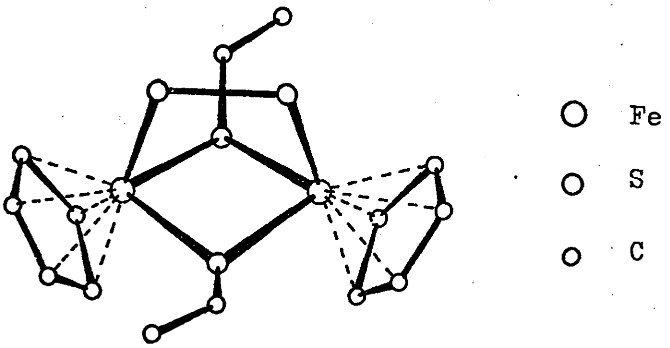
Table 2.13

N.m.r. parameters of complexes $[Fe(CO)_3SR]_2CF_3C_2R'$

	^{19}F (ppm)				
	(CF_2S)			(CF_3C)	
Compound	δ(1) syn	δ(2) anti	δ(3) anti	δ(4) syn	δ(5) anti
$[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$	38.2	35.7	39.3	48.3	47.6
$[Fe(CO)_3SC_6F_5]_2CF_3C_2CF_3$	-	-	-	45.4	-
$[Fe(CO)_3SCF_3]_2CF_3C_2H$	38.7	36.7	39.9	57.5	56.7
$[Fe(CO)_3SC_6F_5]_2CF_3C_2H$	-	-	-	56.6	-

These observations can be rationalised on the basis of a compromise between various intramolecular forces. Thus, in the equatorial position the organic substituent on sulphur interacts with the basal carbonyl ligands and the bridging alkyne, while in the apical position the R group is repelled by the apical carbonyl groups and by the other substituent on sulphur, if it also has this configuration. The predominance of the syn isomer suggests that the former is the more important, particularly when the substituents on sulphur are bulky, e.g. C_6F_5.

It is thus apparent that the absence of a metal-metal bond, by changing the ring geometry dramatically, changes the relative stability of isomers. In $[CpFe(CO)SPh]_2$[76] and $Cp_2Mo(SBu^t)_2PtCl_2$[80] the most stable form has the syn (e,e) configuration in contrast to $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$ which has the syn (a,a) form, suggesting that the presence of a bridging acetylene in the latter considerably destabilises the equatorial position on sulphur. In the first two complexes, however, the axial position is destabilised by the proximity of the cyclopentadienyl ligands, but it is interesting to note that in [CpFe(SEt)S]$_2$, which has a structure intermediate between these two types,[248] the most stable form in the solid state has the syn (e,e) configuration.



Substitution of carbonyl groups in $[Fe(CO)_3SCF_3]_2$ by triphenylphosphine, as described previously, leads to destabilisation of axial substituents and, in view of this, the above observations prompted similar studies with $[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$. At 20°C, in pentane, a 1:1 molar ratio of the latter and triphenylphosphine reacted to give the disubstituted complex $[Fe(CO)_2(PPh_3)SCF_3]_2CF_3C_2CF_3$, no trace of a mono-substituted derivative being detected. The i.r. spectrum is in accord with the structure in which the CO ligands trans to the olefin bridge have been replaced. Attempts to obtain a mass spectrum of the complex were unsuccessful due to decomposition in the spectrometer source. The solubility of the complex is very low even in polar solvents and this, combined with the observed instability in such solvents, prevented a ^{19}F n.m.r. spectrum from being obtained. The proton spectrum gives a single broad resonance at 2.5τ but, unfortunately, is of little help in elucidating the potentially interesting isomer population in this complex.

Reactions of $CF_3C{\equiv}CCF_3$ and $[CpCoSR]_2$, R = CF_3, C_6F_5

It was considered that the cobalt complexes $[CpCoSR]_2$, R = CF_3,

C_6F_5, with a proposed structure similar to $[Fe(CO)_3SR]_2$, might react similarly with hexafluorobut-2-yne. However, no reaction was observed at low temperatures ($< 70^\circ C$), even under u.v. irradiation, but at $80^\circ C$ complex mixtures of products are obtained. Chromatographic methods enabled separation of some of these, but in very low yield and attempted identification by mass and i.r. spectroscopy was unsuccessful. However, the main product in both reactions is a red crystalline complex $CpCoC_6(CF_3)_6$, XVIII, which, from spectroscopic evidence, appears to be analogous to the rhodium derivative $CpRhC_6(CF_3)_6$, obtained from the reaction of $CpRh(CO)_2$ and $CF_3C{\equiv}CCF_3$.[198]

The mass spectrum of XVIII, in addition to a molecular ion, gives a peak at m/e 486 and fragment ions corresponding to the ligand $C_6(CF_3)_6$, hexakis(trifluoromethyl)benzene. The ^1H n.m.r. spectrum gives a sharp singlet, $\delta = 4.53\tau$, while the ^{19}F n.m.r. contains three complex multiplets at $\delta_1 = 50.2$ ppm, $\delta_2 = 52.0$ ppm and $\delta_3 = 57.2$ ppm, of equal intensity. δ_2 and δ_3 exhibit complex fine structure while δ_1 is broad and poorly resolved. Similar spectra have been reported for $CpRhC_6(CF_3)_6$,[198] $Ru[P(OMe)_3]_2[C_6(CF_3)_6]$[186] and $Rh[(CH_3CO)_2CHC_2(CF_3)_2][C_6(CF_3)_6]$,[199] indicating that in $CpCoC_6(CF_3)_6$, as with these three compounds, only four of the six carbon atoms of the benzene ring are bonded to the metal. The free double-bond of the ring generally gives rise to a C=C stretching mode in the i.r. spectrum above 1620 cm^{-1} and in $CpCoC_6(CF_3)_6$ this is observed at 1622 cm^{-1}. Strong C-F stretching modes at 1207 cm^{-1}, 1199 cm^{-1}, 1194 cm^{-1}, 1181 cm^{-1} have an intensity and frequency distribution comparable to those of the cyclopentadienyl rhodium complex.

An X-ray diffraction study of $CpRhC_6(CF_3)_6$[197] has shown that the $C_6(CF_3)_6$ ring is non-planar, the uncoordinated double bond lying above the plane of the other four carbon atoms with a dihedral angle of

48° (see page 81). The C-C separation of the terminal butadiene fragment, 2.56 Å, is significantly shorter than in the free ligand, 2.80 Å, and this accounts for this large distortion from planarity on the basis of arguments presented previously with $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$. A similar structure is therefore proposed for $CpCoC_6(CF_3)_6$.

It has been shown that in the related derivative $CpRhC_6(COOMe)_6$[249] the tetrahapto ring becomes fluxional at 155°C according to n.m.r. data but this was not observed with the corresponding iridium complex, suggesting that in the latter the M-C bonds are probably stronger. These results are in contrast to the fluxional behaviour of dihapto nickel complexes of $C_6(CF_3)_6$[250] with which it has not proved possible to stop 'ring whizzing' even at -90°C. However, at this temperature the frozen structure of the analogous platinum complex $(PEt_3)_2PtC_6(CF_3)_6$ was detected by n.m.r. spectroscopy.[251]

Reaction of $CF_3C{\equiv}CCF_3$ and $CpCo(CO)(SC_6F_5)_2$

This reaction proceeded slowly at room temperature, but rapidly at 60°C, to give good yields of the known hexakis(trifluoromethyl)cyclopentadienone complex $CpCoC_4(CF_3)_4CO$[232] and $C_6F_5SSC_6F_5$ only. No complexes containing C-S bonds were detected, nor was $CpCoC_6(CF_3)_6$, implying that, as with the high temperature reaction of $[Fe(CO)_3SR]_2$ and $CF_3C{\equiv}CCF_3$, attack of the cyclising acetylenes on coordinated carbon monoxide is the most favourable process.

Mechanisms of Reactions

The reaction of $Fe(CO)_5$ and $CF_3C{\equiv}CCF_3$, which gives the cyclopentadienone derivative $Fe(CO)_3[C_4(CF_3)_4CO]$ according to Green,[186] involves only mononuclear reaction intermediates in an ionic reaction mechanism which can effectively explain the formation of $CpCo[C_4(CF_3)_4CO]$ from

$CpCo(CO)(SC_6F_5)_2$. However, $Fe(CO)_3[C_4(CF_3)_4CO]$, when produced from $[Fe(CO)_3SR]_2CF_3C_2CF_3$, is probably formed *via* a dinuclear intermediate since four molecules of CO are required for every molecule of product obtained. The reactions of iron carbonyls with thianapthene,[60] 2,2-dithenyl and[252] tellurophene[235] in each case give a product with the following basic structure.

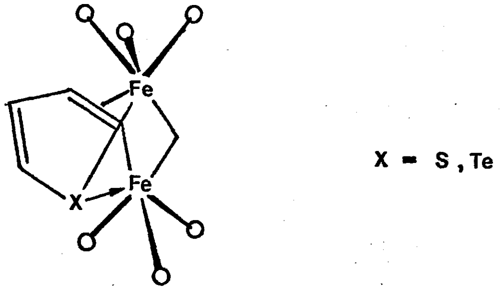


Fig. 2.11

On thermal decomposition of the tellurophene derivative a ferracyclopentadiene compound, $Fe_2(CO)_6(C_4H_4)$, is obtained and complexes of this type are known to undergo thermal decomposition to cyclopentadienone complexes, $Fe(CO)_3[C_4R_4(CO)]$.[129,152] Thus, although $Fe(CO)_3[C_4(CF_3)_4CO]$ is probably produced by direct attack of the cyclising fluorocarbon chain on coordinated CO, it is not possible to eliminate initial attack on sulphur followed by thermal decomposition of the resulting complex.

Although not isolated, an adduct $[CpCoSR]_2CF_3C_2CF_3$ could be involved in the reaction of $CF_3C{\equiv}CCF_3$ and $[CpCoSR]_2$ in view of the similarity of the latter complex to $[Fe(CO)_3SR]_2$, but further reaction of such an intermediate to give a cyclopentadienone complex is obviously not possible. As observed in the reactions of hexafluorobut-2-yne with $CpRh(CO)_2$[198] or $Ru[P(OMe)_3]_2(CO)_3$[186] an alternative pathway leading to a hexakis(trifluoromethyl)benzene complex is possible and consequently $CpCo(C_6CF_3)_6$ is produced. The ruthenium complex $RuP(OMe)_3(CO)_2C_6(CF_3)_6$, described by Green, was produced from Ru$[P(OMe)_3]_2(CO)_3$ and $CF_3C{\equiv}CCF_3$ via a metalocyclopentadiene intermediate (see introduction Fig. (iii)). The final step in the reaction to produce the arene complex could be achieved by 1,4 addition of an alkyne to the five-membered ring of this intermediate. An alternative mechanism considered for this reaction involves ring expansion to give a metalocycloheptatriene complex which undergoes a σ-π transformation to produce a dihapto benzene derivative. On CO expulsion the final tetrahaptobenzene complex is obtained. The latter mechanism was considered less likely by previous workers,[60] but this conclusion now seems rather premature in view of the recent isolation of nickel and platinum compounds containing rings of this type.[251]

Dickson has reported[198] that the mass spectrum of the rhodium arene compound $CpRhC_6(CF_3)_6$ gives a peak at m/e 822 which he assigned to the dinuclear complex $(CpRh)_2[C_6(CF_3)_6]$ and it seems probable that this results from reaction within the mass-spectrometer. It was therefore proposed that this complex may be an intermediate in the reaction of $CpRh(CO)_2$ and $CF_3C{\equiv}CCF_3$ and, on thermal decomposition, gives $CpRhC_6(CF_3)_6$. The mass spectrum of $CpCo[C_6(CF_3)_6]$ similarly gives an ion at m/e 734 assigned to $(CpCo)_2C_6(CF_3)_6$. Attempts to prepare the latter were made by irradiating a pentane solution of the monomer, XVIII, and $CpCo(CO)_2$ but, after several weeks, no reaction was observed. The evidence for a dinuclear reaction intermediate of this type must therefore remain, at best, extremely tenuous.

The lack of isolable intermediates in the reactions of $[CpCoSR]_2$ and hexafluorobut-2-yne obviously prevents further discussion of a possible reaction mechanism at this point, although it is not considered unreasonable to suggest that $CpCoC_6(CF_3)_6$ may be formed via $[CpCoSR]_2CF_3C_2CF_3$ and a metalocyclopentadiene derivative. However, the cyclotrimerisation of hexafluorobut-2-yne in the presence of transition metal complexes will be considered in more detail in Chapter V.

Reaction of $CF_3C{\equiv}CCF_3$ and $[Co(CO)_3SC_6F_5]_2$

As pointed out in the introduction, the reactions of acetylenes with cobalt derivatives are influenced to a great extent by the ligands coordinated to the metal. This is further illustrated by the reaction of hexafluorobut-2-yhe and $[Co(CO)_3SC_6F_5]_2$ which, unlike those involving cyclopentadienyl cobalt derivatives, gave a product $Co_2(CO)_6[C_4(CF_3)_4S]$,* XIX, which is considered to result from attack of cyclising fluorocarbon on a sulphur atom. Other products of this reaction, obtained in low yield, are the known derivatives $[Co(CO)_3]_2CF_3C_2CF_3$[180] and $Co_2(CO)_4[C_6(CF_3)_6]$.[253]

$Co_2(CO)_6[C_4(CF_3)_4S]$ is a dark green air stable solid, very soluble in organic solvents and subliming at 30°C in high vacuum. This is in accord with its dinuclear formulation although it was not possible to confirm this by mass spectroscopy since no molecular ion was observed. Very weak ions in the spectrum were present up to m/e 650 but could not be identified. The highest identifiable ion at m/e 356 is fairly intense and corresponds to $[C_4(CF_3)_4S]^+$. The subsequent fragmentation pattern, involving loss of F and CF_3 groups, is in accord with this formulation and indicates that XIX contains such a ligand bridging two cobalt tricarbonyl moieties. The ^{19}F n.m.r. spectrum, which shows four multiplets at 50.7 ppm, 54.3 ppm, 58.0 ppm and 65.2 ppm, indicates that all four CF_3 groups are in different environments, the spectrum being very similar to that of $CpRu(PPh_3)[C_4(CF_3)_4H]$[163] (described in the introduction), in which all four CF_3 substituents on the C_4 chain are mutually <u>cis</u>.

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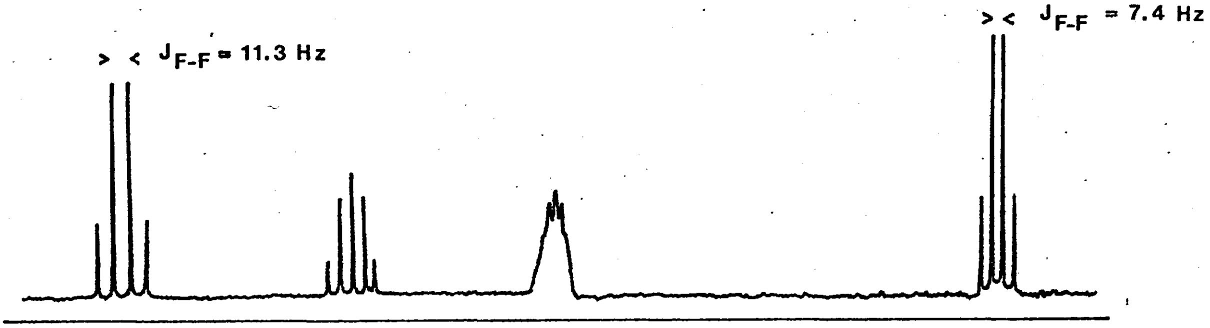
* see Appendix p. 244

^{19}F n.m.r. spectrum $Co_2(CO)_6[C_4(CF_3)_4S]$



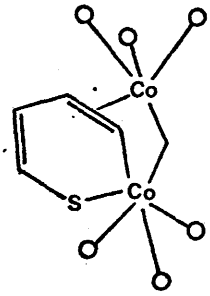
The i.r. spectrum further substantiates a dinuclear structure since the four strong CO stretching modes above 2000 cm^{-1} have an intensity and frequency distribution very similar to that found in the precursor $[Co(CO)_3SC_6F_5]_2$ and isostructural complexes $Co_2(CO)_6CF_3C_2CF_3$ and $[Fe(CO)_3SR]_2$.

Table 2.14

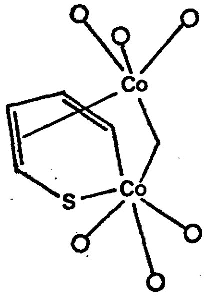
I.r. spectrum of $Co_2(CO)_6[C_4(CF_3)_4S]$ (cm^{-1})*	
νCO	νCF
2105.2m, 2078vs, 2068w, 2062m, 2053m, 2028vw, 2024.2vw, 2019.7vw, 2013.6vw	1269w, 1223wm, 1190m, 1174wm 1149w, 1136w, 1098vw

* Cyclohexane

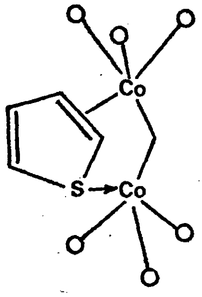
The intensity and frequency separation of the two high energy bands in particular indicate the presence of a cobalt-cobalt[6,57,103] bond and, on the above evidence, five structures (a), (b), (c), (d) and (e) can be considered.



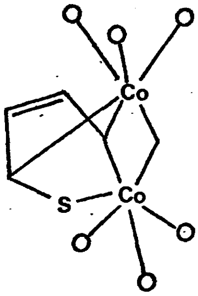
(a)



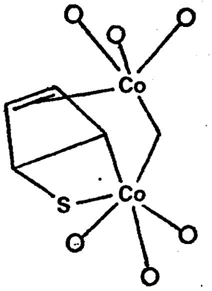
(b)



(c)



(d)



(e)

(a), (b), (c) and (d) contain an uncoordinated C=C bond so that the absence of an olefinic C-C stretching mode in the i.r spectrum would apparently eliminate such structures, particularly since this band is very prominent near 1650 cm^{-1} in the spectra of the related complexes $CpRu(PPh_3)[C_4(CF_3)_4H]$ and $CpNi[C_4(CF_3)_4H]$. The latter is described in Chapter III. However, this is only negative evidence and it is notable that the C=C stretching frequencies of $Mn(CO)_4[(CF_3C_2H)_2SC_6F_5]$ are extremely weak. The absence of a νC=C mode could however be explained by the existence of a cyclobutene ring as in (e). In support of this structure it has been found that on photolysis tetrakis(trifluoromethyl)thiophene isomerises to a cyclobutene derivative,[254] and the ability of electronegative substituents to stabilise small rings is, of course, well known.[255]

The stereochemistry of sulphur, phosphorus and nitrogen bridged dimers was discussed in the introduction to Chapter I and it was pointed out that in certain cases, e.g. $[Fe(CO)_3X]_2$ and $[CpCoX]_2$, the ring system is puckered due to the tendency of the metal to achieve octahedral stereochemistry. On this basis structure (c) is unlikely since the cobalt atoms are five coordinate (including the metal-metal bond). This is also true of one of the cobalt atoms in (a), (b) and (e) unless the bonding approximates to the metalocyclopropane bonding situation found in Pt(0) complexes of olefins and acetylenes bearing electronegative substituents.[130,137] The σ bonded structure of (d) effectively overcomes this difficulty and one of the carbon atoms is linked to both cobalt atoms, as in the carbene complex $Co_2(CO)_7C(CF_3)_2$.[68]

The basic structure of XIX is rather similar to that of several derivatives formed by the reactions of iron carbonyls with heterocyclic compounds similar to thiophene. The reaction of thiophene itself results in complete desulphurisation to give a metalocyclopentadiene complex[1], but with tellurophene[235] a complex $Fe_2(CO)_6C_4H_4Te$ can also be isolated, which is considered to have a structure analogous to XIX, but with the chalcogen bonded to both iron atoms (Fig. 2.11). Related complexes have similarly been isolated from the reactions of thianapthene[60] and 2,2'-dithienyl[252] with iron carbonyls. These derivatives must result from C-X, (X = S, Te), bond scission within the five membered heterocyclic ring, many examples of this being known in the reactions of metal carbonyls with organosulphur compounds.[1] However, the synthesis of XIX suggests that the reactions of heterocyclic chalcogen compounds with cobalt carbonyls might also be a fruitful area of research.

Mechanism

Again the lack of intermediates prevents a full discussion of the reaction mechanism but the similarity of the six membered $CoSC_4$ ring in XIX to that in $Mn(CO)_4[(CF_3C_2H)_2SC_6F_5]$ suggests, either successive insertion of acetylenes into an M-S bond of $[Co(CO)_3SC_6F_5]_2$ or, alternatively, build up of a linear butadiene chain Co-C=C-C=C <u>via</u> an ionic mechanism, followed by attack of the terminal carbon atom on sulphur. Ultimately, expulsion of $(C_6F_5)_2S$ would give the final product, although the sulphide was not isolated from the product mixture. Such a mechanism could also explain the formation of $Co_2(CO)_4C_6(CF_3)_6$, since it obviously does not result from the reaction of $Co_2(CO)_6CF_3C_2CF_3$ and $CF_3C{\equiv}CCF_3$ at the rather low temperature at which the reaction was carried out.[253] $Co_2(CO)_6[C_4(CF_3)_4S]$ can also be excluded on the same basis since it only reacts above 75-80°C with excess alkyne to give the tetracarbonyl compound. If, prior to attack on sulphur, the butadiene chain is intercepted by a molecule of alkyne, a hexatriene chain will be produced which can attack the other cobalt atom and, on elimination of $C_6F_5SSC_6F_5$, give $Co_2(CO)_4[C_6(CF_3)_6]$.

Conclusions

Perhaps the most intriguing aspect of reactions involving acetylenes with transition metal complexes is their unpredictability and this is well illustrated by the reactions described in this chapter. However, with hindsight, it is possible to observe some trends which are worthy of note, but the element of unpredictability still remains.

In reactions of trifluoromethylthio-and pentafluorophenylthio-complexes with $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CH$ leading to cyclisation of the acetylene, three alternative pathways are available to the cyclising fluorocarbon chain. (1) Cyclisation involving only acetylenes which leads, ultimately, to arene rings. (2) Cyclisation in which coordinated carbon monoxide is incorporated into the final ring system. (3) Cyclisation in which sulphur is incorporated into the ring.

Type (1) was only observed in the reactions of $[CpCoSR]_2$ and $[Co(CO)_3SC_6F_5]_2$ with hexafluorobut-2-yne and, in general, is mainly found with complexes of the group VIII metals.[186,198,250] The second class of reaction, involving formation of cyclopentadienone derivatives, occurs more generally throughout the transition series[129,152] as the isolation of $CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$ shows. The third reaction type, (3), which leads to C-S bond formation appears, from the limited studies carried out, to be restricted to derivatives of metals which are capable of forming stable complexes with one, three and five electron ligands, e.g. $[Mn(CO)_4SR]_2$, $CpFe(CO)_2SR$ and $[Co(CO)_3SC_6F_5]_2$. The fact that $CpM(CO)_3SCF_3$, M = Mo, W, and $[CpMo(CO)_2SCF_3]_2$ did not undergo such reactions is in line with the observed trend of greater reactivity of metal-sulphur bonds towards the right-hand side of the periodic table. Accordingly, the products obtained from the reaction of $[CpNiSCF_3]_2$ and hexafluorobut-2-yne described in Chapter III, suggest that Ni-S bond cleavage occurs very readily.

In almost all the cyclisation reactions observed only one type of reaction is observed to the exclusion of the other two, suggesting that in most circumstances one is distinctly more favourable than the others. Even in the reaction of $[Co_2(CO)_3SC_6F_5]_2$ and $CF_3C{\equiv}CCF_3$, the only example in which two types are observed, (1) and (3), one of these, (1), from the relative yields of products appears to be only a minor side reaction.

The two main factors controlling the cyclisation process in individual reactions appear to be the substituents on the acetylene and the nature of the transition metal. The isolation of $CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$

and $Mn(CO)_4(CF_3C_2H)_2SC_6F_5$ from reactions involving $CF_3C{\equiv}CH$ contrasts with $CpMo(CO)_2(CF_3C_2CF_3)SCF_3$ and $Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$ obtained from $CF_3C{\equiv}CCF_3$. These observations, coupled with the formation of the polymer $(CF_3C{\equiv}CH)_n$ in the reactions of $CF_3C{\equiv}CH$ and $[Mn(CO)_4SR]_2$, R = CF_3, C_6F_5, indicate that the propyne has a significantly greater tendency to undergo polymerisation than the disubstituted acetylene $CF_3C{\equiv}CCF_3$. Since cyclisation of fluoroacetylenes is considered to proceed <u>via</u> ionic mechanisms, this can be attributed, perhaps, to the polar nature of $CF_3C{\equiv}CH$ stabilising ionic intermediates. Thus, before attack on coordinated sulphur, carbon monoxide or the metal can occur, the ionic intermediate is intercepted by a second molecule of acetylene. This follows directly from the mechanism proposed in Fig. 2.9.

The effect of the transition metal on the cyclisation process is determined to a great extent by the tendency to attain the favoured eighteen electron configuration but other effects are noticeable, as will now be discussed.

With the cyclopentadienyl cobalt complex $CpCo(CO)(SC_6F_5)_2$ reaction types (1) and (2) are obviously possible but only the cyclopentadienone derivative is produced. This is also true of the reaction of $CpCo(CO)_2$ and $CF_3C{\equiv}CCF_3$,[180] which also gives the cyclopentadienone exclusively. The reaction of $CF_3C{\equiv}CCF_3$ and $[Fe(CO)_3SR]_2$ could possibly follow all three pathways to give $Fe(CO)_3[C_6(CF_3)_6]$, $Fe(CO)_3[C_4(CF_3)_4CO]$ and $Fe_2(CO)_6[C_4(CF_3)_4S]$ but, as with $CpCo(CO)(SC_6F_5)_2$ and $Fe(CO)_5$,[180] only a cyclopentadienone derivative is formed. Since pathways (1) and (2) are both observed in the reaction of $CpRh(CO)_2$[198] and ruthenium carbonyl derivatives[186] with $CF_3C{\equiv}CCF_3$, it appears that carbon monoxide coordinated to first row transition metals is more reactive towards cyclising hexafluorobut-2-yne, than when coordinated to second, and possibly third row metals.

When ligand synthesis occurs during the reactions of acetylenes with transition metal complexes the type of ligand formed depends, to a large extent, on the magnitude of overlap between the metal and acetylene orbitals.[129] This overlap will obviously be sensitive to other types of ligand coordinated to the metal, to substituents on the acetylene and, perhaps most significantly, to changes in the effective nuclear charge on descending a triad from a first to a third row metal. These factors can explain on a general basis the observations discussed above, in particular the predominance of a certain type of reaction when different pathways are potentially available.

It has been observed previously[190,195,256] that second row metals have a greater tendency to promote cyclotrimerisation of acetylenes than first row metals, and it has been suggested[256] that the low lying unoccupied orbitals on the larger second row metal may be closer in energy to the filled orbitals, thereby facilitating coordination of acetylene molecules. It can therefore be concluded that the reactions of fluoroacetylenes with mercapto derivatives of second and possibly third row transition metals may be even more interesting and complex than those of the first row metals described in this chapter, since more than one reaction pathway may be energetically favourable with the heavier metals.

CHAPTER III

REACTIONS OF HEXAFLUOROBUT-2-YNE WITH SOME CYCLOPENTADIENYL NICKEL COMPLEXES

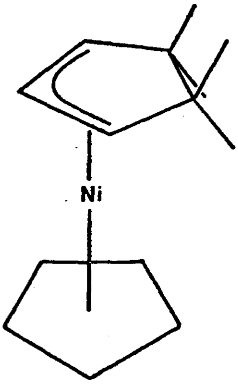
INTRODUCTION

The discovery of ferrocene in 1951,[257] and subsequent elucidation of its structure, led to the synthesis of many other bis-cyclopentadienyl complexes, among these being nickelocene, Cp_2Ni. Ferrocene, which has the favoured eighteen electron configuration, is fairly inert to ring substitution, although a vast organic chemistry of the aromatic rings is now known.[258] Cobaltocene, Cp_2Co, having a nineteen electron configuration, in many respects behaves like a delocalised radical and, if the analogy is carried one step further, nickelocene, with two unpaired electrons, can be considered to have a free double bond.[201]

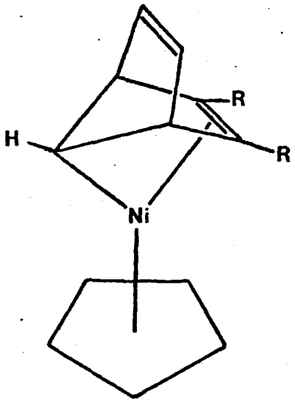
The structure of gaseous nickelocene, according to electron diffraction,[259] is similar to the familiar ferrocene 'sandwich' but with weaker M-C(ring) bonding and slight evidence was obtained for differences in M-C distances. Contemporary[260] theories of the bonding in Cp_2Fe and Cp_2Ni suggests that in the former, all eighteen electrons in the iron atom outer shell are distributed among bonding and non-bonding orbitals. In nickelocene however, the additional pair of electrons most likely go into anti-bonding orbitals (the identity of which are uncertain), thus accounting nicely for the observed weaker bonding in the molecule.

The effect of this weak metal-ring bonding is to make nickelocene very reactive towards nucleophiles, ring substitution occurring readily to give stable complexes,[258,261] e.g. $CpNi(PR_3)Cl$, $Ni(PR_3)_4$ in which the metal has attained the favoured eighteen electron configuration. This can also be achieved by 1,2 or 1,4 addition to one of the Cp rings. 1,2 Addition of hydrogen[262] or fluoroolefins[263] gives complexes containing a cyclopentenyl ring bonded to the metal by a

π- allyl three point attachment (i). Electrophilic acetylenes such as dimethylacetylenedicarboxylate in contrast give 1,4 addition products with the norbornadiene type of structure[264] (ii). Due



(i)



(ii)

to significant differences in the chemical shifts of protons on the fused rings of (i) and (ii) it is possible, by n.m.r. methods, to distinguish clearly between 1,2 and 1,4 addition products.[263]

Certain addition reactions of nickelocene could proceed <u>via</u> preliminary coordination of the attacking agent to the nickel atom followed by a $\pi-\sigma$ rearrangement of a cyclopentadienyl ring.[258] An excellent confirmation of this can be obtained from the structure of the norbornadiene complex (ii). Coordination of the acetylene gives transition state X, Fig. 3.1. which undergoes an internal Diels-Alder reaction without rupture of any of the bonds holding the reacting groups to the metal. This adequately explains why nickel becomes coordinated at the double-bond located between the carbon atoms carrying the electronegative substituents.

Many reactions of nickelocene leading to ring substitution have also been mechanistically interpreted[258] in terms of initial coordination of the attacking substrate, again leading to a $\pi-\sigma$ transformation. The isolation of a stable nickel compound $CpNi(\sigma\text{-}C_5H_5)[(CH_3)_2C{:}\overline{C(CH_3)_2COO}]$, containing both π and σ-bonded cyclopentadienyl rings, lends support to

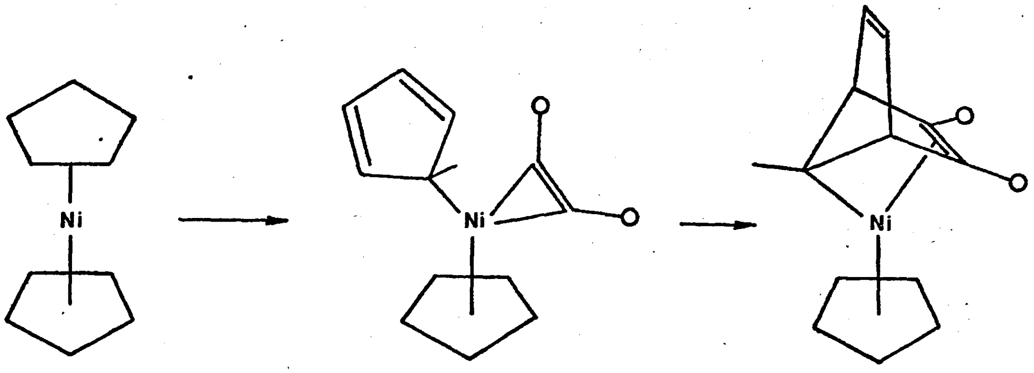


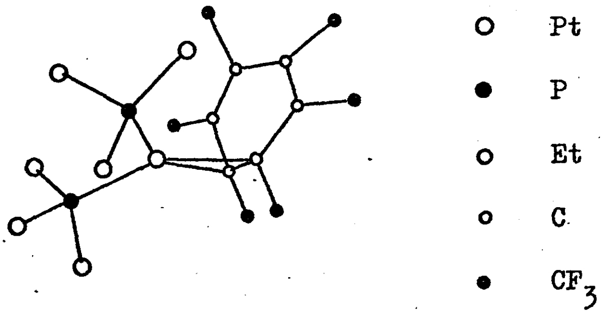
Fig. 3.1.

this theory.[265] Recent work by Werner[266] suggests that the coordination of the incoming nucleophile, in some cases, may be preceded by formation of a charge-transfer complex. The structure of a similar complex, formed by the reaction of ferrocene and tetracyanoethylene, has been solved by X-ray methods.[267] This illustrates that nickelocene is also susceptible to initial attack at the aromatic ring, thus accounting for the higher reaction temperature required for 1,2, as opposed to 1,4 addition.

