THE REACTION OF ELECTROPHILIC KETONES OLEFINS AND ACETYLENES WITH SOME GROUP VIII METAL COMPLEXES.

A thesis presented for the

Degree of Doctor of Philosophy

in the

Faculty of Science

by

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University of Leicester

August 1976

STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of The University of Leicester, between October 1973 and August 1976, under the supervision of Dr. R.D.W. Kemmitt. The work has not been and is not concurrently being, presented for any other degree.

David A. Clarke.

August 1976.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. R.D.W. Kemmitt, for his advice, criticism, tuition and constant enthusiasm, all of which have greatly helped in expanding my understanding of organometallic chemistry.

I would like to acknowledge the contribution of the X-ray crystallographic department of this University whose X-ray crystal structure determinations have added immensely to the understanding of the chemistry studied in this work. Similar thanks are also extended to the operators of the n.m.r. machines, whose many hours spent recording spectra have been of great value.

I am also grateful to Mrs E. Hargreaves-Turner for typing this thesis, and displaying a great deal of tolerance in the process.

Finally I would like to thank the Science Research Council for a grant which has enabled me to do the research now reported.

CONTENTS

SUMMARY

Chapter 1 presents a review on the reactions of electrophilic ketones with palladium and platinum compounds. Further reactions of various palladium(0) platinum(0) and platinum(II) complexes with the electrophilic ketones hexafluoropropan-2-one, chloropentafluoropropan-2-one 1,3-dichlorotetrafluoropropan-2-one, 1,1,3-trichlorotrifluoropropan-2-one, acetonedicarboxylic acid dimethyl ester and diethyl ketomalonate are described.

Chapter 2 contains the results of some investigations into the reactivity of some iridium(I) olefin complexes towards hexafluorobut-2-yne and dimethylacetylenedicarboxylate; hexafluorobut-2-yne reacts with complexes of the type $[IrCl(cod)]_2$ and $[Ir(dithio)(cod)]$ to produce previously unknown olefin-acetylene complexes.

Chapter 3 discusses the preparation of the fluoro-olefin complexes $[IrCl(cod)(CF_2{=}CFX)]$ and $[Ir(dithio)(cod)(CF_2{=}CFX)]$ where X=F, Cl, Br, H, CF_3. Studies of their ^{19}F n.m.r. spectra indicates the presence of two isomers in many of these fluoro-olefin complexes.

ABBREVIATIONS

Å	Angström unit
acac	Anion of acetylacetone
ADCADME	acetonedicarboxylic acid dimethyl ester
bipy	2,2′-bipyridyl
br	broad
C_4H_6	buta-1,3-diene
C_8H_{14}	cyclo-octene
cod	cis-cis-cyclo-octa-1,5-diene
d	doublet
DMA	dimethylacetylenedicarboxylate
dmtc	dimethyldithiocarbamate anion
dptc	diphenyldithiocarbamate anion
dtc	diethyldithiocarbamate anion
dtp	diethyldithiophosphate anion
hfa	hexafluoropropanone
i.r.	infra-red
L	Ligand
m	multiplet
mHz	mega-hertz
n.m.r.	nuclear magnetic resonance
q	quartet
quin	quintet
p.p.m.	parts per million
s	singlet
t	triplet
t-Bu	tertiary butyl
T.M.S.	tetramethylsilane

FOR MY PARENTS

AND DIANA

CHAPTER ONE

THE REACTIONS OF ELECTROPHILIC KETONES WITH LOW VALENT PALLADIUM AND PLATINUM COMPOUNDS.

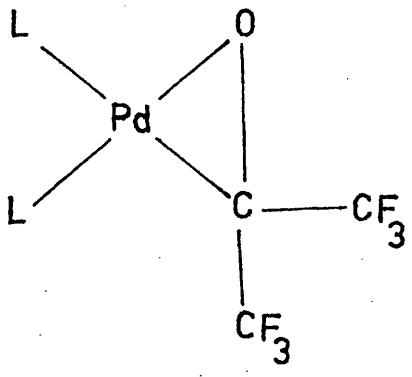
1:1 INTRODUCTION

Since the discovery that hexafluoropropanone can co-ordinate to zero valent platinum or palladium via its p π - p π orbitals[1] a number of analogous molecules e.g. trifluoroacetonitrile,[2] hexafluoroisopropylideneamine,[3] N-methylhexafluoroisopropylideneamine,[4] and trifluoroacetylcyanide,[5] have all been shown to co-ordinate in a similar way to low-valent complexes of the Group VIII metals.

