

TRANSITION METAL FLUOROCARBON ^{COMPLEXES} ~~COMPLEXES~~

A thesis submitted by

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For my parents, in grateful memory.

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ABSTRACT

In this thesis is described the preparation and structure determination of several new transition metal fluorocarbon complexes derived from fluoro-olefins.

Perfluorobutadiene (C_4F_6) reacts with $Fe(CO)_5$ giving the heterocyclic complex $C_4F_6Fe(CO)_4$. With $Co_2(CO)_8$ a complex of stoichiometry $C_4F_6Co_2(CO)_6$ is obtained, which co-ordinates additional ligands to form the complexes $C_4F_6Co_2(CO)_6L_2$ [$L = PPh_3$, PBu_3 , $AsPh_3$ or $L-L = \text{dipyridyl}$]. The diene also reacts with $(PPh_3)_3RhCl$ and $(AsPh_3)_3RhCl$ to give complexes having the stoichiometry $(PPh_3)_2RhCl.C_4F_6$ and $(AsPh_3)_2RhCl.C_4F_6$. With $[Rh(CO)_2Cl]_2$ the dimeric complex $[Rh(CO)_2Cl.C_4F_6]_2$ is obtained. The structures of these complexes are discussed from a consideration of their spectral properties.

Perfluorobut-2-ene (C_4F_8) reacts with $Co_2(CO)_8$ at 150° , giving the complex $Co_4(CO)_{12}C_8F_{12}$, with loss of fluorine from the olefin. This compound reacts with further ligands to give dimeric complexes of stoichiometry $Co_2(CO)_6C_4F_6.L_2$ [$L = PPh_3$, $AsPh_3$ or $L-L = (Ph_2PCH_2)_2$]. The olefin has also been found to react with palladium and platinum triphenylphosphine and arsine compounds to give the expected complexes $(PPh_3)_2PdC_4F_8$ and $L_2PtC_4F_8$ [$L = PPh_3$, $AsPh_3$]. The spectral properties are again discussed with respect to the proposed structures.

Tetrakis(trifluoromethyl)cyclopentadienone ($C_9F_{12}O$) reacts with PPh_3 and $(Ph_2PCH_2)_2$ to give compounds of stoichiometry

$C_9F_{12}O.PPh_3$ and $(C_9F_{12}O)_2(Ph_2PCH_2)_2$, which are considered to contain a 3-membered heterocyclic structure. The colourless compounds formed between this dienone and amines have been shown to be amine fluorides.

The heterocyclic rhodium cyclobutanone complex $[(C_4H_6O)RhCOCl]_2$ has been studied. The structure of the compound is discussed. Further cleavage products have been prepared, and the nature of these complexes is shown to fall into one of two categories, a covalent complex with a Rh-Cl covalent bond, or an ionic complex containing a Rh complex cation.

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INTRODUCTION

Hydrocarbon complexes of transition metals have been known for over 100 years. The beginning of this subject can really be taken back to the work of Zeise, who in 1837 prepared the complex $\text{KCl.PtCl}_2.\text{C}_2\text{H}_4.\text{H}_2\text{O}$ (1) by co-ordination of ethylene to platinum. However the nature of the bonding in such complexes remained vague until comparatively recently, when the complex ferrocene (2) was prepared and its structure elucidated (3). This has led to a great deal of interest in the preparation and bonding of complexes which contain a transition metal directly bonded to carbon.

A transition metal can be bonded to carbon in two ways; firstly through a single electron pair bond, and secondly through a link possessing multiple bond character. The single covalent bond is analogous to that found with main group metals, as in $\text{Pb}(\text{CH}_3)_4$, the bond being formed by overlap of two orbitals along the line joining the two atoms, a σ -bond. The second type of bonding involves not only overlap of a carbon sp orbital with a vacant metal hybrid orbital, but also overlap of a filled d orbital on the metal with an antibonding p^* orbital of correct symmetry on the ligand. This type of bonding, a π -type bond, is prevalent with compounds of sp or sp^2 hybridised carbon, such as olefins and acetylenes. Filled or partially filled d orbitals are necessary for this type of bonding, hence it does not occur with non-transition metals, and it also means that bonds between π -electron donors and transition metals are stronger than those

between simple alkyls. It is also found however that transition metal alkyls are much less stable than alkyls of the main group metals, many of the simple transition metal alkyls existing only at low temperatures and being sensitive to air and moisture.

Jaffe and Doak (4) in 1953 calculated that a transition metal carbon σ -type bond will be weaker than those to main group metals because they have only about one third of the ionic resonance energy which stabilises alkali metal alkyls, and only about half the covalent energy that leads to stable bonds to other main group elements. Chatt and Shaw (5) then isolated several σ -bonded platinum alkyls. They considered that the instability of σ -bonds to transition metals may be because electrons can easily be promoted from the relatively high energy filled d orbitals into antibonding σ orbitals of the M-C bond. The formation of stable organometallic compounds would therefore require more than a certain minimum difference in energy between the highest energy orbital which contains electrons and the lowest energy orbital which is vacant, and that in most transition metal compounds with their rather close d energy levels this minimum is not attained. They postulated that the best way to increase this energy difference was to lower still further the energy of the non σ -bonding d orbitals by combining them with π -type orbitals of low energy in a suitable ligand, which is one capable of forming strong dative bonds. In agreement with these ideas they succeeded in synthesising several σ -bonded platinum-alkyl complexes in which

the metal was further co-ordinated to tertiary phosphines.

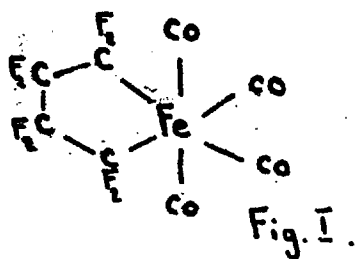
Following the ideas of Jaffe and Doak, it was considered that if the electronegativity difference between the transition metal and the organic moiety could be increased, there should be a corresponding increase in the ionic resonance energy, and hence stabilise the bond. This electronegativity can be effected by substituting the protons in the alkyl group by fluorines. In 1959 it was found that $\text{CF}_3\text{Mn}(\text{CO})_5$ could be prepared by an analogous scheme to the methyl complex (6,7):



This led to an upsurge of interest in σ -complexes of fluoroalkyls and a range of products were made covering a range of transition metals with different fluoroalkyl homologues. The following review is by no means comprehensive, but rather it attempts to illustrate the large variety of transition metal fluorocarbon complexes which have been prepared, and also to describe some of the methods available for elucidating the structures of the compounds obtained. Stone (8) has written reviews of the subject in *Advances in Organometallic Chemistry* and in *Endeavour* (9), and there is a Russian review dealing specifically with conditions favouring the formation and stabilisation of the carbon-transition metal σ -bond (10).

Although σ -bonded transition metal complexes are somewhat uncommon, since the discovery of ferrocene a large number of π -bonded olefinic complexes have been prepared. The first attempt

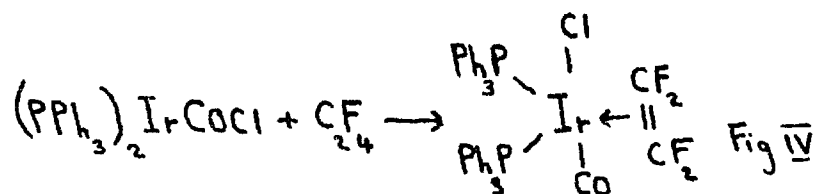
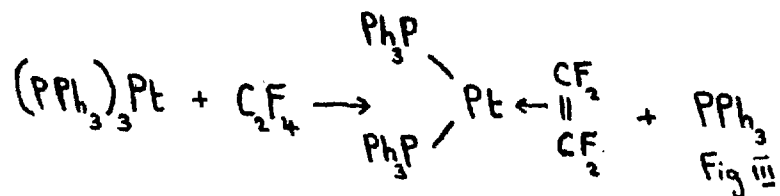
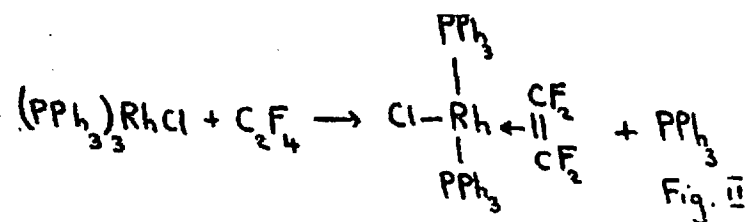
to make a fluoro-olefin complex using tetrafluoroethylene and pentacarbonyliron (11,12) revealed a notable difference, the



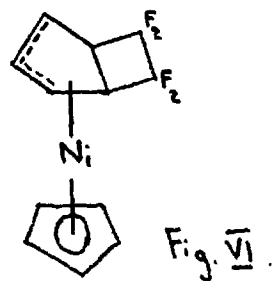
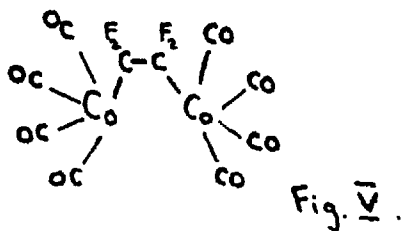
compound obtained was not π -bonded but a heterocyclic σ -bonded complex (I). Since the characterisation of this complex, the co-ordination chemistry of

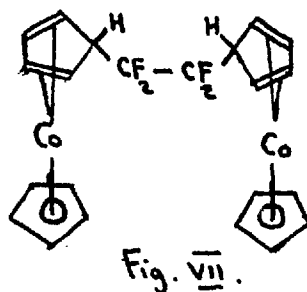
tetrafluoroethylene has been fully studied and has produced many novel complexes (13,14). Studies have proceeded utilising three types of reaction: (i) insertion into a metal hydride to give σ -bonded complexes; (ii) co-ordination with tertiary phosphine complexes in which the bond to the olefin is at right angles to the line of the C-C bond; and (iii) reaction with metal carbonyls or π -cyclopentadienyl carbonyls to give complexes of widely structurally different types. Studies involving insertions as in (i) have been carried out with pentacarbonyl manganese hydride (15), $\text{HMn(CO)}_5 + \text{C}_2\text{F}_4 \longrightarrow \text{HCF}_2\text{CF}_2\text{Mn(CO)}_5$, the proton migrating to the end of the carbon chain. The reaction has been widely used to prepare such compounds as $\pi\text{-cpMo(CO)}_3\text{CF}_2\text{CF}_2\text{H}$ (16), $(\text{HCF}_2\text{CF}_2)_2\text{Fe(CO)}_4$ (17), $\text{K}_3\text{Rh(CN)}_5\text{C}_2\text{F}_4\text{H}$ (18). Reaction type (ii) has been used where the tetrafluoroethylene replaces in solution, a labile triphenylphosphine, as in reactions (a) and (b), or simply adds to a free co-ordination position on the metal as in (c).

The third type of co-ordination involving cyclopentadienyls or carbonyls leads to much less predictable products, this being



well shown by its reactions with octacarbonyl dicobalt (12),
 di π -cyclopentadienyl nickel (14) and di π -cyclopentadienyl cobalt
 (12) which give the complexes (V), (VI) and (VII) respectively.





For the second type of complexes the type of bonding is

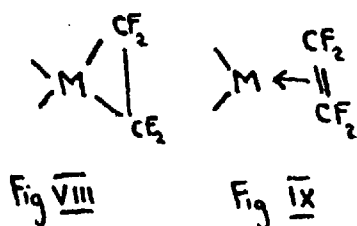
still unclear, it may be via two

σ -bonds as in (VIII), or it may

be via a π -type bond as in (IX).

Decision on the type of bond formed

is extremely difficult. In favour



of a π -type bond is the labile nature of the fluoro-olefin, the formation of the iridium complex (IV) being reversible at room temperature. However the infrared spectrum shows no peak assignable to a carbon-carbon stretch, and the ^{19}F geminal coupling constant in the platinum complex (X) shows a geminal F,F coupling constant of 200 c/s which is of the order observed in saturated fluorocarbon systems (20).

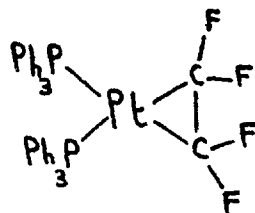


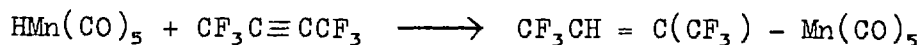
Fig. X

Another unsaturated fluorocarbon which has been widely

studied is perfluorobut-2-yne. It was initially considered that a perfluorinated acetylene should give stable organometallic compounds either more stable, or of a different nature from the well-known hydrocarbon complexes (22). Many complexes have been obtained, often by using similar preparative procedure as used for tetrafluoroethylene complexes.

The acetylene has again been found to insert into metal hydrides (23), act as a bridging ligand (20), and react with phosphine transition metal complexes to give analogous σ -, π -type compounds to those obtained with tetrafluoroethylene (19). As will be seen later, with these latter acetylene compounds a more fruitful consideration of the bonding can be made than with the olefin complexes.

Insertion into a transition metal hydride gives a compound with an olefin directly σ -bonded to the metal, an example being the insertion into pentacarbonyl manganese hydride (23).



The bridging role of the ligand is shown in its reactions with octacarbonyl dicobalt and π -cyclopentadienyldicarbonyl nickel dimer, which give the complexes (XI) and (XII) respectively (20).

The reaction with di π -cyclopentadienyl nickel has produced equal quantities of the complex (XII) and a new complex (XIII) (20), but the reaction with tetracarbonyl nickel gives a 30% yield of a tetrameric complex $[(\text{CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_3$.

The reactions of perfluorobut-2-yne with transition metal

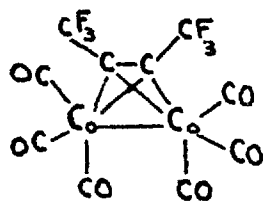


Fig. XI.

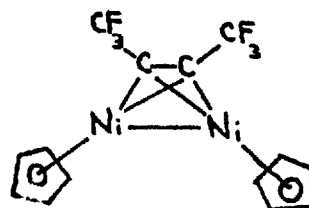


Fig. XXII.

carbonyls have in some instances produced complexes derived from tetrakis(trifluoromethyl)cyclopentadienone (XIV) (22), which has

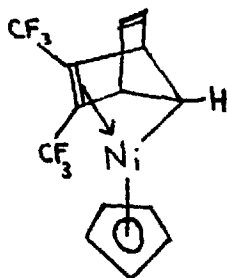


Fig. XIII.

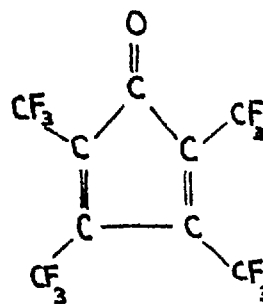
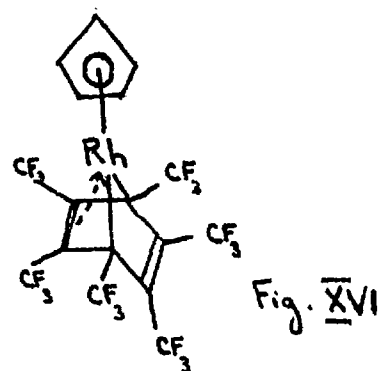
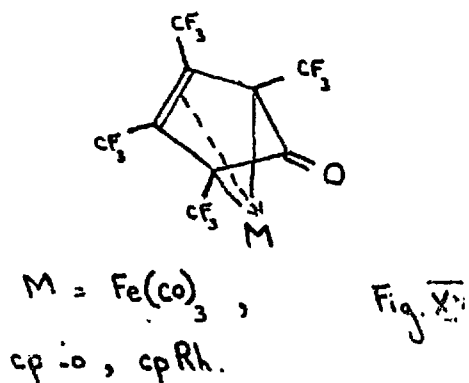


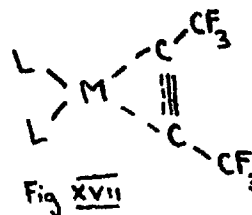
Fig. XIV.

been produced in situ by dimerisation and cyclisation of the acetylene with carbon monoxide inclusion. This type of reaction has been found with pentacarbonyliron, cyclopentadienyl cobalt dicarbonyl (22) and cyclopentadienyl rhodium dicarbonyl (XV) (25). The reaction with cyclopentadienyl rhodium dicarbonyl also gives a second product (XVI), which involves co-ordination of a cyclic perfluorobut-2-yne trimer.