Very few reactions between hexafluorobut-2-yne and complexes of nickel have so far been reported. $CF_3C{\equiv}CCF_3$ reacts with either $[CpNi(CO)]_2$[180] or Cp_2Ni[201] at room temperature, to give the acetylene bridged species $(CpNi)_2CF_3C_2CF_3$, a second product in the nickelocene reaction, $CpNi[C_5H_5C_2(CF_3)_2]$, being formed by 1,4 addition of the acetylene to one of the cyclopentadienyl rings, (c.f. Cp_2Ni + $COOMeC{\equiv}CCOOMe$).[264] Tetrafluorobenzyne, C_6F_4, also adds to one of the rings in nickelocene to give a similar 1,4 adduct, but in addition gives the 1,2 adduct[161] related to $CpNi[C_5H_5C_2F_4]$ mentioned previously.

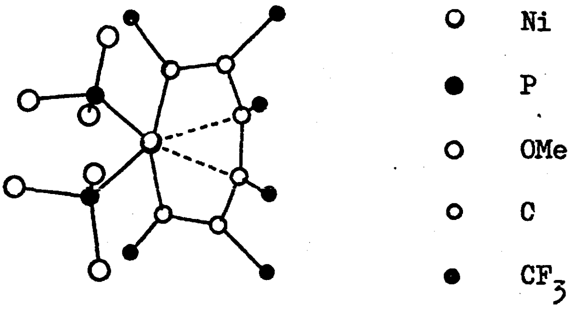
Hexafluorobut-2-yne displaces 1,5 cyclooctadiene, (Cod), from $(Cod)_2Ni$ to give $(Cod)NiC_6(CF_3)_6$ and $(Cod)_2Ni_2C_6(CF_3)_6$. Cod is displaced by phosphines and arsines, (L), to give complexes

$L_2NiC_6(CF_3)_6$ and $L_4Ni_2C_6(CF_3)_6$ respectively.[250] These derivatives are considered to contain a hexakis(trifluoromethyl)benzene ring which undergoes rapid fluxional motion, according to n.m.r. data. Later X-ray studies of a related platinum complex, $(PEt_3)_2PtC_6(CF_3)_6$, revealed the following structure containing a dihapto $C_6(CF_3)_6$ ligand,[251]



and a similar structure is possible for the monomeric nickel derivatives. As with the latter, the platinum complex exhibits fluxional behaviour, but a fixed conformation was detected at -90°C.

The reaction of $L_2NiC_6(CF_3)_6$, $L = P(OMe)_3$, $AsMe_2Ph$, and hexafluorobut-2-yne gave an isomeric complex of identical formula, but different physical and spectroscopic properties, and the following crystal structure has been solved.[251]



The reactions of a range of transition metal trifluoromethylthio and pentafluorophenylthio derivatives with hexafluorobut-2-yne and 3,3,3 trifluoropropyne have already been described and the reaction of $[CpNiSCF_3]_2$ and $CF_3C{\equiv}CCF_3$, which was subsequently investigated, gave a variety of interesting complexes. This led to further studies of reactions involving this acetylene and other cyclopentadienyl-nickel derivatives, the results of which are now described.

SUMMARY OF REACTIONS

(1) $$\begin{aligned}\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{[CpNiSCF_3]_2} \xrightarrow{30^\circ\mathrm{C}} {} & \mathrm{(CpNi)_2CF_3C_2CF_3} + \mathrm{(CCF_3)_6} \\ & + \mathrm{CpNi[C_4(CF_3)_4H]} + \mathrm{Cp_2Ni_3C_6(CF_3)_6} \\ & + \mathrm{(CpNi)_2C_6(CF_3)_6} + \mathrm{CpNi[(C_5H_5)C_6(CF_3)_6]}\end{aligned}$$

(2) $$\begin{aligned}\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{Cp_2Ni} \xrightarrow{85^\circ\mathrm{C}} {} & \mathrm{(CpNi)_2CF_3C_2CF_3} + \mathrm{(CCF_3)_6} + \\ & \mathrm{CpNi[(C_5H_5)C_2(CF_3)_2]} + \mathrm{CpNi[(C_5H_5)C_4(CF_3)_4]} \\ & + \mathrm{[C_5H_5NiC_2(CF_3)_2]_4}\end{aligned}$$

(3) $$\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CpNi[(C_5H_5)C_2(CF_3)_2]} \xrightarrow{85^\circ\mathrm{C}} \mathrm{CpNi[(C_5H_5)C_4(CF_3)_4]}$$

(4) $$\mathrm{CF_3CF{=}CF_2} + \mathrm{CpNi[(C_5H_5)C_2(CF_3)_2]} \xrightarrow{85^\circ\mathrm{C}} \mathrm{CpNi[(C_5H_5)C_4(CF_3)_4]}$$

(5) $$\mathrm{CF_2{=}CFCl} + \mathrm{CpNi[(C_5H_5)C_2(CF_3)_2]} \xrightarrow[h\nu\ 20^\circ\mathrm{C}]{85^\circ\mathrm{C}} \text{no reaction}$$

(6) $$\begin{aligned}\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{CpNi[(C_5H_5)C_2F_3Cl]} \xrightarrow{55^\circ\mathrm{C}} {} & \mathrm{CpNi_2[C_4(CF_3)_4][(C_5H_5)C_2F_3Cl]} \\ & + \mathrm{(CpNi)_2CF_3C_2CF_3}\end{aligned}$$

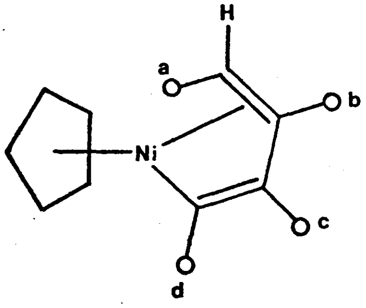
(7) $$\begin{aligned}\mathrm{CF_3C{\equiv}CCF_3} + \mathrm{(CpNi)_2CF_3C_2CF_3} \xrightarrow{90^\circ\mathrm{C}} {} & \mathrm{Cp_2Ni_3C_6(CF_3)_6} + \mathrm{(CCF_3)_6} + \\ & \mathrm{CpNi[(C_5H_5)C_4(CF_3)_4]} + \mathrm{[C_5H_5NiC_2(CF_3)_2]_4}\end{aligned}$$

RESULTS AND DISCUSSION

Reaction of $CF_3C{\equiv}CCF_3$ and $[CpNiSCF_3]_2$

The reaction of $CF_3C{\equiv}CCF_3$ and $[CpNiSCF_3]_2$, in pentane, at temperatures between 20°C and 50°C, gave a complex mixture of products which were separated by chromatography over florisil, eluting with pentane. The main products, $(CpNi)_2CF_3C_2CF_3$[180] and hexakis(trifluoromethyl) benzene $C_6(CF_3)_6$,[268] have been synthesised previously by other workers. The reaction gave four other products in lower yield, which have been identified as $CpNi[C_4(CF_3)_4H]$, I, $Cp_2Ni_3C_6(CF_3)_6$, II, $(CpNi)_2C_6(CF_3)_6$, III, and $CpNi[(C_5H_5)C_6(CF_3)_6]$, IV.

$CpNi[C_4(CF_3)_4H]$ is a volatile, brown crystalline solid, air stable in the solid state, and for a limited period of time, in solution. Of the three structures considered, I(1) is most consistent with spectroscopic data although anomalies do exist, as will be revealed.



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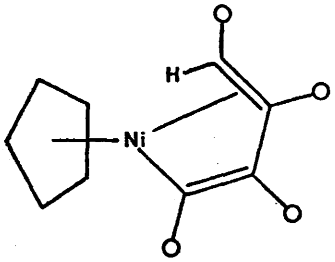

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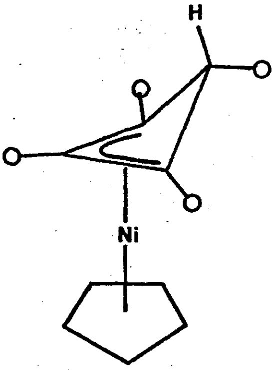

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The ^{19}F spectrum, Fig. 3.2., shows four multiplets of equal intensity, indicating four CF_3 groups in different environments, thus eliminating structure (3). The multiplets are assigned as follows. The broad doublet a', $J_{F-H} = 6.7$ Hz, is due to the terminal CF_3 group, (a), gem to the unique proton. The broadening probably arises from coupling with the trans CF_3 group (b), but is not large enough to be resolved.

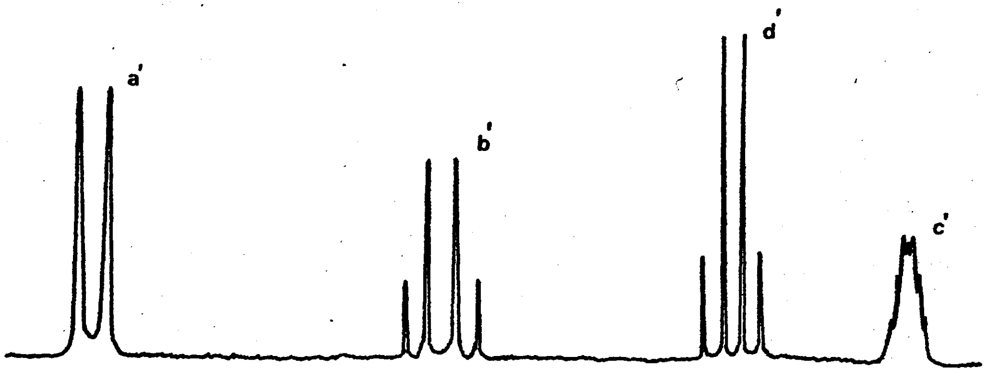


Fig. 3.2.

Quartet b', J_{FF} = 10.6 Hz, is also broadened slightly as a result of coupling with a and the cis proton. The complex multiplet c' is undoubtedly due to c, while the sharp quartet d', J_{FF} = 6.7 Hz, can be assigned to d. c' can be analysed as a quartet of quartets using the coupling constants of b' and d'.

The alternative structure (2), with all CF_3 substituents mutually cis, can be eliminated on the basis of the ^{19}F n.m.r. spectrum since three complex multiplets and only one quartet would be expected as found with $CpRu(PPh_3)[C_8F_{12}H]$,[163] which has been shown by n.m.r. and X-ray studies to have the all cis structure analogous to structure (2).

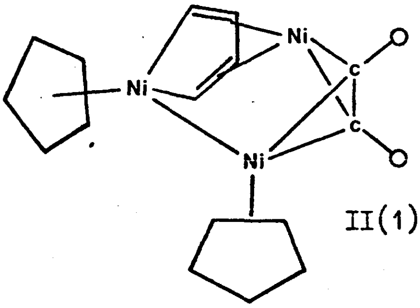
The proton n.m.r. spectrum of I contains two resonances of integrated intensities 5:1; a sharp singlet attributed to the π-cyclopentadienyl group and a quartet centred at 5.6τ due to a single proton coupled to the gem CF_3 group (a), J_{F-H} = 6.75 Hz. The cis CF_3(b)-H coupling was not resolved although the quartet peaks were broadened slightly. The chemical shift of the unique proton is rather low when compared with that in $CpRu(PPh_3)[C_4(CF_3)_4H]$,[163] 7.98τ, and is, in fact, closer to that in $CpRu(PPh_3)_2[C(CF_3)=C(CF_3)H]$, 5.22τ, suggesting that, as in the latter, the hydrogen atom is attached to an uncoordinated C=C bond. Since both ruthenium complexes have the *cis* olefinic structure the validity of such a comparison is not certain and in the *trans* olefinic isomer of $Cp_2MoH(C(CF_3)=C(CF_3)H]$[164] the chemical shift of the analogous proton is 3.3τ. If both the olefinic bonds in I were not coordinated the most favoured structure would probably be the *trans* butadiene form on steric and electronic grounds.

However, this would result in a significant reduction in the coupling constant $J_{CF_3(b)-CF_3(c)}$ since *trans* CF_3 groups have coupling constants near 2 Hz,[189] but *cis* $J_{CF_3-CF_3}$ values are usually greater than 11 Hz.[163] Thus the ^{19}F n.m.r. spectrum is more compatible with structure (1), as is the i.r. spectrum, which gives a single C=C stretching mode at 1661 cm^{-1}, comparable to that of $CpRu(PPh_3)[C_4(CF_3)_4H]$ which is observed at 1641 cm^{-1}. The abnormally low chemical shift of the proton in I must therefore be due to its exposed position in the molecule.

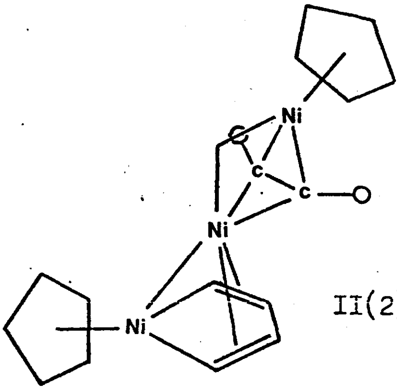
The mass spectrum of I, besides giving expected features such as a molecular ion and nickel containing fragments $CpNiF^+$ and $CpNi^+$, also gives interesting organic ions. A peak due to $[C_4(CF_3)_4H]^+$ is observed which loses F, HF and CF_3 groups in a predictable fragmentation process. However, less predictable and rather interesting is the presence of ions which are assigned to $[(C_5H_5)C_4(CF_3)_4H]^+$ and fragments, which possibly result from expulsion of nickel from the molecular ion and subsequent combination of the two ligands.

The other complex obtained in moderate yield, II, is an air stable, black solid which analyses as $Cp_2Ni_3C_6(CF_3)_6$. The proton n.m.r., which gives two sharp singlets near 4τ, indicates the presence of two chemically distinguishable π-cyclopentadienyl ligands, while the ^{19}F

n.m.r. shows three signals of equal area, one of which is somewhat sharper than the other two. The two highly coupled peaks are similar to those of ring systems $[C_4(CF_3)_4X]$, X = CO,[180] Rh,[269] SR.[222] The presence of a hexakistrifluoromethylbenzene ring can be ruled out on this evidence since one of the peaks would be very broad as in $CpCo(CF_3C)_6$, a conclusion supported by the mass spectrum, which does not give a characteristic ion at m/e 486 and subsequent fragments. Instead, the molecular ion at m/e 790 = $[(Cp)_2Ni_3C_6(CF_3)_6]^+$, undergoes loss of C_4F_6 as an important primary fragmentation process giving $[(Cp)_2Ni_3C_4(CF_3)_4]^+$. Other significant ions can be assigned to $[(CpNi)_2C_4(CF_3)_4]^+$, $[CpNiC_8F_{12}]^+$ and $[CpNiC_8F_{11}]^+$, the last two being particularly prominent, so it would appear, from this evidence, that complex II contains a nickelatetrakis(trifluoromethyl)cyclopentadiene ring. This further suggests that a coordinated hexafluorobut-2-yne ligand is also present, which accounts for the C≡C stretching mode at 1591 cm^{-1} in the i.r. spectrum. This is rather low for a monodentate acetylene ligand, e.g. $(Ph_3P)_2NiCF_3C_2CF_3$, νC≡C = 1790 cm^{-1},[137] but is in the region characteristic of bidentate acetylenes as found in $(CpNi)_2CF_3C_2CF_3$, the νC≡C frequency of which appears at 1597 cm^{-1}, (i.r. spectrum of authentic sample).



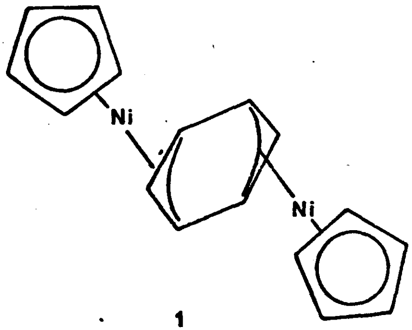
II(1)



II(2)

On this evidence two structures are possible, II(1) and II(2), but the following facts favour the latter. In II(2) each nickel atom has the favoured eighteen electron configuration while in II(1), one of the three has a sixteen electron configuration. The acetylene bridge in II(2), unlike that in II(1), is complemented by a metal-metal bond and no complex containing a bidentate bridging acetylene has yet been reported, which does not also contain a metal-metal bond. Finally, II(2) is structurally related to $(CpNi)_2CF_3C_2CF_3$,(also formed in the reaction of $[CpNiSCF_3]_2$ and hexafluoro-but-2-yne), but with a cyclopentadienyl ligand replaced by the metalocyclopentadiene ring $CpNiC_4(CF_3)_4$.

Two other complexes isolated in trace yields from this reaction are considered, on the basis of i.r. n.m.r. and mass spectroscopy, to have the stoichiometries $(CpNi)_2C_6(CF_3)_6$, III, and $CpNi[C_5H_5C_6(CF_3)_6]$, IV. The former is a dark red, crystalline solid, the mass spectrum of which gives a peak of highest m/e 732 with a double nickel isotope pattern suggesting,(if this is a molecular ion), the above formula. This ion loses a fluorine and then, interestingly, CpNi to give $[CpNiC_{12}F_{17}]^+$, the only other nickel containing ions being $CpNi^+$ and $CpNiF^+$. The rest of the mass spectrum consists of organic fragments with an ion at m/e 486 = $[C_6(CF_3)_6]^+$ which undergoes an almost identical fragmentation process to that of hexakis(trifluoromethyl)-benzene, therefore, indicating the presence of a distinct $C_6(CF_3)_6$ group. On this evidence three structures are possible.



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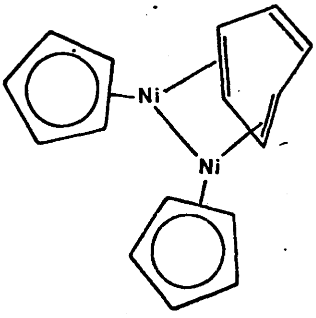

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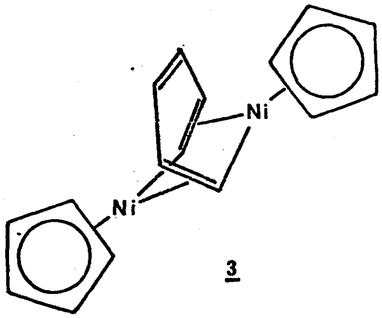


3

A fourth structure similar to III(1), but with both cyclopentadienyl nickel groups on the same side of the ring,would probably be unstable on steric grounds.

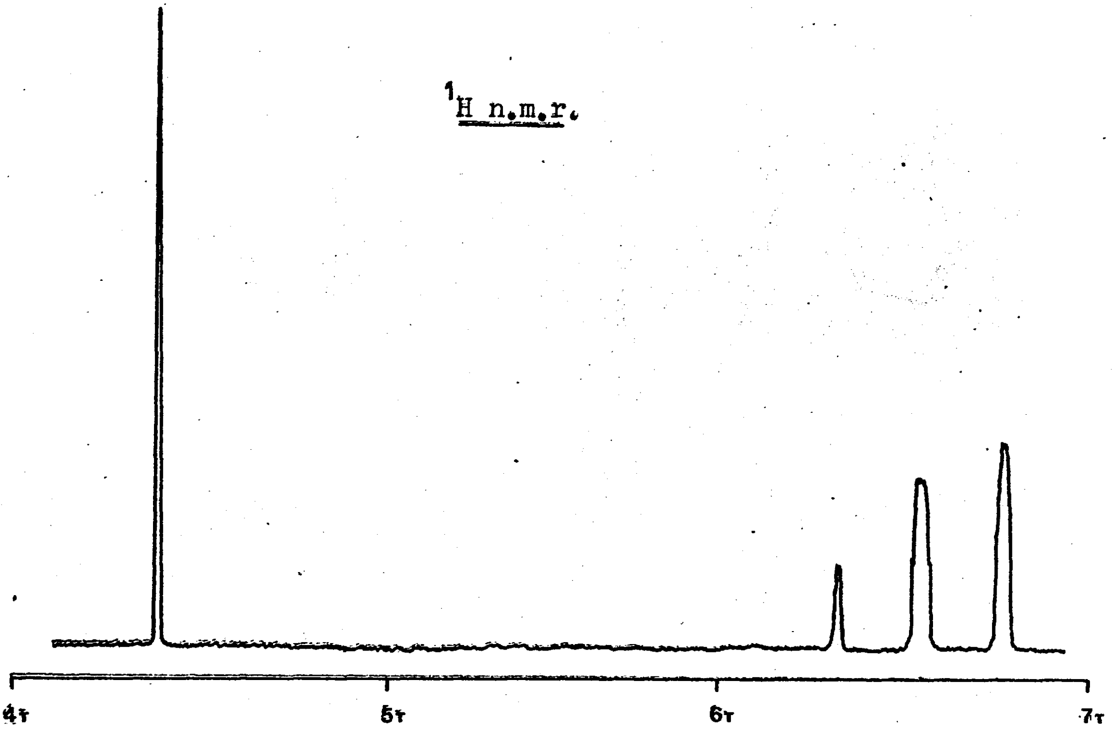
Unfortunately the small quantities of complex available prevented a ^{19}F n.m.r. spectrum from being obtained, but this would not distinguish between (2) and (3) in any case. Similarly, the proton n.m.r. spectrum is of little value, but the single sharp resonance at 4.55τ does confirm the presence of π bonded cyclopentadienyl groups. The i.r. spectrum in the C-F region is very simple in agreement with the reasonably symmetrical rings in (1) and (2). This would appear to rule out (3) which is similar to $Co_2(CO)_4C_6(CF_3)_6$,[253] the i.r. spectrum of which gives a greater number of C-F stretching modes near 1200 cm^{-1}. Structure (3) is, in any case, considered unlikely, since in all other complexes involving flyover structures, e.g. $Co_2(CO)_4(RC)_6$,[129] $Fe_2(CO)_7(RC)_4$,[129] and $(CpM)_2C_6(CF_3)_6$, M = Co,[222] Rh,[198] the bridge system is stabilised by a metal-metal bond. The absence of a C=C stretching mode in the i.r. spectrum would therefore eliminate (2), but this is at best negative evidence. (2) is structurally related to $(CpPt)_2C_{10}H_{10}$[270] which has two metal-metal bonded π-cyclopentadienyl platinum units, π-bonded to a butadiene residue. This structure, and that of $CpMC_6(CF_3)_6$, M = Rh,[197] Co,[222] would therefore imply that the arene ring in (2) is non planar, the free double bond lying above the plane of the other four carbon atoms and away from the metal atoms. Structure (1) also involves localisation of the arene ring bonds but in this case to give a bis π-allyl structure. Structural analogues of this, $(L_2Ni)_2C_6(CF_3)_6$, L = $P(OMe)_3$, $PMeC(CH_2O)_3$, have been prepared by Stone.[250]

The mass spectrum of the other red complex isolated in trace amounts gives an ion of highest m/e at 672 = $[CpNiC_5H_5C_6(CF_3)_6]^+$ with a single nickel isotope pattern. A ligand $[C_5H_5C_6(CF_3)_6]$ is suggested by the presence of an organic ion at m/e 551 which undergoes loss of F, HF and CF_3. The absence of ions due to the arene ring $C_6(CF_3)_6$, indicates that the C_5H_5 moiety is not bonded in a simple manner to such a ring. A large variety of structures can be envisaged for this complex and it is impossible on spectroscopic evidence to be unequivocal, but the following n.m.r. evidence, although not completely satisfactory, allows a tentative prediction of structure. The ^1H n.m.r. spectrum (Fig. 3.3) gives a sharp singlet at 4.36τ due to a π-bonded cyclopentadienyl group and three multiplets at 6.54τ, 6.72τ and 7.02τ,(ratio 1:2:2). This is the pattern expected for a cyclopentenyl ligand as found in $CpNi[C_5H_5C_2F_4]$[263] but the chemical shifts of the two peaks associated with the π-allyl portion of the ring are far too high to be considered olefinic. An alternative explanation is that both 1,2 and 1,4 addition to the C_5H_5 ring has occurred to give a norbornene complex similar to $CpNi[(C_5H_5)C_4(CF_3)_4]$ described later, although the reason for the change in the order of the chemical shifts of the ring protons is not understood.

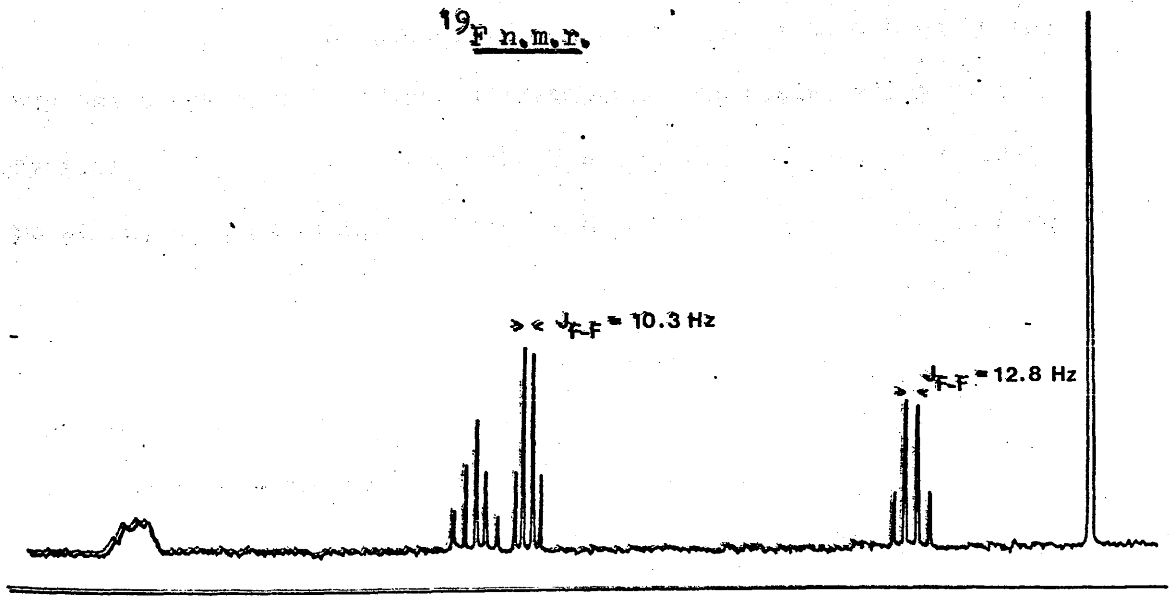
The ^{19}F n.m.r. was only obtained with difficulty due to the small sample size and is consequently of poor quality. However, as shown in Fig. 3.3., five distinct CF_3 environments are indicated by the spectrum, the singlet corresponding to two CF_3 groups in magnetically equivalent situations. The coupling observed on the other resonances suggests a butadiene ring in an asymmetric environment as found in I and $Co_2(CO)_6C_4(CF_3)_4S$, described in chapter II. The i.r. spectrum in the C-F stretching region is complex and a band at 1711 cm^{-1} indicates the presence of an uncoordinated $CF_3C{=}CCF_3$ group, since it is comparable to the C=C stretching mode in the i.r. spectrum of $CpNi[(C_5H_5)C_4(CF_3)_4]$, observed at 1710 cm^{-1}.

On this evidence structures IV(1) and IV(2) are tentatively proposed

Fig. 3.3. N.m.r. spectra of $CpNi[(C_5H_5)C_6(CF_3)_6]$

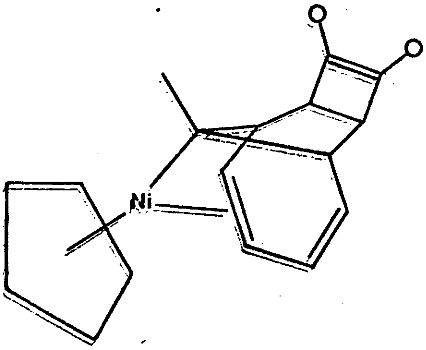


^1H n.m.r.

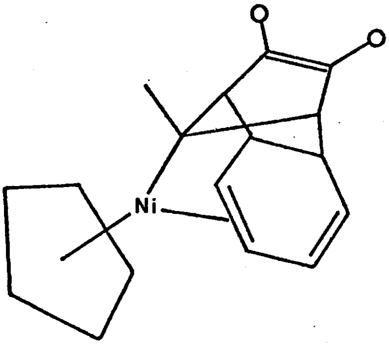


^{19}F n.m.r.

for complex IV. In the former a tetrakis(trifluoromethyl)butadiene



1



2

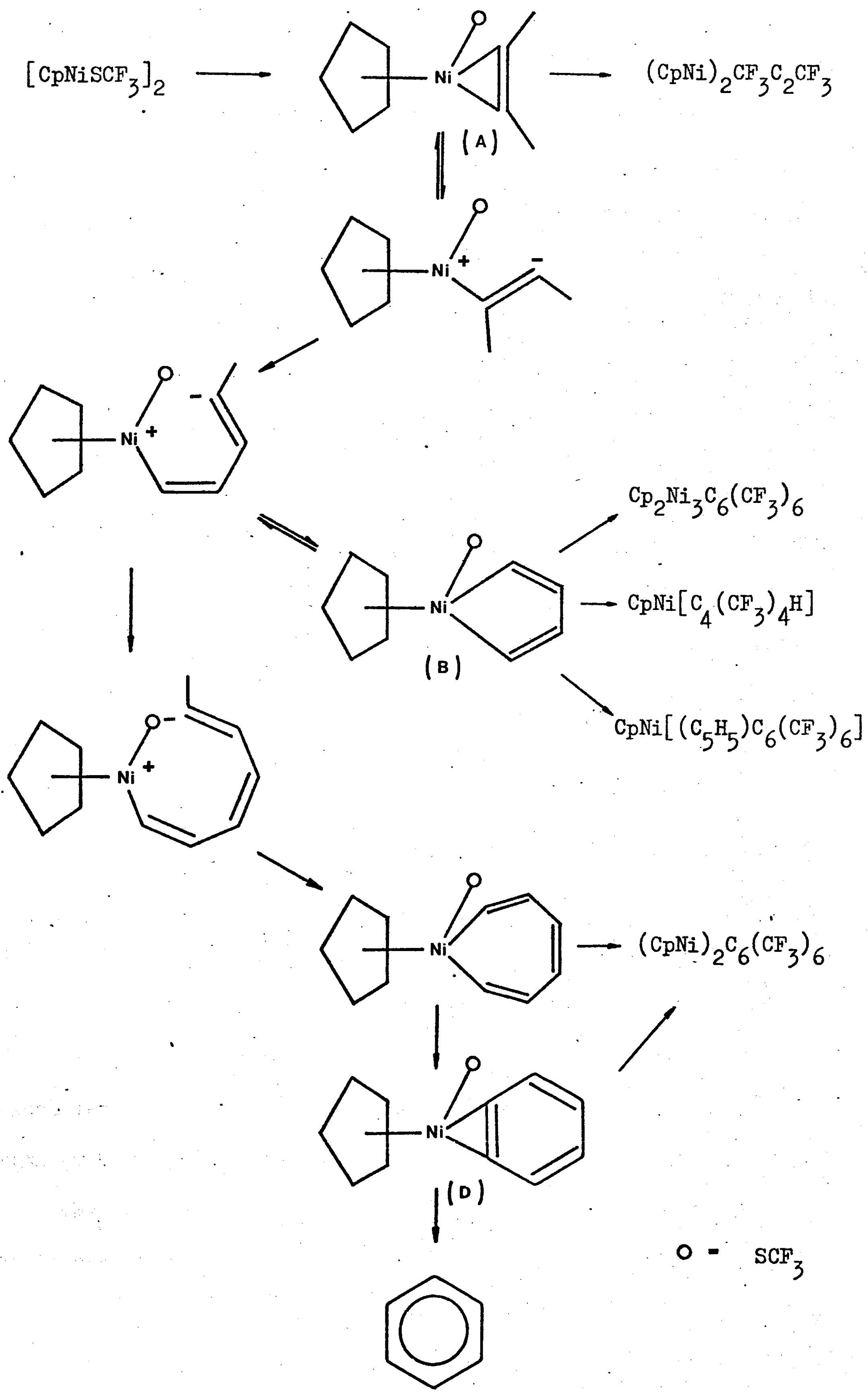
moiety has undergone 1,4 addition to a cyclopentadienyl ring while hexafluorobut-2-yne has added to the remaining olefinic bond to produce a cyclobutene ring. The latter, IV(2), results from 1,4 addition of the alkyne to the ring and 1,2 addition of the butadiene. On the evidence available it is impossible to distinguish between these two structures.