The molecules are analogous to fluoro-olefins and acetylenes since the presence of highly electron withdrawing groups in these molecules reduced the electron density at the unsaturated centre and so enhances their reactivity towards the excess electron density present in a low-valent metal complex.

The complexes formed with palladium or platinum can be formulated as either trico-ordinate Pt(0) or Pd(0) or as tetraco-ordinate Pt(II) or Pd(II). A common reaction of this three membered ring system is ring expansion to five, and seven, membered rings in the presence of an electron deficient unsaturated system.

Tetrakis(triphenylphosphine)palladium(0),[1] tetrakis(triphenylphosphite)palladium(0)[6] and tetrakis(methyldiphenylphosphine)palladium(0)[6] react with hexafluoropropanone to give three membered ring complexes. Hexafluoroisopropylideneamine also reacts with tetrakis(triphenylphosphine) palladium(0)[3] to give a three membered ring complex, $[(PPh_3)_2Pd\overline{C(CF_3)_2NH}]$.



($L=PPh_3$, $P(OPh)_3$, $MePPh_2$).

FIGURE 1:1

In contrast to these reactions bis(t-butylisocyanide)palladium(0)[3] tetrakis(triphenylphosphite)palladium(0),[6] tetrakis(dimethylphenylphosphonite)palladium(0)[6] and tetrakis(dimethylbenzylarsine)palladium(0)[6] react with hexafluoropropanone to give five membered ring complexes (Figure 1:2) (X=O; $L=Bu^tNC$, $P(OMe)_3$, $PPh(OMe)_2$, $Me_2As(CH_2Ph)$), Similarly hexafluoroisopropylideneamine reacts with bis(t-butylisocyanide)palladium(0) and tetrakis(dimethylphenylarsine)palladium(0) to give five membered ring systems,[3] (Figure 1:2) (X=NH, $L=Bu^tNC$, Me_2AsPh).

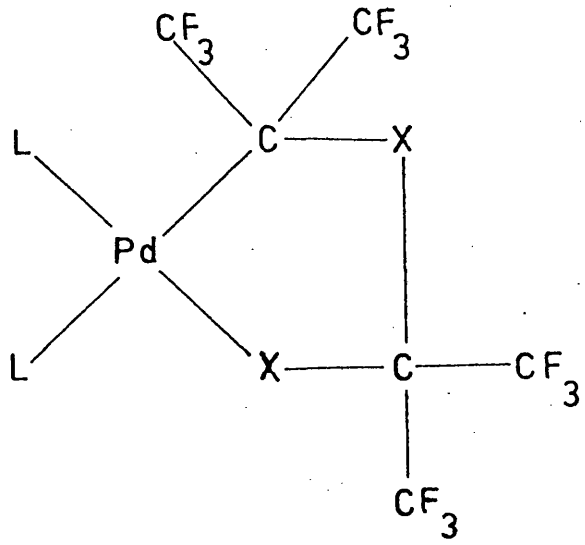
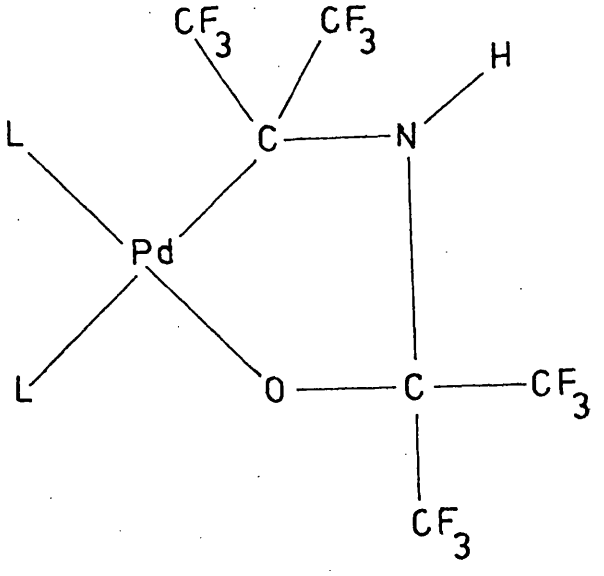