The reactions involving simultaneous co-ordination of two atoms of the acetylene to one metal atom are obtained with chlorotris(triphenylphosphine)rhodium(I) (19), tetrakis(triphenylphosphine)platinum (26) and palladium(0) (27), π -cyclopentadienyl manganese tricarbonyl (26) and chlorobis(triphenylphosphine)carbonyl iridium(I) (21), and have the structure (XVII).

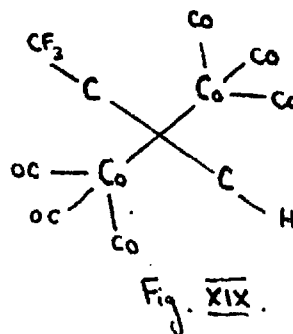
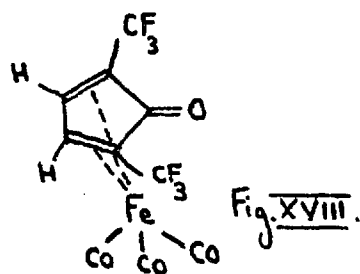
Co-ordination of the acetylene in this manner reduces the C-C bond order, and its position in the i.r. spectrum can be useful in determining the type of



bonding involved. This occurs at 1917 cm^{-1} in the complex $(\text{PPh}_3)_2\text{RhClC}_4\text{F}_6$, which indicates a π -bonded acetylene complex, but in the $(\text{PPh}_3)_2\text{IrCOClC}_4\text{F}_6$ complex this occurs at 1773 cm^{-1} , which corresponds more closely to an olefinic bond.

Very recently trifluoropropyne ($\text{CF}_3\text{C}\equiv\text{CH}$) (28,29) has been reacted with pentacarbonyliron and octacarbonyldicobalt. The former

gives a bis(trifluoromethyl)cyclopentadienone complex (XVIII) and the latter gives two complexes, depending on the quantity of

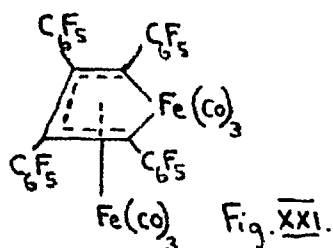


trifluoroacetylene employed.

The acetylene decafluorotolan ($C_6F_5C \equiv CC_6F_5$) has recently been prepared, and a cursory study made of its use as a suitable ligand for metal carbonyl complexes. With octacarbonyl dicobalt the product is structurally analogous to that

obtained from diphenylacetylene (31), the acetylene bridging the two cobalt atoms. With pentacarbonyliron a complex of molecular

formula $Fe_2(CO)_6(C_6F_5C \equiv CC_6F_5)_2$ is formed, (XXI), together with tetrakis(pentafluorophenyl)cyclopentadienone.



Recent fluorocarbon studies have also been concentrated on the preparation of organometallics from dienes. The first study of this kind was concerned with octafluorocyclohexa-1,3-diene (12). This olefin reacts with dodecacarbonyl tri-iron to give the complex of stoichiometry $C_6F_8Fe(CO)_3$ and the structure suggested, (XXII), consists of a π -bonded delocalised system, although the possibility of a structure with two Fe-C

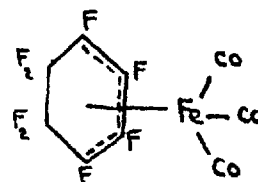


Fig. XXII.

σ -bonds and one co-ordinated double bond is not excluded (10). However this complex has been later found to react with caesium fluoride to give the anionic complex which represents the first definite example of a perfluoro- π -allylic metal complex (32). Octafluorocyclohexa-1,3-diene reacts with both octacarbonyl dicobalt and di π -cyclopentadienyl nickel to give the novel complexes (XXIII) and (XXIV) (33), the structure

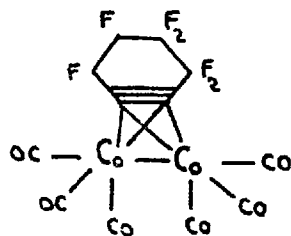


Fig. XXIII.

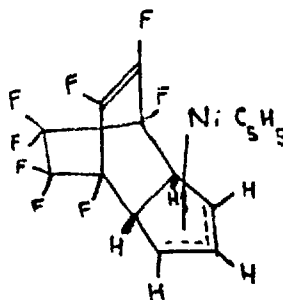


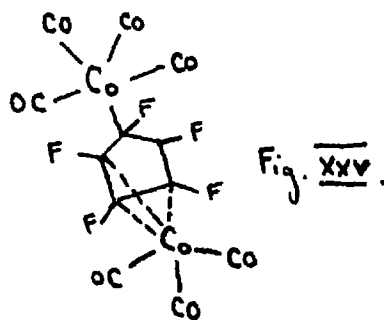
Fig. XXIV.

of (XXIII) having been verified by X-ray crystallography.

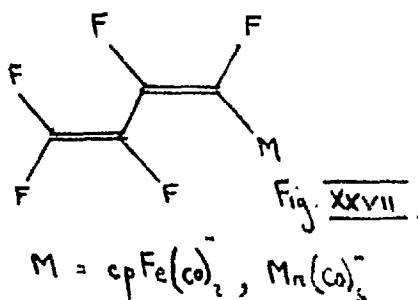
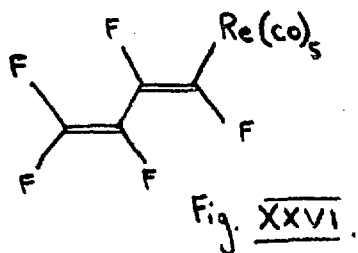
A recent communication describes complexes formed from

the reaction of perfluorocyclopentadiene with octacarbonyl dicobalt, π -cyclopentadienylcobalt dicarbonyl and pentacarbonyliron (35). The complexes obtained have stoichiometries $[C_5F_6 \cdot Co(CO)_2]_2$, $\pi-C_5H_5Co(CO)C_5F_6$ and $Fe_2(CO)_8C_5F_6$. The authors do not discuss the bonding in detail but consider it unlikely that π -bonding occurs.

An X-ray structure determination of the complex from $Co_2(CO)_8$ however has shown the complex to be $Co_2(CO)_7C_5F_6$ and have a structure containing a bridged perfluorocyclopentadienyl group (36). This structure involves the cobalt tricarbonyl moiety being bonded to a fluoro-allyl fragment, and the cobalt tetracarbonyl being σ -bonded to the cyclic ligand.



There is a relative paucity of work on the simplest of the fluorinated dienes, perfluorobutadiene. There is a mention that it forms an unstable platinum complex (37), and a brief description of the products of



the reaction with the carbonyl anions $[\text{Re}(\text{CO})_5]^-$, $[\pi\text{-cpFe}(\text{CO})_2]^-$ and $[\text{Mn}(\text{CO})_5]^-$ to form either cis (XXVI) or trans (XXVII) σ -bonded complexes (38)

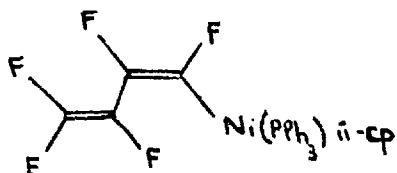


Fig. XXVIII.

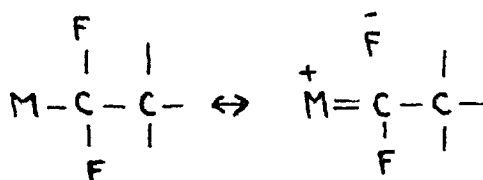
The only other perfluorobutadienyl complex was obtained in an attempt to make $\pi\text{-cpNi}(\text{CO})\text{CF}=\text{CF}_2$ from perfluorovinylMgBr and π -cyclopentadienyl nickel carbonyl iodide (39).

Treatment of the product with triphenylphosphine yields the trans-perfluorobutadienyl nickel complex (XXVIII).

Probably the most significant feature of transition metal complexes derived from fluoro-olefins is the predominance of σ -bonding in the compounds obtained. This is quite different from the hydrocarbon derivatives where the bonding tends to be of a π -type, and often the bonding is from a delocalised system. A good example of this is in cyclopentadienyl complexes where each carbon atom is the same distance from the metal; the first structural studies on a perfluorocyclopentadiene complex (XXV) have shown this to be quite different, being bound at one end by a σ -bond.

At present there is no satisfactory explanation for the relatively high stability of a transition metal fluorocarbon σ -bond. However several X-ray crystallographic structural studies have been carried out on fluoroalkyl complexes which have revealed several definite features. Churchill first studied the complex

$\pi\text{-cpRh}(\text{CO})\text{ICF}_2\text{.CF}_3$ (40) and found the Rh-C bond length significantly shorter, and the C-C bond length longer, than had been anticipated. Also he found the angles Rh-C-F and Rh-C-C to be large. These features are discussed both on a V.B. and M.O. treatment. The former theory accounts for this by invoking the structure as a resonance hybrid, the no-bond resonance structure (B) being responsible for the change in bond lengths. The increase



in bond angles is due to increased electrostatic repulsion between the Rh-C₂F₅ bond, and the other bond involving the

alpha carbon atom. The M.O. theory explains these features as being attributable to back bonding from a filled metal d orbital to a vacant antibonding (σ^*) orbital of suitable energy and symmetry on the fluoroalkyl group. Several other X-ray crystallographic studies have been carried out which substantiate the general features observed by Churchill (41,42).



The most significant study is that of $\pi\text{-cpMo}(\text{CO})_3\text{C}_3\text{F}_7$ (43) since the corresponding parameters of the ethyl complex, $\pi\text{-cpMo}(\text{CO})_3\text{C}_2\text{H}_5$ had been previously determined. The

relative M-C bond lengths are 2.282 (Mo-C₃F₇) and 2.397 (Mo-C₂H₅), the former representing a bond order of ~ 1.17 . Also the bond angle M-C-C in the fluorocarbon complexes studied is always greater than the tetrahedral angle, although more X-ray structural studies are required since the angle in $\text{cpMo(CO)}_3\text{C}_2\text{H}_5$ is also 121° , hence this value may not necessarily be a reflection of back bonding in the fluoroalkyl complexes. A further X-ray study has been carried out on $\text{cis-CFH=CFMn(CO)}_5$ (44). Characterisation of this complex had previously been somewhat doubtful since the $J_{\text{F-F(cis)}}$ coupling constant had been found to be only 2 c.p.s. instead of the expected 80 c.p.s. coupling for olefinic fluorines (45). The X-ray work however confirms the postulated structure, but the n.m.r. anomaly could be due to the non-olefinic nature of the double bond caused by $d_\pi - \sigma^*$ back bonding.

A rather cursory study of the infrared spectrum of $\text{CF}_3\text{Mn(CO)}_5$ has also been made by Cotton (46). He finds that the position of the C-F stretch modes in the complex are shifted considerably from the positions in various CF_3X compounds. On average the positions have been lowered by about 100 cm^{-1} which represents a drop of roughly 10% in the C-F force constant, the author suggesting this being due to a drift of electrons from the appropriate d_π orbitals of manganese (d_{xz} , d_{yz}) into the C-F antibonding orbitals of the CF_3 group.

Although the theoretical nature of the difference in stability between σ -bonded hydrocarbon and fluorocarbon complexes

is only incompletely understood, there is a distinct difference when one considers the experimental thermal stabilities.

<u>Fluorocarbon complexes</u>	<u>Hydrocarbon complexes</u>
$C_2F_5Mn(CO)_5$ Stable to 120°	$C_2H_5Mn(CO)_5$ Existence unproven
$CF_3Co(CO)_4$ Can be distilled at 91°	$CH_3Co(CO)_4$ Stable below 0°
$(C_2F_5)_2Fe(CO)_4$ Stable to 100°	$(C_nH_{2n} + 1)_2Fe(CO)_4$ Attempts at synthesis failed
$cpNi(CO)R_F$ Indefinitely stable at room temperature in vacuo	$cpNi(CO)Me$ Transient existence at room temperature

Two extremely useful methods of structure determination in transition metal fluorocarbon chemistry have been infrared and nuclear magnetic resonance spectroscopy. The former is often used as a diagnosis whether a preparation has been successful, since fluorocarbons show a very strong absorption in the $1000-1400\text{ cm}^{-1}$ region (C-F stretch) (8). Although many fluorocarbons have been studied, there is little correlation between the position of the C-F stretch and the C-F environment. Although co-ordinated double bonds may not be observed, an unco-ordinated fluoro-olefinic C=C stretch occurs between 1550 and 1750 cm^{-1} and can prove useful when assigning a structure to a complex. The simultaneous co-ordination of fluorocarbon and carbonyl groups affects the position of the metal carbonyl. The electron withdrawing effect of the fluorocarbon reduces the back bonding to the carbonyl, and

thereby increasing the frequency of the M-C O absorption.

The only naturally occurring isotope of fluorine is fluorine 19, which possesses a nuclear spin of $1/2$. Unlike most of the heavier nuclei it has a favourable spin-lattice relaxation time for nuclear magnetic resonance spectroscopic studies. In comparison with the proton it has a relative n.m.r. sensitivity of 94% and so one can obtain a favourable signal to noise ratio with the resonances (47,48). Kaesz has recently written a comprehensive review (49) on the application of n.m.r. spectroscopy to organometallics, and he has included details of many of the known transition metal fluorocarbon complexes. Compared to ^1H n.m.r. the chemical shifts are extremely large; this means that the spectra can almost invariably be treated as first order, the chemical shifts being very large compared to the coupling constants ($\nu_0 \gg J$). This leads to a more facile interpretation of the spectra obtained. A most useful feature of the spectra is that a fluorine attached to a carbon atom alpha to a transition metal atom experiences a deshielding and so occurs at a low chemical shift. This has proved extremely useful in structure determination since it identifies certain fluorines.

SECTION A

COMPLEXES DERIVED FROM PERFLUOROBUTADIENE

(i) Introduction

Perfluorobutadiene is a colourless gas (b.p. 5.8° at 760 mm.) which may be obtained from chlorotrifluoroethylene and iodine monochloride (50). Irradiation of the resultant chloro-fluoroiodo-compound produces a hexafluorotetrahalogenobutane which can be dehalogenated with zinc to give perfluorobutadiene. Butadiene itself (C_4H_6) has been co-ordinated to transition metals with the formation of π -complexes (51,52,53), but the only known complexes of the fluorinated analogue are the σ -bonded complexes with Mn and Re carbonyl anions (38). Several complexes have been obtained from perfluorocyclohexadiene and organometallic compounds which have proved to be structurally interesting (12,33), and it is to be expected that perfluorobutadiene, the simplest of the fully fluorinated dienes, should give similar complexes and the lesser complexity of the ligand ought to make structure determination easier.

This section describes some compounds which have been obtained by reacting perfluorobutadiene with several transition metal carbonyl and phosphine complexes, and also discusses the structures of the products on the basis of their chemical and spectral properties.