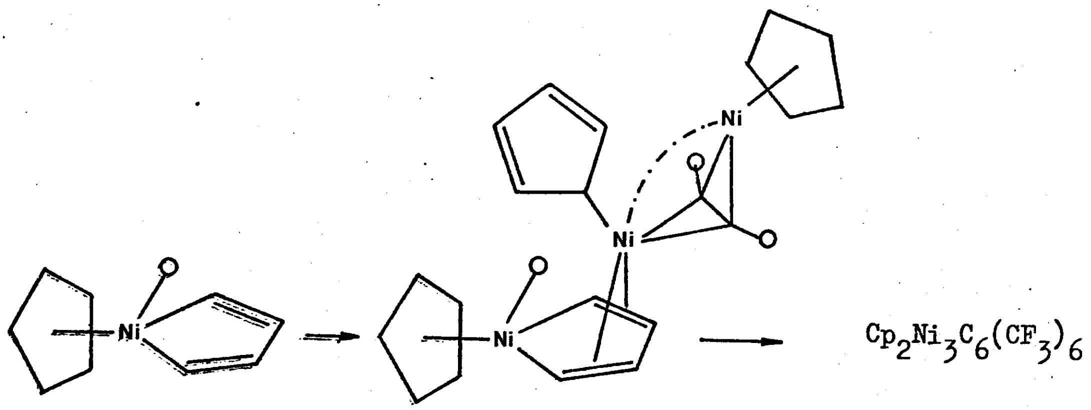
Mechanism

The nature of the products obtained in this reaction would seem to suggest successive build-up of acetylenes into chains which then cyclise. As each acetylene unit adds on, different products are possible, so that higher members in the series are isolated in lower yield. The following mechanism, Fig. 3.4, is tentatively put forward to account for this.

The formation of II from intermediate B and $(CpNi)_2CF_3C_2CF_3$ is suggested by the proposed structure of this complex. Nucleophilic attack of the electron-rich metalocyclopentadiene ring on one of the nickel atoms of $(CpNi)_2CF_3C_2CF_3$ will lead to a π-σ rearrangement, and M-C and M-S bond scission will give the product.

Fig. 3.4.


[CpNiSCF3]2
Ni
(CpNi)2CF3C2CF3
(A)
Ni+
−
Ni+
−
Cp2Ni3C6(CF3)6
Ni
CpNi[C4(CF3)4H]
(B)
CpNi[(C5H5)C6(CF3)6]
O−
Ni+
Ni
(CpNi)2C6(CF3)6
Ni
(D)
○ - SCF3



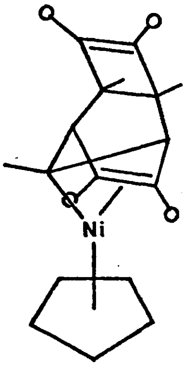
The formation of I may also occur <u>via</u> B and requires hydrogen abstraction, probably from the reaction solvent, hexane. Several examples of this process have been described, of particular relevance being the isolation of <u>trans</u> $CpFe(CO)_2[C(CF_3):C(CF_3)H]$ in low yield from the reaction of $CpFe(CO)_2SnMe_3$ and hexafluorobut-2-yne in hexane.[175] This complex was considered to result from radical formation and a similar mechanism could explain the exclusive formation of the <u>trans</u> isomer of $CpNi[C_4(CF_3)_4H]$. Thus, ring opening in B gives the sterically favoured <u>trans</u> structure, which can abstract a hydrogen atom to give the product. An alternative mechanism, involving formation of an intermediate hydride complex, is considered unlikely, since metal participation would give the <u>cis</u> isomer I(2), as found with $CpRu(PPh_3)[C_4(CF_3)_4H]$.[163]

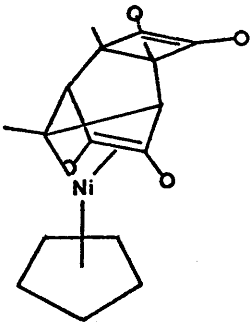
The addition of a third acetylene unit to B to give products containing a six-membered carbon ring, may occur <u>via</u> C, a metalocycloheptatatriene intermediate, which could rearrange to give a dihapto-hexakis(trifluoromethyl)benzene complex D, for reasons discussed in chapter II. On thermal decomposition, hexakis(trifluoromethyl)-benzene is obtained, (cf. $L_2NiC_6(CF_3)_6$),[250] or alternatively, reaction with another cyclopentadienyl nickel complex, possibly $[CpNiSCF_3]_2$, will give $(CpNi)_2C_6(CF_3)_6$. The relative yields of these two products suggest that formation of the benzene is more favourable, possibly due to the delocalisation energy acquired. Moreover, collision of C or D with $[CpNiSCF_3]_2$ to give $(CpNi)_2C_6(CF_3)_6$, is probably a much slower process than simple unimolecular decomposition to the benzene.

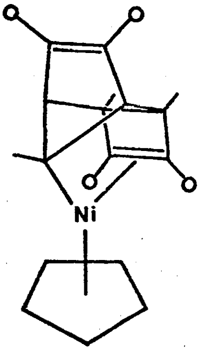
The proposed structure of IV suggests it is produced in some way from intermediate B but it is not possible to postulate any mechanism with certainty.

Reaction of $CF_3C{\equiv}CCF_3$ and Cp_2Ni

This reaction has been reported to give $(CpNi)_2CF_3C_2CF_3$ and 1,4 addition product $CpNi[(C_5H_5)C_2(CF_3)_2]$ at 20°C.[201] However, at 80°C the following products were obtained, $(CpNi)_2CF_3C_2CF_3$, (25% yield), $CpNi[(C_5H_5)C_2(CF_3)_2]$, (trace), $C_6(CF_3)_6$, (trace), $[C_5H_5NiC_2(CF_3)_2]_4$, (trace), and $CpNi[(C_5H_5)C_4(CF_3)_4]$, V (37% yield). $[C_5H_5NiC_2(CF_3)_2]_4$ probably results from the reaction of hexafluorobut-2-yne and $(CpNi)_2CF_3C_2CF_3$ which is described later. The other new compound, from spectroscopic evidence, is a 1,4 addition product for which any one of the three structures shown, is possible.







o = CF_3

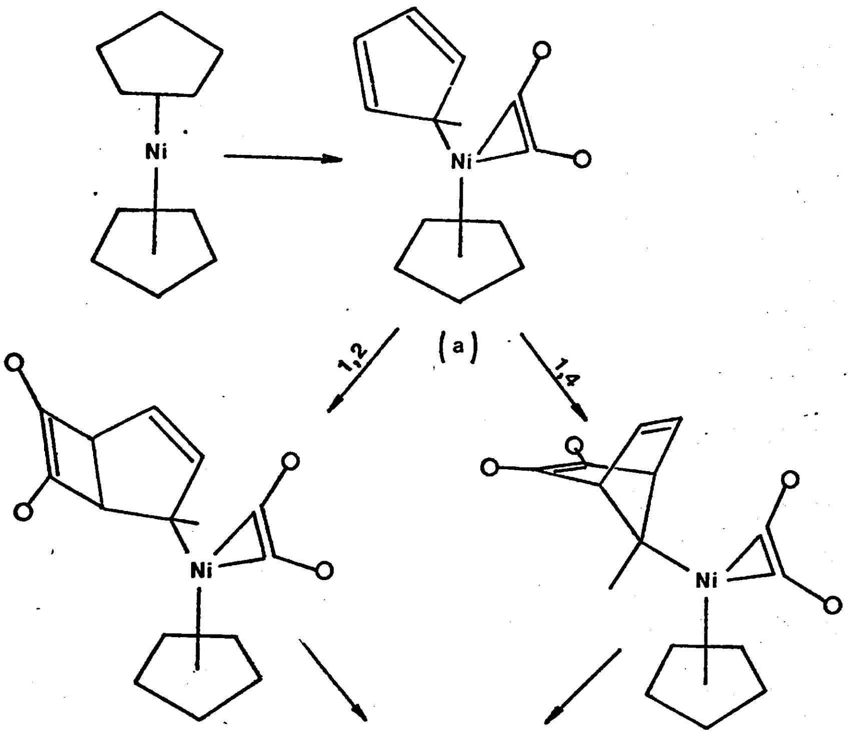
The proton n.m.r. of V is comparable to that of the other 1,4 addition complex $CpNi[(C_5H_5)C_2(CF_3)_2]$, formed in reasonable yields in the low temperature reaction, but only in trace yield at 80°C. However, the resonance at 3.2τ in the spectrum of the latter, due to the olefinic protons has shifted upfield to 7.05τ in the spectrum of V and, in accord with the proposed structures, this peak can be assigned to two equivalent protons on the sp^3 hybridised carbons of the cyclobutene ring. The mass spectrum of V gives a molecular ion and ions due to the ligand $[(C_5H_5)C_4(CF_3)_4]$ and fragments.

The structures proposed for V suggest that 1,2 addition of the alkyne to the free olefinic bond in $CpNi[(C_5H_5)C_2(CF_3)_2]$ has occurred, and the resulting fluoroolefin double-bond would account for the C=C stretching mode observed in the i.r. spectrum at 1710 cm^{-1}. However, although $CpNi[(C_5H_5)C_2(CF_3)_2]$ and hexafluorobut-2-yne were subsequently found to give V at 80-85°C, the reaction is very slow relative to that of nickelocene, as can be seen from the following yields.

	yield	Reaction time
$CF_3C{\equiv}CCF_3 + Cp_2Ni \xrightarrow{80^o} CpNi[(C_5H_5)C_4(CF_3)_4]$	0.5g.	10 hr
$CF_3C{\equiv}CCF_3 + CpNi[(C_5H_5)C_2(CF_3)_2] \xrightarrow{80^o} CpNi[(C_5H_5)C_4(CF_3)_4]$	0.02g.	70 hr

These results rule out the low temperature product as an intermediate in the high temperature reaction and the formation of V at 80°C must proceed <u>via</u> a more efficient pathway, possibly that illustrated in Fig. 3.5.

With $CF_3C{\equiv}CCF_3$ and nickelocene initial coordination of the alkyne to give intermediate (a)[256] is possible in both low and high temperature reactions. Since $(CpNi)_2CF_3C_2CF_3$ is also produced in both reactions, (a) must exist for a reasonable time so that reaction with a second molecule of nickelocene can occur to give the dinuclear product. Thus



$CpNi[(C_5H_5)C_4(CF_3)_4]$

Fig. 3.5.

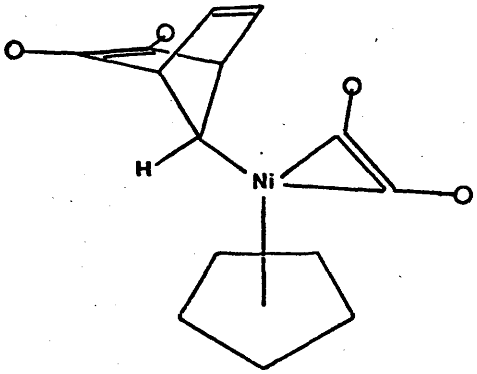
collision of (a) with a molecule of acetylene is highly probable, but at 20°C no reaction occurs. However, at 80°C, direct 1,2 or 1,4 addition to the σ bonded diene ring is possible, and a further intramolecular reaction with the coordinated alkyne gives $CpNi[(C_5H_5)C_4(CF_3)_4]$. Hexafluorobut-2-yne and cyclopentadiene, C_5H_6, have been found to undergo 1,4 cycloaddition[271] favouring such a mechanism in the above reaction, but 1,2 addition cannot be ruled out completely in view of the reported 1,2 and 1,4 addition of tetrafluoroethylene to the latter.[272]

Reactions of CF_2=CFX, X = Cl, CF_3, and $CpNi[(C_5H_5)C_2(CF_3)_2]$

In an attempt to add fluoro-olefins to the uncoordinated double bond of $CpNi[(C_5H_5)C_2(CF_3)_2]$, the latter was reacted with chlorotrifluoroethylene and perfluoropropene. No photochemical or thermal reaction was observed with the former, but the latter, in a reproducible reaction, surprisingly yielded CpNi[$(C_5H_5)C_4(CF_3)_4$], V, identical to the product obtained from hexafluorobut-2-yne. The presence of small quantities of the alkyne in the perfluoropropene can be discounted since it was not detected by i.r. spectroscopy, nor did the sample of olefin react with nickelocene to give the expected products. It is thus apparent that a rearrangement reaction of olefin to acetylene has occurred, possibly via coordination of $CF_3CF{=}CF_2$ to the nickel. Many reactions are known in which coordination of a fluorocarbon leads to fluorine transfer, and in some cases, fluoro acetylenes are produced from fluoroolefins.[160,273]

In all cases the product V, obtained by three different methods, has the same melting point and spectroscopic properties, despite the fact that three different structural isomers exist. This suggests possibly, that one isomer is thermodynamically favoured, and also that all three reactions have a common intermediate X.

Fig. 3.6.



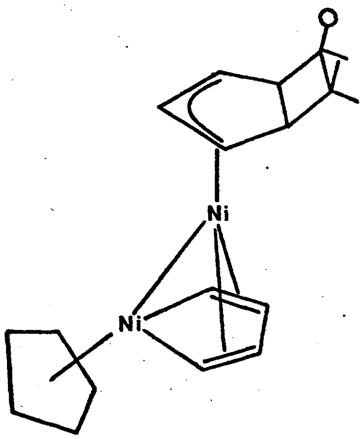
(X)

Intermediate X may be accessible from (i) Cp_2Ni as already discussed, (ii) CpNi[$(C_5H_5)C_2(CF_3)_2$] by coordination of the alkyne leading to cleavage of the nickel-olefin coordinate bond, (iii) CpNi[$(C_5H_5)C_2(CF_3)_2$]

and two molecules of $CF_3CF=CF_2$ by some unknown mechanism which probably involves metal participation. This intermediate effectively explains why the last two reactions are relatively slow since cleavage of metal-fluoroolefin bonds is not an easy process due to the well known ability of fluorocarbon substituents to stabilise metal-carbon σ and π bonds.[145,218]

Reaction of $CF_3C\equiv CCF_3$ and $CpNi[(C_5H_5)C_2F_3Cl]$.

The high temperature reaction of nickelocene and $CF_3C\equiv CCF_3$, as illustrated in Fig. 3.5., could involve 1,2 or 1,4 addition of $CF_3C\equiv CCF_3$ to a C_5H_5 ligand, and in an effort to clarify the situation the 1,2 addition product, $CpNi[(C_5H_5)C_2F_3Cl]$, (obtained from the reaction of nickelocene and chlorotrifluoroethylene),[263] was reacted with hexafluorobut-2-yne at 70°C. In addition to small quantities of $(CpNi)_2CF_3C_2CF_3$, a brown crystalline complex, formulated as $CpNi_2[C_4(CF_3)_4][(C_5H_5)C_2F_3Cl]$, VI, was obtained in 62% yield and the following structure is proposed from spectroscopic evidence.



○ = Cl

CF_3 groups omitted

The mass spectrum gives a molecular ion at m/e 628 which loses C_2F_3Cl in an important primary fragmentation process, the significance of which will be discussed later. Support for a nickelatetrakis-(trifluoromethyl)cyclopentadiene ring is obtained from the presence of strong ions at m/e 447 and m/e 428 assigned to $[CpNiC_8F_{12}]^+$ and $[CpNiC_8F_{11}]^+$. It is recalled that similar ions were also observed in the mass spectrum of $Cp_2Ni_3C_6(CF_3)_6$, II, described earlier. The proton n.m.r. of VI is virtually identical to that of the precursor $CpNi[(C_5H_5)C_2F_3Cl]$, confirming the presence of a π-bonded cyclopentadienyl ligand, and a π-cyclopentenyl group bonded via a three point attachment to a nickel atom. The ^{19}F n.m.r. exhibits two highly coupled peaks in the CF_3 region but the low solubility prevented the resonancesof the C_2F_3Cl substituent being detected clearly. The situation was also complicated by isomerism,(as found in the precursor), which possibly results from different orientations of the chlorine atom.[261] The number of signals observed in the ^{19}F n.m.r. spectrum clearly indicate the presence of more than one isomer, although chromatography of the sample over florisil only gave partial separation of the isomer bands. Finally, no acetylenic or olefinic C-C stretching modes are observed in the i.r. spectrum between 2000 cm^{-1} and 1500 cm^{-1}, which indicates that coordinated acetylenes, or uncoordinated olefinic bonds, are not present, in agreement with the proposed structure. Further supporting evidence is obtained from the crystal-structure of $[C_5H_5NiC_2(CF_3)_2]_4$ described later,and from the structure of $[(CO)_3Fe(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$, obtained from the reaction of $Fe_3(CO)_{12}$ and $(CH_3C)_4NiCl_2$ by Maitlis and co-workers.[274]

An X-ray study of both has revealed a pseudo sandwich structure, as in VI, a metalocyclopentadiene ring functioning as one of the aromatic rings of the sandwich.

Assuming the proposed structure is correct,the formation of VI may occur via the following mechanism,Fig. 3.7.

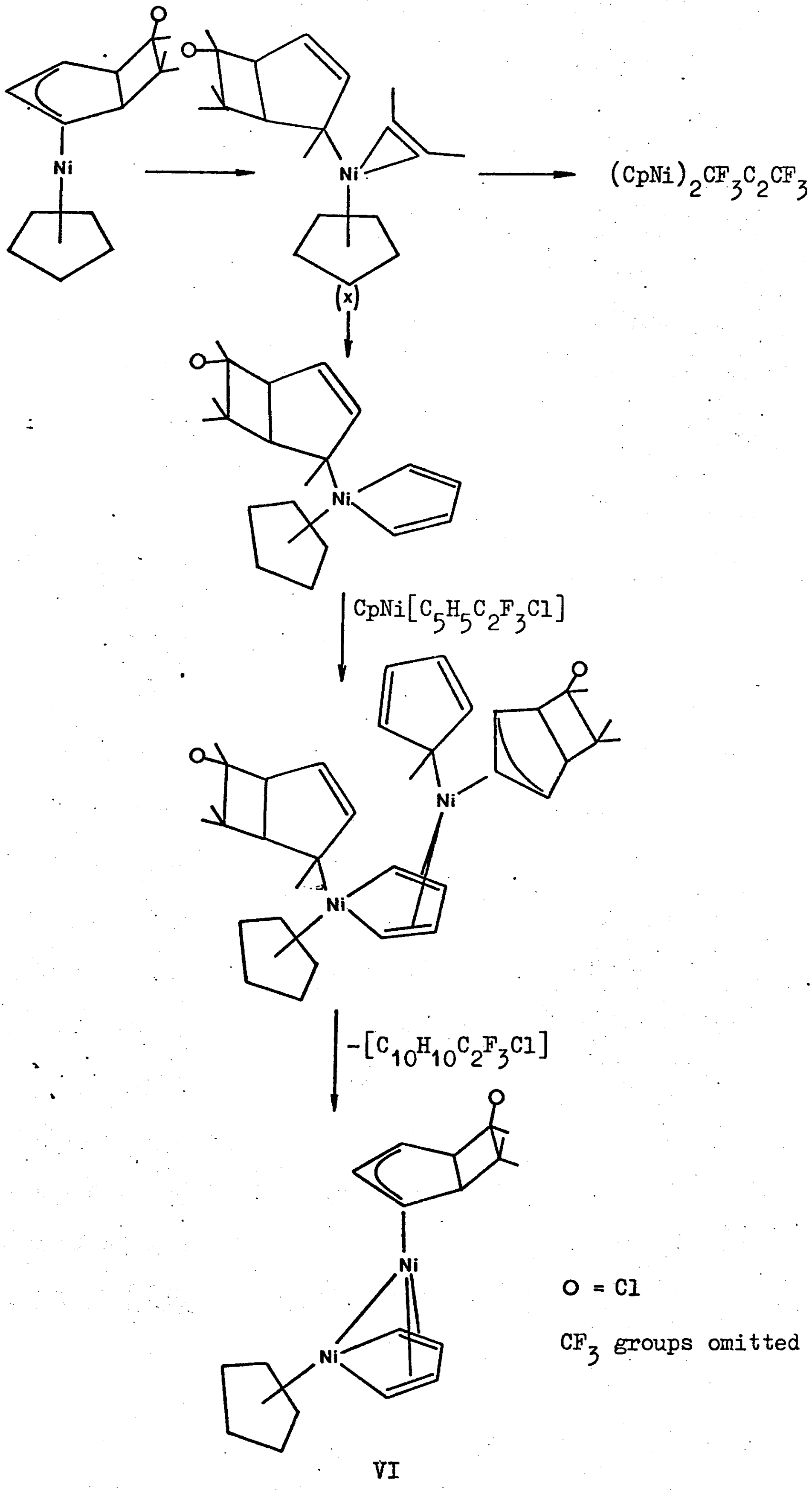

Ni
Ni
$(CpNi)_2CF_3C_2CF_3$
(x)
Ni
$CpNi[C_5H_5C_2F_3Cl]$
Ni
Ni
$-[C_{10}H_{10}C_2F_3Cl]$
Ni
Ni
VI
O = Cl
CF_3 groups omitted

Fig. 3.7.

π-σ Transformations of cyclopentadienyl ligands have already been described and similar π-σ rearrangements of π-allyl groups is also a well known phenomenon,[275] so that the first step in this mechanism is not entirely unprecedented. The intermediate formed, x, besides explaining the small quantity of $(CpNi)_2CF_3C_2CF_3$ isolated in this reaction, does not appear to undergo an intramolecular 1,4 addition, suggesting that formation of $CpNi[(C_5H_5)C_4(CF_3)_4]$ from nickelocene at 80° probably involves direct 1,4 addition of hexafluorobut-2-yne to the σ bonded cyclopentadienyl ligand of (a) Fig. 3.5. to produce intermediate (X), (see Fig. 3.6.).

Reaction of $CF_3C{\equiv}CCF_3$ and $(CpNi)_2CF_3C_2CF_3$

Complexes $Co_2(CO)_6CF_3C_2CF_3$, $[Fe(CO)_3SR]_2$, and $[CpCoSR]_2$, R = CF_3, C_6F_5, besides their structural similarity, all react with hexafluorobut-2-yne to give interesting products formed by cyclisation of the acetylene. The reaction of the structurally related nickel complex $(CpNi)_2CF_3C_2CF_3$ and hexafluorobut-2-yne was therefore investigated and, after 90 hours at 90°C, a complex reaction mixture was obtained, from which was isolated hexakis(trifluoromethyl)benzene, (trace), $CpNi[(C_5H_5)C_4(CF_3)_4]$, (V), (trace), $Cp_2Ni_3C_6(CF_3)_6$, (II), (trace), and a black crystalline solid $[C_5H_5NiC_2(CF_3)_2]_n$, (VII), (72% yield), mentioned previously.

The stoichiometry of $[C_5H_5NiC_2(CF_3)_2]$, suggested by elemental analyses, is verified by the mass spectrum in which a strong peak occurs at m/e 570 = $[C_5H_5NiC_2(CF_3)_2]_2^+$, indicating at least a dimeric structure in the vapour phase. Very weak ions with a triple nickel isotope pattern were observed above m/e 570, but m/e values could not be assigned with certainty, thus precluding identification. The low volatility and solubility of VII suggested a larger value for n in solution and the solid state and this was subsequently confirmed by the proton n.m.r. spectrum. Three sharp singlets near 4τ are observed, indicating three magnetically non equivalent π-cyclopentadienyl groups. A fourth C_5H_5 moiety, resulting from 1,2 addition to a cyclopentadienyl ring, is indicated by the chemical shifts of the three lower intensity resonances of integrated ratio 1:2:2. Thus the value n = 4 indicated, is more compatible with the physical properties of the complex. The ^{19}F n.m.r. appears anomolous in that only three highly coupled resonances are observed, integrated ratio 1:1:2, but this difficulty can be overcome by considering that two multiplets are coincident, accounting for the lack of fine structure on the more intense peak. Since no bands are observed in the i.r. spectrum between 2000 cm^{-1} and 1500 cm^{-1}, the presence of uncoordinated olefinic bonds can be ruled out.

Comparison of the mass spectrum with those of the complexes $Cp_2Ni_3C_6(CF_3)_6$,(II), and $CpNi_2[C_4(CF_3)_4][(C_5H_5)C_2F_3Cl]$,(VI), is particularly informative since in all three, ions corresponding to the dimer $[CpNiC_2(CF_3)_2]_2$ and fragments are present. In II these ions are rather weak, no doubt because transfer of a remote Cp ring to the $CpNi_2C_4(CF_3)_4$ framework is involved. However, in the mass spectrum of VI, loss of C_2F_3Cl from the molecular ion to give $[CpNiC_2(CF_3)_2]^+$ is a highly favourable process, as indicated by the high intensity of this ion. In all three cases strong peaks corresponding to $[CpNiC_4(CF_3)_4]^+$ and fragments are also observed suggesting that, like II and VI, the tetranuclear complex VII also contains a metalocyclopentadiene ring.

In an effort to ascertain the correct molecular structure of $[C_5H_5NiC_2(CF_3)_2]_4$ a single crystal X-ray diffraction study of the complex was carried out by Drs. K. Muir and Lj. Manojlovic-Muir of this department and Dr. Rajna Herak of the Institute 'Boris Kidrich' Belgrade, Yugoslavia. Crystals for X-ray study were prepared by slow recrystallisation of the complex from benzene solution.

X-ray Structure of $[C_5H_5NiC_2(CF_3)_2]_4$

The complex crystallises in the space group P1, Dc = 2.015, $z = 2$. Triclinic, $a = 9.322$, $b = 16.520$, $c = 12.777$ Å, $\alpha = 103.76$, $\beta = 97.83$, $\gamma = 85.89^{\circ}$.

Diffractometer data;(Mo-K_{α} radiation) current, R = 9.0% for 3526 independent reflections. All atoms except hydrogens were located by Patterson and Fourier methods.

The molecular structure of the complex is illustrated in Figs. 3.8. and 3.9. and structural parameters are listed in Table 3.1.

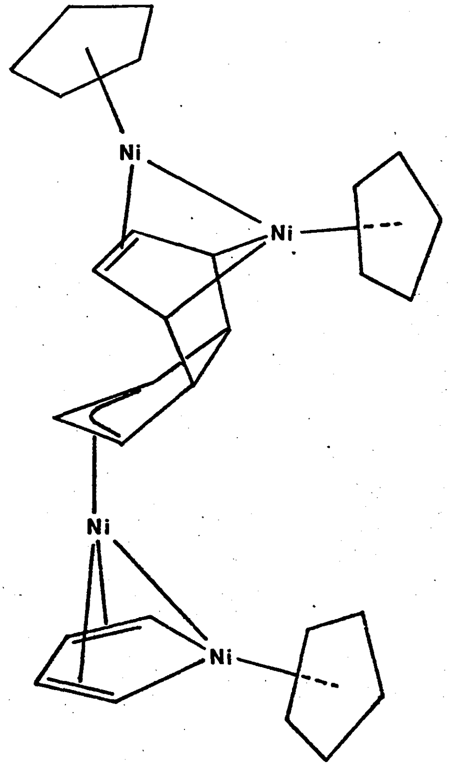


Fig. 3.8.

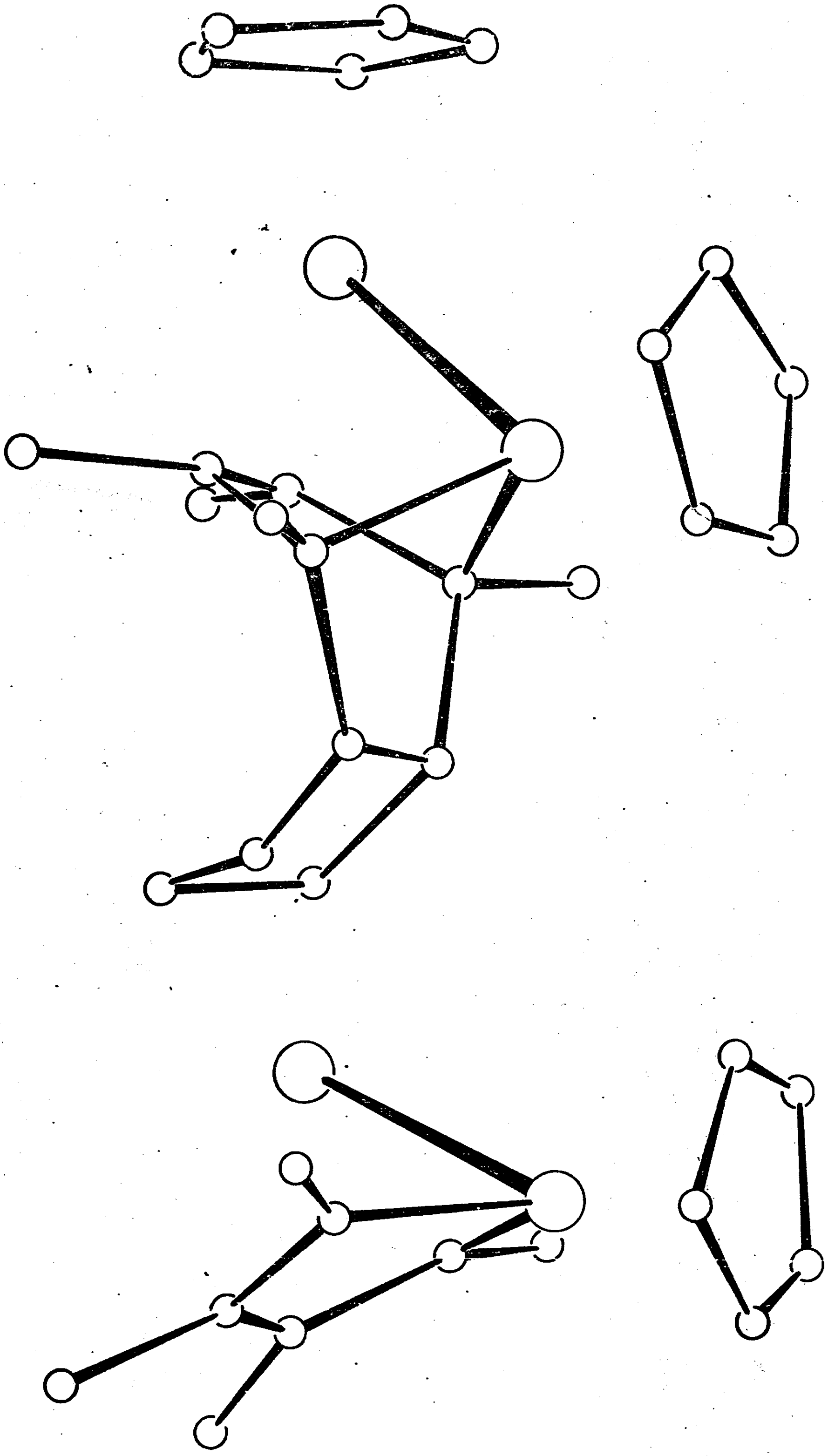


Fig. 3.9 a

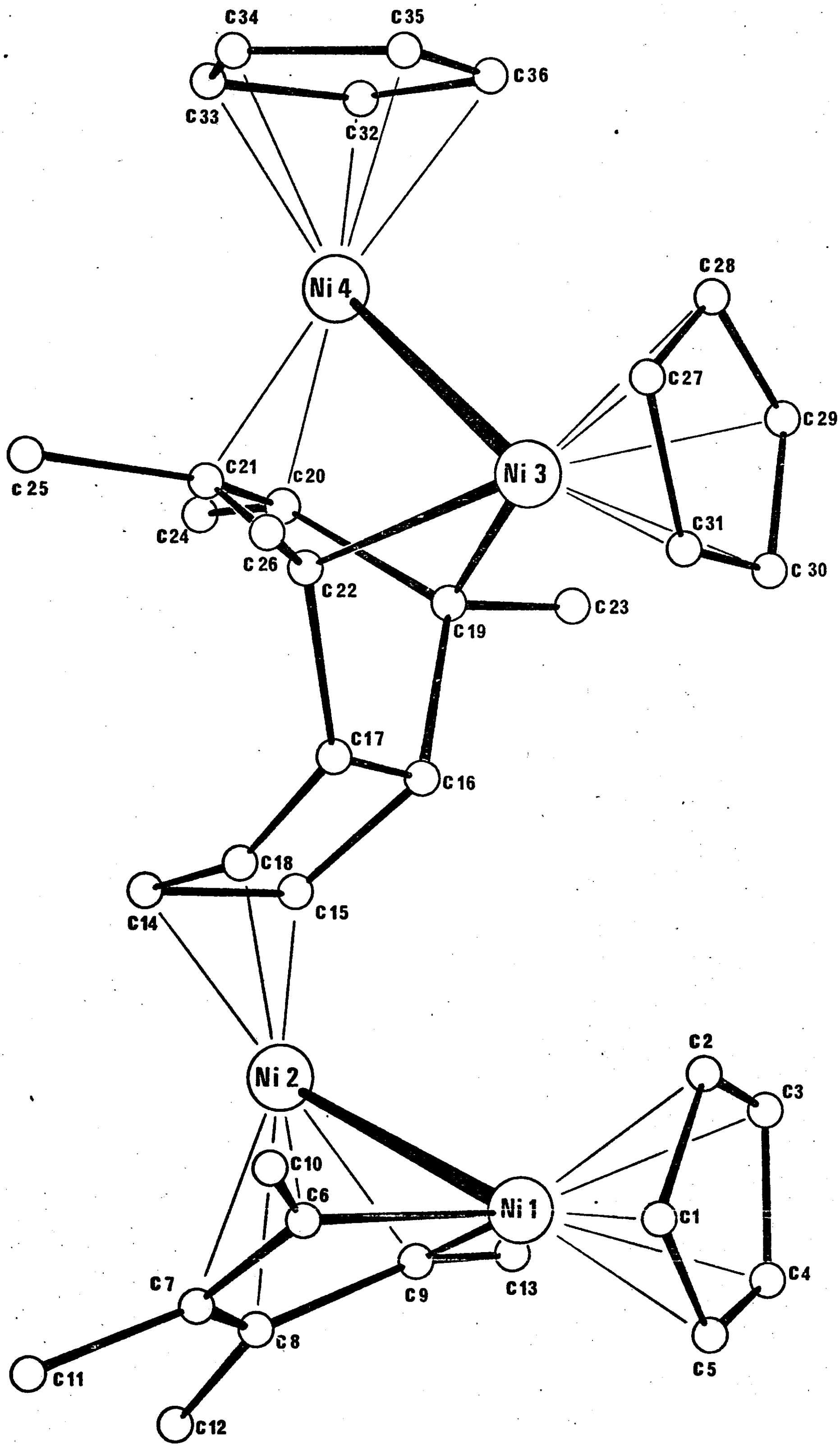

C34
C35
C36
C33
C32
Ni 4
C28
C27
C29
C25
C21
C20
Ni 3
C24
C26
C22
C31
C30
C19
C23
C17
C16
C18
C14
C15
Ni 2
C2
C3
C10
C6
Ni 1
C1
C9
C13
C4
C7
C8
C5
C11
C12

Fig 3.9 b

Table 3.1.