FIGURE 1:2

The complexes $[L_2PdC(CF_3)_2X]$ (X=O; L=P(OPh)$_3$[6], PPh$_3$[3] and X=NH;[3] L=PPh$_3$) could not be ring expanded with hexafluoropropanone or hexafluoroisopropylideneamine. This suggests that the ligands P(OPh)$_3$ and PPh$_3$ have a deactivating effect to ring expansion reactions. Direct formation of five membered ring systems $[L_2PdC(CF_3)_2XC(CF_3)_2X]$ (X=O; L=Bu^{t}NC, P(OMe)$_3$, PPh(OMe)$_2$, Me$_2$As(CH$_2$Ph) and X=NH; L=Bu^{t}NC, Me$_2$AsPh) suggest, assuming that five membered ring formation goes through a reactive three membered ring intermediate, that the ligands Bu^{t}NC, (POMe)$_3$, PPh(OMe)$_2$, Me$_2$As(CH$_2$Ph) and Me$_2$PPh have an activating[6] effect on ring expansion reactions.

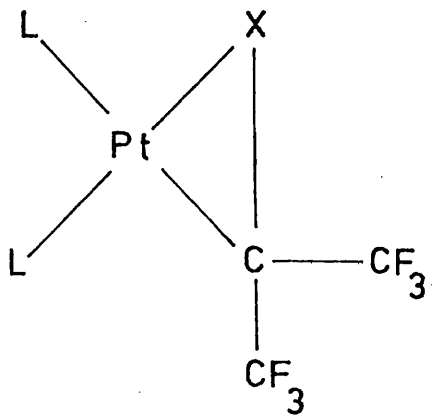
The complexes $[(MePPh_2)_2\overline{PdC(CF_3)_2O}]$ and $[(Ph_2PCH_2)_2\overline{PdC(CF_3)_2O}]$ react with hexafluoropropanone, on prolonged heating at 60°C to give ring expanded products[6] (Figure 1:2) (L=$MePPh_2$ or L_2=$(Ph_2PCH_2)_2$). Hexafluoroisopropylideneamine also ring expands the complex $[(Ph_2PCH_2)_2\overline{PdC(CF_3)_2O}]$, and from ^{19}F n.m.r. spin decoupling data and by analogy to the nickel complex of proven structure,[7] $[(Bu^tNC)_2\overline{NiC(CF_3)_2NHC(CF_3)_2O}]$ the product is assigned the structure shown below[6] (Figure 1:3).



(L=$(Ph_2PCH_2)_2$)

FIGURE 1:3

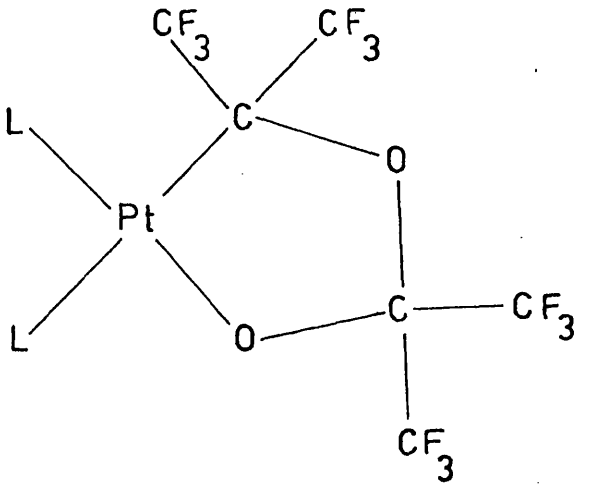
Tetrakis(triphenylphosphine)platinum(0)[1] tetrakis-methyldiphenylphosphine)platinum(0)[1] and tetrakis(triphenylphosphite)-platinum(0)[8] react with hexafluoropropanone to give three membered ring systems, which show in the ^{19}F n.m.r. spectrum a triplet of double doublets due to cis-and trans-^{31}P coupling and ^{195}Pt satellites. Analogous hexafluoroisopropylideneamine and N-methylhexafluoroiso-propylideneamine ring complexes can be prepared by the displacement of trans-stilbene from trans-stilbenebis(triphenylphosphine)platinum(0)[4].