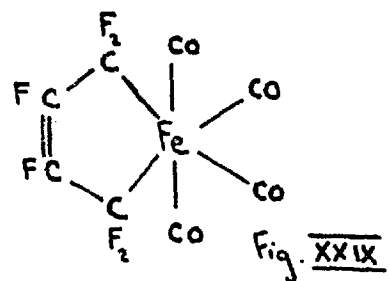
(ii) Interaction with Pentacarbonyliron

Perfluorobutadiene and pentacarbonyliron, in petroleum solution, interact under mercury-sensitised ultra-violet radiation to give a yellow solid, which on vacuum sublimation yields transparent greenish yellow plates. The complex melts sharply at $61-61.5^{\circ}$ and analyses as $C_4F_6Fe(CO)_4$. The i.r. shows four terminal carbon monoxide stretching frequencies, bands due to C-F stretch, and in addition a single sharp band at 1752 cm^{-1} . This latter band is correctly placed for a C=C stretch, and since it is a strong absorption it is probable that it is due to an unco-ordinated double bond.

The ^{19}F n.m.r. spectrum shows two peaks at -4.0 and $+71.9$ p.p.m. relative to benzotrifluoride (a +ve sign indicating an upfield shift), the area ratios being 2:1 respectively. Because of its low chemical shift, the large peak must be due to a $-\text{CF}_2-$ group which is directly σ -bonded to the Fe atom (54). Whereas the low field peak consists of a doublet ($J_{\text{F-F}} = 6.8$ c.p.s.), the high field one is more complex, and the splittings have not been completely resolved, but the chemical shift is consistent for the resonance to be assigned as being due to an olefinic fluorine atom. The spectral data is adequately explained by the structure (XXIX), which involves re-arrangement of the butadiene fragment leading to a heterocyclic σ -bonded mono-olefin. This structure closely resembles that of the compound formed between pentacarbonyliron and tetrafluoroethylene (12), except that in this case the heterocyclic

ring consists of a fully saturated perfluoromethylene chain.

This structure has now been confirmed by an X-ray crystallographic analysis (55). The coordination symmetry of the iron is closely octahedral having a Fe-C(F₂) bond length of 2.00 Å and Fe-C(O) length of 1.82 Å. The C₄Fe ring is planar, but it is thought that in addition to the σ-bonds formed between the 1,4 carbon atoms and the metal, there is some interaction between the metal and the 2,3-ethylenic type bond.



A σ-bonded fluorocarbon group, with its high electronegativity, withdraws electrons from the orbitals of the transition metal and thereby denuding somewhat those available for back bonding with the carbonyl. This affects the bond order in the carbonyl, and results in a shift of the carbonyl stretch to higher wave numbers. Table 1 shows the observed positions of the carbonyl

Table 1

<u>Complex</u>	<u>$\nu_{\max}$; M-C O (cm.⁻¹)</u>	<u>Ref.</u>
C ₄ F ₆ Fe(CO) ₄	2153, 2097, 2092, 2076	
C ₄ F ₈ Fe(CO) ₄	2160, 2108, 2088, 2055	(12)
C ₄ H ₆ Fe(CO) ₃	2051, 1978	(52)

stretching frequencies of this new complex and compares them with those of similar complexes to illustrate this effect.

The structure of this complex is however quite different from that of the compound formed from butadiene and pentacarbonyl-iron. The stoichiometry of this complex is $C_4H_6Fe(CO)_3$, and although it was considered initially to have a similar σ -bonded structure (56), an X-ray crystallographic structure determination has shown that the olefin is π -bonded (57). This leads to the molecule being square pyramidal, two corners of the square being occupied by carbonyl carbon atoms, and two by the 1,4 carbon atoms of the butadiene moiety.

The preparation and structure determination of this new complex well illustrates the difference in type of the compounds formed by fluoro-olefins; thus whereas butadiene forms a π -type bond and remains in a similar configuration when co-ordinated, perfluorobutadiene forms two σ -type bonds with internal re-arrangement within the olefin.

(iii) Interaction with Octacarbonyldicobalt

The thermal interaction of octacarbonyldicobalt and perfluorobutadiene yields two products, one a non-volatile red substance, and the other a volatile yellow compound. The former is insoluble in organic solvents, is non-crystalline, and the i.r. spectrum does not show any bands due to C-F stretches. The compound is not a cobalt fluorocarbon complex and has not been characterised. The other compound can readily be purified by vacuum sublimation

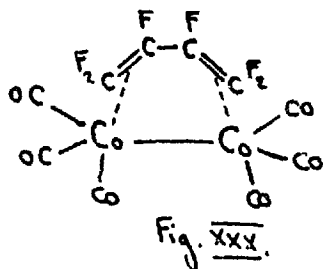
or can be crystallised from petroleum as large yellow needles.

This compound analyses as $C_4F_6Co_2(CO)_6$, the molecular formula being substantiated by the determination of the molecular weight in solution. The mass spectrum of the complex shows a value of 448 for the molecular ion, although the exact determination of its position is somewhat imprecise. The spectrum shows strong peaks corresponding to the lower masses of 420, 392, 364, 336, 308 and 280. The numerical difference between these mass peaks is 28, which corresponds to the CO molecule; and hence these peaks represent the progressive loss of the six carbon monoxide molecules from the complex. The observance of these peaks shows that the loss of carbon monoxide occurs before the complete fragmentation of the molecule, which has recently been found for pure metal carbonyls (58). However there is no evidence for a species in which only the fluorocarbon has been lost which is consistent with the observed strong binding of fluoro-olefins to cobalt carbonyl (59).

The i.r. spectrum in solution shows bands due to three terminal carbon monoxide groups which are at a high frequency due to the co-ordination of the fluorocarbon and bands assignable to C-F stretches. There are no bands due to bridging carbonyls, showing that it is these two carbon monoxides which have been replaced by the fluoro-olefin, and there are no bands due to an olefinic double bond.

The ^{19}F n.m.r. spectrum consists of two peaks of relative area 1:2 centred at 26.2 p.p.m. and 36.7 p.p.m. upfield of benzo-

trifluoride. The high field line is obtained as a sharp doublet ($J_{F-F} = 16.5$ c.p.s.), but the low field line is unusually poorly defined and broad (75 c.p.s.). The poor resolution of this peak is probably due to the proximity of the fluorine to the cobalt atom. Cobalt 59 has a nuclear spin of $7/2$, and this quadrupole moment should cause the ^{19}F resonance to be split into eight lines. In practice however it is unusual for these splittings to be resolvable at room temperature, the resonance normally appearing as just a broad peak. From this n.m.r. spectrum it is unlikely that one of the carbon atoms is directly σ -bonded to the cobalt, since the fluorine attached to this α -carbon would have been observed at a lower chemical shift. The structure best consistent with the



spectral evidence is one involving a cobalt dimer unit bridged by the perfluorobutadiene (XXX).

The structure of low valent first row transition metal complexes can often be decided by consideration of the empirical inert gas rule (60).

This formulates such complexes with the metal atom surrounded by that number of electrons which is required to achieve the electronic structure of the next highest inert gas. In the structure suggested for this complex one considers each carbonyl donates two electrons, and each double bond two electrons to a cobalt atom. Since cobalt(I) has the

electronic structure d^8s^2 , the total number of electrons surrounding each cobalt atom will be 18, which corresponds to the electronic structure of the next highest inert gas, krypton. Although this rule is by no means rigorous, it is a useful guide when assigning a structure to a low-valent organometallic complex, and although it can be used throughout the transition metal series, it is more closely adhered to for the first row elements. This complex has also been found to be diamagnetic which is what would be expected for such an electronic structure.

The bonding in the complex cannot be definitely concluded from the spectral evidence. The two possibilities are a π -bonded structure, with a π -bond between the double bonds and the respective cobalt atoms, or a structure in which each double bond is co-ordinated to the cobalt atom by two σ -bonds. The latter structure is possibly correct since this would lead to the fluorines of the CF_2 groups being in equivalent environments, which is shown by the occurrence of only the one resonance in the n.m.r. spectrum for the CF_2 group. This would mean that the cobalt atoms were formally cobalt(III). This implies a useful criterion when considering synthetic routes to fluoro-olefin complexes; since the bonding of the olefin to the metal formally involves the formation of two σ -bonds, the oxidation state of the metal is increased by two, and success is more likely to be achieved by starting with a metal in such an oxidation state that it can be increased by two to form a stable species. This is well illustrated with the perfluorobutadiene complex of pentacarbonyl-

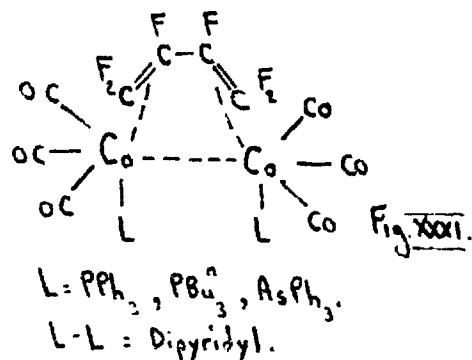
iron where the iron has increased its oxidation number from zero to two on complex formation.

Although an X-ray crystallographic structure determination would be necessary before the bonding could be assigned, it has been found that this is very difficult because the molecule possesses a large unit cell, and the only confirmation of the structure which has been obtained is that the cobalt-cobalt distance seems short enough to satisfy the criterion for metal-metal bonding (61).

The complex is quite air and moisture stable, and it is not decomposed by bromine or iodine at 80° or by the action of strong acids. With carbon monoxide however at 150° and 150 atmosphere, partial conversion to octacarbonyldicobalt occurs. An attempt was made to cleave the metal-metal bond and produce a dimeric cobalt hydride species. When sodium amalgam is added to a bright yellow solution of the complex in tetrahydrofuran under nitrogen, the colour of the solution is lost. Filtration, acidification and concentration gives a colourless solution but the n.m.r. spectrum failed to show any resonance in the usual position for metal hydrides. The non-observance could be because the electron withdrawing effect of the fluorocarbon ligand makes such a species unstable, or it could be that a sufficiently concentrated solution could not be obtained.

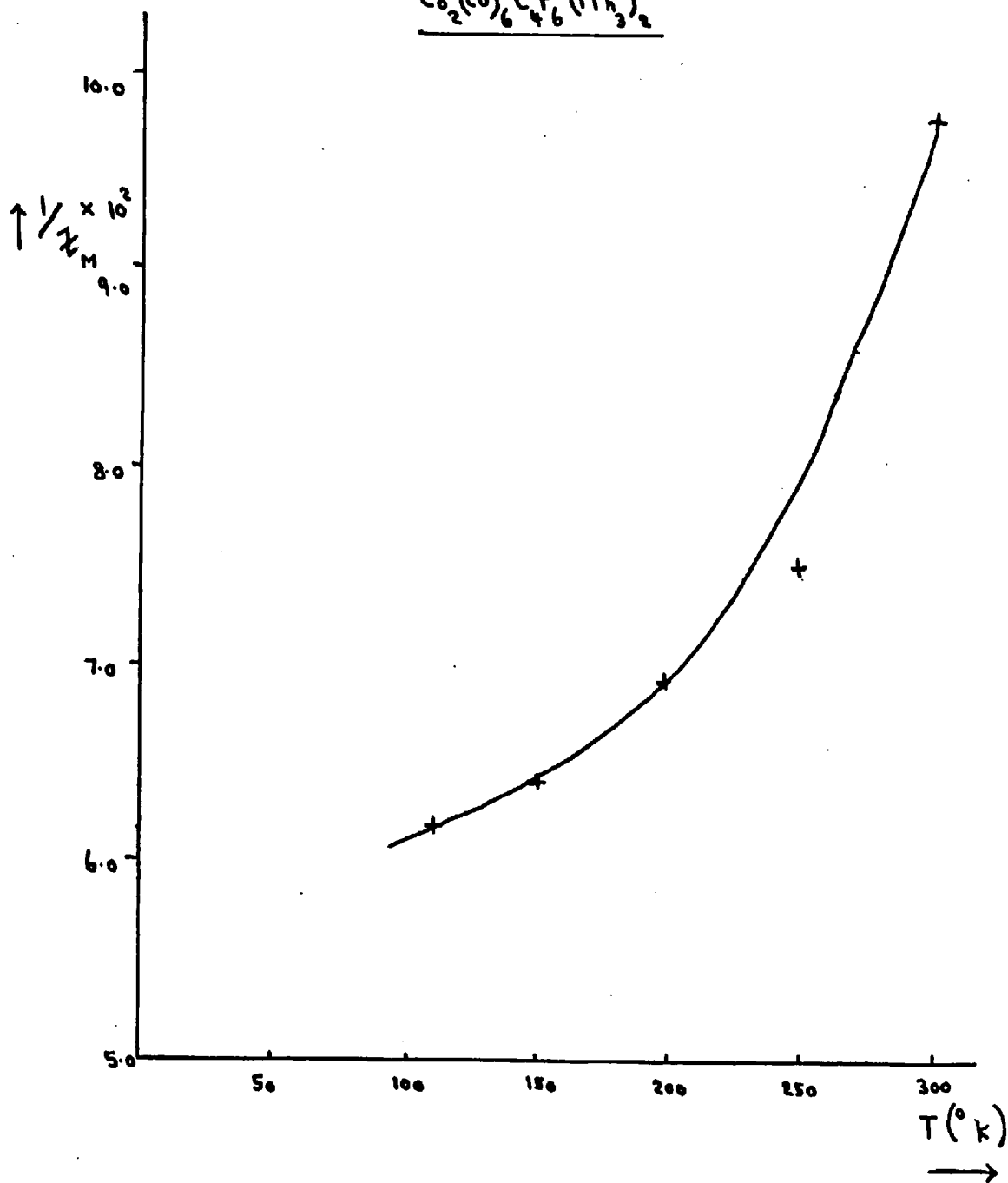
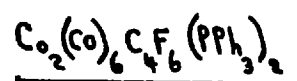
Whilst attempts at substituting either the carbonyl or fluorocarbon ligands have proved unsuccessful, the complex readily reacts with Lewis bases by additional ligand co-ordination to yield

paramagnetic complexes which have the structure (XXXI). The first of these to be obtained was formed by refluxing $C_4F_6Co_2(CO)_6$ with two moles of triphenylphosphine in petroleum. The adduct is obtained as a very sparingly soluble precipitate which analyses as $C_4F_6Co_2(CO)_6-(PPh_3)_2$. This compound is paramagnetic, the magnetic moment by the Gouy method being 2.0 B.M. at room temperature. This is equivalent to a magnetic moment of 1.4 B.M. for each cobalt atom, and although this value is too high for the cobalt to be diamagnetic, it is too low for the metal atom having one unpaired electron. According to the Curie-Weiss law the paramagnetic susceptibility should be inversely proportional to the temperature, and often a simple linear relationship is obtained (59). The paramagnetic susceptibility of $C_4F_6Co_2(CO)_6(PPh_3)_2$ has been measured at temperatures down to $100^\circ K$. The reciprocal of the susceptibility does decrease on lowering the temperature, but the relationship more closely fits a curve than a straight line.



Many copper(II) complexes are known which have an anomalously low magnetic moment (62). These compounds are bridged complexes containing either a three atom e.g. copper acetate, or a single atom e.g. CuO, bridge. The temperature variation of

Temperature dependence of the paramagnetism of



copper acetate is somewhat typical, passing through a maximum at 270°K and then decreasing rapidly as the temperature is lowered. It is deduced that the lower magnetic moment is a consequence of the stronger copper-copper linkage. From this it is concluded that the magnetic interaction should become larger as the metal-metal distance decreases, and this is what is found in practice. The paramagnetism of this complex could be due to the similar effect of a short Co-Co distance.

The presence of incompletely paired electrons on the cobalt is verified by the e.s.r. spectrum of the powder. The spectra at 78° and 295°K are almost identical in position and strength, and show three rather poorly resolved lines at $g = 1.95, 2.67$ and 2.95 , which are correctly placed for a cobalt spectrum. As with the n.m.r. spectrum, the nuclear spin of $7/2$ should lead to the occurrence of an 8 line spectrum, but again this detailed fine structure is not usually resolvable.