Intramolecular bond distances and angles

(A) Bond Distances (Å)

Metalocyclopentadiene Ring		$Ni(1)[C_4(CF_3)_4]$	
Ni(1) - C(6)	1.910	Ni - C(9)	1.909
C(6) - C(7)	1.480	C(7) - C(8)	1.433
C(8) - C(9)	1.400		

Ni(2) - X Distances			
Ni(2) - Ni(1)	2.466		
Ni(2) - C(6)	2.054	Ni(2) - C(9)	2.006
Ni(2) - C(7)	2.152	Ni(2) - C(8)	2.152
Ni(2) - C(14)	1.954		
Ni(2) - C(15)	2.035	Ni(2) - C(18)	2.033
Ni(2) - C(16)	2.728	Ni(2) - C(17)	2.715

Cyclopentenyl Ring			
C(14) - C(15)	1.38	C(14) - C(18)	1.38
C(15) - C(16)	1.53	C(18) - C(17)	1.58
C(16) - C(17)	1.55		

$(Cp)_2Ni(3)Ni(4)[C_4(CF_3)_4]$			
C(16) - C(19)	1.58	C(17) - C(22)	1.56
C(19) - C(20)	1.54	C(22) - C(20)	1.56
C(20) - C(21)	1.42		
Ni(3) - Ni(4)	2.370		
Ni(3) - C(19)	2.029	Ni(3) - C(22)	2.000
Ni(4) - C(20)	1.940	Ni(4) - C(21)	1.950

Table 3.1. (cont'd)

Ni-C (cyclopentadienyl) Distances

Ni(1) - C(1)	2.146	Ni(3) - C(27)	2.152
Ni(1) - C(2)	2.143	Ni(3) - C(28)	2.148
Ni(1) - C(3)	2.106	Ni(3) - C(29)	2.160
Ni(1) - C(4)	2.075	Ni(3) - C(30)	2.166
Ni(1) - C(5)	2.118	Ni(3) - C(31)	2.153
Ni(4) - C(32)	2.126		
Ni(4) - C(33)	2.146		
Ni(4) - C(34)	2.092		
Ni(4) - C(35)	2.125		
Ni(4) - C(36)	2.095		

(B) Bond Angles (degrees)

Metalocyclopentadiene Ring :- $CpNi(1)[C_4(CF_3)_4]$

Ni(1) - C(6) - C(7)	111	Ni(1) - C(9) - C(8)	113
C(6) - C(7) - C(8)	112	C(7) - C(8) - C(9)	114
C(6) - Ni(1) - C(9)	84		

Cyclopentenyl Ring

C(14) - C(15) - C(16)	109.5	C(14) - C(18) - C(17)	108
C(15) - C(16) - C(17)	103	C(16) - C(17) - C(18)	103
C(15) - C(14) - C(18)	110		

$(Cp)_2Ni(3)Ni(4)[C_4(CF_3)_4]$

C(17) - C(16) - C(19)	109	C(22) - C(17) - C(16)	108
C(16) - C(19) - C(20)	112	C(21) - C(22) - C(17)	111
C(19) - C(20) - C(21)	113	C(20) - C(21) - C(22)	110
C(22) - Ni(3) - C(19)	78	C(21) - Ni(4) - C(20)	42.8

Table 3.1. (cont'd)

Angles round C(19)		Angles round C(22)	
C(16) - C(19) - C(20)	112	C(17) - C(22) - C(21)	111
C(16) - C(19) - C(23)	111	C(17) - C(22) - C(26)	111
C(20) - C(19) - C(23)	122	C(21) - C(22) - C(26)	119

Distances of atoms from Planes (Å)

C(6), C(7), C(8), C(9)

Ni(1)	-0.475	Ni(2)	+1.573
C(10)	+0.099	C(13)	-0.082
C(11)	-0.008	C(12)	-0.045

C(14), C(15), C(18)

Ni(2)	-1.679		
C(16)	+0.664	C(17)	+0.649

C(19), C(20), C(21), C(22)

Ni(3)	+1.390	Ni(4)	+1.800
C(16)	-1.255	C(17)	-1.255
C(23)	+0.258	C(26)	+0.278
C(24)	-.0510	C(25)	-0.589

The structure of $[C_5H_5NiC_2(CF_3)_2]_4$ shown in Figs. 3.8. and 3.9. confirms the general conclusions reached from spectroscopic evidence and appears to result from condensation of two dinuclear units, $[C_5H_5NiC_2(CF_3)_2]_2$. The similarity to the proposed structure of $CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$ can therefore explain the high intensity of the ions $[(C_5H_5)_2Ni_2C_8F_{12}]^+$ and $[(C_5H_5)_2Ni_2C_5F_{11}]^+$ in the mass spectra of both complexes. The process which produces these ions constitutes a reversal of a Diels-Alder condensation reaction, although it is not known if the reverse reaction is thermal in origin, or only occurs under electron impact, since mass spectroscopic studies involving variation of source temperature and electron beam energy were inconclusive. It is significant however, that many retro Diels-Alder reactions, observed in the mass spectra of certain organic molecules, are considered to be induced by electron impact.[276]

The structure of the tetramer provides one of the most striking examples of the tendency of transition metals in low oxidation states to attain the stable eighteen electron configuration, each of the nickel atoms having achieved this by a different method. The reactivity of nickelocene has already been explained on this basis and it is possible that the reaction of $(CpNi)_2CF_3C_2CF_3$ and $CF_3C{\equiv}CCF_3$ gives initially $[C_5H_5NiC_2(CF_3)_2]_2$, with a structure similar to nickelocene, but with a five membered ring $CpNiC_4(CF_3)_4$ replacing one of the cyclopentadienyl rings, (see Fig. 3.10). This intermediate can achieve the stable configuration by 1,2-addition of the metalocyclopentadiene ring to a Cp ring of a second molecule of dimer. The presence of a ring $CpNiC_4(CF_3)_4$, π-bonded to a nickel atom therefore provides further evidence that $Cp_2Ni_3C_6(CF_3)_6$ and, in particular $CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$, have the structures proposed earlier. Several other transition metal complexes containing metalocyclopentadiene rings are known[274] but these are the first examples in nickel chemistry.

Structure of $[C_5H_5NiC_2(CF_3)_2]_4$

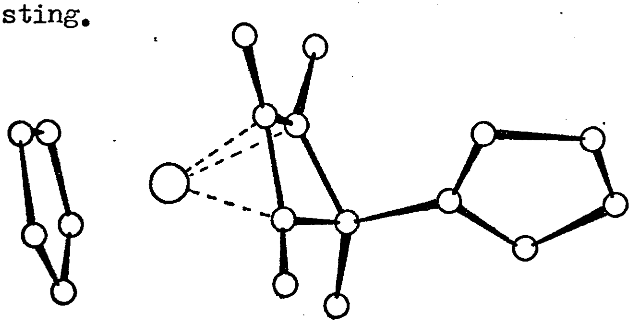
The π-electron-density of the five membered ring, $Ni(1)C_4(CF_3)_4$, appears to be delocalised over all four carbon atoms of the ring, the C-C distances being equal within experimental error, with an average value of 1.44 Å. Some delocalisation over the $Ni(1)-C_6$, C_9 bonds is also suggested by the average Ni-C distance of 1.91 Å, which is significantly shorter than the average $Ni(3)-C_{19}$, C_{22} separation, (2.015 Å), where little if any double-bond character is expected, since C_{19} and C_{22} are sp^3 hybridised. Delocalisation of ring electron density over the Rh-C σ bonds in the rhodiacyclopentadiene complex $RhCl(SbPh_3)_2[C_4(CF_3)_4]$ has also been reported although interestingly in the related six coordinate complex $RhClH_2O(AsPh_3)_2[C_4(CF_3)_4]$ a reduction in delocalisation has been found.[277] Such observations must however, be treated with caution at the present time.

As with uncoordinated cyclopentadienes[278] the five membered ring in these rhodium compounds is planar but in VII, Ni(1) lies below the plane defined by C_6, C_7, C_8 and C_9 by 0.48 Å, to give a dihedral angle of 19.6° between these four coplanar atoms and C_6, Ni(1), C_9. This bending phenomenon, common in metalocyclopentadiene rings coordinated to a metal,[274] probably results from twisting of the orbitals on C_6 and C_9 to achieve maximum overlap with the Ni(2) orbitals as already discussed in some detail in Chapter II.

Nonetheless, it is difficult to explain the high degree of non-planarity of the Ni(1) C_4 ring in the nickel complex when compared with comparable iron and cobalt complexes. In $Fe(CO)_3(PhC_2C_6H_4C_2Ph)_2Fe(CO)$ the MC_4 ring metal atom lies 0.31 Å below the plane of the four carbon atoms while in $[Fe(CO)_3(MeC_2Me)_2]Ni[C_4Me_4]$ this is reduced to 0.24 Å and in $(CpCo)_2(C_4H_4)$, to 0.15 Å.[287] However, the dihedral angle and hetero-atom displacement are significantly lower than in $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$, (30.8° and 0.67 Å), and this is considered to result from the constraining effect of the metal-metal bond between Ni(1) and Ni(2). The overall geometry of the metalocyclopentadiene ring must reflect a compromise between the Ni(2)-C_6, C_9 and Ni(1)-Ni(2) orbital overlaps. Consequently, the Ni(1)-Ni(2) bond distance, at 2.466 Å, is appreciably longer than the relatively unstrained Ni(3)-Ni(4) separation, 2.37 Å, which is closer to the average nickel-nickel bond length of 2.39 Å in $(CpNi)_3(CO)_2$.[279]

The transformation of a π cyclopentadienyl group to a cyclopentenyl ligand is well documented in the literature[262] but this provides the first opportunity to examine the structural alterations which result from 1,2 addition to a π-C_5H_5 ring. The Ni(2) carbon distances clearly indicate that the five membered ring functions as a three electron donor, only C_{18}, C_{14} and C_{15} lying within bonding distance of Ni(2). The Ni(2)-C_{18}, C_{15} separations, 2.033 Å and 2.035 Å, are slightly less than the average Ni-Cp bond lengths but slightly greater than the Ni(2)-C_{14} distance, and this results in a dihedral angle of 19.9° between the two planes of the sandwich, C_{14}, C_{15}, C_{18} and C_6, C_7, C_8, C_9. This phenomenon, common in π allyl complexes, is considered by Kettle and Mason[280] to result from contributions from two different bonding situations, but it is perhaps pertinent to point out that simple orbital twisting at C_{15} and C_{18} as discussed in Chapter II, may also account, to a certain extent, for the observed distortions.
Differences in M-C distances in cyclic butadiene complexes probably result from similar effects and it is also of interest to note that such diene ligands also have dihedral angles greater than expected values.[280]

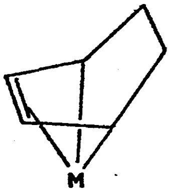
The allylic nature of the five membered cyclopentenyl ring is also reflected in the C-C bond lengths, $C_{14}-C_{18}^{218}$ and $C_{14}-C_{15}$, each having a typical π allyl distance of 1.38 Å, while the three other C-C distances are in the region of 1.56 Å as expected for C-C single bonds.[226] Most π-allyl ligands have central C-C-C angles close to the ideal sp^2 angle of $120^{o}C$[281] but the constraining effect of the five membered ring reduces this to 110^{o} in $[C_5H_5NiC_2(CF_3)_3]_4$. In the cyclobutenyl complex $CpNi[C_4(CH_3)_4C_5H_5]$[282] this is further reduced to 89^{o}. The four membered ring in the latter is non-planar with the non-bonded carbon atom lying above the plane of the three allylic carbon atoms to give a dihedral angle of 24.9^{o}, probably as a result of orbital twisting.

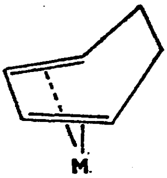


This also occurs in the cyclopentenyl ring of VII and the comparable dihedral angle between C_{14}, C_{15}, C_{18} and C_{15}, C_{16}, C_{17}, C_{18}, 25.70^{o}, reflects a similar degree of orbital twisting at C_{15}, C_{18}.

As a result of the sp^3 character of C_{16} and C_{17} the four carbon atoms, C_{15}, C_{16}, C_{17}, C_{18} make a dihedral angle of 58.1^{o} with the plane defined by C_{16}, C_{17}, C_{19}, C_{22} which further makes a dihedral angle of 57.1^{o} with C_{19}, C_{20}, C_{21}, C_{22}, C_{20}, and C_{18} also being sp^3 hybridised. This is illustrated by the bond angles round these two atoms (see Table 3.1.(B)) and, as a result, Ni(3)-C_{19}, C_{22}, makes a dihedral angle of 62.7^{o} with C_{19}, C_{20}, C_{21}, C_{22}., Ni(3) lying above this plane by 1.39 Å. This contrasts with the analogous values of 19.6^{o} and 0.48 Å for Ni(1)-C_6, C_7, C_8, C_9 where the carbon atoms are all sp^2 hybridised and the metal atom lies on the opposite side of the NiC_4 ring

The unusual manner by which Ni(3) and Ni(4) are attached to the four carbon atoms of the C_6 ring is illustrated by the C-C bond lengths, all of which are single bond distances near 1.56 Å apart from C_{20}-C_{21}, which at 1.42 Å, is typical of a coordinated olefinic bond.[142,143,163] Since the carbon atoms C_{19} and C_{22} are sp^3 hybridised the diene ring C_{19}, C_{20}, C_{21}, C_{22}, has attained the extreme valence-bond structure originally suggested by Mason[218] to contribute to the bonding in e.g. $CpCo[C_4(CF_3)_4CO]$ and $Fe(CO)_3C_6F_8$.





It has already been argued that the terminal carbon atoms of the diene ligand in such derivatives are probably closer to sp^2 hybridisation so that the high degree of non-planarity in the six-membered ring of the nickel tetramer may be ascribed in part to the sp^3 hybridisation of carbon atoms, C_{19} and C_{22}. It is not however, possible to relate the dihedral angle directly to changes in hybridisation in view of the fact that two metal atoms are linked to the diene in VII, but in the otherwise comparable octafluorocyclohexadiene complex $Fe(CO)_3C_6F_8$,[283] with a dihedral angle of 47.3°, only one metal atom is so attached. The metal-carbon orbital overlap considerations must clearly be different in these complexes.

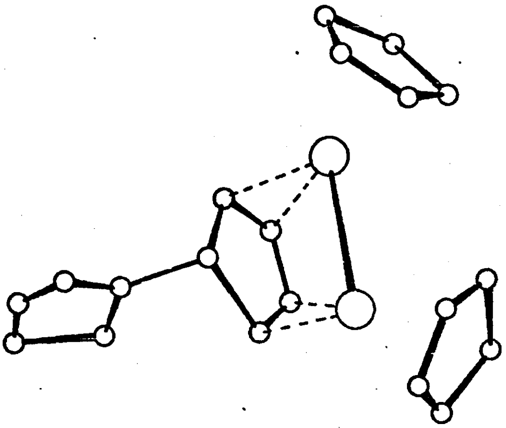
It was originally suggested by Alcock,[219] that if the terminal carbon atoms of a coordinated butadiene were sp^3 hybridised, the substituents on these atoms would lie above the plane of the C_4 ring, away from the metal atom. If however, the atoms retained the sp^2 hybridisation of the uncoordinated state, the result of orbital twisting would be to pull the substituents below the plane of the butadiene towards the metal as is the case in $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ and $CpCo[C_4(CF_3)_4PO_2H]$, the latter of which will be described in Chapter V. It is therefore surprising to find that the CF_3 substituents on the sp^3 hybridised carbon atoms C_{19} and C_{22} are bent below the plane of C_{19}, C_{20}, C_{21}, C_{22} towards Ni(3) and Ni(4) by 0.26 Å and 0.28 Å respectively. It can only be suggested that this anomolous situation is a consequence of the diene being coordinated to two metal atoms instead of one, or else that Alcock's theories have reached the limits of their applicability.

The CF_3 substituents on the other two carbon atoms C_{20} and C_{21} of the diene ring are also bent out of the plane C_{19}, C_{20}, C_{21}, C_{22}, but in this case by 0.51 and 0.59 Å away from Ni(3) and Ni(4), the dihedral angle between the two planes C_{19}, C_{20}, C_{21}, C_{22} and C_{24}, C_{20}, C_{21}, C_{25} being 26.2°. In $CpCo[C_4(CF_3)_4PO_2H]$ the comparable CF_3 groups are also bent away from the metal, but only by 0.063 Å and 0.087 Å, and this significant difference can probably be attributed to the fact that in the cobalt complex, the π electron density is delocalised over all three C-C bonds of the butadiene. As a result of the localised bonding situation found in the nickel derivative, the $Ni(4)-C_{20}-C_{21}$ bonding can be compared with that in simple metal olefin complexes and hence significant bending of the substituents away from the metal can be expected as in, e.g. $CpRh(C_2H_4)(C_2F_4)$.[143] As already discussed in the introduction, with fluoroolefins and fluoroacetylenes these large distortions are a consequence of greater M-C back donation which leads to significant sp^3 character in the coordinated carbon atoms of the olefin. The very small bending of the CF_3 substituents on the C_3 and C_4 positions of the diene in $[CpCoC_4(CF_3)_4PO_2F]$ can therefore be cited as further evidence that the carbon atoms of cyclic dienes in general retain the sp^2 hybridised state upon coordination to a transition metal. This is further substantiated by the very low degree of bending of the CF_3 substituents on the metalocyclopentadiene ring $Ni(1)-C_6$, C_7, C_8, C_9 out of the plane of the four co-planar carbon atoms, (see Table 3.1.(C)).

In many complexes containing small rings bending of the substituents out the plane of the ring by small amounts is frequently observed,[218,244] and this has been attributed to steric effects.[284] However, a more satisfactory explanation of this phenomenon has been put forward by Kettle who considers such changes in geometry to result from interactions between the metal orbitals and the σ framework of the organic ring system.[285]

The different type of bonding of Ni(3) and Ni(4) to the six membered ring in $[C_5H_5NiC_4(CF_3)_2]_4$ is also reflected in the average $Ni(3)-C_{19}$, C_{22} and $Ni(4)-C_{20}$, C_{21} distances, 2.015 Å and 1.94 Å respectively. The larger σ bond distance possible results from the greater covalent radius of sp^3 carbon, 0.77 Å, relative to sp^3 carbon, 0.74 Å[226], in addition to the fact that M-C σ bonds, as discussed earlier, are unlikely to have any double bond character. This possibility however, exists for M-C π bonds.[130]

The bonding of Ni(3) and Ni(4) to C_{19}, C_{20}, C_{21} and C_{22} contrasts with the situation found in $(CpPt)_2C_{10}H_{10}$ which has the structure illustrated.[270]

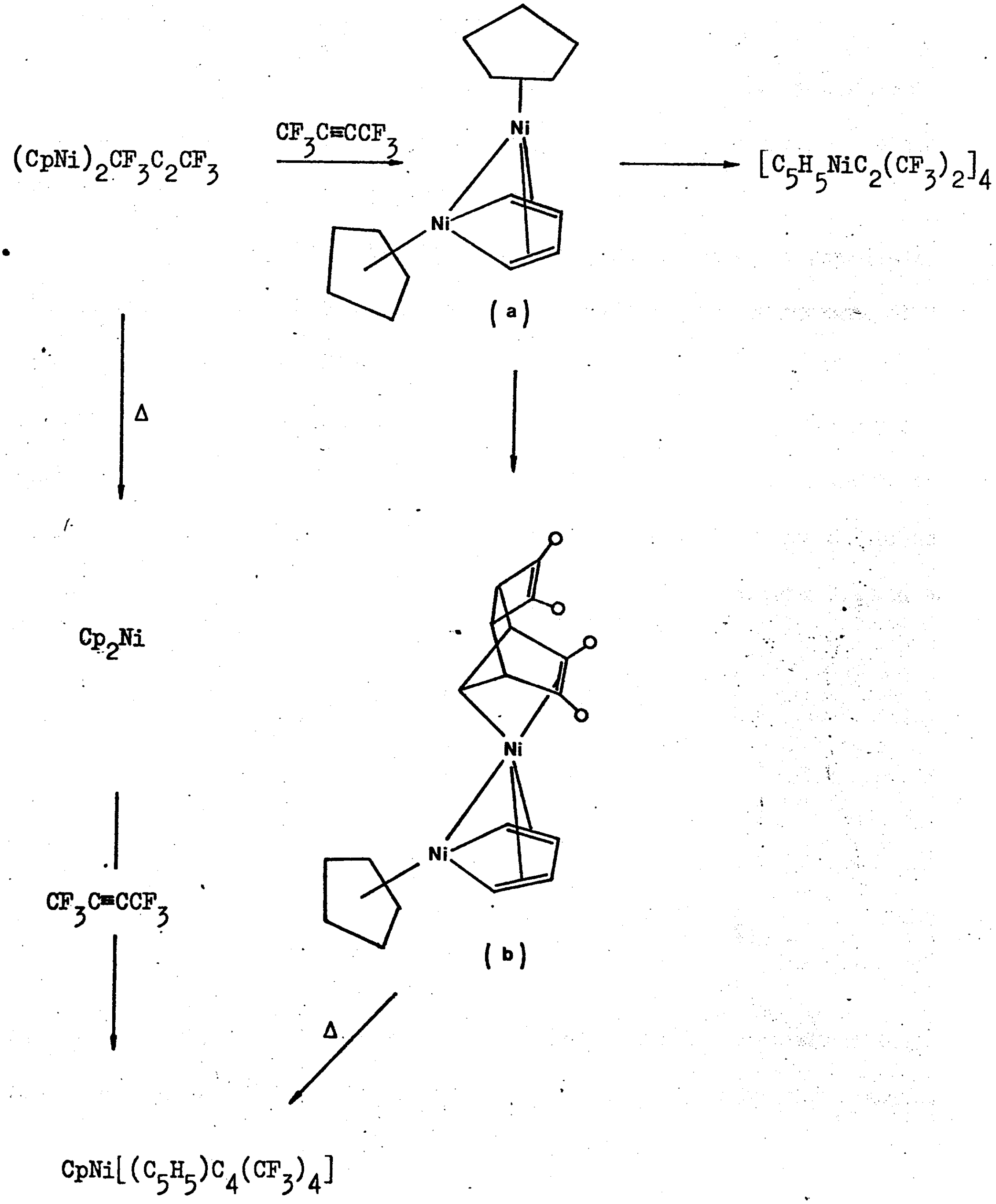


The $2\sigma,\pi$ bonding of the nickel complex may be a consequence of this possibly being formed via a dinuclear intermediate $[C_5H_5NiC_2(CF_3)_2]_2$ which has a σ-π bonded structure, but once the tetramer is formed transformation to the π bonded alternative is obviously not inhibited by stereochemical considerations, as the platinum complex illustrates. That it does not occur may be a reflection of the greater stability of the 2σ π bonded isomer or else a high energy barrier to interconversion. The tendency of fluorocarbon ligands to form σ rather than π bonds[145] to transition metals suggests that the first explanation may be correct, but it would obviously be of great interest to determine the structures of model complexes containing, e.g. a perfluorocyclopentadiene ring and with stoichiometry $(CpM)_2(C_5F_6)$, M = Ni, Pt.

Mechanism

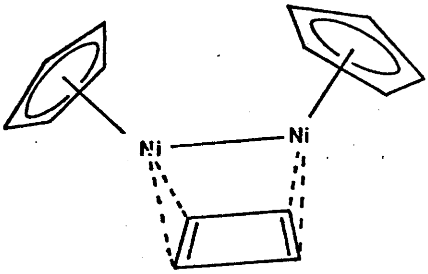
It has been suggested that $[CpNiC_2(CF_3)_2]_4$ is formed by condensation of two dimeric units $[CpNiC_2(CF_3)_2]_2$ and the structure of this intermediate in all probability is similar to that of $CpNi_2[(C_4(CF_3)_4)(C_5H_5)C_2F_3Cl]$, but with a cyclopentadienyl ligand in place of the cyclopentenyl group, (a). Having an unstable twenty electron configuration for one of the nickel atoms, the metalocyclopentadiene ring undergoes a Diels-Alder addition to the 1,2-position of a cyclopentadienyl group in a second molecule of dimer. This could occur in four different ways[263,285] but only one appears to be favourable. A similar 1,2-addition of hexafluorobutadiene to the cyclopentadienyl ring of nickelocene has been reported by Wilkinson[286], the product $CpNi(C_5H_5)C_4F_6$ having a fused C_4, C_6 ring system like the tetramer. To account for the formation of the tetramer and the other products of the reaction the following mechanism is proposed.

Fig. 3. 10.


$(CpNi)_2CF_3C_2CF_3$
$CF_3C{\equiv}CCF_3$
Ni
Ni
(a)
$[C_5H_5NiC_2(CF_3)_2]_4$
Δ
Cp_2Ni
$CF_3C{\equiv}CCF_3$
Ni
Ni
(b)
Δ
$CpNi[(C_5H_5)C_4(CF_3)_4]$

If (a) is the main intermediate it follows that, since it resembles nickelocene, it may react with $CF_3C≡CCF_3$ to give (b). This was not isolated, suggesting that such a reaction does not occur. However, $CpNi[(C_5H_5)C_4(CF_3)_4]$ could be produced by thermal decomposition of (b) although an alternative source of V could be nickelocene, produced possibly by thermal decomposition of $(CpNi)_2CF_3C_2CF_3$. $Cp_2Ni_3C_6(CF_3)_6$ could also be produced from the latter by reaction with a complex containing a metalocyclopentadiene ring, $CpNiC_4(CF_3)_4$, as suggested in the reaction of $[CpNiSCF_3]_2$ and $CF_3C≡CCF_3$, (Fig. 3.4.).

Although the postulated structure of the dimeric intermediate $[CpNiC_2(CF_3)_2]_2$ seems reasonable on the basis of the structure of the tetramer and other metalocyclopentadiene complexes,[274] e.g. $(CpCo)_2(C_4H_4)$,[267] the lack of reactivity of a twenty electron species such as this towards $CF_3C≡CCF_3$ is intriguing. This could be explained by an alternative structure in which two CpNi moieties are attached symmetrically to a tetrakis(trifluoromethyl)cyclobutadiene ligand as illustrated.



As such both nickel atoms have 18 electron configurations which might be expected to stabilise this intermediate to attack by the acetylene until condensation with a second molecule of dimer can occur. In this context it has been found that the reaction of the tetraphenylcyclobutadiene complex $(PhC)_4PdCl_2$ and cyclopentadiene gives a fused ring product[288] remarkably similar to the C_5-C_6 fused rings in $[C_5H_5NiC_2(CF_3)_2]_4$.

Table 3.3.

N.m.r. Parameters of Cyclopentadienyl-Nickel Complexes

Compound	^1H (τ)						^{19}F (ppm)				
	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_1	δ_2	δ_3	δ_4	δ_5
$CpNi[C_4(CF_3)_4H]^*$	4.24(5)	5.63(1)					53.7(1)	56.0(1)	63.5(1)	65.7(1)	
$Cp_2Ni_3C_6(CF_3)_6$	4.39(1)	4.50(1)					47.5(1)	51.8(1)	54.8(1)		
$CpNi[(C_5H_5)C_6(CF_3)_6]^*$	4.36(5)	6.54(1)	6.72(2)	7.02(2)			51.1(1)	55.4(1)	56.0(1)	61.5(1)	64.0(2)
$(CpNi)_2C_6(CF_3)_6^*$	4.55										
$CpNi[(C_5H_5)C_4(CF_3)_4]$	4.52(5)	6.50(2)	7.05(2)	7.61(1)			57.8(1)	66.8(1)			
$CpNi[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$	3.75(1)	4.40(5)	5.05(2)	6.91(2)			49.0(1)	56.7(1)			
$[C_5H_5NiC_2(CF_3)_2]_4$	3.86(1)	4.20(5)	4.24(5)	4.64(5)	4.91(2)	7.18(2)	47.3(1)	50.0(1)	55.0(2)		

Relative intensities in parentheses.

Table 3.2.

I.r. Spectra (cm^{-1}) of Cyclopentadienyl Nickel Complexes

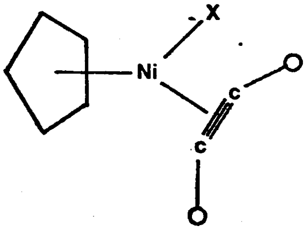
Compound	νC–C	νCF
$CpNi[C_4(CF_3)_4H]^*$	1661w	1293s, 1260s, 1245s, 1214w, 1187s, 1178s, 1160s, 1150sh
$Cp_2Ni_3[C_6(CF_3)_6]$	1589w	1265wm,vb, 1219s, 1189s, 1177m, 1170m, 1147wm, 1134m
$CpNi(C_5H_5)C_6(CF_3)_6^*$	1711w	1299m, 1290wm,sh, 1271wm, 1234wm, 1224wm, 1219m, 1200vs, 1183m, 1168s, 1166s,sh, 1144s, 1126wm, 1116w
$(CpNi)_2[C_6(CF_3)_6]^*$		1296vw, 1237wm, 1205vs, 1188s, 1120vw
$CpNi[(C_5H_5)C_4(CF_3)_4]$	1710w	1287w, 1258s, 1241m, 1235m, 1218w, 1196vs, 1178msh, 1170m, 1145vs,b, 1131vs, 1112m
$CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$	-	1297m, 1294m, 1274wm, 1260wm, 1247wm, 1219vs, 1190s, 1172s, 1133m
$[C_5H_5NiC_3(CF_3)_2]_4$	-	1270wsh, 1247m, 1216s, 1198ms, 1191ms 1173ms,sh, 1161s, 1146m, 1129m

CCl_4 solution or if indicated * cyclohexane solution

Conclusions

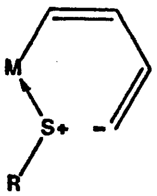
The dominating feature of the reactions of cyclopentadienyl nickel complexes with hexafluorobut-2-yne appears to be the tendency of the metal to achieve the favoured eighteen electron configuration. Although this is not unusual, the manner in which it is accomplished is particularly intriguing. Only three electrons are required by the metal of a CpNi moiety but, as illustrated by the limited studies carried out, the variety of three-electron ligands which can be produced from the three species Cp, Ni and $CF_3C{\equiv}CCF_3$ serves once more to illustrate the unpredictability of reactions involving transition metal complexes and acetylenes.

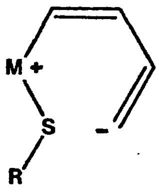
An important feature of the chemistry of nickelocene discussed in the introduction, is the π-σ transformation of one of the cyclopentadienyl groups. Several of the reactions of cyclopentadienyl nickel derivatives described in this chapter have also been rationalised in terms of such rearrangements to give an intermediate of the following form.



A similar type of intermediate may also be involved in the reaction of $CF_3C{\equiv}CCF_3$ and $[CpNiSCF_3]_2$, i.e. X = SCF_3, (Fig. 3.4.). Since in all these reactions $(CpNi)_2CF_3C_2CF_3$ is produced, reaction of $CpNi(CF_3C_2CF_3)X$ with a CpNi complex is obviously possible with cleavage of the Ni-X bond. However, the other products of the reactions suggest that the nature of X also influences the availability of other potential reaction pathways. Thus, with X = C_5H_5, $C_5H_5C_2(CF_3)$, intramolecular condensation reactions involving X and $CF_3C≡CCF_3$ occur exclusively. As already pointed out this does not occur with X = $C_5H_5C_2F_3Cl$, and the alternative reaction with the acetylene gives a metalocyclopentadiene ring complex. This intermediate appears capable of promoting a π-σ interconversion of a cyclopentadienyl group and the dinuclear product $CpNi[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$ is produced.

Particularly interesting is the reaction of $[CpNiSCF_3]_2$ and $CF_3C≡CCF_3$ which, despite the variety of complexes produced, did not yield an organosulphur compound by an intramolecular condensation of the intermediate $CpNi(CF_3C_2CF_3)SCF_3$. The electronic requirements of CpNi are the same as $Mn(CO)_4$ and CpFeCO so that a complex $CpNiC(CF_3)=C(CF_3)SCF_3$ might be expected, by analogy with $Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$ and $CpFe(CO)C(CF_3)=C(CF_3)SR$. Reactions which give such complexes have been postulated to proceed via dipolar intermediates, (Fig. 2.9), and a tentative explanation of the different types of product obtained is suggested by the possible nature of such species. Since in a dipolar intermediate the negative charge will probably be localised on the cyclising fluorocarbon chain, the positive charge will be taken up by the metal, and possibly by ligands coordinated to the metal. It is therefore possible that the location of this positive charge determines, to a certain extent, the reaction pathway taken by the intermediate, and hence the nature of the products. With $[Mn(CO)_4SR]_2$ location of a significant amount of the charge on sulphur, as illustrated in Fig. 2.9., leads to sulphur heterocycles whereas with $[CpNiSCF_3]_2$, positive charge on the metal can explain the absence of such derivatives and the formation of the compounds described earlier, (see Fig. 3.4.). It should be emphasised that the ionic intermediates illustrated are extreme canonical forms and hence must be treated as such. However, they serve as





a basis by which it is possible to attempt to rationalise the various types of product obtained from reactions involving electrophilic acetylenes and transition metal mercapto complexes.

CHAPTER IV

REACTIONS OF ACETYLENES
WITH SOME
CYCLOPENTADIENYL MOLYBDENUM COMPLEXES

INTRODUCTION

Apart from a few isolated studies, the reactions of group VI metal carbonyls and derivatives with acetylenes have been virtually neglected, despite the ready availability of these compounds.

The reaction of $Mo(CO)_6$ and PhC≡CPh has been reported to give a variety of complexes containing tetraphenylcyclobutadiene ligands formed by cyclodimerisation of the acetylene.[179] In contrast cyclopentadienyl molybdenum tricarbonyl derivatives $CpMo(CO)_3X$, X = CH_3,[289] C_2H_5,[290] have been reported to react with PhC≡CPh to give low yields of $[CpMoCO]_2PhC_2Ph$ in which the bridging acetylene is considered to function as a two electron donor to each metal as in $Co_2(CO)_6PhC_2Ph$. When X = CH_3 a second product isolated was tetraphenylcyclopentadiene which may have resulted from insertion of a methyl group into the dimerising acetylene with concomitant hydrogen abstraction. A similar process would account for the formation of the second complex derived from $CpMo(CO)_3C_2H_5$ and diphenylacetylene which is considered to be 1,2,3,4-tetraphenylbenzene(cyclopentadienyl)molybdenum, but this seems unlikely since the molybdenum is assigned a seventeen electron configuration. In the absence of spectroscopic data further comment is not possible except that a re-investigation is desirable.

The products of these reactions compare with the simple substituted derivatives $CpMo(CO)_2RC_2RSCF_3$, described in Chapter II suggesting that the nature of X in $CpMo(CO)_3X$ is important in determining the course of reactions with acetylenes. The formation of the cyclopentadienone compound $CpMo(CO)[(CF_3CCH)_2CO]SCF_3$ from $CpMo(CO)_3SCF_3$ and 3,3,3-trifluoropropyne further suggested that, in some circumstances, the alkyne substituents might also be important and it was therefore decided to study the reactions of $CpMo(CO)_3X$, X = Cl, Br, I, with a variety of acetylenes RC≡CR, R = CH_3, CF_3, C_6H_5.

SUMMARY OF REACTIONS

$$\mathrm{CpMo(CO)_3X + CH_3C{\equiv}CCH_3 \longrightarrow CpMo(CH_3C_2CH_3)_2X + [C_4(CH_3)_4(CO)_2]}$$

$$\mathrm{CpMo(CO)_3X + CF_3C{\equiv}CCF_3 \longrightarrow CpMo(CF_3C_2CF_3)_2X}$$

$$\mathrm{CpMo(CO)_3X + PhC{\equiv}CPh \longrightarrow CpMo(CO)(PhC_2Ph)X}$$

$$\mathrm{CpMo(CO)(PhC_2Ph)X + PhC{\equiv}CPh \longrightarrow CpMo(CO)(PhC)_4X}$$

$$\mathrm{CpMo(CO)(PhC_2Ph)X + CH_3C{\equiv}CCH_3 \longrightarrow CpMo(CH_3C_2CH_2)_2X}$$

$$\mathrm{CpMo(CO)(PhC_2Ph)X + CF_3C{\equiv}CCF_3 \longrightarrow CpMo(CF_3C_2CF_3)_2X}$$

$$\mathrm{CpMo(CF_3C_2CF_3)_2Cl \xrightarrow{h\nu} [CpMo(CF_3C_2CF_3)Cl]_n}$$

$$\mathrm{CpMo(CF_3C_2CF_3)_2Cl + CF_3C{\equiv}CCF_3 \xrightarrow{h\nu} CpMo[C_4(CF_3)_4]Cl}$$

X = Cl, Br, I

RESULTS AND DISCUSSION

Reactions of $CF_3C{\equiv}CCF_3$ and $CH_3C{\equiv}CCH_3$ with $CpMo(CO)_3X$, X = Cl, Br, I

$CpMo(CO)_3X$ and the acetylenes but-2-yne and hexafluorobut-2-yne react with complete decarbonylation to give yellow, orange and red brown crystalline solids of stoichiometry $CpMo(RC_2R)_2X$, $R = CH_3$, CF_3, X = Cl, Br, I. With $R = CH_3$ quantities of tetramethylquinone[291] were also formed. Molecular weight studies of the organometallic products in chloroform solution (vapour phase osmometry), and the vapour phase (mass spectrometry), indicate the existence of only monomeric species and this eliminates a dimeric halogen or acetylene bridged structure which would confer an eighteen electron configuration on the metal. It therefore appears that in these complexes the metal has formally acquired the relatively rare sixteen electron configuration, assuming that each acetylene functions as a two-electron donor.

It is recalled that in complexes $MX(RC_2R)_3$,[155] M = Mo, W, each of the acetylenes is formally required to donate all four π-electrons to the metal which acquires an eighteen electron configuration since two of the electrons are non-bonding.[156] It is conceivable that a similar situation might exist in $CpMo(RC_2R)_2X$ but the i.r. spectra contain C≡C stretching modes near 1800 cm^{-1} indicating that only a partial reduction in triple bond order occurs on coordination of the acetylene, consistent with the ligands acting as two electron donors. These frequencies further indicate that condensation of the two acetylenes to form a cyclobutadiene ring has not occurred. Moreover, the mass spectrum in all cases exhibits a molecular ion which undergoes stepwise loss of acetylene units, in agreement with the above conclusion.

In all cases a singlet is observed in the ^1H n.m.r. spectra of the complexes near 4τ characteristic of a π-bonded cyclopentadienyl ligand. The chemical shift of the Cp protons is virtually invariant to the halogen, having the value for $CpMo(CH_3C_2CH_3)_2X$, $\delta = 4.59\tau$,

Table 4.1.(a)

I.r. Spectra of Complexes $CpMo(CH_3C_2CH_3)_2X^*$ (cm^{-1})			
X	νC–H	νC≡C	Other bands
Cl	3121vw, 2944wm, 2901s, 2833wm	1810w	1445wm,sh, 1430m, 1357m, 1138ms, 1063w, 1042wm, 1030wm, 1019wm, 1000wm,sh, 938w, 839wm, 614wm
Br	3124vw, 2950wm 2900s, 2834wm	1790w, 1747w,	1428m,b, 1356m, 1139ms, 1063w, 1040wm, 1019m, 1000wmsh, 935w, 905vw, 839wm, 615wm
I	3120vw, 2944wm, 2899s, 2833wm	1829vw, 1810vw 1790w, 1770vw	1446wm,sh, 1427m, 1326wm, 1137m, 1063w, 1041wm, 1019wm, 999wm, 955vw, 910vw, 839m, 613wm

* CCl_4

Table 4.1.(b)

I.r. Spectra of Complexes $CpMo(CF_3C_2CF_3)_2X^*$ (cm^{-1})			
X	νC–H	νC≡C	νC–F
Cl	3119vw	1799w, 1782w	1282s,sh, 1277s, 1234vs, 1203vs, 1173vs,b
Br	3120vw	1792w, 1775w	1279s,sh, 1274s, 1232vs, 1203vs, 1169vs,b
I	3120vw	1788w, 1770w	1282s,sh, 1277s, 1234vs, 1206vs, 1172vs,b

* CCl_4

and for $CpMo(CF_3C_2CF_3)_2X$, δ = 3.95τ. However, as the above values show, the chemical shift is sensitive to the nature of the substituents on the acetylene. These results appear to be quite general in that only very small changes in the chemical shift of the cyclopentadienyl protons in $CpFe(CO)_2X$, X = Cl, Br, I,[292] are observed, while in complexes containing unsaturated organic ligands such as cyclopentadienones e.g. $CpCo[C_4R_4CO]$, the aromatic protons are very sensitive to the electron withdrawing ability of the substituents R on the organic species.[190]

The proton n.m.r. of the but-2-yne complexes show a broad singlet near 7τ due to the methyl protons of the acetylene ligands, the chemical shift again being relatively insensitive to the halogen. At low temperatures this splits into two slightly coupled resonances which are probably quartets, but only splitting of the two central peaks could be resolved due to the low coupling constant, J_{H-H} = 0.7 Hz. The ^{19}F n.m.r. spectra of the hexafluorobut-2-yne derivatives are similar, giving a singlet at room temperature and two peaks at low temperature but no distinct coupling could be observed in the latter. These results suggest fluxional motion of some description involving exchange of CF_3 or CH_3 groups between two non-equivalent sites in the molecule.

X-ray studies of the sixteen electron chromium complex $CpCr(NO)N(Ph)_2I$,[293] show that the metal is octahedrally coordinated with the cyclopentadienyl group occupying one of the faces of the octahedron and a similar geometry can be adopted by the complexes $CpMo(RC_2R)_2X$. The acetylenes, according to the n.m.r. data, must take up a preferred conformation at low temperatures such that only two chemically distinguishable R groups are present. A preferred orientation can be explained by considering the metal-acetylene bond as described in the introduction for Pt(0) and Pt(II) complexes. The acetylene will take up a conformation which enables maximum π-back-bonding to occur from filled d orbitals on the metal to π^* orbitals on the C≡C bond. Since in an octahedral complex only the dxy, dyz and dzx orbitals are available for back-donation, two conformers (a) and (b) are possible, but only one is preferred at low temperature.

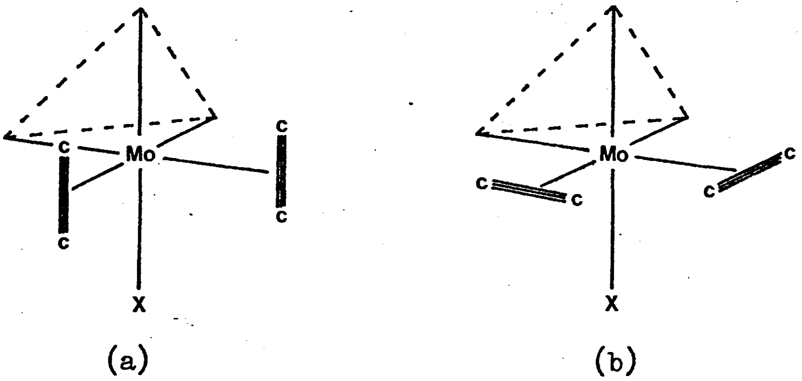


Fig. 4.1.

Steric interactions may also contribute to conformational stability and in (a) repulsion between the acetylene substituents R is at a minimum whereas repulsion between R and the other ligands Cp and X is maximised. In contrast, repulsion between acetylenes is probably significant in (b) but interaction with the other ligands is reduced. However, the orientation of acetylenes in (a) leads to overlap of the π^* orbitals of an acetylene with the dxz orbitals while the dyz overlap with the other acetylene. Both these orbitals are also available for back-donation to the halogen but since this has no energetically available orbitals to accept electron density the acetylenes will accept most of the dπ electron density. In (b) both acetylenes share the dxy orbital which obviously leads to weaker metal-acetylene back-bonding and hence a less stable conformation. Provided that steric interactions are not excessive isomer (a) would appear to be preferred on electronic grounds. However, since steric considerations favour (b) full variable temperature n.m.r. data were obtained over the range -80 to +34°C for all six compounds in an effort to clarify the situation.

Table 4.2.

N.m.r. Parameters of Complexes $CpMo(RC_2R)_2X$

$CpMo(CH_3C_2CH_3)_2X$	$\delta_1(Cp)(\tau)$	$\delta_2(CH_3)$, 34°C	$\delta_2(a)(-80°C)$	$\delta_2(b)(-80°C)$
X = Cl	4.59	7.39	7.08	7.65
Br	4.59	7.34	7.07	7.56
I	4.59	7.25	7.05	7.42
	^1H		^{19}F (ppm)	
$CpMo(CF_3C_2CF_3)_2X$	$\delta Cp(\tau)$	$\delta_1(CF_3)$, 34°C	$\delta_1(a)(-80°C)$	$\delta_1(b)(-80°C)$
X = Cl	3.94	56.85	56.05	57.66
Br	3.94	56.80	55.90	57.70
I	3.95	56.68	55.74	57.61

From these data the rate of exchange at coalescence k_c has been calculated using the approximate formula[294]

$$k_c = \frac{\pi}{\sqrt{2}} \cdot \Delta\nu_c$$

$\Delta\nu_c$ = difference in chemical shift of two peaks at coalescence (Hz). $\Delta\nu_c$ was obtained from a graph of a $\Delta\nu$/temperature, the linear part of the graph being extrapolated to the coalescence temperature, T_c. From k_c the free energy of activation, ΔG_c, for the exchange at T_c, was calculated using the Eyring equation[295]

$$\Delta G_c = R.T_c.\mathrm{Ln}(Tc/kc \cdot k/h)$$

The values of T_c, k_c and ΔG_c are given in Table 4.3.

Table 4.3.

Complex	T_c (K)	$\Delta\nu_c$ (Hz)	k_c (sec^{-1})	ΔG_c (k.cal.mol)
$CpMo(CH_3C_2CH_3)_2X$				
X = Cl	286.5	52.23	116.0	9.326
Br	292	43.4	96.5	14.42
I	289.4	29.53	65.6	12.69
$CpMo(CF_3C_2CF_3)_2X$				
X = Cl	243.3	159	353.6	11.160
Br	249	179	398	11.515
I	240.5	186	413.4	11.085

Several mechanisms may be considered for the equilibration of protons or fluorine atoms in these complexes[296] but only two seem probable. (1) Exchange of acetylene molecules by a dissociative mechanism, by a bimolecular mechanism without dissociation of acetylenes or by an intramolecular mechanism. (2) Rapid rotation of the acetylene molecules about the metal acetylene axes. In a series of elegant experiments Cramer was able to show that the latter mechanism accounts for proton equilibration in a variety of ethylene and monofluoroethylene complexes of rhodium.[141,296] Propeller rotation of ethylene in platinum complexes has subsequently been detected by Lewis[297] and recently rotation of coordinated acetylene molecules has also been described.[298,299] However, when all the protons of ethylene are replaced by fluorine the increased M-C back-donation appears to stabilise one particular olefin conformation and no rotation of coordinated tetrafluoroethylene was observed in the complex, $CpRh(C_2H_4)(C_2F_4)$, even at 100°C.[141] Since in the complexes $CpMo(RC_2R)_2X$, X = Br, I, the ΔG_c and k_c values for the rate of exchange of coordinated hexafluorobut-2-yne and but-2-yne imply a greater degree of mobility for the former, it would appear that the n.m.r. data of these complexes is unlikely to be accounted for by propeller rotation.

Fluxional behaviour in the sixteen electron complex $(acac)Rh(C_2H_4)_2$ is considered to be due to a bimolecular exchange mechanism and exchange between free and coordinated ethylene occurs even at -58°C.[296] However, addition of varying amounts of free but-2-yne to a CD_2Cl_2 solution of $CpMo(CH_3C_2CH_3)_2I$ produced no effect on the spectrum above or below the coalescence temperature, which was also unaffected. The coalescence temperatures also appear to be independent of complex concentration, and on this evidence it is concluded that the variable temperature n.m.r. spectra of the complexes $CpMo(RC_2R)_2X$ can be best reconciled with an intramolecular exchange process involving the coordinated acetylene ligands. An exchange reaction of this type probably proceeds <u>via</u> a square planar intermediate considering the cyclopentadienyl group to occupy one of the corners of the square. As can be seen this process can proceed by two different routes, depending on whether an acetylene or halogen atom is <u>trans</u> to the cyclopentadienyl ligand in the transition state, (Fig. 4.2.).

However, it is impossible to decide which of these two mechanisms is responsible for CH_3 or CF_3 equilibration from the limited data available, although speculative attempts have been made with related systems.[211] It is significant that the orders of ΔG_c values calculated for both but-2-yne and hexafluorobut-2-yne complexes follow a similar trend with a maximum occurring at the bromo derivative in each

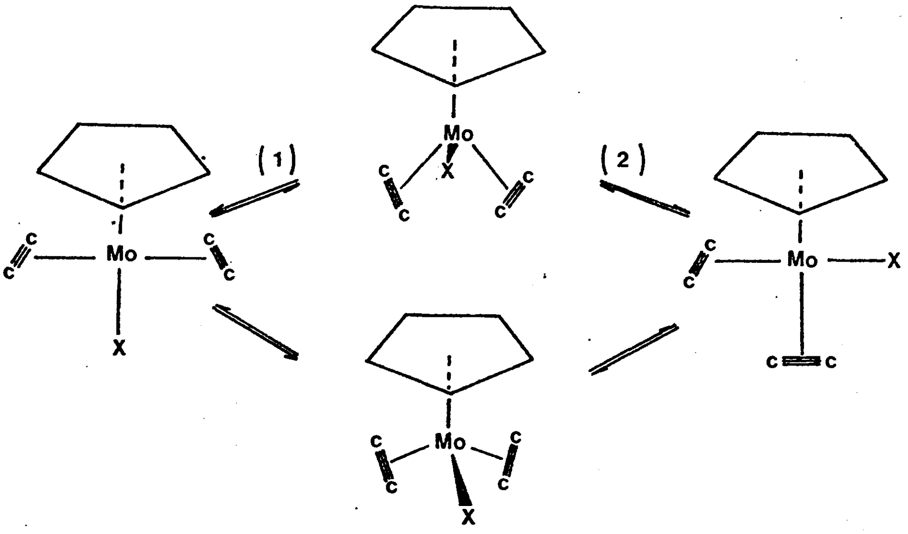


Fig. 4.2.

case. It was suggested earlier that both steric and electronic factors may affect the conformation of the acetylenes in the low temperature form of the complexes and the observed trend would seem to imply that they also influence the thermodynamics of the exchange reaction. Since the trend is not uniform, i.e. does not follow the increasing size or electronegativity of the halogen, it would appear that these factors have opposite effects on the ΔG_c values.

Although ΔG_c for both sets of complexes follows the same trend it is noticeable that the values for the but-2-yne derivatives vary by over 3 k.cal/mol whereas those of the hexafluorobut-2-yne complexes are all within 0.3 k.cal/mol of 11.25 k.cal/mol. The significance of this difference is not immediately apparent but it is obvious that the nature of the halogen affects the thermodynamics of the equilibration reaction of the but-2-yne complex to a much greater extent. This could be compatible with the exchange process for $CpMo(CH_3C_2CH_3)_2X$ following a different pathway to that of $CpMo(CF_3C_2CF_3)_2X$, (Fig. 4.2.), but differences in the metal-acetylene bond type prevent this from being anything more than speculation.

Another difference between the but-2-yne and hexafluorobut-2-yne complexes is the rate of exchange, k_c, which is much greater with the latter, again implying differences in the equilibration mechanism. This is further suggested by the different trends in the value of k_c which, with the but-2-yne derivatives, decreases in the order Cl > Br > I whereas with the hexafluorobut-2-yne compounds k_c increases in this order.

Reactions of PhC≡CPh and $CpMo(CO)_3X$, X = Cl, Br, I

The tricarbonyls $CpMo(CO)_3X$, X = Cl, Br, reacted with diphenylacetylene in pentane at temperatures below 50°C to give high yields of the green solids $CpMo(CO)(PhC_2Ph)X$. The bromo derivative, as might be expected, reacted more slowly since not only are the M-CO bonds stronger (lower νCO frequencies), but the bromine atom, being more bulky, probably inhibits the reaction through steric interaction with PhC≡CPh. Attempts to obtain the analogous iodo derivative $CpMo(CO)(PhC_2Ph)I$, by a thermal reaction were unsuccessful due to further reaction with the acetylene to give $CpMoCO(PhC)_4I$ at the higher temperature (~70°), required for a reaction to take place. Traces of a green solid were detected during this reaction and it was subsequently found that the photolytic reaction proceeded rapidly to give high yields of the required product, $CpMo(CO)(PhC_2Ph)I$. As with $CpMo(RCCR)_2X$, solution studies and mass spectroscopy indicate a monomeric structure and again the molybdenum atom is assigned a sixteen electron configuration. Solution i.r. spectra of the complexes could not be obtained due to their instability in CCl_4 and $CHCl_3$, solvents in which they are soluble. However, K Br discs of the compounds reveal a single C-O stretching mode near 2000 cm^{-1}, but as with $CpMo(CO)_2(PhC_2Ph)SCF_3$ it was not possible to detect the C≡C stretching mode of the coordinated acetylene, and the extent to which the triple bond is modified on coordination remains unknown. The proton n.m.r. gives a single sharp

Table 4.4.

I.r. Spectra of Complexes CpMo(CO)(PhC$_2$Ph)X* (cm^{-1})

X	νCH	νCO	Others
Cl	3129w, 3118w, 3097w 3048vw	1964vs, 1912w	1444wm, 1441wm, 1426wm, 1072w, 1068w, 1012w, 1005w, 920w, 910w, 831m, 814wm, 794m, 977m, 767m, 753w, 707m, 696wm, 687m
Br	3120w, 3102w, 3086w 3045vw	1963vs, 1911w	1439wm, 1436wm, 1421wm, 1068w, 920wmb, 832m, 818wm, 797m, 779m, 769m, 756wm, 709m, 698wm, 689m
I	3118w, 3100w, 3070w 3040w	1964vs, 1914w	1440wm, 1436wm, 1422wm, 1068wm, 1020w, 1004w, 950w, 916w, 833m, 820wm, 800m, 778m, 770m, 760w, 708m, 696m, 690m.

* K Br disc

peak at 4.30τ due to the cyclopentadienyl group and the chemical shift is again invariant to the halogen. In addition a broad resonance near 2.4τ is present in each case due to the phenyl protons, and although of limited usefulness as a structural probe, differences were observed with different halogens. With the chloro and bromo complexes the fine structure was fairly symmetric while the iodo derivative exhibited a grossly distorted signal, suggesting structural differences.

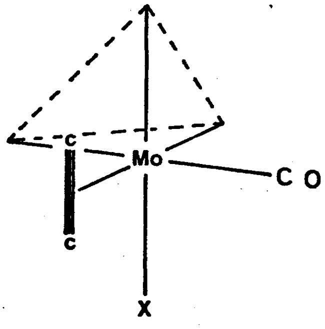
A structure based on that proposed for CpMo(RC$_2$R)$_2$X can be envisaged with a carbonyl group replacing an acetylene ligand on one

Table 4.5.

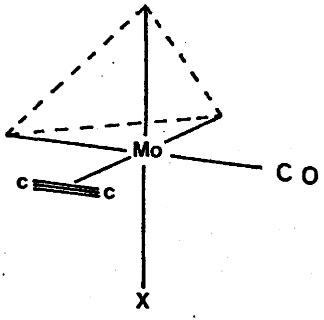
^1H n.m.r. Parameters of Complexes $CpMo(CO)(PhC_2Ph)X$

Compound	δ Cp	δ (Ph) 34°C
X = Cl	2.42	4.30
Br	2.40	4.30
I	2.43	4.30

of the octahedral sites as in $CpCr(CO)(NO)(HC_2H)$.[298] As with these complexes isomerism is possible due to different conformations available to the acetylene but the most stable structure is probably that in which greatest π donation from metal to acetylene occurs. On the basis that CO is a strong π acceptor and halogens are if anything π donors[300] isomer (a) is the more stable. However, in this conformation steric repulsion will be greater between the bulky C_6H_5 group and the halogen which, although perhaps insignificant in the chloro and bromo derivatives, may be sufficient to destabilise the iodo complex with respect to isomer (b). This could account for the differences in the appearance of the phenyl proton resonances already described, although an alternative explanation assumes that rotation of the acetylene can occur in the chloro and bromo complexes giving a time averaged symmetrical spectrum. In the iodo derivative



(a)

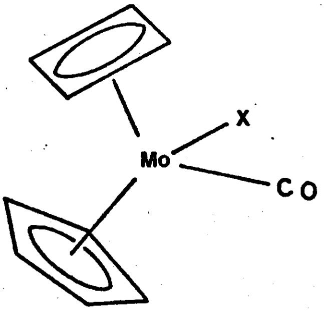


(b)

greater steric crowding may freeze out one or both rotational isomers, giving rise to the observed asymmetry in the phenyl resonances.

As mentioned earlier at temperatures above 70°C, $CpMo(CO)_3I$ reacts with diphenylacetylene to give $CpMo(CO)(PhC)_4I$, and the related chloro and bromo complexes were subsequently obtained from the appropriate tricarbonyl derivative. The reactions involve the monocarbonyls, $CpMo(CO)(PhC_2Ph)X$, as intermediates and as in the formation of the latter, the reaction is successively slower on going from chloro to bromo to the iodo complex. Purification was achieved by recrystallisation from benzene or CH_2Cl_2 but with the latter the complexes crystallise with a solvent molecule of crystallisation.

The complexes $CpMo(CO)(PhC)_4X$, X = Cl, Br, are identical to the tetraphenylcyclobutadiene derivatives of this stoichiometry isolated in low yield from the reactions of $[CpMo(CO)_3]_2$ with the tetraphenylcyclobutadiene compounds $(PhC)_4PdX_2$,[301] X = Cl, Br. All the spectral features are consistent with the structure proposed for these complexes and there seems no reason to formulate alternatives for the iodo compound.



(phenyl groups omitted)

Table 4.6.

I.r. Spectra of Complexes $CpMo(CO)(PhC)_4X$, CH_2Cl_2* (cm^{-1})			
X	νCH	νCO	Others
Cl	3114w, 3088w, 3058w, 3024w	1960vs, 1915w	1596wm, 1571w, 1524w, 1497m, 1451w, 1441wm, 1414w, 1273w, 1066w, 1026w, 995w, 925wm, 780w, 770wm, 730, 691m, 616w
Br	3110w, 3080w 3058w, 3025w	1960vs, 1915	1594wm, 1570w, 1520w, 1495m, 1439wm, 1410w, 1269w, 1064w, 1022w, 1014w, 995w, 909w, 821wm, 771w, 729m, 690m, 618w
I	3110w, 3080w, 3059w, 3022w	1965vs, 1920w	1598m, 1572w, 1573w, 1498m, 1451w, 1441wm, 1413w, 1269w, 1066wm, 1026wm, 1015w, 990w, 909w, 821wm, 780w, 769m, 728m, 690m, 612w

* K Br disc

In the proton n.m.r. at 34°C the phenyl proton resonance in each case appears as a broad peak near 2.8τ but on cooling to -60°C the signal splits to give the spectrum shown in Fig. 4.2. and this is considered to be due to freezing out of preferred conformation(s) at low temperature. At room temperature the tetraphenylcyclobutadiene ring is probably rotating rapidly in a manner similar to π-cyclopentadienyl ligands but the bulky phenyl substituents of the former must contribute to a much higher energy barrier to rotation. Thus at -60°C the rotation has stopped and the phenyl substituents on the ring are no longer magnetically equivalent. These observations could also be explained by a polytopal rearrangement similar to that

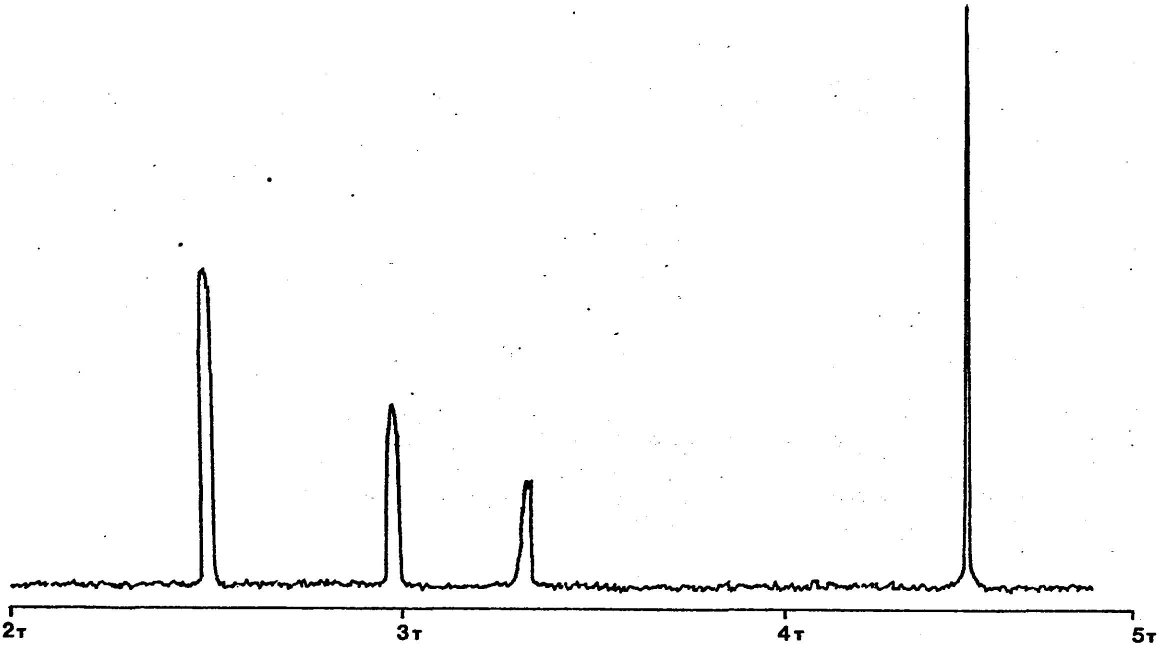


Fig. 4.3.

discussed for CpMo(CO)[$(CF_3C_2H)_2CO$]SCF_3, but the appearance of only one phenyl resonance at 34°C seems more compatible with restricted rotation of the cyclobutadiene.

Table 4.7.

^1H N.m.r. Parameters of Complexes CpMo(CO)$(PhC)_4X$*

X	δCp	δPh (34°C)	δPh (-60°C)		
Cl	4.50	2.80	2.54	2.97	3.35
Br	4.50	2.80	2.55	2.98	3.35
I	4.50	2.80	2.43	2.86	3.19

* CD_2Cl_2 solution

Photolysis of $CpMo(CF_3C_2CF_3)_2Cl$

It was noted in the introduction that no complex has yet been isolated containing a tetrakis(trifluoromethyl)cyclobutadiene ligand and it was suggested that, since metalocyclopentadiene rings are frequently the precursors to cyclobutadiene ligands, the stability of M-C σ bonds when electronegative substituents are attached to carbon may prevent the required σ - π rearrangements in such cases. This effect was also discussed with respect to the structure of the six membered ring in $[C_5H_5NiC_2(CF_3)_2]_4$. The isolation of complexes $CpMo(CF_3C_2CF_3)_2X$ in which two coordinated acetylenes have not undergone condensation to a metalocyclopentadiene ring, therefore provided an opportunity to attempt syntheses of complexes containing a π-bonded $C_4(CF_3)_4$ ligand. Although incomplete the brief studies which were carried out suggest that the above comments may be at least partially correct.

$CpMo(CF_3C_2CF_3)_2Cl$ when irradiated in pentane with u/v light for 24 hr. gave dark-red insoluble crystals and traces of a very unstable, pentane soluble compound, which was not characterised. Due to the small quantity of red crystals obtained only partial characterisation was possible and only i.r. and mass spectra were obtained. The crystals are insoluble in all common solvents suggesting a polymeric nature but in the mass spectrum the highest peak is observed at m/e 716, corresponding possibly to $[CpMo(CF_3C_2CF_3)Cl]_2^+$ and in accord with this a double molybdenum isotope pattern is observed, having taken into account the chlorine isotopes. The i.r. spectrum (K Br disc), gives bands between 1500 cm^{-1} and 1600 cm^{-1} suggesting bridging acetylenes, while strong, broad νCF modes are present near 1200 cm^{-1}. It would appear, on this evidence, that the compound possibly contains acetylenes bridging two molybdenum atoms which are linked to other dimeric units by chlorine bridges.