$C_4F_6Co_2(CO)_6$ also reacts readily with tributylphosphine, triphenylarsine and dipyridyl to give adducts which have the same stoichiometry as the triphenylphosphine compound. The PBu_3^n complex is rather unstable and has not been studied but the $AsPh_3$ compound is an air stable yellow precipitate. Unlike the PPh_3 compound this one is readily soluble in chloroform, acetone and benzene; this has allowed an osmometric determination of the molecular weight to be carried out which confirms that the structure is dimeric like the parent $C_4F_6Co_2(CO)_6$. The complex is similar to the PPh_3 derivative

being paramagnetic with a magnetic moment of 2.6 B.M. at 292°K. The e.s.r. again shows a peak in the correct position for an unpaired electron on cobalt at $g = 2.35$, the single resonance being broad and unresolved.

The addition complex with dipyridyl has the correct stoichiometry, $C_4F_6Co_2(CO)_2(dipy)$ for the ligand acting as a bidentate and bridging the two cobalt atoms. Since the two atoms are already bridged by the perfluorobutadiene fragment, for the introduction of a second chelating ligand the cobalt atoms must be held close together. This prerequisite forestalls the possibility that the two metal atoms are well apart in a transoid arrangement with the double bonds of the butadiene.

(iv) Interaction with Tris(triphenylphosphine)chlororhodium(I)

When a solution of tris(triphenylphosphine)chlororhodium^I in benzene is heated with perfluorobutadiene in the absence of air, a yellow compound is obtained, which can readily be recrystallised from hot benzene or dichloromethane and methanol to give pale yellow needles. The same compound can also be prepared from bis(triphenylphosphine)ethylene chlororhodium^I (63) which is more favourable since the former method gives also one mole of triphenylphosphine per mole of compound. Since this has similar solubility properties to the compound required, contamination leads to erratic analytical results. The latter method gives one mole of ethylene per mole of required compound which leads to no contamination difficulties. Microanalysis shows that the compound can be formulated as $(PPh_3)_2RhC_4F_6Cl$, and

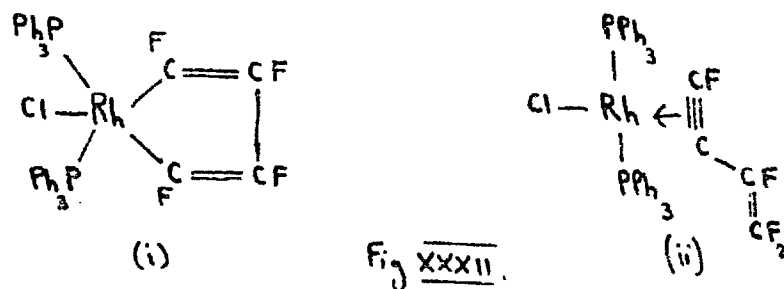
osmometric molecular weight determination verifies the complex monomeric, the product being formed with the unexpected loss of two fluorines from the diene.

The i.r. spectrum of the complex in solution shows the expected bands due to triphenylphosphine and carbon-fluorine bonds. In addition there are two bands at 1739 and 1672 cm^{-1} which are in the correct position to be assigned as olefinic carbon-carbon bonds. In addition there is a sharp band at 303 cm^{-1} , which is probably due to the Rh-Cl stretch. No comprehensive study has been made of the theoretical or observed positions of this infrared active mode, but in a recent paper (64) a number of complexes having a rhodium-chlorine bond have been investigated in this region. This work has shown that a terminal $\text{Rh}^{\text{I}}\text{-Cl}$ stretch appears at 300-310 cm^{-1} , and a bridging $\text{Rh}^{\text{I}}\text{-Cl}$ at the somewhat lower value of 280-290 cm^{-1} . From this it appears that the band is due to a terminal Rh-Cl bond, showing that the chlorine is not bridging and also has not transferred to the fluorocarbon ligand.

The n.m.r. spectrum consists of three resonances centred at -9.96, +64.77 and +74.08 p.p.m. relative to benzotrifluoride, the area ratios being 2:1:1 respectively. The low field peak consists of 14 lines, the middle peak of 6, and the high field peak is poorly resolved consisting of 3 equal lines.

From the spectral data two structures can be considered possible, one where the fluorine atoms have been lost from the 1,4, and the other from the 1,2 positions of the perfluorobutadiene. These

structures are shown in Fig. (XXXII).



Mays and Wilkinson (19) have prepared several fluorocarbon complexes from tris(triphenylphosphine)chlororhodium(I) and tetrafluoroethylene, chlorotrifluoroethylene and perfluorobut-2-yne. In these compounds the fluorocarbon is rather readily eliminated and they consider that the fluorocarbon is π -bonded. This new complex obtained from perfluorobutadiene also has a readily eliminated fluorocarbon moiety. If carbon monoxide is passed through a benzene solution of the complex at room temperature however, there is no evidence for the formation of a Rh(III) carbonyl, and only slight formation of the Rh^{I} carbonyl; the fluorocarbon is removed though when a benzene solution at 60° is held under a carbon monoxide pressure of 50 atmos., or when the complex is refluxed in ethanol. The complete removal of the fluorocarbon is also readily effected when the complex is dissolved in pyridine, the pyridine co-ordinating to the rhodium triphenylphosphine complex. This lability of Group VIII triphenylphosphine fluoro-olefin complexes seems to be fairly general since

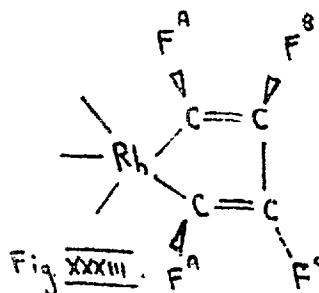
the addition complexes of bis(triphenylphosphine)iridium^I carbonyl chloride are also extremely labile (21).

The full analysis of the n.m.r. spectrum of a 7 spin system is obviously extremely complex, but the spectrum is still useful for differentiating between the two structures. The middle peak is well resolved into a double triplet ($J = 21.5$ c.p.s.), the triplets being separated by 9.0 c.p.s. In structure (ii) this resonance would be associated with the acetylenic fluorine with couplings between rhodium ($J_{F-103Rh} = 9.0$ c.p.s.) and phosphorus ($J_{F-3,P} = 21.5$ c.p.s.). For structure (ii) though, the low field peak must be associated with a CF_2 group which is not directly σ -bonded to a transition metal. Some complexes are known with perfluorobut-2-yne, such as $(PPh_3)_2PtC_4F_6$ (26), where a low shift n.m.r. peak is not associated with a CF_3 group directly bonded to a transition metal. In these cases however the n.m.r. of the free ligand shows a resonance at low field, and the n.m.r. spectrum of the complex is doubtless due to the similarity to the free ligand. The n.m.r. of perfluorobutadiene shows three equal resonances centred at 30.8, 44.8 and 116.0 p.p.m. upfield of benzotrifluoride. Also if structure (ii) were correct one would expect to see cis and trans couplings of the order of 80 and 120 c.p.s. for the olefinic $CF=CF_2$ group.

The n.m.r. spectrum is probably better explained in terms of structure (i). The large peak centred at low field now accords with the general theory of being due to a CF group directly σ -bonded to a metal. Since two further resonances are obtained, the other

fluorine atoms must be non-equivalent, which can be achieved if the two fluorine atoms are arranged so that one is cis and the other trans.

The low field line consists of 14 lines arranged in two groups of 7 symmetrical about a gap in the centre. This



complex splitting is due to the coupling between F^A and the nuclei F^B , F^C , ^{103}Rh and ^{31}P each of which has a nuclear spin ($I = 1/2$). With this structure one would again expect the cis and trans olefinic couplings between F^A and F^B , F^C to be observed. A recent paper describes the preparation of cis-1,2-difluorovinylpentacarbonylmanganese, which contains a double bond in a similar environment, namely $\begin{array}{c} \text{F} \quad \text{F} \\ | \quad | \\ \text{M} - \text{C} = \text{C} - \end{array}$. They report that the n.m.r. shows an F-F olefinic coupling constant of only 2 c.p.s. (45).

The structure has since been confirmed by an X-ray crystallographic structure (44) determination, and it is considered that the olefinic bond is affected by the close proximity of the metal atom. This causes a drift of d_π electrons from the metal into the antibonding orbitals of the C-F bond, which leads to an anomalous F-F interaction, and it is quite probable that a similar effect is affecting the double bond in this rhodium complex.

Although the fine structure of the n.m.r. spectrum is probably better explained by structure (ii), the positions of the peaks, and

the non-observance of the olefinic coupling constants is better explained by the σ^- -bonded structure, and this one is the more favoured.

Although the fluorocarbon group can be readily eliminated it has not been possible to obtain any gaseous product from the decomposition. If however the complex is refluxed overnight in methanol, and the residue extracted with ether, the extract contains a solid product which shows i.r. bands due to C-F groups, and a band due to an olefinic double bond. It seems likely that the ligand is not liberated free but that it undergoes polymerisation to a higher fluoro-olefin which is not gaseous.

Similarly from tris(triphenylarsine)chlororhodium(I) and perfluorobutadiene one again obtains a yellow compound which can be recrystallised from a dichloromethane, methanol mixed solution to give pale yellow crystals.

The i.r. spectrum shows the expected bands due to triphenylarsine and a fluorocarbon, and two bands at 1645 and 1567 cm^{-1} which are again correctly placed to be assigned to olefinic double bonds, occurring in the same region as those for the phosphine complex. The i.r. also shows bands attributable to the Rh-Cl stretch at 341, 332 and 299 cm^{-1} .

The complex is analogous to the phosphine complex and to the other rhodium fluoro-olefin in the lability of the fluorocarbon, refluxing in alcohol readily giving bis(triphenylarsine)chloro carbonyl rhodium(I) in good yield.

Because of the somewhat limited solubility and stability

in solution, the n.m.r. spectrum has not been obtained under high resolution. The low resolution spectrum shows the expected three peaks (area ratio 2:1:1) centred at -9.6, +60.4 and +71.1 p.p.m. from benzotrifluoride respectively which compares closely with the n.m.r. spectrum of the phosphine complex (-9.96, +64.77, +74.08 p.p.m.). Analytical data shows that the compound has the molecular formula $(AsPh_3)_2RhClC_4F_4$, and from the spectral evidence the structure is doubtless entirely analogous to the phosphine complex.

An attempt to obtain a third similar complex from tris(tri-phenylstibine)chlororhodium(I) and perfluorobutadiene has given a brown solid from which no identifiable compound can be isolated.

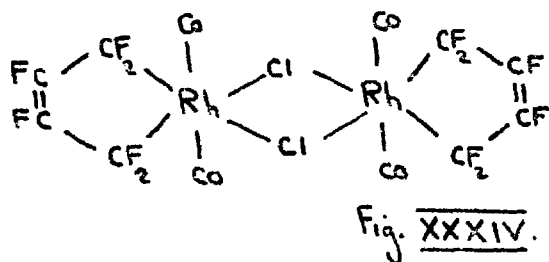
(v) Interaction with Rhodium carbonyl chloride

Rhodium carbonyl chloride slowly reacts with perfluorobutadiene at 30° to give a fawn coloured solid. The compound is somewhat soluble in CH_2Cl_2 , but addition of petroleum readily reprecipitates it.

Microanalytical data shows the complex to have the stoichiometry $C_4F_6Rh(CO)_2Cl$, and osmometric determination of the molecular weight gives a value of 706, which is very close to the value required for the complex being dimeric. The i.r. spectrum shows two strong well-separated bands in the carbonyl region at 2110 and 2029 cm^{-1} , bands due to C-F groups, and a strong band at 1678 cm^{-1} . The spectrum also shows a band at 285 cm^{-1} , which is in the correct position for a bridging Rh-Cl stretch, the value for rhodium carbonyl chloride itself being at 277 cm^{-1} (64).

The complex is too insoluble for an n.m.r. spectrum to be

obtained, but from the i.r. spectral data a heterocyclic structure (XXXIV) is probable. From this structure the band at 1678 cm^{-1}



must be due to the olefinic double bond. The other possibility is a heterocyclic 6-membered ring complex formed by carbonyl insertion, making one of the carbonyls ketonic.

A similar type of ketonic complex is obtained from $\text{Rh}(\text{CO})_2\text{Cl}$ and cyclopropane (65). The complex shown however is favoured since it contains Rh(III) in its most common co-ordination number of 6, and is further favoured since a 5-membered ring is the most favoured heterocyclic system (66). The formation of a ketonic ring would lead to each rhodium having only one non-ketonic carbonyl. Since it is very unlikely that the metal atoms are in widely differing structural environments, this structure would not explain the observation of two well-separated bands in the carbonyl region of the i.r.

The complex reacts with pyridine, but the expected cleavage of the Rh-Cl bridge occurs with the simultaneous removal of the fluoro-carbon group. A similar reaction occurs with triphenylphosphine, the product being $(\text{PPh}_3)_2\text{RhCOCl}$.

EXPERIMENTALInteraction of perfluorobutadiene with pentacarbonyliron

An excess of perfluorobutadiene (2 ml.) and pentacarbonyliron (1.5 ml.) in a sealed glass tube containing a little mercury, was irradiated with ultra-violet light for 24 hours. After removal of the excess liquid in vacuum, the residue was crystallised from petroleum at -40° . The solid was then sublimed in vacuum from room temperature to a water-cooled probe to give the pure complex as transparent green plates. Yield ca. 100 mg., m.p. $61-61.5^{\circ}$. [Found: C, 29.0; F, 34.3; Fe, 17.0. $C_8F_6FeO_4$ requires C, 29.1; F, 34.5; Fe, 16.9.] $\nu_{(max)}$ (cyclohexane): 2153s, 2097s, 2092s, 2076s, 1752s, 1344m, 1310s, 1287sh, 1122s, 1090m, 1059m, 977s, 928s, 815m.

On standing for 3 months the complex changed colour to pink. When this material was sublimed on to a water-cooled probe a colourless compound was obtained which was spectroscopically and analytically analogous to the initial complex, but there remained a non-volatile red residue which was probably iron.

Interaction of perfluorobutadiene with octacarbonyldicobalt

An excess of perfluorobutadiene (3.5 ml.) and octacarbonyldicobalt (4 g.) in a thick-walled glass tube were heated at 100° for 24 hours. After opening and removal of excess C_4F_6 , the residue was extracted with petroleum (b.p. $40-60^{\circ}$) to leave a red residue. The solution was evaporated and the dark residue sublimed in vacuum at 60° to a water-cooled probe. Two crystallisations from petroleum produced yellow needles of the complex. Yield, ca. 4 g., m.p. $85-85.5^{\circ}$.

[Found: C, 27.1; Co, 26.3; F, 25.4. $\bar{M}$, 460 (benzene). $C_{10}Co_2F_6O_6$ requires C, 26.8; Co, 26.4; F, 25.4. $\bar{M}$, 448.] ν _(max) (cyclohexane): 2132s, 2096s, 2079s, 1284m, 1244m, 1199s, 1100s, 994s, 888m, 730s, 665s.

The complex is soluble in all common organic solvents.