If the highest peak in the mass spectrum is the molecular ion for the dimeric species, irradiation of $CpMo(CF_3C_2CF_3)_2Cl$ must result in loss of one molecule of acetylene per molecule of complex and the experiment was therefore repeated in the presence of $CF_3C{\equiv}CCF_3$, in an attempt to prevent this. This reaction proved to be somewhat irreproducible but the first experiment carried out gave, after prolonged irradiation, a mixture of starting material and a second fluorocarbon complex (X), which could not be separated completely due to the similarity in physical properties of the two compounds. However, a small sample of almost pure X was obtained by repeated sublimation and recrystallisation from CH_2Cl_2/hexane and this enabled i.r. and mass spectra to be obtained.

The former indicates that no coordinated acetylenes or uncoordinated olefinic bonds are present, the region 2000 cm^{-1} to 1500 cm^{-1} being free from νC-C bands. The CF stretching region is somewhat less complex than in the spectrum of $CpMo(CF_3C_2CF_3)_2Cl$ and contains three strong bands close together, as found with $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ and $CpCo[C_4(CF_3)_4CO]$.

Table 4.8.

I.r. Spectra (cm^{-1})

	νCH	νC≡C	νCF
$[CpMo(CF_3C_2CF_3)Cl]_n$ *	3120w	1550w, 1521wm	1275m, 1180s, 1167s, 1118s, 1105s
$CpMoC_4(CF_3)_4Cl$ †	3120w	=	1227m, 1211vs, 1192s 1184ssh, 1167msh, 1146m, 1109wm

* K Br disc † CCl_4

The mass spectrum of the complex gives an ion of highest m/e at 520 with a single molybdenum isotope pattern, corresponding to the molecular ion of the starting material $CpMo(CF_3C_2CF_3)_2Cl$. This suggests that the new complex and the latter have identical stoichiometries but the relative intensities of the ions shown in Table 4.9. indicate different structures.

Table 4.9.

		$CpMo(CF_3C_2CF_3)_2Cl$	X
m/e	Ion	% Abundance	% Abundance
520	$CpMoC_8F_{12}Cl$	0.2	23
501	$CpMoC_8F_{11}Cl$	0.25	10
482	$CpMoC_8F_{10}Cl$	0.6	1.3
451	$CpMoC_7F_9Cl$	0.5	1
358	$CpMoC_4F_6Cl$	2.9	17.5
386	C_8F_{10}	4	1.5
267	C_8F_9	6.6	5
234	$CpMoF_2Cl$	0	15
215	CpMoFCl	40	100
196	CpMoCl	100	50

It can be seen that significant differences are observed in the relative abundances of some ions in the spectra of the two compounds. Weak ions corresponding to $[C_8F_{10}]^+$ and $[C_8F_9]^+$ are observed in both spectra suggesting that a ligand $C_4(CF_3)_4$ is at least formed in the mass spectrometer, although spectroscopic data precludes the existence of such a ligand in $CpMo(CF_3C_2CF_3)_2Cl$. Particularly significant are the relative abundances of the ion $[M-(CF_3C_2CF_3)]^+$, $(M = CpMoC_8F_{12}Cl)$, which is fairly weak in the spectrum of X but strong in the spectrum of $CpMo(CF_3C_2CF_3)_2Cl$. This could be reconciled with the presence of a distinct tetrakis(trifluoromethyl)cyclobutadiene ligand in X although the lack of an ion due to the complete ligand suggests that it must fragment fairly easily when removed from the complex.

The proton n.m.r. of the less pure sample of X shows two sharp singlets near 4τ,* the weaker of which corresponds to $CpMo(CF_3C_2CF_3)_2Cl$. The singlet due to the latter is also observed in the ^{19}F n.m.r. spectrum in addition to two multiplets of equal intensity (δ_1 = 52.14 ppm, δ_2 = 53.97 ppm), which can be assigned to two sets of two CF_3 groups. The fine structure of the peaks, which are due to X, is virtually identical to that of $CpCo[C_4(CF_3)_4CO]$ and similar complexes in which a cyclic butadiene fragment, $C_4(CF_3)_4$, is present giving rise to two sets of non-equivalent CF_3 groups.

On this evidence it is tentatively suggested that complex X is the sought for tetrakis(trifluoromethyl)cyclobutadiene compound $CpMo[C_4(CF_3)_4]Cl$, although, to account for the non-equivalence of the CF_3 substituents, the C_4 ring must be considered to have a fixed conformation at room temperature in contrast to the situation found in $CpMo(CO)(PhC)_4X$ where steric interactions appear to be greater. This apparent contradiction may be explained by a greater barrier to rotation of the $C_4(CF_3)_4$ ring being induced by strong M-C back-donation. To achieve maximum overlap of the π^* orbitals of the C_4 ring with the d orbitals of the metal a conformation related to that of the acetylenes in the complex $CpMo(CF_3C_2CF_3)_2Cl$ seems most probable, giving the following structure illustrated overleaf.

Miscellaneous Reactions

Several attempts were made to prepare mixed acetylene complexes by reacting $CpMo(CO)(PhC_2Ph)X$ with $CH_3C{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$ but only

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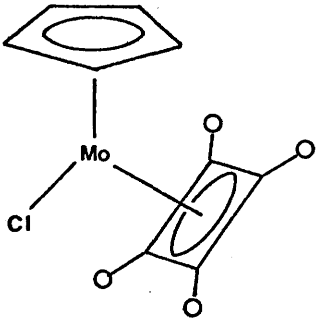
* δ Cp(X) = 4.02τ



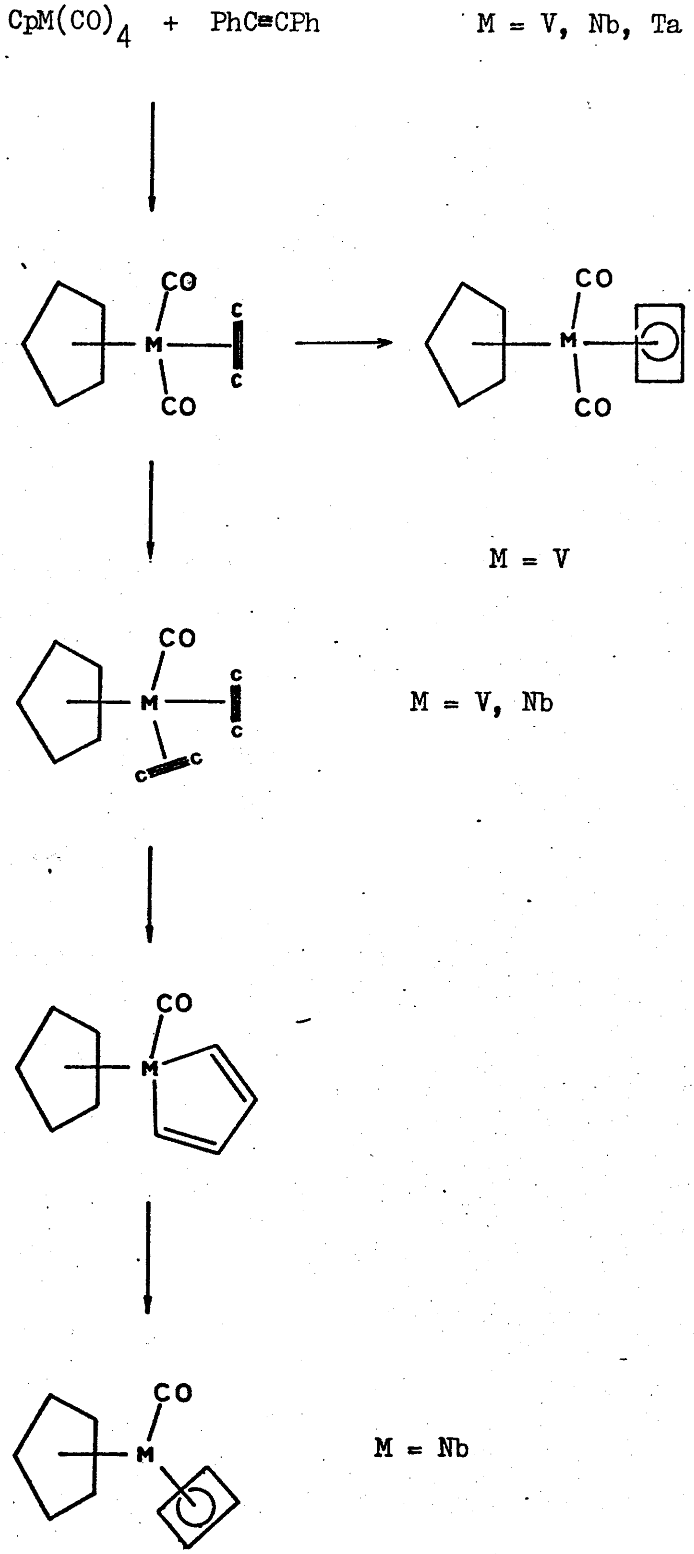
$CpMo(CH_3C_2CH_3)_2X$ and $CpMo(CF_3C_2CF_3)_2X$ were isolated respectively. Similarly the reaction of $CpMo(CH_3C_2CH_3)_2Cl$ and $CF_3C{\equiv}CCF_3$ gave only $CpMo(CF_3C_2CF_3)_2Cl$. Although unsuccessful in certain respects these reactions are of some synthetic value since the products $CpMo(RC_2R)_2X$ were generally obtained in higher yield and with shorter reaction times than from the tricarbonyls $CpMo(CO)_3X$.

Conclusions

It is apparent from the results described that the reactions of complexes $CpMo(CO)_3X$, (X = alkyl group, halogen, SCF_3,) and acetylenes are sensitive to the nature of X and the substituents on the acetylene. However, with X = halogen only slight effects are observed on varying the halogen from Cl to I, the reactions becoming less facile in accord with stronger M-CO bonding and increased steric repulsion between X and the incoming acetylene.

Since $CH_3C{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$ both yielded complexes of stoichiometry $CpMo(RC_2R)_2X$ the electronegativity of the substituent R appears to be relatively unimportant but the formation of $CpMo(CO)(PhC_2Ph)X$ suggests that steric factors may influence the reaction. Since a monocarbonyl species was detected in the reaction of $CpMo(CO)_3I$ and $CF_3C{\equiv}CCF_3$, it is interesting to speculate that complexes $CpMo(CO)(RC_2R)X$ may be unstable intermediates in reactions which give compounds $CpMo(RC_2R)_2X$, $R = CH_3$, CF_3. However, coordination of a second acetylene molecule must lead to CO expulsion whereas with diphenylacetylene the carbonyl ligand is retained and condensation of two molecules of PhC≡CPh occurs. Condensation of acetylenes to form four membered rings appears to occur most readily with diphenylacetylene[191] whereas with $CH_3C{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$ inclusion of coordinated carbon monoxide usually occurs to give cyclopentadienone compounds.[129,152] In addition, but-2-yne sometimes forms quinone derivatives[129,152] and the formation of tetramethylquinone in the reactions of $CpMo(CO)_3X$ and $CH_3C{\equiv}CCH_3$ probably results from thermal decomposition of an unstable complex of this ligand. However, it is interesting to note that the reactions of $CpMo(CO)_3X$ and $CF_3C{\equiv}CCF_3$ did not give tetrakis(trifluoromethyl)quinone,in spite of the reactivity of this acetylene towards coordinated carbon monoxide discussed in Chapter II.

The reaction of $CpMo(CO)_3X$ and PhC≡CPh in some ways parallels the reaction of this acetylene with $CpCo(PPh_3)I_2$ which gives initially $CpCo(PPh_3)(PhC_2Ph)$ containing a coordinated acetylene ligand.[194] Further reaction with a second molecule of the acetylene gives the tetraphenylcyclobutadiene complex $CpCo(PhC)_4$ and it was shown that this is formed <u>via</u> a metalocyclopentadiene intermediate,$CpCo(PPh_3)(PhC_2Ph)_2$. This suggests that $CpMo(CO)(PhC)_4X$ may be produced from $CpMo(CO)(PhC_2Ph)X$ <u>via</u> a related complex $CpMo(CO)(PhC_2Ph)_2X$,the vacant orbital on the sixteen electron complex perhaps facilitating coordination of a second molecule of the acetylene . Support for such a mechanism is obtained from the reactions of $CpM(CO)_4$, M = V, Nb, Ta,and PhC≡CPh described by Nesmeyanov.[177,178] The following reaction schemes have been elucidated and comparison with the reactions of $CpMo(CO)_3X$ and PhC≡CPh is perhaps informative.


CpM(CO)$_4$ + PhC≡CPh
M = V, Nb, Ta
CO
M
C
C
CO
CO
M
CO
M = V
CO
M
C
C
C
C
M = V, Nb
CO
M
CO
M
M = Nb

CHAPTER V

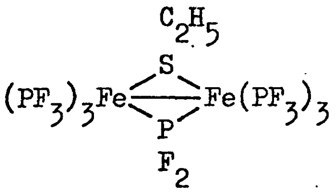
REACTIONS OF ACETYLENES
WITH SOME
TRANSITION METAL TRIFLUOROPHOSPHINE COMPLEXES

INTRODUCTION

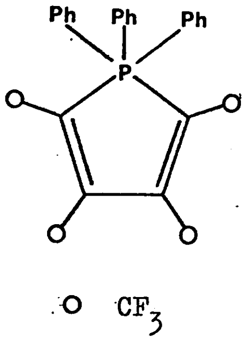
The bonding in transition-metal carbonyl complexes which, until recently, have held a unique place in coordination chemistry, has been of interest ever since the first known derivative $Ni(CO)_4$,was discovered by Mond.[302] The bonding in simple terms has been described as (i) a σ bond contribution from the lone-pair on the carbon atom into suitable empty orbitals of the metal and (ii) d – p π-bonding which involves back-donation of electron density from filled dπ-orbitals of the metal into the empty π^* orbitals of the CO ligand, such a system operating synergically.[223]

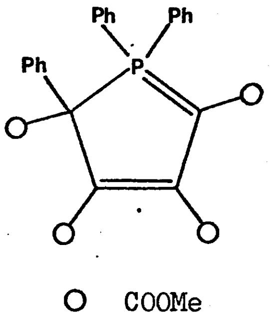
Chatt's work on $[PtCl_2PF_3]_2$[303] and the synthesis of $Ni(PF_3)_4$ in 1951 by Wilkinson,[304] subsequently focussed attention on the coordinating properties of trifluorophosphine, PF_3. Since then the transition metal chemistry of this ligand has expanded rapidly, particularly in the past ten years, and the ability of PF_3 to stabilise low oxidation states of metals in a manner similar to carbon monoxide has attracted much interest, both from the synthetic and the theoretical chemist.[305,306] The presence of highly electronegative fluorine atoms in PF_3 significantly lowers the ability of phosphorus to donate its lone pair to an acceptor atom and simultaneously increases its ability to accept metal dπ electrons into empty d orbitals. The importance of π-bonding in phosphine complexes of the transition metals in their usual oxidation states has recently been questioned and the soft character of phosphine ligands attributed to σ-bonding effects.[307] It is however, generally considered that these conclusions are less likely to be valid with trifluorophosphine derivatives of low and zero-valent transition metals such as $Ni(PF_3)_4$ and $Fe(PF_3)_5$.[308] Evidence for double-bond character in the metal-phosphorus bond of PF_3 complexes has been obtained from i.r. and photoelectron spectroscopy , electron diffraction and X-ray crystallographic studies.[305,306]

Physically and chemically the similarity between metal carbonyls and their PF_3 analogues is striking and PF_3 readily substitutes many, if not all the carbonyl groups in carbonyl complexes, being almost unique in this respect.[306] Recent reports indicate that PF_3 complexes react with a variety of ligands in a manner similar to their carbonyl analogues. Hydrides $HM(PF_3)_4$, M = Co, Rh, and $H_2M(PF_3)_4$, M = Fe, Ru, Os, have been prepared which prove to be more stable than the corresponding carbonyls.[305] Oxidative addition of halides and pseudohalides to PF_3 complexes has been observed[309] and neutral organic ligands displace PF_3 to give complexes similar to known carbonyl derivatives.[305, 306,310] However, differences are observed when the ligand is also capable of reacting with the P-F bonds and the reaction of $Fe(PF_3)_5$ and C_2H_5SH results in HF elimination to give the hetero-bridged complex



Since many interesting and unusual reactions have been observed between transition metal carbonyls and acetylenes it was considered that similar reactions might be obtained by reacting acetylenes with trifluorophosphine complexes. Of particular interest is the formation of phosphorus heterocycles in a manner similar to that which produces cyclopentadienone, quinone and tropone derivatives from metal carbonyl compounds. This would possibly require oxidation of phosphorus III to phosphorus V. In this context it has recently been reported that the cyclic phosphorane $[C_4(CF_3)_4PPh_3]$ is produced in the reaction of $CpRu(PPh_3)_2H$ with hexafluorobut-2-yne[163] while the direct reaction of triphenylphosphine and dimethyl acetylenedicarboxylate gives a different type of heterocycle, $[C_4(COOMe)_4PhPPh_2]$, in which migration of a phenyl group from phosphorus to carbon has occurred.[312] This suggests that

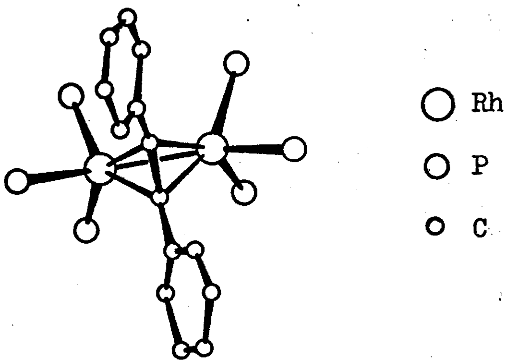




heterocycles of phosphorus V are most likely to be obtained from acetylenes bearing electronegative substituents which is not unexpected in view of the well known ability of such groups, e.g. F, CF_3, to stabilise high oxidation states.

During the course of this work Whimp et al. reported that the reactions of acetylenes and $Rh_2(PF_3)_8$ give complexes $Rh_2(PF_3)_6RC_2R$.[312] An X-ray study of the substituted diphenylacetylene derivative $Rh_2(PF_3)_4(PPh_3)_2PhC_2Ph$ has revealed an acetylene bridged structure, (i) analogous to $Co_2(CO)_6PhC_2Ph$. However, no reactions of PF_3 complexes with acetylenes have yet been reported in which oxidative addition of the acetylene(s) to the phosphorus occurs.

(substituents on phosphorus omitted for clarity)



(i)

SUMMARY OF REACTIONS

(1) $\mathrm{Ni(PF_3)_4 + CF_3C{\equiv}CCF_3 \longrightarrow C_6(CF_3)_6 + Ni_3C_3F_5 + PF_3}$

(2) $\mathrm{CpCo(PF_3)_2 + CF_3C{\equiv}CCF_3 \longrightarrow CpCo[C_4(CF_3)_4PF_3]}$

(3) $\mathrm{CpCo[C_4(CF_3)_4PF_3] \xrightarrow{H_2O} CpCo[C_4(CF_3)_4POF]}$

(4) $\mathrm{CpCo[C_4(CF_3)_4POF] \xrightarrow{H_2O} CpCo[C_4(CF_3)_4PO_2H]}$

(5) $\mathrm{CpCo(PF_3)_2 + RC{\equiv}CR \longrightarrow}$ no reaction

$\mathrm{R = CH_3,\ Ph}$

(6) $\mathrm{CpRh(PF_3)_2 + CF_3C{\equiv}CCF_3 \longrightarrow}$ no reaction

RESULTS AND DISCUSSION

Reactions of RC≡CR, R = Ph, CF_3, with $Ni(PF_3)_4$.

Attempts to obtain an acetylene derivative of $Ni(PF_3)_4$ by the reaction of the latter with the acetylenes hexafluorobut-2-yne and diphenylacetylene, under a variety of conditions, were unsuccessful. In general few acetylene derivatives of the corresponding carbonyl complex $Ni(CO)_4$ are known, although the reaction of this complex with PhC≡CPh at 110°C has been reported to give the bistetraphenylcyclopentadienone derivative, $[(PhC)_4CO]_2Ni$, in 50% yield.[313] However, no complex was isolated from the reaction of $Ni(PF_3)_4$ and PhC≡CPh at 80°C, the only products being insoluble organic material which was not investigated further.

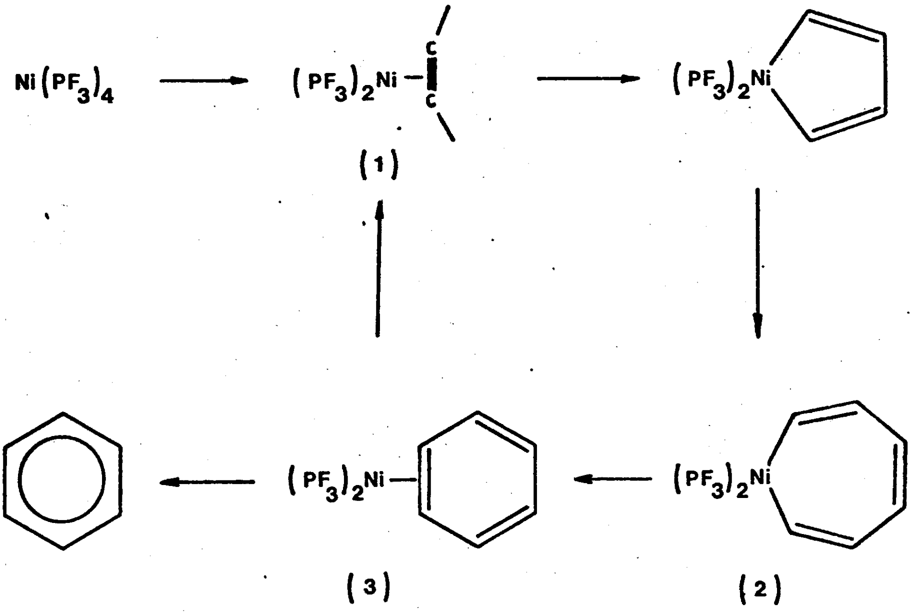
A consideration of the electronic structure of $Ni(CO)_4$ and of the mechanism of its ligand-exchange reactions led to the suggestion that only olefins and acetylenes which permit extensive metal-ligand back-bonding, either by having electron withdrawing substituents or low-lying unoccupied molecular-orbitals, will be able to form stable π-complexes with $Ni(CO)_4$.[314] The validity of this suggestion was subsequently demonstrated by the reaction of $Ni(CO)_4$ and hexafluorobut-2-yne which yielded $Ni_4(CO)_3(CF_3C_2CF_3)_3$, and a structure has been proposed based on a trigonal pyramidal array of nickel atoms, the coordinated acetylenes retaining their identity.[315]

The reaction of $Ni(PF_3)_4$ and $CF_3C{\equiv}CCF_3$, in contrast, does not yield an analogous complex. With a large excess of alkyne, at temperatures above 50°C, $Ni(PF_3)_4$ reacts to produce reasonable yields of the cyclic trimer, hexakis(trifluoromethyl)benzene, and a pale yellow insoluble powder which analyses as $Ni_3C_3F_5$. The presence of broad C-F stretching modes in the i.r. spectrum near 1200 cm^{-1} suggests the latter is probably a mixture of a nickel compound and a linear polymer, perhaps $[C_2(CF_3)_2]_n$.

With 1:1 acetylene/$Ni(PF_3)_4$ molar ratio deep blue-purple and green solutions were observed after short reaction times, possibly due to complex formation, but on removal of reactants these colours disappeared and no complex could be isolated.

The formation of the trimer of hexafluorobut-2-yne in this reaction is not surprising in view of the well-known catalytic activity of zero-valent nickel complexes in the trimerisation of $CF_3C{\equiv}CCF_3$ and other acetylenes to substituted benzenes.[180,250,251] With many such catalytic reactions decomposition of the nickel complex is frequently observed[316] and the reaction of $Ni(PF_3)_4$ and $CF_3C{\equiv}CCF_3$ is no exception since, particularly with high temperatures and long reaction times, small amounts of PF_3 were detected.

A mechanism involving a cyclobutadiene intermediate has been proposed for the cyclooligomerisation of disubstituted acetylenes by $Ni(CO)_2(PPh_3)_2$,[139b,316] but in the present case, the following mechanism is considered more probable.



Isolation of phosphine complexes analogous to intermediates(1) by Maitlis,[137] and (2) and (3) by Stone,[250,251] supports such a mechanism. The stability of the dihapto complexes (3) has been found to depend on the π-acceptor ability of the phosphine, being lower with derivatives of strong π-acids like $P(OMe)_3$. It was also found that attempted displacement of phosphines with carbon monoxide resulted in decomposition of the complexes with release of the benzene. It seems probable that the high π-acceptor ability of PF_3 destabilises $(PF_3)_2NiC_6(CF_3)_6$, (3), to the extent that it cannot be isolated, but as with $Ni[C_6(CF_3)_6][P(OMe)_3]_2$, reaction with $CF_3C{\equiv}CCF_3$ can occur to give $L_2NiC_6(CF_3)_6$, (2), with release of the hexa-substituted benzene.[250] Thus the L_2Ni fragment effectively catalyses the cyclotrimerisation of hexafluorobut-2-yne.

Reaction of RC≡CR, R = CF_3, Ph, with $CpM(PF_3)_2$, M = Co, Rh.

$CpCo(PF_3)_2$ has been prepared previously from cobaltocene and PF_3 at 170°C/350 atm.[305] However, reasonable yields of this complex were obtained by irradiating pentane solutions of $CpCo(CO)_2$ and PF_3, (10 atm), the evolved carbon monoxide being removed at intervals. To prepare substantial quantities by this method is rather tedious, very long irradiation times being required, (6-9 months).

The reaction of $CpCo(PF_3)_2$ and $CF_3C{\equiv}CCF_3$ at 20°C, in pentane, gave good yields of a yellow solid which was shown to be $CpCo[C_4(CF_3)_4POF]$, indicating that hydrolysis must occur during the reaction. This complex proved to be susceptible to further hydrolysis in the presence of moist air, or on refluxing in aqueous acetone solution, giving a second yellow solid, $CpCo[C_4(CF_3)_4PO_2H]$, the X-ray structure of which has been solved by Prof. G. Sim and Dr. M.J. Barrow. Orange crystals of the complex were obtained by slow crystallisation from Analar acetone.

X-ray Structure of $CpCo[C_4(CF_3)_4PO_2H]$

The complex crystallises in the space group $P2_12_12_1$, $Z = 4$, Dc = 2.05. Orthorhombic : $a = 9.353(7)$, $b = 9.893(7)$, $c = 17.923(10)$Å. Diffractometer data : (Mo-K_α radiation); current, R = 6.3% for 1918 reflections with $I > 3\sigma(I)$.

The molecular structure of the complex is illustrated in Figs. 5.1., 5.2. and 5.3.

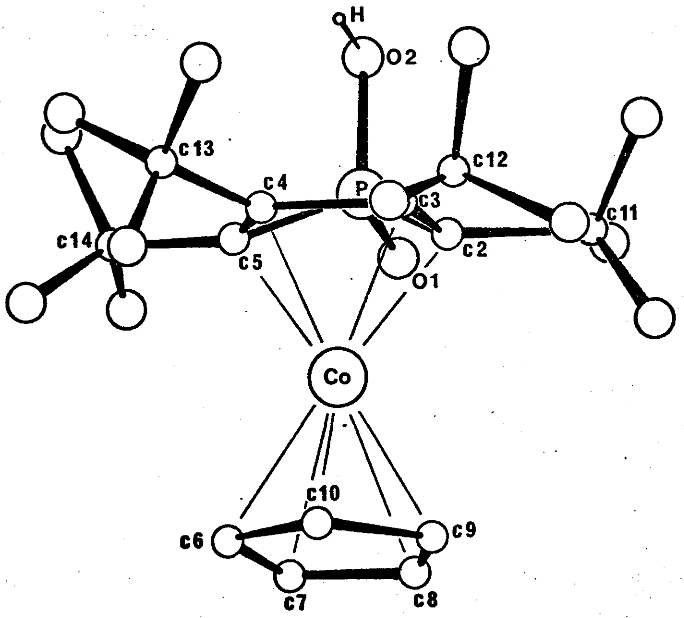


Fig. 5.1.

Table 5.1.

Intramolecular Bond Distances and Angles

(A) Bond Distances (Å)

Co - P	2.730	Co - C(6)	2.026
Co - C(2)	2.040	Co - C(7)	2.051
Co - C(3)	1.962	Co - C(8)	2.035
Co - C(4)	1.961	Co - C(9)	2.016
Co - C(5)	2.036	Co - C(10)	2.039
C(2) - C(3)	1.434	C(3) - C(4)	1.418
C(4) - C(5)	1.436		
P - C(2)	1.768	P - C(5)	1.764
P - O(1)	1.492	P - O(2)	1.545
C(2) - C(11)	1.503	C(3) - C(12)	1.499
C(4) - C(13)	1.491	C(5) - C(14)	1.505
C(6) - C(7)	1.373	C(7) - C(8)	1.349
C(8) - C(9)	1.406	C(9) - C(10)	1.389
C(10) - C(6)	1.390		

(B) Bond Angles (degrees)

C(2) - C(3) - C(4)	110.710	C(3) - C(4) - C(5)	110.11
P - C(2) - C(3)	109.62	P - C(5) - C(4)	110.02
C(5) - P - C(2)	86.45	O(1) - P - O(2)	109.33
C(5) - P - O(1)	117.54	C(5) - P - O(2)	113.23
C(2) - P - O(1)	116.58	C(2) - P - O(2)	112.24

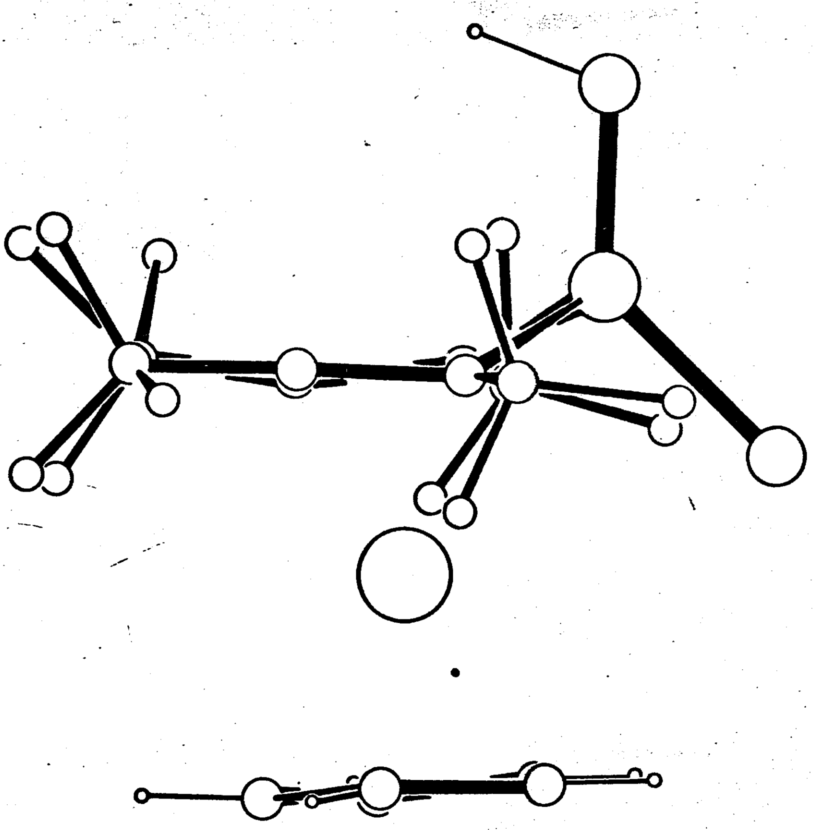


Fig. 5.2

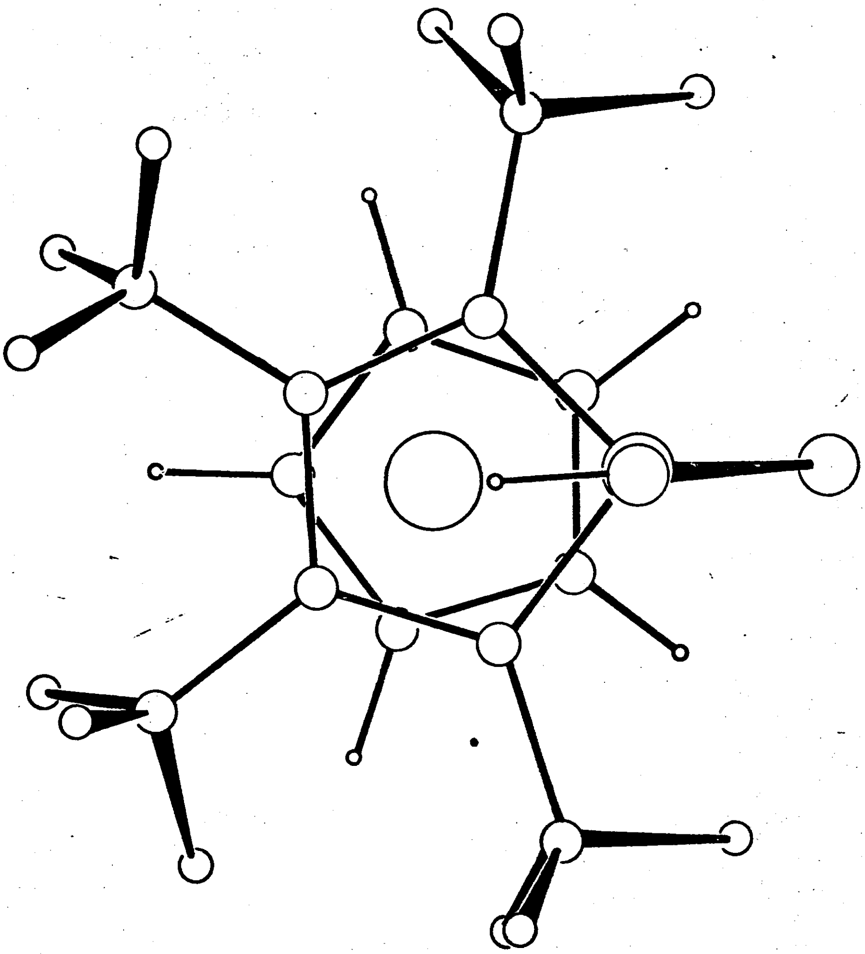


Fig. 5.3

The structure revealed consists of a cyclopentadienyl-cobalt moiety π-bonded to a 1-hydroxy-2,3,4,5-tetrakis(trifluoromethyl)phosphole-1-oxide ligand, $C_4(CF_3)_4PO_2H$. The heterocyclic ring appears to have resulted from condensation of two acetylene units and incorporation of a phosphorus ligand into a cyclic diene ligand.

The five membered phosphole-oxide ring is non-planar with a dihedral angle of 32.2° between the two planes defined by C_2, P, C_5 and C_2, C_3, C_4, C_5. The phosphorus lies above the plane of the four carbon atoms of the butadiene moiety by 0.686 Å and the Co-P distance, 2.730 Å, must be considered non-bonding. This is to be expected since the four carbon atoms of the ring provide the four electrons required by cobalt to achieve the stable eighteen electron configuration. As with $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$ the metal-C(ring)separations vary such that M-C_2, C_5 are equal, but slightly longer than M-C_2, C_3. Again the three C-C distances of the ring imply delocalisation of electron density over all four carbon atoms. The C_2, C_5-P distances, 1.77 Å and 1.76 Å, are close to the sum of the covalent radii of carbon and phosphorus 1.84,[226] so that little double-bond character is evident. The slight reduction observed can be accounted for by the reduction in radius of phosphorus in the pentavalent oxidation state.

An interesting feature of the structure is the strong hydrogen bonding between the P=O and P-OH groups on adjacent molecules (O-H-O distance 2.45 Å) and this results in molecules of complex being aligned in infinite chains throughout the crystal. This explains the peculiar physical properties of the compound which, although monomeric in the vapour state, (mass spectrometry), is virtually insoluble in all but the most polar organic solvents such as acetone. The melting-point of the complex could not be obtained, the hydrogen-bonding being sufficient to maintain the crystallinity of the compound above 300°C.

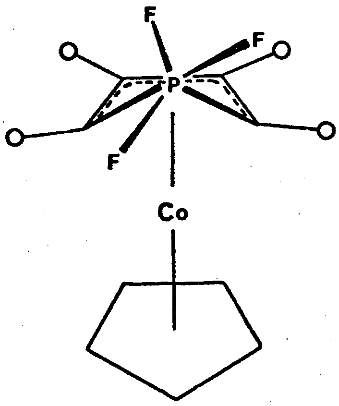
The structural similarity of CpCo[$C_4(CF_3)_4PO_2H$] and CpCo[$C_4(CF_3)_4CO$] makes it possible to analyse the effect of replacing a ketonic carbonyl group in the tetrahapto ring, by an atom with different hybridisation. The dihedral angle of fold of the ring in the phosphorus derivative, (32.2°), is comparable to that found in $Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$, 30.8°, but considerably in excess of 21° in the cyclopentadienone cobalt complex. This appears to be the only significant structural alteration resulting from this change and further substantiates the conclusions reached in Chapter II, on the basis of Churchill[233] and Alcocks[219] theories, that the non-planarity of five membered cyclic butadiene rings in transition metal complexes is a function of the dimensions of the triangle C_2-X-C_5, and hence of the radius and hybridisation of the hetero atom X. In the sulphur and phosphorus heterocycles these factors are almost identical and lead to similar dihedral angles but in CpCo[$C_4(CF_3)_4CO$], the smaller C-X distance and greater C-X-C angle allowed by sp^2 hybridised carbon, leads to a lesser angle. This difference seems impossible to explain in terms of π^* orbital population changes required by Mason's theory.[218]

Minor differences between the cyclopentadienone and phosphole-oxide complexes are of course observed, such as the slightly greater average C-C distance in the butadiene moiety of the former, but this is probably not significant. However, the CF_3 substituents on atoms C_2 and C_5 of the phosphole ring are displaced towards the cobalt atom by 0.081 Å and 0.075 Å respectively, while in the cyclopentadienone complex they are virtually in the plane of the butadiene ring. This, as explained in Chapters II and III, may again be a confirmation of Churchill and Alcock's theories, a larger displacement towards the metal being required by a greater degree of orbital twisting and non-planarity (Fig. 2.7.). However, in view of the situation found in $[C_5H_5NiC_2(CF_3)_2]_4$ such a conclusion must be treated with some caution.

The question arises as to the mechanism by which $CpCo[C_4(CF_3)_4POF]$ and $CpCo[C_4(CF_3)_4POH]$ are produced from $CpCo(PF_3)_2$ and hexafluorobut-2-yne, at some stage oxidation of coordinated phosphorus having occurred, in addition to hydrolysis of P-F bonds.

The mass spectra of freshly prepared samples of $CpCo[C_4(CF_3)_4POF]$ usually contained weak ions at m/e 536 and 517 which can be attributed to $CpCo[C_4(CF_3)_4PF_3]^+$ and $[CpCo[C_4(CF_3)_4PF_3]-F]^+$. This suggests that this complex is formed initially, but hydrolyses rapidly to $CpCo[C_4(CF_3)_4POF]$. An alternative mechanism, involving fluorine substitution to give $CpCo[C_4(CF_3)_4PF]$ which is oxidised to the phosphole oxide, seems less probable, particularly in view of the isolation of the P V heterocycle $[C_4(CF_3)_4PPh_3]$, from the reaction of $CpRu(PPh_3)_2H$ and $CF_3C{\equiv}CCF_3$.[163] Assuming the correctness of the above conclusions, the reactions of hexafluorobut-2-yne with $CpCo(PF_3)_2$ and its carbonyl analogue $CpCo(CO)_2$ are comparable, in each case a ligand being incorporated into the cyclic butadiene group of the resulting complex.

The stereochemistry of five coordinate phosphorus compounds is usually based on a trigonal bipyramidal arrangement of substituents[12] and in cyclic phosphoranes, e.g. $[C_4(CF_3)_4PPh_3]$, the ring occupies an axial and an equatorial position.[317] On this basis the following structure for $CpCo[C_4(CF_3)_4PF_3]$ is considered probable.



The manner by which hydrolysis of $CpCo[C_4(CF_3)_4PF_3]$ occurs, is not known with certainty. Although the solvents were dried carefully over molecular sieves, minute traces of moisture could catalyse the hydrolysis by reacting to give $CpCo[C_4(CF_3)_4POF]$ and HF. The latter could then attack the glass reaction vessel to give SiF_4 and regenerate H_2O.

The primary hydrolysis product $CpCo[C_4(CF_3)_4POF]$ is a yellow powder, air and moisture sensitive in both the solid state and solution. The i.r spectrum is similar to that of $CpCo[C_4(CF_3)PO_2H]$ in the C-F stretching region, suggesting a similar structure. A band at 847 cm^{-1} is assigned to a P-F stretching mode since this disappeared gradually as the sample was allowed to hydrolyse. The mass spectrum is also in accord with the presence of a heterocyclic $[C_4(CF_3)_4POF]$ ring with a variety of ions being assigned to fragments of this species, although an ion due to the complete ligand was not observed.

The ^{19}F n.m.r. spectrum contains two highly coupled resonances indicating two different CF_3 environments and, although the low field signal was slightly broader than the other peak, no distinct coupling to phosphorus was observed. Due to the fairly low solubility of the complex it was not possible to detect the expected doublet of the unique fluorine attached to phosphorus. Two sharp singlets, one of which is rather weak; are observed in the proton n.m.r., assignable to π-cyclopentadienyl groups. This can either be explained by the presence of small quantities of $CpCo[C_4(CF_3)_4PF_3]$ as an impurity in the sample, or perhaps by the occurrence of isomerism which could arise from the presence of both an endo and an exo oxygen atom. Support for the latter conclusion comes from the observation that no change in the relative intensities of the two peaks was observed as the complex was allowed to hydrolyse slowly in the n.m.r. tube. If $CpCo[C_4(CF_3)_4PF_3]$

was responsible for the weaker resonance, its decomposition might be expected to be more rapid. This follows from the fact that the main product of the reaction of $CpCo(PF_3)_2$ and $CF_3C{\equiv}CCF_3$ is $CpCo[C_4(CF_3)_4POF]$ according to elemental analysis, i.r., and mass spectroscopy, suggesting that $CpCo[C_4(CF_3)_4PF_3]$ undergoes hydrolysis more readily than the phosphole-oxide.

The terminal hydrolysis product $[CpCoC_4(CF_3)_4PO_2H]$, is an orange crystalline solid, air stable in the solid state and, for a reasonable length of time, in solution. The spectroscopic properties are almost identical in every respect to those of the POF complex apart from the absence of a P-F stretching mode in the i.r. spectrum.

A variety of phosphole and phosphole-oxide complexes of iron have been isolated from the reactions of such ligands with iron carbonyls[318,319] but the complexes described in this chapter appear to be the first examples containing a cyclopentadienyl cobalt moiety. The cyclic phosphorane $[C_4(CF_3)_4PPh_3]$ mentioned previously, was isolated from the reactions of triphenylphosphine complexes and hexafluorobut-2-yne,[163] but no complexes containing a coordinated heterocycle were detected. No reaction was observed between the alkyne and uncoordinated PPh_3, in contrast to the reaction of the latter with dimethyl acetylenedicarboxylate which gives $[C_4(COOMe)_4PhPPh_2]$.[312] When this reaction was carried out at -50°C an unstable zwitterion intermediate was detected, possibly indicating that an ionic mechanism is involved. As noted frequently throughout this thesis cyclooligomerisation of hexafluorobut-2-yne in the presence of transition metal compounds is also considered to occur <u>via</u> an ionic mechanism, so that incorporation of PF_3 into the cyclising fluorocarbon chain to give $CpCo[C_4(CF_3)_4PF_3]$ may also occur in a similar manner. A mechanism comparable to that formulated by Green[186] to account for the formation of tetrakis(trifluoromethyl)cyclopentadienone complexes of the iron group (Fig. (iii), p. 79) is therefore probable.

Table 5.2.

I.r. Spectra of Cyclopentadienyl-Cobalt Complexes		
Compound	νCF	νPF
$CpCo[C_4(CF_3)_4POF]^*$	1311m, 1299m, 1266w, 1234msh, 1221vs, 1196vs, 1183vs, 1152m, 1129wm	847
$CpCo[C_4(CF_3)_4PO_2H]^\dagger$	1230ssh, 1219vs, 1187s, 1161m, 1132wm	

* CCl_4 † CH_3CN

Table 5.3.

N.m.r. Spectra of Cyclopentadienyl-Cobalt Complexes				
	^1H		^{19}F	
Compound	$\delta_1(Cp)$	$\delta_2(Cp)$	$\delta_1(CF_3)$	$\delta_2(CF_3)$
$CpCo[C_4(CF_3)_4POF]$	4.35	4.44^a	50.3	51.3^b
$CpCo[C_4(CF_3)_4PO_2H]^*$	4.36^c		51.6	52.8^d

[a] CD_2Cl_2 [b] CH_2Cl_2

[c] acetone-d_6 [d] acetone

* hydroxyl proton resonance not detected

Miscellaneous Reactions

In contrast to the high yield formation of $CpCo[C_4(CF_3)_4PF_3]$ and its hydrolysis products from $CF_3C≡CCF_3$ and $CpCo(PF_3)_2$ no reaction was observed between the latter and acetylenes PhC≡CPh and $CH_3C≡CCH_3$, in pentane, up to 90°C, when decomposition became appreciable. This of course, may be due to the inability of such acetylenes to promote oxidation of the PF_3 ligand to give a phosphorus V species.

Perhaps more surprising was the negative result obtained when $CpRh(PF_3)_2$ and hexafluorobut-2-yne were allowed to react in pentane at 85°C, particularly when the reactivity of $CpRh(CO)_2$ towards this acetylene is recalled.[198] It was suggested in Chapter II that the reactivity of coordinated carbon monoxide towards $CF_3C{\equiv}CCF_3$ may be lower in carbonyls of the second and third row transition metals and, if this conclusion is valid for PF_3 with similar coordinating abilities, a tentative explanation is provided. However, cyclopentadienyl rhodium compounds frequently exhibit high catalytic activity in promoting the cyclotrimerisation of acetylenes[195,256] so that the failure to isolate $CpRhC_6(CF_3)_6$, or the free benzene $[C_6(CF_3)_6]$, from this reaction is difficult to explain. Such a reaction may perhaps require preliminary coordination of the alkyne and displacement of PF_3, which may not be thermodynamically feasible, but in the absence of additional data, no further conclusions can be reached.

Conclusions

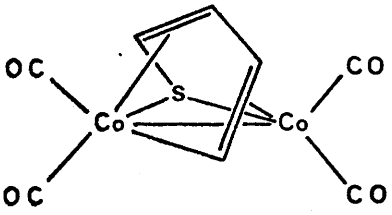
The results of the work described in this chapter suggest that, in certain cases, reactions of acetylenes with trifluorophosphine complexes are analogous to those with transition metal carbonyls, while in other cases no resemblance is apparent. It is obvious from these observations that the reactivity of coordinated PF_3 depends on the complex and on the reacting acetylene, so that further investigations are therefore desirable. Unlike the C-O bond of carbon monoxide the P-F bond of PF_3 is fairly reactive towards certain substrates and the chemistry of uncoordinated PF_3 is being studied increasingly.[306] Consequently it may be possible to investigate, not only the reactions of acetylenes with transition metal complexes of PF_3, but also of PF_2X, X = NR_2, CN. The isolation of the heterocycle $[C_4(CF_3)_4PPh_3]$, from the reactions of triphenylphosphine complexes with $CF_3C{\equiv}CCF_3$, lends support to this hypothesis. A variety of different products have been isolated from the reactions of tertiary phosphines with electrophilic olefins and acetylenes and the facile nature of many of these reactions has been ascribed to the nucleophilicity of the lone pair of electrons on the phosphine.[320] However, it is apparent from the isolation of $CpCo[C_4(CF_3)_4PO_2H]$ and its precursors and $[C_4(CF_3)PPh_3]$, that other factors must also influence the reaction since, on coordination, the lone pair can no longer function as a reactive site for electrophilic attack. It is perhaps significant that in reactions involving uncoordinated phosphine, the products obtained are in most cases, linear whereas in the two reactions involving coordinated phosphines heterocyclic products were obtained.[320] If this observation proves to be of greater generality, new routes to heterocyclic phosphorus V derivatives may become available using transition metal phosphine derivatives as precursors. In a more general theme the demonstration that heterocyclic sulphur complexes can be also formed in a similar manner (Chapter II this thesis) leads to the conclusion that oxidative addition of acetylenes to a wide range of inorganic ligands may be possible. The chemistry of coordinated inorganic ligands in this respect appears to have been neglected to a great extent and the potential revealed in a modest fashion by some of the work described in this thesis, must clearly be investigated by future work.

APPENDIX

Reaction of $CF_3C{\equiv}CCF_3$ and $[Co(CO)_3SC_6F_5]_2$

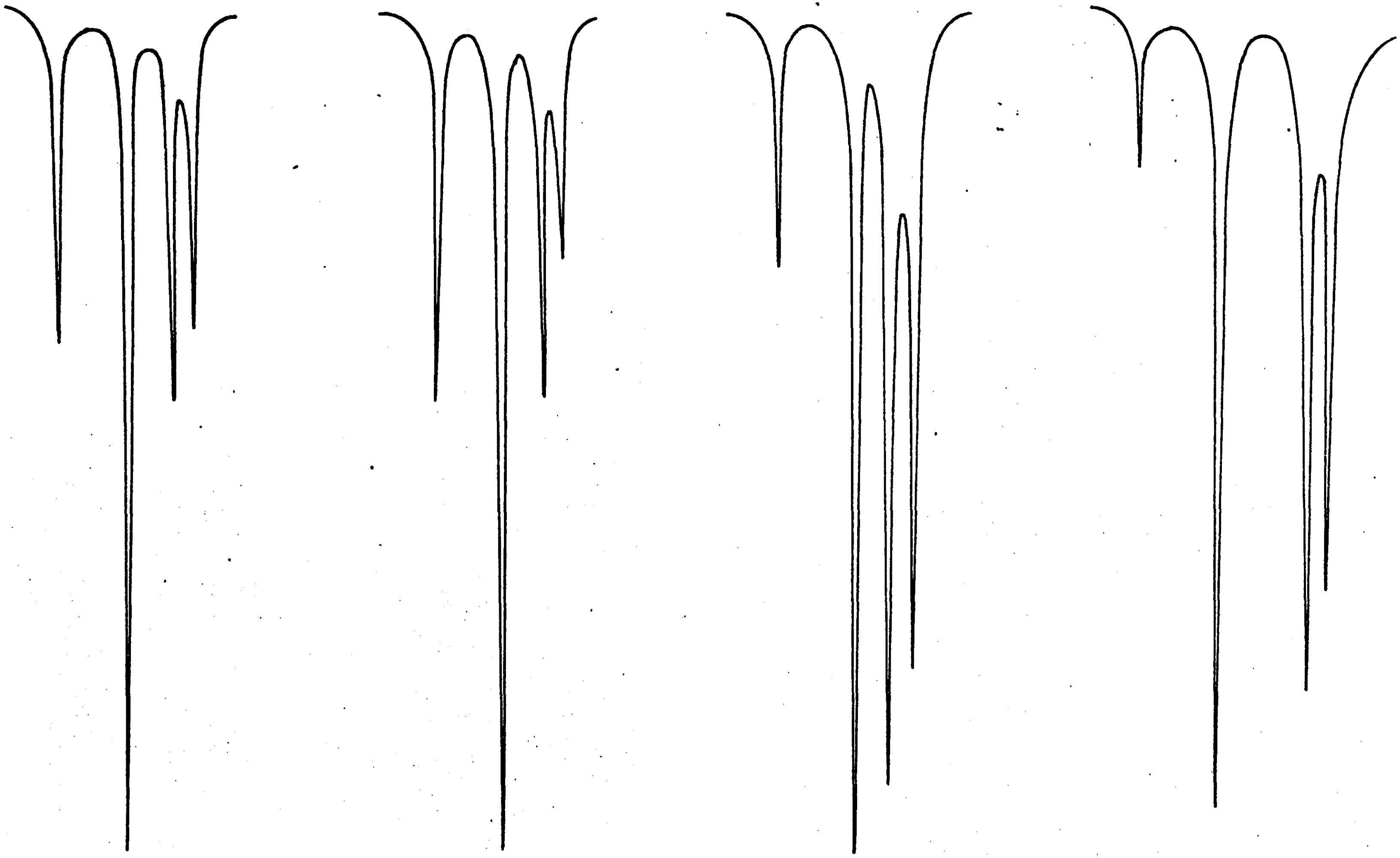
As stated in Chapter II the formulation of the dark-green organosulphur complex obtained from the reaction of $[Co(CO)_3SC_6F_5]_2$ and $CF_3C{\equiv}CCF_3$ as the hexacarbonyl complex $Co_2(CO)_6[C_4(CF_3)_4S]$, is somewhat unsatisfactory in that no C=C stretching mode is observed in the i.r. spectrum. An alternative stoichiometry, $Co_2(CO)_4[C_4(CF_3)_4S]$, is now considered more likely in view of recent analytical results, which suggest that the original analyses for C and F were inaccurate.

A structure analogous to $Co_2(CO)_4(CF_3C_2H)_3$[188] is considered probable for the complex, but with one of the C_2 units of the C_6 chain replaced by sulphur.



As such both olefinic bonds are coordinated, thus accounting for the lack of νC=C modes in the i.r. spectrum. The coordination of one of the sulphur lone pairs to a cobalt atom also seems more satisfactory in view of the well-known ability of sulphur to form coordinate bonds to cobalt.[1] The i.r. spectrum in the CO stretching region can possibly be reconciled with both a hexacarbonyl or a tetracarbonyl species, but, as Fig. (i) reveals, the relative intensities of the bands seem more compatible with the latter. X-ray crystal studies of the compound are at present being carried out by Professor G.A. Sim and Dr. M.J. Barrow in order to clarify

Fig. (1) νCO modes



the situation.

It was pointed out in Chapter II that the formation of $Co_2(CO)_4[C_6(CF_3)_6]$ in the reaction which produced $Co_2(CO)_4[C_4(CF_3)_4S]$ is unusual in view of the mild conditions employed. However, the formation of the tetracarbonyl organosulphur complex is less unexpected since it is probably produced via a $Co_2(CO)_6C_4(CF_3)_4S$ with one of the structures a or b originally considered for the complex (page 149). Subsequent coordination of sulphur and an olefinic bond is obviously possible and decarbonylation occurs under the mild conditions employed.

EXPERIMENTAL

Chapter I. Preparation and Reactions of Trifluoromethylthio and Pentafluorophenylthio-Metallates.

Reagents

CF_3SSCF_3, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $[CpMo(CO)_3]_2$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Fe_2(CO)_9$, $[CpFe(CO)_2]_2$, $Co_2(CO)_8$, $CpCo(CO)_2$ and $[CpNiCO]_2$ were obtained from Strem Chemicals Inc. and Cp_2Ni from Alpha Inorganics. $C_6F_5SSC_6F_5$,[321] $[CpW(CO)_3]_2$,[322] $CpMo(CO)_3I$,[323] and $CpFe(CO)_2Cl$[324] were prepared by standard methods.

Method

The general experimental methods employed have already been described on page 16.

Photolytic Reactions

Since most of the photolytic reactions employed similar techniques a general reaction will be described.

In a typical reaction ≈1 g. metal complex and excess disulphide were transferred to a flat-bottomed pyrex reaction vessel, capacity ~ 200 ml. This was evacuated and cooled to -196°C and ~75 ml. of dry, deoxygenated pentane condensed in. The flask was then sealed and allowed to warm to room temperature. The reaction mixture, which was stirred continuously, was then irradiated for ~30 hrs. at a distance of 10 cm^{-1} from a u/v lamp. After this time the volatiles were removed in vacuo, the crude product mixture dissolved in a small quantity of CH_2Cl_2, and a few millilitres of hexane added. This was centrifuged for 15 min. and the clear solution decanted off. Solvent was then removed slowly in a stream of nitrogen to give crystals of the product. Further purification, if necessary, was achieved by second and third slow recrystallisations from

CH_2Cl_2/hexane or from hexane at -24°C.

The reaction of $Mn_2(CO)_{10}$ and CF_3SSCF_3 and $[CpNiCO]_2$ and the disulphides RSSR, R = CF_3, C_6F_5, as described in Chapter I, gave initially, unstable species $Mn(CO)_5SCF_3$ and CpNi(CO)SR respectively.

These were detected by i.r. spectroscopy prior to work-up as described on pages 22 and 33. Cooling of the reaction vessel to -10°C prior to solvent removal enabled a sticky yellow product mixture to be obtained from the manganese carbonyl reaction. Slow recrystallisation of the centrifuged product from CH_2Cl_2/hexane, at -10°C gave, initially $[Mn(CO)_4SCF_3]_2$ and small amounts of monomer, but as the recrystallisation proceeded the product colour became pale yellow as the proportion of more soluble monomer, $Mn(CO)_5SCF_3$, increased. The final batch of pale yellow crystals were ≈90% monomer according to the ^{19}F n.m.r. spectrum, (integration of signals). Attempts to isolate CpNi(CO)SR, R = CF_3, C_6F_5, by similar methods were unsuccessful due to rapid decarbonylation to $[CpNiSR]_n$, even on cooling the solution to -20°C.

Decarbonylation of $CpMo(CO)_3SCF_3$

0.4.g. complex, when heated in pentane at 80°C in a sealed tube, gave a black solution after 25 hr. Solvent was removed and the product sublimed at 90°C. The brown product obtained was recrystallised from CH_2Cl_2/hexane to give black crystals of $[CpMo(CO)_2SCF_3]_2$. The residue from sublimation was extracted with large quantities of hexane and the pale green solution thus obtained, filtered. Removal of solvent gave small quantities of the green solid $[CpMoCOSCF_3]_3$.

Reactions of CF_3SSCF_3 and $M(CO)_6$, M = Mo, W

The product mixture from these reactions contained large quantities of unreacted hexacarbonyl and the product was separated by extraction with small quantities of hexane. This solution was then chromatographed over florisil, eluting with pentane. The hexacarbonyl was eluted first as a colourless solution followed by a green band which was collected and, following removal of solvent, the product sublimed at 50°C to give a green-blue solid which gave black crystals from pentane at -78°C.

Reactions of CF_3SSCF_3 with $Fe(CO)_5$ and $Fe_2(CO)_9$

Repeated recrystallisation of the centrifuged products from these reactions from pentane at -24°C gave $[Fe(CO)_3SCF_3]_2$ as red, air-sensitive crystals. The residues from recrystallisation were combined, dissolved in a small quantity of hexane, and chromatographed over florisil. Four bands separated on elution with hexane and these were each collected and on removal of solvent, the residues sublimed at 60°C to give $Fe_3(CO)_9S_2$, (trace), $[Fe(CO)_3SCF_3]_2$, (trace), $[Fe_2(CO)_6SCF_3]_2S$, (1% yield) and $[Fe(CO)_3S]_2$, (trace), $Fe_3(CO)_9S_2$ and $[Fe(CO)_3S]_2$ were identified by comparison of their i.r. spectra and melting point with those reported in the literature.[325]

Reaction of CF_3SSCF_3 and $Co_2(CO)_8$

The product mixture from this reaction contained quantities of unreacted $Co_2(CO)_8$. Sublimation at 40°C gave a mixture of $Co_2(CO)_8$ and $Co_3(CO)_9CF$, according to i.r. spectra. The mixture was allowed to sit open to the atmosphere for 24 hrs. when $Co_2(CO)_8$ decomposed and pure $Co_3(CO)_9CF$ was obtained by resublimation.

The residue from the first sublimation was extracted with methylene chloride to give a red solution which was shown by i.r. spectroscopy to contain small quantities of $[Co_2(CO)_5S]_2$.[326]

Reactions of $C_6F_5SSC_6F_5$ and $CpCo(CO)_2$

(1) Pentane solutions of $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$, molar ratio

1:2, were mixed under nitrogen and then transferred to a reaction tube which was sealed. This was shaken for three days at 20°C when black crystals formed. These were filtered off and recrystallised from CH_2Cl_2/hexane to give $CpCo(CO)(SC_6F_5)_2$ in 75% yield.

(2) In a separate experiment the solution, as prepared above, was allowed to warm over a period of three days from -78°C. No reaction was observed up to -10°C when crystals of $CpCo(CO)(SC_6F_5)_2$ began to form. The reaction mixture was kept at this temperature for a further three days after which $CpCo(CO)(SC_6F_5)_2$ was filtered off in 63% yield. The green, pentane soluble residues were centrifuged, and on removal of solvent, sublimed at 50°C to give $C_6F_5SSC_6F_5$ in small quantities. Recrystallisation of the residues of sublimation from pentane gave small quantities of $[CpCoSC_6F_5]_2$.

(3) In a third experiment $CpCo(CO)_2$ and $C_6F_5SSC_6F_5$, in pentane, were irradiated for 8 hrs. in a pyrex reaction vessel (unstirred). Large crystals of $[CpCoSC_6F_5]_2$ and $CpCo(CO)(SC_6F_5)_2$ formed on the side of the reaction vessel adjacent to the u/v source. Crystals of the monomer formed in lower concentration on other parts of the reactor. The products were separated as described in (2). Yields : $[CpCoSC_6F_5]_2$, 4%, $CpCo(CO)(SC_6F_5)_2$ 36%.

(4) $C_6F_5SSC_6F_5$ was added to $CpCo(CO)_2$ in a glass reactor in the absence of solvent when rapid evolution of carbon monoxide was observed. The flask was evacuated and heated for 24 hrs. at 40°C. Extraction with pentane followed by centrifuging and recrystallisation gave $[CpCoSC_6F_5]_2$ in 32% yield. The residue from the extraction contained only insoluble decomposition material.

Thermal decarbonylation of $CpCo(CO)(SC_6F_5)_2$

0.3 g. complex in pentane was heated in a sealed flask at 90°C for 40 hr. The pentane soluble residue was centrifuged and solvent removed slowly to give small quantities of $[CpCoSC_6F_5]_2$. The insoluble residues were extracted with CH_2Cl_2, hexane added and the solution centrifuged. Slow removal of solvent gave the dark green solid $CpCo_2CO(SC_6F_5)_3$ in 34% yield.

Reactions of $CpCo(CO)_2$ and CF_3SSCF_3

A series of reactions similar to those carried out with $C_6F_5SSC_6F_5$ was carried out. The thermal reaction, in all cases, gave purple black mixtures from which was isolated by extraction with petroleum ether, a red black oily solid in small quantities. This showed one CO stretching mode in the i.r. spectrum above 2000 cm^{-1} and strong C-F stretchingmodes near 1100 cm^{-1}. Due to its instability and low yield this compound could not be characterised further.

Extraction of the remaining product mixture with CH_2Cl_2 gave a black solid in low yield. Due to its low solubility n.m.r. spectra could not be obtained, although an i.r. spectrum gave strong C-F stretching modes but no νCO frequencies. The analysis, which confirms the presence of Co, C, S and F, does not correspond to any intelligible empirical formula and suggests that the black solid is probably a mixture of compounds.

On irradiation $CpCo(CO)_2$ and CF_3SSCF_3 in pentane after ~50 hrs. gave a green solution. Removal of volatiles followed by sublimation at 80°C gave $[CpCo(SCF_3]_2$ as a green air sensitive powder.

Table (1)

			Analytical Data*						
Compound	Mp(K)	Colour	%C	%H	%S	%F	%M	M.Wt.[a]	Yield(%)
$CpMo(CO)_3SCF_3$	343- 347d	Orange Yellow	31.6 (31.2)	1.5 (1.4)	9.2 (9.2)	16.8 (16.5)	27.9 (27.8)	346 (346)	82
$[CpMo(CO)_2SCF_3]_2$	436- 440	Brown Black	31.0 (30.2)	1.8 (1.6)	9.8 (10.1)	16.8 (17.9)			46
$[CpMo(CO)SCF_3]_3$	468d	Green	-						
$CpW(CO)_3SCF_3$	378- 381d	Orange Yellow	25.2 (24.9)	1.0 (1.2)	7.5 (7.4)	13.4 (13.1)	42.7 (42.4)	434 (434)	74
$[CpFe(CO)SCF_3]_2$(A)	377d	Olive Brown	33.1 (32.9)	2.1 (1.7)	12.5 (12.6)	23.4 (23.5)	22.8 (21.9)	500 (500)	†
$[CpFe(CO)SCF_3]_2$(B)	386d	Olive Brown	33.6 (32.9)	2.0 (1.7)	12.8 (12.6)	22.8 (23.5)	22.4 (21.9)	500 (500)	†
$[CpNiSCF_3]_2$	390- 396	Purple Black	32.4 (32.1)	2.1 (2.2)	14.2 (14.3)	25.1 (25.4)	26.4 (26.1)	448 (448)	83
$CpNiPPh_3SCF_3$	415d	Yellow Brown	57.5 (58.0)	4.1 (4.1)	6.2 (6.4)	11.2 (11.7)	6.8[c] (6.4)		85
$[Mo(CO)_4SCF_3]_2$	363d	Blue Black	19.1 (19.4)		10.2 (10.4)	17.8 (18.4)	30.6 (31.1)	618 (618)	5.5
$[W(CO)_4SCF_3]_2$	381d	Blue Black	15.6 (15.1)		7.8 (8.1)	14.0 (14.4)	45.5 (46.3)	794 (794)	8.0

Table (1) (cont'd)

$[Fe(CO)_3SCF_3]_2$	350	Red	20.1 (19.9)		13.2 (13.3)	24.0 (23.6)	22.9 (23.2)	482 (482)	30.0
$[Fe_2(CO)_6SCF_3]_2S$	407- 408	Red	-					794 (794)	
$[Fe(CO)_2PPh_3SCF_3]_2$	450- 452	Red Black	53.5 (53.1)	3.2 (3.2)	11.6 (12.0)	11.2 (11.8)	6.0^c ((6.5)		89
$[Fe(NO)_2SCF_3]_2$	324	Brown	5.2 (5.5)		14.4 (14.7)	26.9 (26.3	25.4 (25.8)	434 (434)	72
$[CpCoSCF_3]_2$	355d	Green Black	31.6 (32.0)	1.9 (2.2)	14.3 (14.2)	26.0 (25.3)	25.6 (26.2)	450 (450)	63
$CpCo(CO)(SC_6F_5)_2$	370d	Black	39.5 (39.3)	1.0 (0.9)	12.5 (11.6)	33.2 (34.5)	11.0 (10.7)	495^b (550)	†
$CpCo_2(CO)(SC_6F_5)_3$	463d	Green Black	35.3 (35.6)	1.0 (0.6)	11.0 (11.9)	34.5 (35.3)	14.0 (14.6)		34
$[CpCoSC_6F_5]_2$	423d	Green Black	40.0 (40.9)	1.2 (1.5)	9.7 (9.9)	30.6 (29.4)	17.7 (18.3)	646 (646)	†

* calculated values in parentheses

d decomposed

a molecular ion in mass spectrum

b vapour phase osmometry ($CHCl_3$ solution)

c phosphorus analysis

† see text

Chapter II. Reactions of Trifluoromethylthio-and Pentafluorophenylthio-Metallates with Acetylenes $CF_3C{\equiv}CCF_3$ and $CF_3C{\equiv}CH$

Reagents

$CF_3C{\equiv}CCF_3$ was obtained from Peninsular Chem. Research Inc. $CF_3C{\equiv}CH$ from Fluorochem. Ltd., and $CH_3C{\equiv}CCH_3$ and PhC≡CPh from Koch-light Lab. Ltd. The metal-SCF_3 and SC_6F_5 derivatives were prepared by methods described in Chapter I. Florisil (100-200 mesh) was obtained from Koch-Light Lab. Ltd., activated alumina (neutral) from Woelm.