Bis(triphenylphosphine)perfluorobutadiene hexacarbonyldicobalt

Perfluorobutadiene hexacarbonyldicobalt (0.2 g.; 1 equiv.) and triphenylphosphine (0.24 g.; 2 equivs.) in petroleum (20 ml., b.p. 60-80°) were refluxed for 2 hours. The yellow-orange precipitate of the complex was filtered off and washed with petroleum and acetone. Yield, quantitative; m.p. 146-150° [Found: C, 56.6; H, 3.4; F, 12.5. $C_{46}H_{30}Co_2F_6O_6P_2$ requires C, 56.8; H, 3.1; F, 11.7.] ν _(max) (nujol mull): 2073s, 2048s, 2024s, 2018s, 1236s, 1186s, 1164m, 1098m, 1088m, 1070m, 1042m, 1000m, 977m, 969s, 880s, 715s, 696s. The magnetic moment (from susceptibilities by the Gouy method, corrected for diamagnetism of ligands), μ_{eff} in B.M., °K: 2.0, 297°; 1.9, 254°; 1.8, 204°; 1.6, 155°; 1.4, 113°.

Bis(tri-n-butylphosphine)perfluorobutadiene hexacarbonyldicobalt

In a similar way using stoichiometric quantities with tri-n-butylphosphine to yield an orange tar after removal of petroleum. This material was dissolved in methanol and cooled to -40° to give orange crystals of the complex which were collected and dried in vacuum. Yield, ca. 70%; m.p. 77.5-78°. [Found: C, 48.0; H, 6.6; Co, 14.0; F, 13.7. $C_{34}H_{54}Co_2F_6O_6P_2$ requires C, 47.9; H, 6.3; Co, 13.9; F, 13.4.] ν _(max) (cyclohexane): 2058s, 2027s, 2008s, 1993m, 1381s,

1274s, 1230s, 1186s, 1092s, 1071s, 1053s, 977s, 882s, 775m, 712s.

Bis(triphenylarsine)perfluorobutadiene hexacarbonyldicobalt

Again in a similar way using triphenylarsine to give an essentially quantitative yield of the yellow complex, m.p. 110° (decomp.). [Found: C, 52.2; H, 2.9; F, 10.8; M, 1080 (CHCl₃).

C₄₆H₃₀As₂Co₂F₆O₆ requires C, 52.1; H, 2.8; F, 10.8. M, 1060.]

ν_(max) (CH₂Cl₂): 2110m, 2045s, 2018s, 1931s, 1709w, 1597w, 1399m, 1220s, 1183s, 1157sh, 1073s, 1050ms, 977s, 878s. The magnetic moment μ_{eff}: 2.6 B.M. at 297°.

The complex is soluble in dichloromethane and chloroform but only slightly soluble in petroleum.

2,2'Dipyridyl perfluorobutadiene hexacarbonyldicobalt

Perfluorobutadiene hexacarbonyldicobalt (0.1 g.; 1 equiv.) and 2,2'dipyridyl (0.2 g.; 1 equiv.) in ethanol (20 ml.) were refluxed under nitrogen for 3 hours. On allowing to stand for 24 hours ruby crystals were formed which were filtered off and dried in vacuum. Yield, 0.76 g.; m.p. 230° (decomp.). [Found: C, 39.2; H, 1.3. C₁₈H₆Co₂F₆O₆ requires C, 39.7; H, 1.3.] ν_(max) (nujol mull): 2083s, 2036s, 2020s, 2004s, 1595w, 1277s, 1235m, 1190s, 1065s, 1046s, 980s, 965s, 881s, 721s.

Interaction of perfluorobutadiene with tris(triphenylphosphine)chlororhodium(I).

An excess of perfluorobutadiene (3 ml.) and tris(triphenylphosphine)chlororhodium(I) (1 g.) in a hard glass tube containing benzene (10 ml.) was kept at 60° for 12 hours. After allowing to

cool, the excess C_4F_6 was removed and the crystals washed out of the tube. The compound was either crystallised from hot benzene or by the addition of methanol to a boiling solution in dichloromethane, giving the complex as yellow needles which were dried in vacuum. Yield, 0.7 g.; m.p. 185-195° (decomp.). [Found: C, 60.7; H, 4.3; Cl, 4.4; F, 9.4; P, 7.4. M , 835, 828 ($CHCl_3$). $C_{40}H_{30}ClF_4P_2Rh$ requires C, 61.1; H, 3.8; Cl, 4.5; P, 9.7. M , 787.] ν (max) (solution in CH_2Cl_2): 1737s, 1672s, 1577m, 1312s, 1188m, 1095s, 985s, 933s. ν (max) (vaseline mull): 303 cm^{-1} .

The complex is soluble in CH_2Cl_2 , THF and hot benzene, but insoluble in MeOH.

The complex was also obtained from ethylene bis(triphenylphosphine)chlororhodium(I) and perfluorobutadiene in a hard glass tube with dichloromethane at 20°.

Interaction of perfluorobutadiene with tris(triphenylarsine)chlororhodium(I)

In a similar way using triphenylarsine to give the complex which can be recrystallised again from CH_2Cl_2 : MeOH, the yellow needles being dried in vacuum. M.p. 182-3°. [Found: C, 53.4; H, 4.1; Cl, 3.4. $C_{40}H_{30}As_2ClF_4Rh$ requires C, 54.9; H, 3.5; Cl, 4.0.] ν (max) (nujol mull): 1695m, 1645s, 1567s, 1285s, 1157w, 1074s, 1009s, 941sh, 930s, 914s, 736s, 691s. ν (max) (vaseline mull): 341s, 332s, 299s.

Interaction of perfluorobutadiene with rhodium carbonyl chloride

An excess of perfluorobutadiene (3 ml.) was condensed into

a thick-walled glass tube containing rhodium carbonyl chloride (0.2 g.) which was kept at 40° for 48 hours. After opening and removal of excess C_4F_6 , the beige solid was washed out with warm petroleum to give the complex. Yield, essentially quantitative. [Found: C, 20.1; F, 32.1. $\underline{M}$, 706 ($CHCl_3$). $C_{12}Cl_2F_{12}O_4Rh_2$ requires C, 20.2; F, 32.0. $\underline{M}$, 713.] ν _(max) (solution in $CHCl_3$): 2110s, 2096sh, 2029s, 1701sh, 1678s, 1618sh, 1590s, 1309s, 1131m, 1005s, 990s, 947sh, 926s, 868m.

SECTION B

COMPLEXES DERIVED FROM PERFLUOROBUT-2-ENE

(i) Introduction

Perfluorobut-2-ene is a colourless gas (b.p. $0.4-3^{\circ}$ at 760 mm.) which can be prepared from 1:2:3:4-tetrachlorohexafluorobutane (50). Dehalogenation by refluxing with zinc in dioxan gives 1:4-dichlorohexafluorobut-2-ene, which reacts with a fused antimony trifluoride, chlorine mixture to give perfluorobut-2-ene.

Although this fluoro-olefin has been known since 1948 there have been no complexes of it with transition metals previously reported. Recently a large number of fluoro-olefins have become commercially available and their complexing ability with organometallics has been studied. Among those studied are trifluoroethylene, 1,1-difluoroethylene, trifluorostyrene(13), perfluorocyclobutene (67), perfluorocyclopentene and perfluorocyclohexene (68).

The more highly fluorinated olefins normally are more reactive because of the high electronegativity of the fluorine atom. Tetrachloroethylene has been considered as a ligand for transition metals, but the only well-documented complex is $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{Cl}_4$, obtained from $\text{Pt}(\text{PPh}_3)_4$ and the olefin (69). On this basis one would expect perfluorobut-2-ene to be less reactive than C_2F_4 , because the electronegativity of the CF_3 group is only 3.3 as against 4.0 for the fluorine atom itself (70).

The only previous mention of perfluorobut-2-ene as a ligand

is that it does not insert into hydridopentacarbonyl manganese to form a fluoroalkyl complex (8). The complexes described in this section are the first ones known using this olefin, although it has now been shown that it will insert into hydridopentamminerhodium^{III} sulphate to form the expected fluoroalkyl complex (71).

(ii) Interaction with Octacarbonyldicobalt

When a mixture of perfluorobut-2-ene and octacarbonyldicobalt is kept at 150°C for 12 hours a deep red waxy solid can be obtained in good yield, which is extremely volatile and sublimes at room temperature. The i.r. spectrum of the complex shows bands due to C-F stretches and terminal carbon monoxide groups, but no bands due to bridging carbon monoxide groups. In addition there is a strong sharp band at 1600 cm.⁻¹ which is correctly placed for an olefinic double bond.

After sublimation of this product, there remains a non-volatile pink solid. This residue dissolves somewhat in hot water, which on filtration yields a pink solution. This solution gives a positive test for fluoride ion (72) and is probably cobalt fluoride. A recent communication (73) mentions the action of fluoro-olefins as fluorinating agents for octacarbonyl dicobalt, although no other complexes were formed in reasonable yields in the reactions reported.

The ¹⁹F n.m.r. spectrum of the complex shows a single very sharp peak at -10.26 p.p.m. relative to benzotrifluoride. The observance of only a single resonance must be either due to the presence of only equivalent fluorines, or to a rapid equilibration

of all the fluorines in the molecule. Spectroscopically this complex is very similar to the one obtained from octacarbonyl dicobalt and perfluorobut-2-yne (22). This deep red volatile complex also shows a single n.m.r. resonance at -10.0 p.p.m. and a peak in the i.r. spectrum at 1600 cm^{-1} . This complex differs from the one formed from perfluorobut-2-yne in that the molecular weight is not 448, but closer to 800. The complex is quite air stable, but unlike the fluoroacetylenic complexes of $\text{Co}_2(\text{CO})_8$ derived from perfluorobut-2-yne (22) and perfluorocyclohex-1-yne-3-ene (33) which are very unreactive, this complex readily reacts with triphenylphosphine, triphenylarsine and 1,2-bis(diphenylphosphino)ethane.

These further compounds are obtained by refluxing the waxy solid with the appropriate ligand which gives the complexes as pure and crystalline. The i.r. spectra of these derivatives show bands due to terminal carbonyls and to double bonds, the main features of the spectra being collected in Table 2. The bands due to the C=C stretch are less strong than those of the parent complex and have also moved to lower wave numbers.

Except for the case of the 1,2-bis(diphenylphosphino)ethane complex, the derived complexes show only a single fluorine resonance downfield of benzotrifluoride, as shown in Table 2. In view of a single n.m.r. line being obtained from a complex derived from perfluorobut-2-ene the spectrum was more closely studied at 94.1 Mc/s. The spectrum of the parent complex at 30° still consists

Table 2

Spectroscopic data for cobalt fluorocarbon complexes						
Complex	¹⁹ F n m.r. ^a				I.r. ^d	
	30°	Δ ¹ /2 c.p.s.	-60°	Δ ¹ /2 c.p.s.	CO stretch	C=C stretch
Co ₄ (CO) ₁₂ C ₈ F ₁₂	-10.26	2.5	-9.52	7.5	2123s, 2088s, 2058, 2024w	1600s
					2119s, 2086s, ^e 2056s, 2022w	
Co ₂ (CO) ₆ C ₄ F ₆ (PPh ₃) ₂	-15.08	6.5	-14.86	14.5	2096s, 2049s, 2024s, 2000s.	1560ms
Co ₂ (CO) ₆ C ₄ F ₆ (AsPh ₃) ₂	-15.1 ^b				2096s, 2049s, 2020s, 1996s	1536m
Co ₂ (CO) ₆ C ₄ F ₆ (diphos)	-13.4 ^{b,c}					

^a against benzotrifluoride at 94.1 Mc/sec. ^b at 56.45 Mc/sec.

^c triplet, J_{P-F} = 9.4 c.p.s. ^d in CCl₄ ^e in cyclohexane

of a sharp resonance line, which at -60° broadens somewhat. At this lower temperature the resonance line is 3 times broader at half height than it was at 30° , but there is no evidence for the peak splitting into a multiplet which is what would be expected if the equivalence of the fluorine atoms was being effected by a rapid equilibration of non-equivalent fluorines. The single resonance of the triphenylphosphine complex is broader at 30° than that of the parent complex, but it does not show a resolvable coupling with the ^{31}P . This may be due to the ^{31}P - ^{19}F coupling constant being less than 1 c.p.s., or because the nuclear quadrupole moment of the cobalt atom affects the spin-lattice relaxation of the fluorine causing a broadening of the observed resonance. Cooling the solution to -60° produces a further broadening of the peak without any splitting. The broadening of the spectrum on lowering the temperature is probably again due to the increased effect of the cobalt quadrupole.

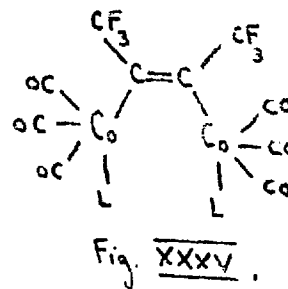
From Table 2 it is evident that there is a large change in chemical shift with change in temperature of the solution, which would usually be interpreted as being due to an exchange process; however from the probable structure of the complexes this appears unlikely. An alternative explanation is that the position of the fluorine resonance is simply a function of temperature. Evans (74) has found that the position of the ^{19}F resonance in benzotrifluoride itself is very sensitive to temperature, a lowering of temperature causing a shift to lower field. Since the resonance position of the

complex apparently increases with reduction of temperature, the shift of the resonance position of the complex must vary less with temperature than that of benzotrifluoride. This is what would be expected since the fluorine atoms in benzotrifluoride are less shielded to the effect of solvent than those of a more intricate structure.

The n.m.r. spectrum was also used to unequivocally show that the triphenylphosphine complex contained only six fluorine atoms, and not eight undergoing interconversion. This complex was chosen in favour of the parent because of its greater ease of handling, and also, since it is non-volatile, a possible error in the weighing and transfer into solution is eliminated. The area of the n.m.r. resonance is directly proportional to the fluorine concentration of the solution. A mixed solution in dichloromethane was made up containing known weights of the phosphine complex, and a compound $C_9F_{12}O PPh_3$ which is a pure solid of known stoichiometry. The whole spectrum was integrated, and since the weight of each compound is known, and the areas of the peaks produced by the fluorine atoms in the compounds can be obtained, the number of fluorine atoms can be found. The value obtained was six for each cobalt dimer unit, making the stoichiometry $Co_2(CO)_6C_4F_6(PPh_3)_2$.

From the spectral and analytical data, the complexes obtained by ligand co-ordination almost certainly have the structure shown in Fig. (XXXV). A decision on the structure of such complexes is often difficult since there is no unambiguous way of deciding the assignment

of the bonding. The structure below would be expected to show i.r. bands for terminal carbon monoxide groups and for a double bond. The postulated structure does not involve a metal-metal bond between the cobalt atoms since this would lead to a structure with cobalt having one more electron than that



required for the next higher inert gas. The structure shown involves the metal atom being surrounded by 18 electrons and is structurally analogous to the organometallic $\text{Co}(\text{CO})_4\text{H}$, which is confirmed by the observed diamagnetism of the complex.

This complex differs structurally from the one previously prepared from octacarbonyldicobalt and perfluorobut-2-yne since this compound contains a metal-metal bond, and each carbon atom of the acetylene is attached to each cobalt, the structure again conforming to the inert gas rule.

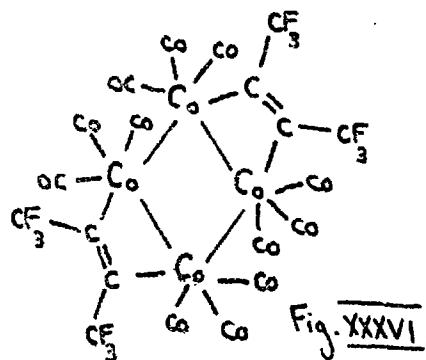
The proposed structure allows the possibility of a cis and a trans isomer. In the case of the diphosphine complex however the product must have the CF_3 group cis, in order that the cobalt atoms are close enough together for the chelating phosphine to act as a bridge. Although it cannot be determined unequivocally it is probable that the PPh_3 and AsPh_3 complexes are also cis, although an X-ray structure determination which is at present in progress

should elucidate the problem.