Method

In a typical reaction ~0.4 g. complex was transferred to a thick glass reaction vessel with a teflon stopcock. This was evacuated, cooled to -196°C and pentane, (~15 ml), and the acetylene, (~ 2.5 g.), condensed in. (With the reaction of $CpMo(CO)_3SCF_3$ and PhC≡CPh both reactants were weighed out into the reactor prior to evacuation.) The reaction mixture was then allowed to warm slowly to room temperature and placed in an oven, (or irradiated), at the temperature given in Table 2. The reaction was followed by i.r. spectroscopy in the νCO and νCF region and, after several hours, (see Table 2), the reaction stopped and volatiles removed <u>in vacuo</u>. The product was then extracted with CH_2Cl_2, hexane added and the solution centrifuged. Solvent was then removed slowly (under a stream of nitrogen) from the decanted solution to give the crystalline product. Repeated recrystallisation gave analytically pure samples. Complexes requiring alternative separation and purification techniques are as follows :

<u>$CpM(CO)_2(RC_2R)SCF_3$</u>: repeated fractional sublimation at 25°C, I and II, 35°C, III and IV.

<u>$Mn(CO)_3[C_4(CF_3)_4SCF_3]$</u>: chromatographed over florisil, eluting with

pentane, followed by slow crystallisation from pentane at -24°C.

$Mn(CO)_3[(CF_3C_2R)(CF_3C_2H)_2SC_6F_5]$, R = CF_3, H : chromatographed over florisil, eluting with hexane/benzene mixture 5:1, followed by sublimation at 60°C. This did not result in isolation of completely pure products.

$CpFe(CO)C(CF_3)=C(CF_3)SR$, R = CF_3, C_6F_5 : as above but with R = CF_3 two bands were eluted and shown to be $CpFe(CO)C(CF_3)=(CF_3)SCF_3$ and $CpFe(CO)_2SCF_3$.

$Co_2(CO)_4[C_4(CF_3)_4S]$: the product mixture from the reaction of $[Co(CO)_3SC_6F_5]_2$ and $CF_3C{\equiv}CCF_3$ was chromatographed over florisil and eluted with petroleum ether to give three bands; (1) purple, $Co_2(CO)_4C_6(CF_3)_6$, (2) orange, $Co_2(CO)_6CF_3C_2CF_3$, (3) green, $Co_2(CO)_4[C_4(CF_3)_4S]$. These were each collected, and following removal of solvent, (1) and (2) sublimed at 40°C to give solid products, identified by comparison of i.r. spectra with authentic samples.[180,253] (3) was recrystallised from pentane at -24°C.

Table (2)

Reactants	Temp. (^{o}C)	Time (hr)	Products	Yield (%)
$CpMo(CO)_3SCF_3 + CF_3C{\equiv}CCF_3$	30	90	$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$	36
" $+ CH_3C{\equiv}CCH_3$	30	20	$CpMo(CO)_2(CH_3C_2CH_3)SCF_3$	77
" $+ PhC{\equiv}CPh$	30	20	$CpMo(CO)_2(PhC_2Ph)SCF_3$	84
$CpW(CO)_3SCF_3 + CF_3C{\equiv}CCF_3$	60	200	$CpW(CO)_2(CF_2C_2CF_3)SCF_3$	30
" $+ CH_3C{\equiv}CCH_3$	60	100	$CpW(CO)_2(CH_3C_2CH_3)SCF_3$	57
$CpMo(CO)_3SCF_3 + CF_3C{\equiv}CH$	35	120	$CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$	32
$CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$	hν/20	60	$[CpMo[(CF_3C_2H)_2CO]SCF_3]_2$	63
$[Mn(CO)_4SC_6F_5]_2 + CF_3C{\equiv}CCF_3$	20	120	$Mn(CO)_4C(CF_3){=}C(CF_3)SC_6F_5$	73
" + "	80	50	$Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$	84
" $+ CF_3C{\equiv}CH$	20	90	$Mn(CO)_4(CF_3C_2H)_2SC_6F_5$	61
$Mn(CO)_4(CF_3C_2H)_2SC_6F_5$	85	30	$Mn(CO)_3[(CF_3C_2H)_2SC_6F_5]$	-
$[Mn(CO)_4SCF_3]_2 + CF_3C{\equiv}CCF_3$	80	90	$Mn(CO)_3[C_4(CF_3)_4SCF_3]$	72
$CpFe(CO)_2SCF_3$ + "	80	50	$CpFe(CO)_2C(CF_3){=}C(CF_3)SCF_3$	77
$CpFe(CO)_2SC_6F_5$ + "	75	30	$CpFe(CO)_2C(CF_3){=}C(CF_3)SC_6F_5$	69
$CpFe(CO)_2CCF_3{=}CCF_3SCF_3$	hν/20	40	$CpFe(CO)C(CF_3){=}C(CF_3)SCF_3$	72
			$+ CpFe(CO)_2SCF_3$	5

Table (2) (cont'd)

$\mathrm{CpFe(CO)_2C(CF_3){=}C(EF_3)SC_6F_5}$	hν/20	50	$\mathrm{CpFe(CO)C(CF_3){=}C(CF_3)SC_6F_5}$	73
$\mathrm{CpFe(CO)C(CF_3){=}C(CF_3)SC_6F_5}$ + $\mathrm{CF_3C{\equiv}CCF_3}$	hν/20	200	$\mathrm{CpFe[C_4(CF_3)_4SC_6F_5]}$	67
$\mathrm{CpFe(CO)C(CF_3){=}C(CF_3)SC_6F_5}$	90	30	$\mathrm{CpFe(CO)_2C(CF_3){=}C(CF_3)SC_6F_5}$	19
$\mathrm{[Fe(CO)_3SCF_3]_2 + CF_3C{\equiv}CCF_3}$	30	70	$\mathrm{[Fe(CO)_3SCF_3]_2CF_3C_2CF_3}$	72
$\mathrm{[Fe(CO)_3SC_6F_5]_2 + CF_3C{\equiv}CCF_3}$	hν/20	5	$\mathrm{[Fe(CO)_3SC_6F_5]_2CF_3C_2CF_3}$	95
$\mathrm{[Fe(CO)_3SR]_2CF_3C_2CF_3 + CF_3C{\equiv}CCF_3}$	70	40	$\mathrm{Fe(CO)_3[C_4(CF_3)_4CO]}$	30
$\mathrm{[Fe(CO)_3SCF_3]_2 + CF_3C{\equiv}CH}$	hν/20	24	$\mathrm{[Fe(CO)_3SCF_3]_2CF_3C_2H}$	15
$\mathrm{[Fe(CO)_3SC_6F_5]_2 + CF_3C{\equiv}CH}$	hν/20	24	$\mathrm{[Fe(CO)_3SC_6F_5]_2CF_3C_2H}$	17
$\mathrm{[Fe(CO)_3SCF_3]_2CF_3C_2CF_3 + PPh_3}$	20	30	$\mathrm{[Fe(CO)_2(PPh_3)SCF_3]CF_3C_2CF_3}$	64
$\mathrm{[CpCoSCF_3]_2 + CF_3C{\equiv}CCF_3}$	85	8	$\mathrm{CpCoC_6(CF_3)_6}$	18
$\mathrm{[CpCoSC_6F_5]_2 + CF_3C{\equiv}CCF_3}$	80	6	$\mathrm{CpCoC_6(CF_3)_6}$	13
$\mathrm{[Co(CO)_3SC_6F_5]_2 + CF_3C{\equiv}CCF_3}$	40	45	$\mathrm{Co_2(CO)_4C_4(CF_3)_4S}$	29
			$\mathrm{Co_2(CO)_6CF_3C_2CF_3}$	6
			$\mathrm{Co_2(CO)_4C_6(CF_3)_6}$	1

Table (3)

			Analytical Data					
Compound	Mp(K)	Colour	%C	%H	%S	%F	%M	M.Wt.
$CpMo(CO)_2(CF_3C_2CF_3)SCF_3$	334-336	Blue	30.3 (30.4)	1.2 (1.0)	6.6 (6.7)	36.2 (35.6)	21.0 (20.0)	
$CpMo(CO)_2(CH_3C_2CH_3)SCF_3$	327-330	Red Black	38.6 (38.7)	3.2 (3.0)	9.3 (8.6)	16.5 (15.3)	26.7 (25.8)	
$CpMo(CO)_2(PhC_2Ph)SCF_3$	368-370	Blue	54.9 (53.2)	3.2 (2.9)	6.5 (6.5)	11.7 (11.5)	20.3 (19.4)	
$CpW(CO)_2(CF_3C_2CF_3)SCF_3$	347-349	Purple	26.2 (25.3)	1.0 (0.9)	5.4 (5.6)	31.0 (30.1)	32.9 (32.4)	
$CpW(CO)_2(CH_3C_2CH_3)SCF_3$	351-35.3	Red Black	31.4 (31.3)	2.2 (2.4)	7.1 (7.0)	12.9 (12.4)	41.0 (40.0)	
$CpMo(CO)[(CF_3C_2H)_2CO]SCF_3$	424d	Yellow	33.2 (33.2)	1.3 (1.4)	6.4 (6.3)	32.4 (33.8)	19.9 (19.0)	506 (506)
$[CpMo[(CF_3C_2H)_2CO]SCF_3]_2$	488d	Red	33.0 (32.6)	1.3 (1.5)	6.9 (6.7)	34.3 (35.8)	21.3 (20.1)	956 (956)
$Mn(CO)_4C(CF_3)=C(CF_3)SC_6F_5$	347-348	Yellow	31.6 (31.8)		6.3 (6.1)	38.4 (39.6)	11.1 (10.4)	528 (528)
$Mn(CO)_3[C_4(CF_3)_4SC_6F_5]$	370	Orange Yellow	29.9 (30.8)		5.0 (4.8)	49.4 (48.8)	8.6 (8.3)	662 (662)
$Mn(CO)_3[C_4(CF_3)_4SCF_3]$	423	Yellow	26.1 (25.5)		6.0 (5.6)	51.7 (50.5)	10.0 (9.8)	564 (564)

Table (3) (cont'd)

$Mn(CO)_4(CF_3C_2H)_2SC_6F_5$	368- 369	Yellow	35.3 (34.7)	0.5 (0.3)	5.6 (5.8)	37.1 (37.7)	10.3 (9.9)	554 (554)
$CpFe(CO)_2C(CF_3)=C(CF_3)SCF_3$	331- 334	Yellow	34.0 (32.7)	1.1 (1.0)	7.4 (7.3)	37.8 (38.8)	13.0 (12.7)	440 (440)
$CpFe(CO)_2C(CF_3)=C(CF_3)SC_6F_5$	390	Yellow	38.6 (37.9)	0.6 (0.9)	6.2 (5.9)	38.2 (38.8)	11.2 (10.9)	538 (538)
$CpFe(CO)C(CF_3)=C(CF_3)SCF_3$	-	Brown Black	31.9 (32.0)	1.3 (1.2)	7.5 (7.8)	41.9 (41.1)	13.6 (13.6)	412 (412)
$CpFe(CO)C(CF_3)=C(CF_3)SC_6F_5$	-	Brown Black	37.4 (37.7)	1.3 (1.0)	6.3 (6.3)	40.6 (40.9)	11.4 (11.0)	510 (510)
$CpFe[C_4(CF_3)_4SC_6F_5]$	419d	Yellow Brown	35.1 (35.4)	0.8 (0.8)	5.1 (4.9)	48.8 (50.1)	8.3 (8.7)	644 (644)
$[Fe(CO)_3SCF_3]_2CF_3C_2CF_3$	368- 378d	Yellow	23.5 (22.4)		10.5 (10.0)	36.5 (35.4)	18.0 (17.4)	644 (644)
$[Fe(CO)_3SC_6F_5]_2CF_3C_2CF_3$	388 396	Orange Yellow	31.6 (31.4)		7.7 (7.6)	35.7 (36.2)		
$[Fe(CO)_3SCF_3]_2CF_3C_2H$	368 375d	Yellow	22.2 (22.9)	0.3 (0.2)	10.6 (11.1)	30.0 (29.7)	19.9 (19.4)	576 (576)
$[Fe(CO)_3SC_6F_5]_2CF_3C_2H$	377- 379d	Yellow	34.6 (33.9)	0.4 (0.1)	8.6 (8.3)	31.6 (32.0)		
$[Fe(CO)_2PPh_3SCF_3]_2CF_3C_2CF_3$	412 414	Orange	47.9 (49.6)	2.6 (2.7)	6.3 (5.8)	19.9 (20.5)	10.7 (10.1)	
$CpCo[C_6(CF_3)_6]$	453	Red	33.1 (33.4)	0.9 (0.8)		55.3 (56.0)	10.0 (9.7)	610 (610)
$Co_2(CO)_4[C_4(CF_3)_4S]$	369- 370	Green Black	25.2 (24.6)		5.8 (5.5)	39.9 (38.9)	20.4 (20.1)	

Chapter III. Reactions of Hexafluorobut-2-yne with Some Cyclopentadienyl Nickel Complexes

Reagents

$CF_3CF{=}CF_2$ and $CF_2{=}CFCl$ were obtained commercially from Peninsular Chem. Research Inc., $CpNi[(C_5H_5)C_2(CF_3)_2]$.[201] $CpNi\ [(C_5H_5)C_2F_3Cl]$[263] and $(CpNi)_2CF_3C_2CF_3$[180] were prepared by standard methods.

The reactions described in this chapter were carried out in the manner described in Chapter II. Reaction conditions are listed in Table 4.

The following separation and purification techniques were employed

$[CpNiSCF_3]_2 + CF_3C{\equiv}CCF_3$. The product mixture was extracted with petroleum ether ~15 ml, chromatographed over florisil, and eluted with petroleum ether. The first two bands (1) red, and (2) orange, did not separate completely and were re-chromatographed over activated alumina, (grade II), and eluted as before to give clean separation of the bands. These were collected and the two products recrystallised from pentane to give $(CpNi)_2C_6(CF_3)_6$ and $CpNi[(C_5H_5)C_6(CF_3)_6]$. The other bands eluted from the florisil column were, (3) green, $(CpNi)_2CF_3C_2CF_3$, (4) yellow, $CpNi[C_4(CF_3)_4H]$, (5) purple, $Cp_2Ni_3C_6(CF_3)_6$. (3) and (4) were each collected and, on removal of solvent, sublimed at 40°C. (5) was collected and recrystallised from CH_2Cl_2/hexane.

$Cp_2Ni + CF_3C{\equiv}CCF_3$

The products were sublimed at 45°C and the sublimate extracted with pentane. Chromatography over florisil/petroleum ether gave the following bands; (1) yellow, $CpNiC_5H_5C_4(CF_3)_4$, (2) yellow, $[CpNi(C_5H_5)C_2(CF_3)_2]$, (3) green, $(CpNi)_2CF_3C_2CF_3$. These were collected as before and sublimed at 80°C, (1), 30°C, (2) and (3). The residue from the extraction of the first sublimation was recrystallised from CH_2Cl_2/hexane to give small quantities of $C_6(CF_3)_6$. The residue from the first sublimation was sublimed at 80°C to give $CpNi[(C_5H_5)C_4(CF_3)_4]$ which was recrystallised from CH_2Cl_2/hexane. The black solid remaining in the sublimation vessel was dissolved in CH_2Cl_2, hexane added and after being centrifuged, solvent removed in a stream of nitrogen to give a small quantity of $[C_5H_5NiC_2(CF_3)_2]_4$.

$CpNi[(C_5H_5)C_2(CF_3)_2]$ + (1) $CF_3C{\equiv}CCF_3$, (2) $CF_3CF{=}CF_2$

The product mixturesfrom these reactions were sublimed at 40°C to remove unreacted $CpNi[(C_5H_5)C_2(CF_3)_2]$ and the second component of the mixture, $CpNi[(C_5H_5)C_4(CF_3)_4]$, recrystallised from CH_2Cl_2/hexane.

$CpNi(C_5H_5C_2F_3Cl)$ + $CF_3C{\equiv}CCF_3$

The product mixture was sublimed at 50°C leaving a dark-brown solid which was recystallised from CH_2Cl_2/hexane to give brown crystals of $CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$. The sublimate was chromatographed over florisil, eluting with pentane to give $(CpNi)_2CF_3C_2CF_3$ and small quantities of the above product.

$(CpNi)_2CF_3C_2CF_3$ + CF_3CCCF_3

The product mixture was extracted with petroleum ether and on removal of solvent sublimed at 50°C. Extraction of the sublimate with pentane left a small quantity of $C_6(CF_3)_6$ on the cold finger of the sublimation vessel. The residue in the sublimation vessel and the pentane soluble extract were combined and chromatographed over florisil, eluting with pentane, to give (1), $CpNi[(C_5H_5)C_4(CF_3)_4]$, (2), $(CpNi)_2CF_3C_2CF_3$, (3), $Cp_2Ni_3C_6(CF_3)_6$ and (4), $[C_5H_5NiC_2(CF_3)_2]_4$. The last complex was obtained in quantity from the residue of the product mixture not removed in the petroleum ether extraction, by recrystallisation from CH_2Cl_2/hexane.

Table (4)

Reactants	Temp (^{o}C)	Time (hr)	Products	Yield
$[CpNiSCF_3]_2 + CF_3C{\equiv}CCF_3$	45	60	$(CpNi)_2CF_3C_2CF_3$	28
			$C_6(CF_3)_6$	15
			$CpNi[C_4(CF_3)_4H]$	5
			$Cp_2Ni_3C_6(CF_3)_6$	8
			$CpNi[(C_5H_5)C_6(CF_3)_6]$	trace
			$(CpNi)_2C_6(CF_3)_6$	trace
$Cp_2Ni + CF_3C{\equiv}CCF_3$	85	10	$(CpNi)_2CF_3C_2CF_3$	25
			$C_6(CF_3)_6$	trace
			$CpNi[(C_5H_5)C_2(CF_3)_2]$	trace
			$CpNi[(C_5H_5)C_4(CF_3)_4]$	37
			$[C_5H_5NiC_2(CF_3)_2]_4$	trace
$CpNi[(C_5H_5)C_2(CF_3)_2] + CF_3C{\equiv}CCF_3$	80	70	$CpNi[(C_5H_5)C_4(CF_3)_4]$	8*
" $+ CF_3CF{=}CF_2$	85	80	"	6
$CpNi[(C_5H_5)C_2F_3Cl] + CF_3C{\equiv}CCF_3$	70	90	$(CpNi)_2CF_3C_2CF_3$	6

Table (4) (cont'd)

$(CpNi)_2CF_3C_2CF_3 + CF_3C{\equiv}CCF_3$	90	90	$CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]$	62
			$C_6(CF_3)_6$	trace
			$CpNi[(C_5H_5)C_4(CF_3)_4]$	trace
			$Cp_2Ni_3C_6(CF_3)_6$	trace
			$[(C_5H_5)NiC_2(CF_3)_2]_4$	72

* see text page 173

Table (5)

Compound	Mp(K)	Colour	%C	%H	%F	%M	M.Wt.*
$CpNi[C_4(CF_3)_4H]$	327	Brown	35.3 (34.8)	1.5 (1.3)	49.8 (50.9)	13.4 (13.1)	448 (448)
$Cp_2Ni_3[C_6(CF_3)_6]$	461d	Black	33.7 (33.3)	1.2 (1.3)	42.6 (43.1)	21.9 (22.2)	790 (790)
$CpNi[(C_5H_5)C_6(CF_3)_6]$	431- 433	Orange Red					674 (674)
$(CpNi)_2[C_6(CF_3)_6]$	453	Red					732 (732)
$CpNi[(C_5H_5)C_4(CF_3)_4]$	469- 470	Yellow	41.2 (40.6)	2.1 (2.0)	44.3 (44.4)	11.5 (11.4)	512 (512)
$CpNi_2[C_4(CF_3)_4(C_5H_5)C_2F_3Cl]^{\dagger}$	461d	Brown	35.2 (34.9)	1.5 (1.5)	42.5 (41.5)	17.5 (17.1)	686 (686)
$[C_5H_5NiC_2(CF_3)_2]_4$	538d	Black	37.6 (37.5)	1.9 (1.9)	40.5 (40.0)	21.5 (20.4)	

Calculated values in parentheses

* molecular ion in mass spectrum

† Chlorine analysis :- 4.9 (5.2)

Chapter IV. Reactions of Acetylenes with Complexes $CpMo(CO)_3X$, $X = Cl, Br, I$

Reagents

$CpMo(CO)_3Cl$,[327] $CpMo(CO)_3Br$[327] and $CpMo(CO)_3I$[324] were prepared by standard methods.

Method

Reactions were carried out as described for Chapter II, under the conditions listed in Table 6, the following separation and purification techniques being employed.

$CpMo(CO)_3X + CH_3C{\equiv}CCH_3$

The product mixture was sublimed at 40°C and the sublimate crystallised from pentane at -24°C to give pale yellow crystals of duroquinone $C_4(CH_3)_4(CO)_2$ which was identified by comparison of the i.r. spectrum, (Sadtler Index) and melting point,[291] with those given in the literature. Recrystallisation of the sublimation residue from CH_2Cl_2/hexane gave yellow crystals of $CpMo(CH_3C_2CH_3)_2X$, X = Cl, Br, I.

$CpMo(CO)_3X + CF_3C{\equiv}CCF_3$

Repeated recrystallisation of the product from CH_2Cl_2/hexane gave yellow, X = Cl. orange, X = Br, or red brown, X = I, crystals of the complex $CpMo(CF_3C_2CF_3)_2X$. Very poor yields of the iodide were obtained, mainly insoluble decomposition material being produced. The reactions were followed by i.r. spectroscopy and in the case of the iodide a species giving a single CO stretching mode above 2000 cm^{-1} was detected, but attempted isolation by recrystallisation and chromatography was unsuccessful.

$\underline{\mathrm{CpMo(CO)_3X + PhC{\equiv}CPh\ (low\ temperature\ or\ u/v\ irradiation)}}$

Recrystallisation of the product from these reactions from CH_2Cl_2/hexane gave $CpMo(CO)(PhC_2Ph)X$ as a green powdery solid.

$\underline{\mathrm{CpMo(CO)_3X\ or\ CpMo(CO)(PhC_2Ph)X + PhC{\equiv}CPh\ (80^{o}C)}}$

The product was recrystallised from CH_2Cl_2/hexane to give a red-brown powder $CpMo(CO)(PhC)_4X.CH_2Cl_2$, X = Cl, Br, I, or as described in the literature[301] when red brown crystals of $CpMo(CO)(PhC)_4X$ were obtained.

$\underline{\mathrm{CpMo(CO)(PhC_2Ph)X + RC{\equiv}CR,\ R = CF_3,\ CH_3}}$

$\underline{\mathrm{CpMo(CH_3C_2CH_3)_2X + RC{\equiv}CR,\ R = CF_3}}$

The products of these reactions $CpMo(RC_2R)_2X$,were isolated by repeated recrystallisation from CH_2Cl_2/hexane.

$\underline{\mathrm{CpMo(CF_3C_2CF_3)_2Cl + CF_3C{\equiv}CCF_3\ (u/v\ irradiation)}}$

The pentane soluble material was removed, centrifuged, and recrystallised from CH_2Cl_2/hexane to give a mixture of a yellow complex and starting material. Repeated recrystallisation and fractional sublimation, (65°C), gave a small quantity of almost pure complex $CpMo(CF_3C)_4Cl$? , which is fractionally more volatile and soluble in organic solvents than $CpMo(CF_3C_2CF_3)_2Cl$.

$\underline{\mathrm{CpMo(CF_3C_2CF_3)_2Cl}}\ \xrightarrow{h\nu}$

The product of this reaction, dark red crystals, was washed with pentane but, due to insolubility in all common solvents, could not be purified further.

Table (6)

Reagents	Temperature	Time (hr)	Products	Yield (%)
$CpMo(CO)_3X + CH_3C{\equiv}CCH_3$			$CpMo(CH_3C_2CH_3)_2X$	
X = Cl	65°C	60		40
			$+ C_4(CH_3)_4(CO)_2$	11
Br	65°C	60		35
			$+ C_4(CH_3)_4(CO)_2$	8
I	65°C	100		32
			$+ C_4(CH_3)_4(CO)_2$	9
$CpMo(CO)_3X + CF_3C{\equiv}CCF_3$			$CpMo(CF_3C_2CF_3)X$	
X = Cl	70°C	15		77
Br	75°C	40		29
I	85°C	80		5
$CpMo(CO)_3X + PhC{\equiv}CPh$			$CpMo(CO)(PhC_2Ph)X$	
X = Cl	40°C	30		81
	20°C/hν	20		90
Br	55°C	40		87
	20°C/hν	20		92
I	20°C/hν	20		95
			$CpMo(CO)(PhC)_4X\cdot CH_2Cl_2$	
Cl	90°C	60		61
Br	90°C	48		45
I	85°C	48		49
$CpMo(CO)(PhC_2Ph)X + CF_3C{\equiv}CCF_3$			$CpMo(CF_3C_2CF_3)X$	
X = Cl	65°C	16		70
Br	65 C	20		65
I	70 C	8		17

Table (7)

			Analytical Data					
Compound	Mp(K)	Colour	%C	%H	%F	%X	%M	M.Wt.[a]
$CpMo(CH_3C_2CH_3)_2X$								
X = Cl	427-	Yellow	50.2	5.5		11.4	31.3	304
	429		(51.1)	(5.7)		(11.7)	(31.6)	(304)
Br	437-	Yellow	44.3	5.0		23.6		350
	440		(44.6)	(5.9)		(23.1)		(350)
I	441-	Yellow	39.4	4.3		32.2		385[b]/396
	444		(39.4)	(4.3)		(32.1)		(396)
$CpMo(CF_3C_2CF_3)_2X$								
X = Cl	418	Yellow	31.0	1.3	42.5	7.1	18.9	520
	420		(30.0)	(1.0)	(43.8)	(6.8)	(18.5)	(520)
Br	427	Orange	28.1	1.2	41.3	14.6		566
	428		(27.6)	(0.9)	(40.3)	(14.3)		(566)
I	416	Red	25.3	0.6	37.5	20.0		566[b]/612
	418	Brown	(25.5)	(0.8)	(37.2)	(20.9)		(612)
$CpMo(CO)(PhC_2Ph)X$								
X = Cl	418	Green	59.0	3.7	4.2*	9.2	22.8	374[b]
	420		(59.8)	(3.7)	(4.0)	(8.8)	(23.9)	(402)
Br	415	Green	52.6	3.4	3.4*	17.5		
	417		(53.3)	(3.3)	(3.6)	(18.1)		
I	379	Green	48.5	3.4	3.5*	26.4		
	381		(48.6)	(3.0)	(3.2)	(25.7)		

Table (7) (cont'd)

$CpMo(CO)(PhC)_4X.CH_2Cl_2$								
X = Cl	525d	Red	64.6	4.5		17.6	16.3	552^b
		Brown	(63.2)	(4.3)		(16.8)	(16.6)	(580)
Br	513d	Red	58.6	3.6		10.8		
		Brown	(59.9)	(3.8)		(11.4)		
I	490d	Red	56.3	3.2		17.9		
		Brown	(55.5)	(3.6)		(16.8)		

Calculated values in parentheses

* oxygen analyses

a molecular ion in mass spectrum

b vapour phase osmometry

Chapter V. Reactions of Acetylenes with Some Transition Metal Trifluorophosphine Complexes

Reagents

PF_3 was obtained commercially (Peninsular Chem. Research Inc.) $Ni(PF_3)_4$[328] and $CpRh(PF_3)_2$[329] were prepared by standard methods. $CpCo(PF_3)_2$ was prepared by the following method. 1.0 g $CpCo(CO)_2$ was transferred to a thick glass reaction vessel which was evacuated and ~30 ml pentane (dried over molecular sieves, type 4A) and 3 g PF_3 condensed in at -196°C. The reactor was allowed to warm to room temperature and irradiated at a distance of ~ 5 cm from a Hanovia u/v lamp. Evolved carbon monoxide was removed at intervals by cooling the flask to -196°C and pumping. The reaction was followed by i.r. spectroscopy, small samples being removed at intervals. After ~6 months the reaction was found to be complete and $CpCo(PF_3)_2$ was separated from the other volatiles by fractional distillation under vacuum. The complex collected in a trap held at -24°C.

Method

The reactions of trifluorophosphine complexes with acetylenes were carried out in glass reactors, as described for Chapter II, under the conditions listed in Table 8. $Ni(PF_3)_4/CF_3C{\equiv}CCF_3$ reactions were carried out, without solvent, in glass reactors ($CF_3C{\equiv}CCF_3$ pressure ~4 atmosphere) and with larger quantities of $CF_3C{\equiv}CCF_3$, ~6 g, in Hoke bombs of 80 ml capacity. Purification procedures are as follows.

$Ni(PF_3)_4 + CF_3C{\equiv}CCF_3$

Volatiles were removed under vacuum and separated at -65°C, $Ni(PF_3)_4$, -110°C, $CF_3C{\equiv}CCF_3$ and -196°C, PF_3. Sublimation of the solid product at 50°C gave $C_6(CF_3)_6$ as a white powder. The insoluble, involatile, pale yellow residue analysed as $Ni_3C_3F_5$.

$CpCo(PF_3)_2 + CF_3C{\equiv}CCF_3$

Removal of volatiles left a yellow solid which was washed with dry pentane, ~50 ml, and sublimed at 80°C to give $CpCo[C_4(CF_3)_4POF]$ as a yellow powder.

$CpCo[C_4(CF_3)_4POF] + H_2O$

$CpCo[C_4(CF_3)_4POF]$ 0.2 g was dissolved in Analar acetone ~20 ml and ~10 ml distilled water added. The resulting mixture was refluxed in a conical flask for 2 hr. and then transferred to an evaporating basin and the acetone distilled off. Orange crystals of $CpCo[C_4(CF_3)_4PO_2H]$ settled out and these were filtered off, washed with a small quantity of cold acetone followed by pentane, and dried in air.

Table (8)

Reagents	Temp. (°C)	Time (hr)	Products	Yield (%)
$Ni(PF_3)_4 + CF_3C{\equiv}CCF_3$	100°C	96	$C_6(CF_3)_6$	30
			$Ni_3C_5F_5$?	11
			PF_3	trace
$CpCo(PF_3)_2 + CF_3C{\equiv}CCF_3$	20°C	100	$CpCoC_4(CF_3)_4PF_3$	trace ?
			$CpCoC_4(CF_3)_4POF$	82
$CpCoC_4(CF_3)_4POF + H_2O$	80°C	2	$CpCoC_4(CF_3)_4PO_2H$	100

Table (9)

Compound	Analytical Data						
	Colour	%C	%H	%P	%F	%M	M.Wt.
$CpCo[C_4(CF_3)_4POF]$	Yellow	30.0 (30.3)	0.9 (1.0)	6.3 (6.3)	47.6 (48.2)	12.1 (11.9)	514 (514)
$CpCo[(C_4CF_3)_4PO_2H]$	Yellow	31.2 (30.5)	0.9 (1.1)	6.8 (6.5)	42.4 (44.5)	12.6 (11.5)	512 (512)

Calculated values in parentheses

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