It has been found to be much more difficult to study the parent complex because of the handling and purification problems. Although the microanalytical data is rather unsatisfactory, osmometric molecular weight data consistently gives values of the order of 800, which represents a tetrameric complex of stoichiometry $\text{Co}_4(\text{CO})_{12}(\text{C}_4\text{F}_6)_2$. King et al have found that the reaction between hexafluorobut-2-yne and tetracarbonylnickel gives a complex of stoichiometry $[\pi-(\text{CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_3$ (24). This resembles the present cobalt complex in being extremely volatile for the high molecular weight, and they conclude that the molecule must have a compact spherical structure. The cobalt complex must differ from this stoichiometrically in having only one fluorocarbon moiety for every pair of cobalt atoms, so as to explain why the reaction with additional ligands produces only a single complex which can be formulated $\text{Co}_2(\text{CO})_6\text{C}_4\text{F}_6\text{L}_2$.

The structure is best depicted as in Fig. XXXVI. The precise nature of the bonding is not definite but the fluorocarbon is almost certainly bonded in the same manner as in the dimeric complexes, although the tetramer must be held together by metal-metal bonding.

Although this complex readily reacts with phosphines and arsines, it



is thermally extremely stable. An attempt to liberate the fluorocarbon for identification has been unsuccessful since the complex can be recovered unchanged after keeping overnight in a sealed tube at 200° . The complex reacts with pyridine and 2,2'-dipyridyl but pure products have not been obtained; however the complex could be recovered unchanged from refluxing with anhydrous stannous chloride in a petroleum (60-80 $^{\circ}$):ethanol (10:1) solution.

Recent communications about the reactivity of octacarbonyl dicobalt with fluoro-olefins have either given no isolable product, or have given a complex of the type $\text{Co}_3(\text{CO})_9\text{CCF}_3$ (13,73). Previous to these publications the reaction between octacarbonyl dicobalt and perfluoropropene was studied. Reaction occurs at 110° to give a dark solid in good yield. The product can be sublimed in vacuum at 70° to give black crystals. The i.r. spectrum shows bands due to carbonyls at approximately 2093, 2077, 2055, 2024 and 1867 cm^{-1} which resembles the solution spectrum of $\text{Co}_4(\text{CO})_{12}$ which has bands at 2070, 2062, 2045, 2033 and 1869 cm^{-1} (75). Since the reaction between perfluorobut-2-ene and octacarbonyldicobalt does not occur below 110° , and the product is tetrameric, it is probable that the reaction occurs via $\text{Co}_4(\text{CO})_{12}$ which is produced by heating the lower carbonyl. The fluorocarbon may co-ordinate to this species although it is unclear at what stage the fluorine elimination occurs.

(iii) Interaction with Pentacarbonyliron

Haszeldine has described the preparation of complexes from pentacarbonyliron and chlorotrifluoroethylene, perfluoropropene,

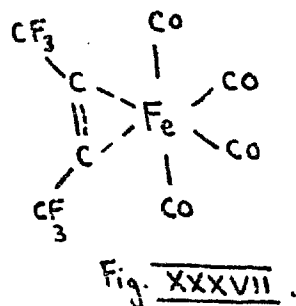
perfluorocyclopentene, perfluorocyclohexene or 1,1-dichlorodifluoro-ethylene of the type $(\text{olefin})\text{Fe}(\text{CO})_4$ (76). The products from the higher olefins are obtained in only poor yield. He has also obtained evidence for the complex $(\text{C}_2\text{F}_4)\text{Fe}(\text{CO})_4$, although prolonged u.v. irradiation gives the previously obtained heterocyclic compound $(\text{C}_2\text{F}_4)_2\text{Fe}(\text{CO})_4$. Perfluorobut-2-ene also reacts with pentacarbonyl-iron under u.v. irradiation to give an erratic yield of a colourless solid. Because of the unreliability of the reaction insufficient quantity of the material has been obtained for purification to analytical quality.

The i.r. spectrum shows four bands due to terminal carbon monoxide groups at 2132, 2070, 2041 and 2008 cm^{-1} which are at higher wave numbers than those in pentacarbonyliron itself, showing that the electron withdrawing effect of the fluorocarbon causes the π -bonded carbonyl stretch to go to higher wave numbers. In addition the spectrum shows bands due to the fluorocarbon moiety.

Haszeldine has been unable to decide whether the fluoro-olefin in the complexes is σ - or π -bonded. The latter is favoured by the ready elimination of the fluoro-olefin from the complex, but the former is favoured by the observation that the coupling constants of the bonded fluoro-olefin differ from those in the pure olefin.

The ^{19}F n.m.r. spectrum of this perfluorobut-2-ene complex consists of two resonances at +4.8 and +11.4 p.p.m. upfield of benzotrifluoride of relative area 3:1, the low field peak being split into a doublet. If the complex had been heterocyclic, like

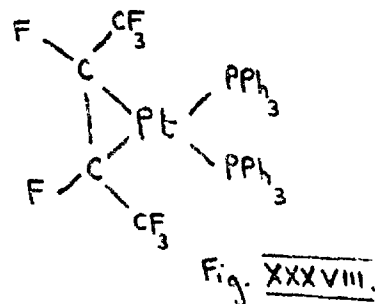
the tetrafluoroethylene compound, the n.m.r. would have shown more than two peaks. The relative positions of the peaks are very similar to those obtained from platinum and palladium complexes of perfluorobut-2-ene, and the complex therefore almost certainly has the stoichiometry $C_4F_8Fe(CO)_4$, and the structure shown in Fig. (XXXVII).



(iv) Interaction with Platinum and Palladium complexes

Perfluorobut-2-ene reacts readily at room temperature with tetrakis(triphenylphosphine)platinum(0) to give bis(triphenylphosphine)perfluorobut-2-ene platinum, $(PPh_3)_2PtC_4F_8$. The analytical data is correct, and the osmometric molecular weight shows the complex to be monomeric. The i.r. spectrum shows bands due to triphenylphosphine and C-F stretches, and the absence of any bands attributable to a carbon-carbon double bond. A communication by Stone (20) has described the preparation of the complexes $(PPh_3)_2Pt(\text{fluoro-olefin})$ using tetrafluoroethylene, chlorotrifluoroethylene and perfluoropropene. By analogy with these compounds it is anticipated that this perfluorobut-2-ene complex has the structure shown in Fig. (XXXVIII). The ^{19}F n.m.r. spectrum consists of two resonances centred at 2.5 and 140 p.p.m. upfield of benzotrifluoride, the relative areas being 3:1 respectively. From

the areas of these two peaks it is the $-\text{CF}_3$ group of the co-ordinated perfluorobut-2-ene which is situated at a markedly down-field chemical shift, and not the fluorine of the CF group. It is the latter which would be expected to be found at low field because if



the σ -bonded structure is correct, this carbon atom is directly bonded to the platinum. It has been noted that in the corresponding complex with perfluorobut-2-yne (26) the low field position of the fluorine resonance is associated with the ligand itself.

To check whether a similar effect was causing the relative positions of the fluorine resonances in the co-ordinated perfluorobut-2-ene, the n.m.r. spectrum of condensed perfluorobut-2-ene itself was obtained. This shows two peaks of relative areas 3:1 centred at 6.1 and 3.5 p.p.m. upfield of benzotrifluoride. The peaks are multiplets, but because the two single fluorines are equivalent the olefinic cis and trans coupling constants are not observed, and the splittings obtained are small. From this the CF_3 resonance in the complex is close to its position in the free ligand, as with the perfluorobut-2-yne spectrum, but the small peak is much further upfield than its position in the free ligand which is rather surprising.

By similar methods it has been possible to prepare the

corresponding complexes from perfluorobut-2-ene and tetrakis(triphenylarsine)platinum(0) and tetrakis(triphenylphosphine)palladium(0). The analytical and molecular weight data show the complexes are monomeric of stoichiometry $L_2MC_4F_8$ ($L = PPh_3$ or $AsPh_3$; $M = Pd$ or Pt). The i.r. spectra again shows the expected bands due to C-F groups, and the absence of any band for an olefinic double bond. The n.m.r. spectra are very similar to that obtained for the platinum phosphine complex, the large peak being at low field and the small peak occurring at over 100 p.p.m. upfield of benzotrifluoride. The spectra of the complexes are shown in Table 3 along with those previously obtained for platinum and palladium fluorocarbon complexes.

Both the ^{31}P and ^{195}Pt isotopes have a nuclear spin (I) equal to $1/2$, but ^{75}As and ^{105}Pd have nuclear quadrupoles ($I > 1/2$) (48). A comparison of the n.m.r. spectra of the three complexes should unequivocally give the values of the $^{31}P-^{19}F$ and $^{195}Pt-^{19}F$ coupling constants, since the corresponding As and Pd complexes will not show the splittings. In practice the limited solubility and high molecular weight of the complexes has limited this study to the large peak, although with the $C_4F_8Pd(PPh_3)_2$ complex the $^{19}F-^{31}P$ coupling constant can be obtained approximately from the small peak.

Since only $1/3$ of the platinum nuclei have a nuclear spin of $1/2$ the ^{19}F spectrum should consist of a singlet with two satellite peaks for the fluorines attached to complexes of ^{195}Pt . In accordance with this the spectrum of $(AsPh_3)_2PtC_4F_8$ is a triplet, and the spectrum of $(PPh_3)_2PtC_4F_8$ a double triplet from coupling with ^{31}P .

Table 3

N.M.R. data of some Pt and Pd fluorocarbon complexes

Complex	δ p.p.m. [‡]	$J_{195\text{Pt}-19\text{F}}$ (c.p.s.)	$J_{31\text{P}-19\text{F}}$ (c.p.s.)	Ref.
$(\text{PPh}_3)_2\text{PtC}_2\text{F}_4$	67.4	288	39, 29	(20)
$(\text{PPh}_3)_2\text{PtC}_4\text{F}_6$	9.0	65	10.3	(26)
$(\text{AsPh}_3)_2\text{PtC}_4\text{F}_6$	9.0	80	-	(26)
$(\text{PPh}_3)_2\text{PdC}_4\text{F}_6$	10.7	-	11.2	(27)
$(\text{PPh}_3)_2\text{PtC}_4\text{F}_8$	2.5(3), 140.0(1)	77.6	9.2	This work
$(\text{AsPh}_3)_2\text{PtC}_4\text{F}_8$	5.0(3), 131.1(1)	93	-	This work
$(\text{PPh}_3)_2\text{PdC}_4\text{F}_8$	4.0(3), 133.0(1)	-	9.5	This work
$(\text{PPh}_3)_2\text{PtC}_3\text{F}_6$	2.9(3), 43.5(1), 56.6(1), 136.4(1)			(20)

[‡] upfield of benzotrifluoride.

Although the previously prepared perfluorobut-2-yne complexes contain the carbon-carbon bond in a different hybridisation state to the perfluorobut-2-ene complexes, the observed coupling constants agree closely. This probably arises because the fluorines in the CF_3 groups in each complex are separated from the metal atom by another carbon atom, and hence through bond coupling would involve a similar distance. The coupling constants in the tetrafluoroethylene compound are much larger because in this case the CF groups studied are directly bonded to the metal.

The perfluoropropene complex should have fluorine atoms in identical environments to those of the different fluorines in perfluorobut-2-ene. The communication (20) however gives no values for the ^{31}P - ^{19}F and ^{195}Pt - ^{19}F coupling constants, but it is interesting to note that the large peak is observed to be closer to benzotri-fluoride than are the other peaks, and this may be a feature of a fluoro-olefin bonded to platinum and palladium in this manner.

When tetrakis(triphenylphosphine)platinum(0) and perfluorobutadiene are placed in a sealed tube with dichloromethane, but in the absence of air, colourless crystals are obtained. Removal of the excess fluoro-olefin, followed by filtration of the solution gives the compound mixed with starting material and a grey solid. The compound is unstable in air and it has not been possible to recrystallise the solid to give the complex in a pure state.

EXPERIMENTALInteraction of perfluorobut-2-ene with octacarbonyl dicobalt

An excess of perfluorobut-2-ene was condensed on to $\text{Co}_2(\text{CO})_8$ in a 25 ml. stainless steel vessel. After 12 hours at 150° the bomb was cooled, the excess olefin removed, and the contents extracted with petroleum. After removal of solvent the residue was sublimed at 25° to an ice-cooled probe giving the complex as deep red, waxy crystals. Yield ca. 70% based on $\text{Co}_2(\text{CO})_8$. [Found: C, 25.0; H, 0.0. $\underline{M}$, 865 (CHCl_3). $\text{C}_{20}\text{Co}_4\text{F}_{12}\text{O}_{12}$ requires C, 26.3; H, 0.0 $\underline{M}$, 896.] The compound is exceedingly volatile and soluble in organic solvents but is not wetted by water. It can be recrystallised from a small volume of petroleum at -40° . Chromatography on silica using petroleum as eluant gives a single band. $\nu_{(\text{max})}$ (solutions in hexane, CCl_4): 1282s, 1190s, 1144s, 956m, 932m, 682s, 661m.

Bis(triphenylphosphine)hexacarbonyl perfluorobut-2-ene dicobalt

On refluxing the above complex (0.3 g.) with excess triphenylphosphine (0.3 g.) in petroleum (20 ml., $60-80^\circ$) for 3 hours, the colour of the solution changes to burgundy. After cooling, the complex was collected and recrystallised by dropwise addition of MeOH to a boiling solution in CH_2Cl_2 until ruby coloured crystals of the complex were formed. These were filtered off and dried in vacuum, m.p. $105-113^\circ$. Yield 0.25 g., 65%. [Found: C, 57.2; H, 3.4; F, 11.5; P, 6.2; $\underline{M}$, 1050 (CHCl_3). $\text{C}_{46}\text{H}_{30}\text{Co}_2\text{F}_6\text{O}_6\text{P}_2$ requires C, 56.8; H, 3.1; F, 11.7; P, 6.4%. $\underline{M}$, 972.] $\nu_{(\text{max})}$ (solution in CCl_4): 1457m, 1433s, 1302w, 1263s, 1183s, 1122s, 1092s, 1027w,

692s, 677s. The complex is soluble in CH_2Cl_2 and C_6H_6 .

Bis(triphenylarsine)hexacarbonyl perfluorobut-2-ene dicobalt

In an analogous way using AsPh_3 , burgundy coloured crystals of the complex were obtained, m.p. $130-135^\circ$. Yield ca. 70%.

[Found: C, 52.9; H, 3.4; As, 15.3; F, 11.2; $\underline{M}$, 875 (CHCl_3).

$\text{C}_{46}\text{H}_{30}\text{As}_2\text{Co}_2\text{F}_6\text{O}_6$ requires C, 52.1; H, 2.9; As, 14.1; F, 10.8%. $\underline{M}$, 1060.] ν (max) (solutions in CS_2 , CCl_4): 1553sh, 1481s, 1433s, 1263s, 1182s, 1121s, 1073m, 1021w, 963w, 691s, 678s, 659sh.

1,2-bis(diphenylphosphino)ethane hexacarbonyl perfluorobut-2-ene dicobalt

Similarly using 1,2-bis(diphenylphosphino)ethane, salmon-pink crystals of the complex were obtained. Yield ca. 75%. [Found:

C, 51.3; H, 3.5; F, 12.8; P, 6.7; $\underline{M}$, 870 (solution in CHCl_3).

$\text{C}_{36}\text{H}_{24}\text{Co}_2\text{F}_6\text{O}_6\text{P}_2$ requires C, 51.1; H, 2.9; F, 13.5; P, 7.3%. $\underline{M}$, 846.]

Bis(triphenylphosphine)perfluorobut-2-ene platinum

A suspension of $\text{Pt}(\text{PPh}_3)_4$ (1.0 g.) in dichloromethane (8 ml.) was sealed in a thick-walled glass tube with excess perfluorobut-2-ene. After shaking for 12 hours, the excess olefin was removed and the solution filtered. To the boiling solution was slowly added methanol until colourless crystals of the complex appeared. After cooling the crystals were collected and vacuum dried, m.p. $229-231^\circ$. Yield 0.45 g., 60%. [Found: C, 52.4; H, 3.9; F, 16.2; $\underline{M}$, 850 (CHCl_3).

$\text{C}_{40}\text{H}_{30}\text{F}_8\text{P}_2\text{Pt}$ requires C, 52.2; H, 3.3; F, 16.5%. $\underline{M}$, 919.]

ν (max) (solution in CCl_4): 1477w, 1435m, 1370w, 1272s, 1180sh, 1172s, 1154s, 1096m, 1041m. The complex is moderately soluble in CH_2Cl_2 and

CHCl_3 , slightly soluble in CS_2 , and insoluble in MeOH or petroleum.

Bis(triphenylarsine)perfluorobut-2-ene platinum

This complex was prepared by a similar procedure using $\text{Pt}(\text{AsPh}_3)_4$ to give colourless crystals of the complex, m.p. $198-200^\circ$. Yield 0.45 g., 65%. [Found: C, 48.5; H, 3.5; F, 15.9; M, 740 (CHCl_3). $\text{C}_{40}\text{H}_{30}\text{As}_2\text{F}_8\text{Pt}$ requires C, 47.7; H, 3.0; F, 15.1%. M, 1008.] ν (max) (solution in CS_2): 1379w, 1269s, 1176sh, 1170s, 1148s, 1125s, 1104m, 1076m, 1021m, 999m, 781s, 691s.

Bis(triphenylphosphine)perfluorobut-2-ene palladium

In a similar way using $\text{Pd}(\text{PPh}_3)_4$ gives colourless crystals of the complex, m.p. $135-137^\circ$. Yield ca. 60%. [Found: C, 57.3; H, 3.7; P, 6.9; M, 865 (CHCl_3). $\text{C}_{40}\text{H}_{30}\text{F}_8\text{P}_2\text{Pd}$ requires C, 57.8; H, 3.6; P, 7.5%. M, 831.] ν (max) (CS_2): 1389w, 1290sh, 1276s, 1261s, 1227s, 1181s, 1174s, 1145s, 1093s, 1050m, 1025m, 740s, 692.

Interaction of perfluorobut-2-ene with pentacarbonyliron

Pentacarbonyliron (1 ml.) was sealed in a thick-walled glass tube with excess perfluorobut-2-ene (2 ml.). The tube was irradiated with ultra-violet light for 24 hours. The tube was opened, the excess fluoro-olefin removed, and the colourless complex filtered off. Yield low. ν (max) (solution in cyclohexane): 2132m, 2070s, 2041s, 2008w, 1284m, 1188s, 1166sh, 1067m.

SECTION C

COMPLEXES DERIVED FROM TETRAKIS(TRIFLUOROMETHYL)CYCLOPENTADIENONE

(i) Introduction

When rhodium carbonyl chloride is heated with perfluorobut-2-yne under a high pressure of carbon monoxide, one obtains a good yield of tetrakis(trifluoromethyl)cyclopentadienone ($C_9F_{12}O$) (25). The reaction yields several products but the dienone is very volatile, and it can readily be obtained as a pungent yellow crystalline solid by sublimation.

The introduction at the beginning of this thesis describes the formation of complexes of this ligand from the reaction of perfluorobut-2-yne with pentacarbonyliron and cyclopentadienyl cobalt dicarbonyl, the dienone having possibly been formed in situ with its subsequent co-ordination. When a mixed solution of $C_9F_{12}O$ and dodecacarbonyltri-iron is refluxed the same complex, $C_9F_{12}O.Fe(CO)_4$, is obtained as was formed by the interaction of perfluorobut-2-yne and pentacarbonyliron (25). Since then the free dienone has been shown to co-ordinate with organometallics, it was considered that it should be possible to make other new compounds between this dienone and other transition metal complexes.

(ii) Interaction with Tertiary Phosphines

When dichloromethane solutions of the dienone and tetrakis(triphenylphosphine)platinum(0) or tris(triphenylphosphine)chlororhodium(I) are mixed at room temperature an immediate reaction occurs.

From the solution can be obtained a colourless crystalline compound, but this product does not contain a metal atom. When this reaction is carried out using triphenylphosphine itself one obtains the same compound in good yield. Microanalytical and molecular weight data show it to be a monomer of stoichiometry $C_{27}H_{15}F_{12}OP$. This formula is further substantiated by a mass spectrometric study on the molecular ion. The mass spectrum shows a molecular ion peak at 614. A spectrum of a mixture of the complex and heptacosafuoro-n-butylamine shows two molecular ion peaks, the ratio of the positions of the complex: standard peaks being 1.000166. Since the molecular weight of heptacosafuoro-n-butylamine is 613.96473, the true molecular weight of the complex is 614.0668, which is so close to the theoretical value of 614.06687 that the formula of the complex must be $C_{27}H_{15}F_{12}OP$.

The complex is soluble in dichloromethane and chloroform, slightly soluble in carbon disulphide, but insoluble in petroleum, methanol or water. As well as bands due to triphenylphosphine and to C-F bonds, the i.r. spectrum shows two medium strong bands at 1582 and 1502 cm^{-1} , the only other band in the 1500-2000 cm^{-1} region being an extremely weak one.

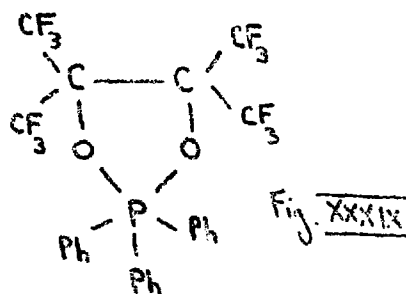
The n.m.r. spectrum at 56.45 Mc/s shows two resonances separated by 43.7 c.p.s., the centre being 11.7 p.p.m. downfield of benzotri-fluoride. The spectrum at 94.1 Mc/s is similar, but now the separation has increased to 79 c.p.s., which shows that the spectrum is to be regarded as two peaks of chemical shift -11.38 and

-12.22 p.p.m., and not one ^{19}F resonance split into a doublet by coupling with the ^{31}P of the phosphine. These values compare closely with those found for tetrakis(trifluoromethyl)cyclopentadienone itself which shows two resonances at -7.9 and -10.1 p.p.m. The peaks are not too well resolved, the upfield one appearing as three equal resonances of separation 6 c.p.s. When each of the peaks in turn is spin decoupled by irradiating it at its own frequency, the other peak collapses into a singlet. This collapsing of the fine structure shows that the multiplicity of the individual peaks is due to F-F coupling, and that the ^{19}F - ^{31}P coupling constants are immeasurably small.

When the reaction is carried out using 1,2bis(diphenylphosphino)ethane instead of triphenylphosphine, a colourless compound is again obtained which has the stoichiometry $\text{C}_{44}\text{H}_{24}\text{F}_{24}\text{P}_2\text{O}_2$ and which can be formulated $(\text{Ph}_2\text{PCH}_2)_2(\text{C}_9\text{F}_{12}\text{O})_2$. This compound is similar to the triphenylphosphine one in having one dienone group co-ordinated to each phosphorus. Using the identical experimental procedure with triphenylarsine there is no reaction, the reactants being recovered unchanged.

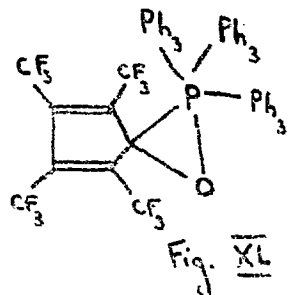
The transition metal complexes of tetrakis(trifluoromethyl)cyclopentadienone contain the ligand bonded via two σ -bonds and one π -bond (77), but these complexes show strong i.r. bands between 1700 and 1750 cm^{-1} . Since the i.r. spectrum of this compound does not show these bands, it is unlikely that a similar structure with two σ -bonds to the phosphorus atom is correct.

Triphenylphosphine has been found to react with hexafluoroacetone to give an adduct of the phosphine with two ketone molecules to give a phospholane (XXXIX) (78). The n.m.r. spectrum shows one



peak at 1.6 p.p.m. upfield of benzo-trifluoride. A similar complex cannot be prepared with triphenylarsine. Since the complex with tetrakis(trifluoromethyl)cyclopentadienone does not show a ketonic stretch in the i.r., it is possible that co-ordination to the phosphorus

is through a similar C-O-P linkage. This structure (XL) would involve a bicyclic compound with 5- and 3-membered rings mutually at right angles. Several other possible structures can be considered, but this structure best explains the spectral data. The structure adequately explains the observed n.m.r. spectrum. The



fluorines are arranged into two sets of equivalent trifluoromethyl groups, and in addition the chemical shifts would be expected to be similar to those in $C_9F_{12}O$ itself, which is as observed. Other structures which can be drawn destroy these two groups of equivalent fluorines and hence cannot be considered. The phosphorus atom is

well separated from the fluorine atoms which explains the observed low or zero $^3\text{P}-^{19}\text{F}$ coupling constants. From this structure the peaks in the i.r. spectrum at 1502 and 1582 cm^{-1} can be assigned to the C-C stretch of the double bonds.

The U.V. spectrum in CH_2Cl_2 shows two peaks at 307 and 267 $\text{m}\mu$, the former being very broad and ill-defined. The relative extinction coefficients are 780 and 12,580. For $\text{C}_9\text{F}_{12}\text{O}$ itself, Dickson (25) reports a single peak at 342 $\text{m}\mu$ ($\epsilon = 360$) for a CH_2Cl_2 solution.

The complex with 1,2bis(diphenylphosphino)ethane has the stoichiometry derived from one molecule of the bidentate phosphine co-ordinated to two molecules of the dienone. The structure of this compound is almost certainly similar to the PPh_3 one, each phosphorus being co-ordinated in a similar manner, the two phosphorus atoms being then joined by a methylene bridge.

(iii) Interaction with Amines

It has been previously reported that tetrakis(trifluoromethyl)cyclopentadienone reacts with amines to give deeply coloured solutions, which on standing deposit colourless crystals (25). Further investigation of this reaction of the dienone has shown that amines give variable yields of impure compounds when either dichloromethane or the liquid amine itself is used as solvent. The addition however of a 20% solution of the amine in ether to a dilute ethereal solution of tetrakis(trifluoromethyl)cyclopentadienone gives a good yield of the colourless compounds. The remaining solution is

often deeply coloured but no pure compound has been isolable.

The colourless crystalline products are insoluble in organic solvents but are quite freely soluble in water. In order to study the nature of these compounds the product obtained from benzylamine was prepared in quantity. An aqueous solution of the compound has been found to be conducting, the conductivity in water being 106 mhos. Addition of an aqueous solution of sodium tetraphenylboron to a solution of the compound gives a colourless precipitate, but no precipitate is obtained on addition of a solution of tetraphenylarsonium chloride. Addition of one drop of a solution of the compound to a small quantity of a zirconium alizarinate solution changes the colour of the solution from red to yellow, showing the presence of the F^- ion in solution (72).

The compound is probably benzylamine hydrofluoride, $C_6H_5CH_2NH_3F$, which has been confirmed by microanalytical data: - Found: C, 65.8; H, 7.5. $C_7H_{10}FN$ requires C, 66.1; H, 7.9%. Further confirmation has been obtained from a study of the n.m.r. spectrum. A solution of the compound in D_2O shows a single broad peak 53.5 p.p.m., upfield of benzotrifluoride as external reference. When some ammonium fluoride is added to the solution no other peak appears, the resonance obtained is more intense but still at the same chemical shift.

EXPERIMENTALInteraction of tetrakis(trifluoromethyl)cyclopentadienone and triphenylphosphine

When a yellow solution of tetrakis(trifluoromethyl)cyclopentadienone (0.12 g., 1 mol) in CH_2Cl_2 is added to a CH_2Cl_2 solution of triphenylphosphine (0.15 g., 1.7 mol) the colour is immediately discharged. Addition of MeOH to the boiling solution gives colourless crystals, which can be recrystallised from CH_2Cl_2 : MeOH to give the complex, m.p. $219-224^\circ$. Yield 0.17 g., 80%. [Found: C, 52.2; H, 3.6; F, 36.8; M, 619 (CHCl_3). $\text{C}_{27}\text{H}_{15}\text{F}_{12}\text{P}_2\text{O}$ requires C, 52.8; H, 2.5; F, 37.1; M, 614.] ν (max) (nujol mull): 1582m, 1502s, 1276s, 1211s, 1189sh, 1107s, 1086sh, 1043s, 995m, 941sh, 934s, 797w, 788m, 752s, 739s, 735sh, 724s, 699s, 686s.

Interaction of tetrakis(trifluoromethyl)cyclopentadienone and 1,2bis(diphenylphosphino)ethane

Using an identical procedure as above but using 1,2bis(diphenylphosphino)ethane, the compound was again obtained as colourless crystals, m.p. 265° (decomp.). [Found: C, 48.3; H, 3.6; F, 39.8. $\text{C}_{44}\text{H}_{24}\text{F}_{24}\text{P}_2\text{O}_2$ requires C, 47.9; H, 2.2; F, 41.4%.] ν (max) (nujol mull): 1742m, 1582m, 1504s, 1282s, 1245s, 1220s, 1188s, 1149m, 1121s, 1091sh, 1032s, 996m, 943s, 930m, 795m, 763sh, 753s, 745s, 737s, 709s, 692sh, 686s.

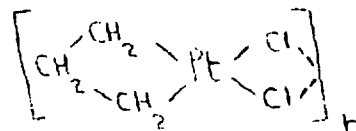
SECTION D

COMPLEXES DERIVED FROM CYCLOPROPANE

Interaction with rhodium carbonyl chloride

D.N. Lawson (65) describes a reaction between rhodium carbonyl chloride and liquid cyclopropane at 40° . The product is a yellow crystalline solid, insoluble in cold organic solvents but it has limited solubility in boiling chloroform. The stoichiometry of the complex, $C_3H_6ClO_2Rh$, shows that no carbon monoxide has been lost. This is confirmed by the i.r. spectrum which shows one terminal carbon monoxide stretch at 2041 cm^{-1} , and a band at 1730 cm^{-1} which is associated with a ketonic stretch.

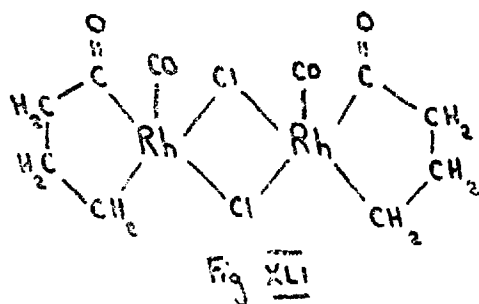
The n.m.r. spectrum shows three broad peaks centred at τ 6.4, 7.28, and 8.35. This is consistent with the presence of a 5-membered heterocyclic ring system involving a co-ordinated tetramethylene-1-one group. Since the complex is only slightly soluble, the molecular weight cannot be determined by osmometric determination. The product of the reaction of cyclopropane with chloroplatinic acid (79) has been shown (80) to be a chloro-bridged polymeric complex of tervalent platinum:



Since $Pt(IV)$ and $Rh(III)$ are isoelectronic Lawson considers that this new rhodium complex is polymeric and of high molecular weight.

Rhodium carbonyl chloride exists as discrete dimeric molecules. Although the product obtained by cyclopropane insertion could be

polymeric, it seems more likely that under the mild conditions of the



reaction the dimeric unit remains intact giving the structure (XLI). The complex has since been shown to show a band in the i.r. spectrum at 288 cm.^{-1}

which is due to a bridging Rh-Cl stretch (64), the value being close to that found for rhodium carbonyl chloride itself which is at 277 cm.^{-1} . Although one of the carbonyl groups is structurally ketonic, its proximity to the rhodium atom precludes it from being chemically ketonic, since it fails to give a positive test with Brady's reagent.

The platinum cyclopropane complex reacts with pyridine to give a compound $\text{C}_3\text{H}_6\text{PtCl}_2\text{py}_2$ for which the structure (XLII) has been confirmed. When this complex is boiled in benzene it undergoes a re-arrangement to give an ylid structure. Although the rhodium complex does not undergo re-

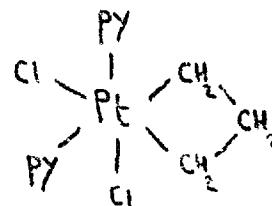


Fig. XLII

arrangement, Lawson considers that an ylid type structure is possible for the product obtained by cleavage of the complex with pyridine, which has the stoichiometry

$(C_4H_6O)RhClCOpy_2$. This complex is a white diamagnetic solid which is insoluble in organic solvents, and the i.r. spectrum shows a terminal carbon monoxide stretch at 2050 cm.^{-1} .

The proposed structure contains a Rh-Cl bond but a careful examination of the i.r. spectrum in the region for the Rh-Cl stretch fails to reveal any bands. Because of the low symmetry of the structure it is very improbable that the non-observance of any bands is because the mode is inactive in the i.r., and from the previously observed intensities of the Rh-Cl stretch it is unlikely that it would be too weak to be observed.

The complex dissolves slightly in warm water, and when a drop of an aqueous solution of $AgNO_3$ is added to this filtered solution, a white precipitate of $AgCl$ is formed. Addition of an aqueous solution of sodium tetraphenylboron to the solution also produces a white precipitate. The compound is therefore ionic, and is doubtless a chloride salt of the 5 co-ordinate rhodium substituted cation (XLIII). Since the chlorine is ionic, the complex would not be expected to show a band in the i.r. spectrum for the Rh-Cl stretch of a covalent metal-chlorine bond.

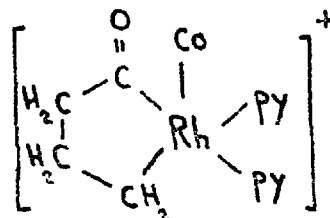


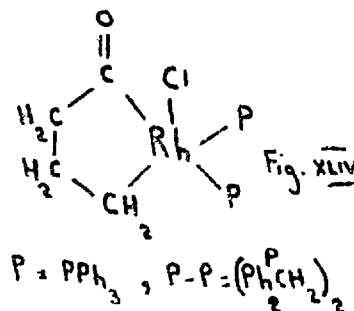
Fig. XLIII.

The complex has also been cleaved by reaction with molten triphenylphosphine. The compound formed is of stoichiometry $(C_4H_6O)RhCl(PPh_3)_2$, and has been formed

with elimination of carbon monoxide from the parent complex. The substitution product with the chelating phosphine, $(\text{Ph}_2\text{PCH}_2)_2$ has now been prepared. The PPh_3 complex is only moderately stable, and slowly decomposes to $(\text{PPh}_3)_2\text{RhCOCl}$ in the course of several weeks. The $(\text{Ph}_2\text{PCH}_2)_2$ complex is less stable, and the colourless compound changes to a yellow colour on the surface in the course of several hours. The complex is moderately soluble in dichloromethane and chloroform, but is quite insoluble in water. The i.r. spectrum shows the characteristic bands for the heterocyclic tetramethylene-one group, and in addition a strong band at 343 cm^{-1} characteristic of a Rh-Cl stretch. From the spectral data the phosphine substituted complexes have a different structure from the pyridine substituted products, and consist of a non-ionic 5-co-ordinate structure (XLIV).

The dimeric complex also reacts with 2,2'-dipyridyl and 1,10-phenanthroline to give monomeric products. There is also formed in the reactions a dark solid which shows no bands in the i.r. for the heterocyclic cyclobutanone ring. Although these

compounds have not been fully characterised they are doubtless compounds of the type LRhCOCl where $\text{L} = \text{dipy}$ or 1,10-phenan. The required products have analogous stoichiometries to the pyridine



substituted complex, their i.r. spectra are similar, and aqueous solutions of the complexes give colourless precipitates with AgNO_3 and NaBPh_4 . The precipitate obtained from aqueous solutions of $(\text{C}_4\text{H}_6\text{O})\text{RhCOCl}(\text{dipy})$ and NaBPh_4 has been characterised, the analytical and i.r. spectral data show the complex to have the stoichiometry $[(\text{C}_4\text{H}_6\text{O})\text{RhCO}(\text{dipy})]^+[\text{BPh}_4]^- \cdot 2\text{H}_2\text{O}$.

The dimeric complex is cleaved at room temperature by triphenylarsine. Addition of petroleum to the CH_2Cl_2 solution gives the addition compound as colourless needles, which slowly turn yellow in the course of several days on exposure to air. The i.r. spectrum of this complex shows bands due to both a Rh-Cl stretch and a terminal carbonyl. The i.r. spectra of all these complexes are collected together in Table 4. The complex is soluble in CH_2Cl_2 but insoluble in water, and from the i.r. data, the structure is one in which the Rh atom is 6 co-ordinate (XLV).

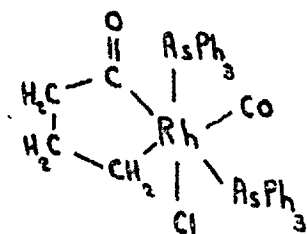


Fig. XLV

The n.m.r. spectrum in CH_2Cl_2 shows peaks at τ 2.58 (AsPh_3) and 8.34, 8.35, and 9.24; although the complex is somewhat unstable in solution and it is not possible to obtain a well resolved spectrum.

This AsPh_3 complex contains 6 co-ordinate rhodium(III), and is almost certainly octahedral. This is the common stereochemistry for the metal in the oxidation state (III), but the other compounds in this

Table 4

Infrared data on the Complexes		
	ν (Rh-C $\equiv$ O) stretch (cm $^{-1}$)	ν Rh-Cl stretch (cm $^{-1}$)
[Rh(CO) $_2$ Cl] $_2$		277
[Rh(C $_2$ H $_4$) $_2$ Cl] $_2$	-	270
[(C $_4$ H $_6$ O)RhCOCl] $_2$	2041	288
(C $_4$ H $_6$ O)RhCl(PPh $_3$) $_2$	-	
(C $_4$ H $_6$ O)RhCl(Ph $_2$ PCH $_2$) $_2$	-	343
(C $_4$ H $_6$ O)RhCOCl(AsPh $_3$) $_2$	2039	325, 310, 291
(C $_4$ H $_6$ O)RhCOCl(py) $_2$	2040	-
(C $_4$ H $_6$ O)RhCOCl(dipy)	2041	-
(C $_4$ H $_6$ O)RhCOBPh $_4$ (dipy)	2066	-
(C $_4$ H $_6$ O)RhCOCl(phenan)	2016	-

series are 5 co-ordinate rhodium(III). Complexes with this coordination number are rather uncommon, although Hieber (81) has recently reported some triphenylstibine complexes of rhodium(I) which are 5 co-ordinate.

Tetramethylene-1-one rhodium carbonyl chloride dissolves slowly in acetonitrile, but the addition of petroleum yields the complex unchanged and analytically pure. The dimer also dissolves slowly in dimethylsulphoxide. No pure complex has been isolated but the yellow solution gives a white precipitate with an aqueous solution of AgNO_3 and probably contains DMSO co-ordinated in a similar manner to the pyridine product.

EXPERIMENTALTetramethylene-1-one 2,2'-dipyridyl rhodium carbonyl chloride

Tetramethylene-1-one rhodium carbonyl chloride (0.1 g.) was dissolved in several small quantities of CH_2Cl_2 (5 ml. portions). To this was added a CH_2Cl_2 solution of 2,2'-dipyridyl (0.4 g.), when the colour of the solution changed from yellow to red. Addition of a small quantity of petroleum gave a dark precipitate which was filtered off. Further addition of petroleum gave colourless crystals of the complex which were filtered off and dried in vacuum, m.p. $197-200^\circ$. Yield 0.05 g. [Found: C, 46.0; H, 4.2. $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{O}_2\text{Rh}$ requires C, 45.9; H, 3.6.] $\nu_{(\text{max})}$ (nujol mull): 2041s, 1695s, 1595m, 1311w, 1276w, 1206m, 1156m, 1098m, 1071m, 1029m, 986s, 896m, 812m, 764s, 731m, 720sh.

The complex is insoluble in organic solvents but is slightly soluble in warm water.

Tetramethylene-1-one 2,2' dipyridyl rhodium carbonyl tetraphenylborate

To an aqueous solution of tetramethylene-1-one 2,2'-dipyridyl rhodium carbonyl chloride was added excess of an aqueous solution of sodium tetraphenylboron. A colourless precipitate was immediately formed which was filtered off and dried in vacuum giving the complex in quantitative yield. [Found: C, 65.4; H, 5.4. $\text{C}_{41}\text{H}_{32}\text{BClN}_2\text{O}_4\text{Rh}$ requires C, 64.7; H, 5.3.] $\nu_{(\text{max})}$ (nujol mull): 3440mw, 2066s, 1618s, 1594s, 1311w, 1246w, 1229w, 1156w, 1120w, 1063w, 1032m, 1009m, 843w, 766s, 748m, 731s, 706s.

Tetramethylene-1-one 1,10 phenanthroline rhodium carbonyl chloride

Using an identical experimental procedure with 1,10 phenanthroline the complex was obtained as colourless crystals which were dried in vacuum, m.p. decompose at 220° . [Found: C, 48.7; H, 3.6; N, 6.8. $C_{17}H_{14}ClN_2O_2Rh$ requires C, 49.0; H, 3.4; N, 6.7.]

λ_{max}^D (nujol mull): 2016s, 1678s, 1342mw, 1305w, 1274w, 1259w, 1222m, 1145m, 1099m, 1072m, 1029m, 992s, 867m, 854s, 815m, 789m, 777m, 738s.

Tetramethylene-1-one 1,2 bis(diphenylphosphino)ethane rhodium carbonyl chloride

To a solution of tetramethylene-1-one rhodium carbonyl chloride (0.1 g.) in CH_2Cl_2 was added CH_2Cl_2 solution of bis(diphenylphosphino)ethane (0.5 g.). The solution immediately changed colour to deep yellow. Methanol was slowly added to the boiling solution until pale yellow crystals were obtained. Recrystallisation in a similar manner gave colourless microcrystals of the complex. [Found: C, 59.8; H, 5.7. $C_{30}H_{30}ClOP_2Rh$ requires C, 59.4; H, 5.0.]

λ_{max}^D (nujol mull): 1618s, 1550s, 1307w, 1272w, 1186m, 1156w, 1093s, 1027w, 984m, 958m, 906w, 742s, 719s, 702s.

Tetramethylene-1-one bis(triphenylarsine)rhodium carbonyl chloride

Solutions of tetramethylene-1-one rhodium carbonyl chloride (0.1 g.) and triphenylarsine (0.1 g.) in CH_2Cl_2 were mixed and allowed to stand overnight at room temperature. The resulting yellow solution was boiled and petroleum added until only a little CH_2Cl_2 remained. On cooling and standing colourless needles of

the complex were obtained, m.p. 247° (decomp.). Yield 0.2 g. (85%).

[Found: C, 57.9; H, 4.4. $C_{41}H_{36}As_2ClORh$ requires C, 58.0; H, 4.3.]

$\nu_{(\max)}$ (nujol mull): 2039s, 1686s, 1570w, 1304w, 1274w, 1202w,
1156w, 1074m, 1022m, 994m, 735s, 731s, 693s.

SECTION E

EXPERIMENTAL PROCEDURE

This section gives a brief description of the spectral equipment used, and indicates any special analytical methods employed in this work. Finally the section describes briefly the preparative procedures used for some of the complexes which were employed as starting materials for the new complexes described in the thesis.

Infrared spectra in the region $4000\text{--}650\text{ cm.}^{-1}$ were recorded on Perkin Elmer 237 or on Grubb-Parson's Spectromaster grating instruments as nujol mulls or as dilute solutions in appropriate solvents. If possible cyclohexane or hexane was used as solvent for measuring spectra in the carbonyl region ($\text{ca. } 2000\text{ cm.}^{-1}$). In the region $500\text{--}200\text{ cm.}^{-1}$ the spectra were recorded on a Grubb-Parson's DM4 instrument as vaseline mulls between polythene discs. The ultra-violet spectrum was recorded on a PE 350 spectrometer as a solution in CH_2Cl_2 .

Nuclear magnetic resonance spectra were obtained on Varian V4311 or HA100 spectrometers operating at 56.45 and 94.1 Mc/s respectively. With the former instrument calibration of the spectrum was by the side band technique from a Muirhead oscillator. Mass spectra were obtained on a MS9 spectrometer. Electron spin resonance spectra were obtained on a Varian Associates V-4502-15 spectrometer as crystalline or amorphous solids.

Except where otherwise stated, petroleum refers to petroleum ether b.p. 30-40°. Microanalyses were performed by the Microanalytical Laboratories, Imperial College, or by A. Bernhardt, Mülheim (Ruhr), Germany. Molecular weights were obtained by Mechrolab osmometer at 37°, the solvent used being shown alongside the value found. Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Magnetic moments were determined by the Gouy method, the values being corrected for the diamagnetism of the tube and the ligands (Pascal's constants).

Perfluorobutadiene, perfluorobut-2-ene, and perfluorobut-2-yne were supplied by Peninsular ChemResearch, Inc., U.S.A.

The fluoride test solution was made up by adding a slight excess of a solution of alizarin in ethanol to a 25% hydrochloric acid solution of zirconium nitrate. The red colour of this solution changes to yellow in the presence of fluoride ion.

Tris(triphenylphosphine)chlororhodium(I) was prepared by mixing hot ethanolic solutions of triphenylphosphine (6 moles) and rhodium trichloride (1 mole), and refluxing for 30 minutes (63,82). The complex precipitated as burgundy-red crystals which were dried in vacuum.

Tris(triphenylarsine)chlororhodium(I) cannot be prepared by an analogous procedure (83). Dichlorotetrakis(ethylene)rhodium^I was first prepared as described by Cramer (84). This complex was then refluxed with excess triphenylarsine under nitrogen for 30 minutes. Further refluxing for 10 minutes after the addition

of ether gave the complex as brown crystals which were dried in vacuum.

Rhodium carbonyl chloride was prepared by the method of McCleverty and Wilkinson (85). Carbon monoxide was slowly passed over rhodium trichloride which was kept at 100° ; the product sublimes away as it is formed and can be collected in a cooler part of the apparatus. If required the complex was recrystallised from petroleum ether at -40° .

Tetrakis(triphenylphosphine)platinum(0) and the corresponding arsine complex (86) were prepared by the dropwise addition of hydrazine to a solution containing chloroplatinite (1 mole) and the phosphine or arsine (6 moles). Recrystallisation of the products gives the tris co-ordinated complex which has been studied structurally (87).

Tetrakis(triphenylphosphine)palladium(0) is prepared similarly except that in this case $(PPh_3)_2PdCl_2$ was first prepared, which was then reduced to the required product with hydrazine in the presence of excess triphenylphosphine (88).

Tetrakis(trifluoromethyl)cyclopentadienone was prepared by heating a mixture of $Rh(CO)_2Cl$ (1.0 g.), perfluorobut-2-yne (12.5 g.) and carbon monoxide (100 atmos.) in a stainless steel reaction vessel at 150° for 20 hours (25). The compound was sublimed out of the vessel into a trap cooled in liquid N_2 and purified by vacuum sublimation on to a water-cooled probe.

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