(X=O; L=PPh_3, $MePPh_2$, $P(OPh)_3$).
(X=NH; L=PPh_3, X=NMe; L=PPh_3).

FIGURE 1:4

Hexafluoropropanone reacts with tetrakis-(trimethylphosphine)platinum(0) to give a five membered ring system[8] (Figure 1:5)



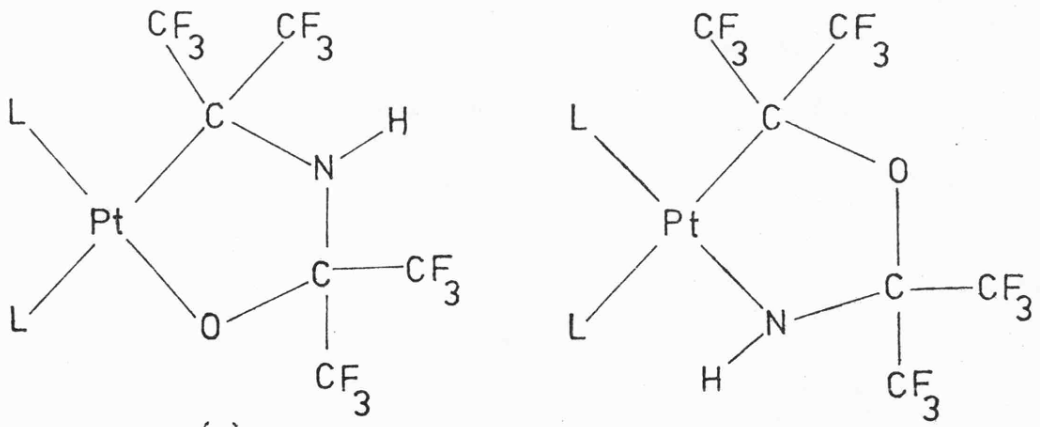
$(L=P(OMe)_3)$

FIGURE 1:5

Assuming this reaction goes via a reactive three membered ring intermediate, it can be seen, as in nickel and palladium systems, how important a role the ligand plays in three to five membered ring expansions. As trimethylphosphite is a more basic ligand than, for example, triphenylphosphite there will be increased electron density on the platinum in the three membered ring system, which will be available for back donation into the π^* orbitals of the second hexafluoropropanone molecule. Five membered ring formation will therefore be more readily accomplished.

$[(PPh_3)_2Pt\overline{C(CF_3)_2O}]$ and $[(P(OPh_3)_2Pt\overline{C(CF_3)_2O}]$ are not ring expanded even after prolonged heating with hexafluoropropanone[8], but $[(Ph_2PCH_2)_2Pt\overline{C(CF_3)_2O}]$ and $[(MePPh_2)_2Pt\overline{C(CF_3)_2O}]$ react slowly with hexafluoropropanone to give ring expanded products showing two ^{19}F n.m.r. signals and are hence assigned the structure in Figure 1:5 ($L=MePPh_2$ $L_2=(Ph_2PCH_2)_2$). Steric effects of the phosphine ligands may also be important in deciding whether the three membered rings can be expanded by hexafluoropropanone.

Hexafluoroisopropylideneamine reacts with $[(MePPh_2)_2Pt\overline{C(CF_3)_2O}]$ and $[(PPh_3)_2Pt\overline{C(CF_3)_2O}]$ to give good yields of the ring expanded products[8] (Figure 1:6) which can be assigned structure (a) or (b)

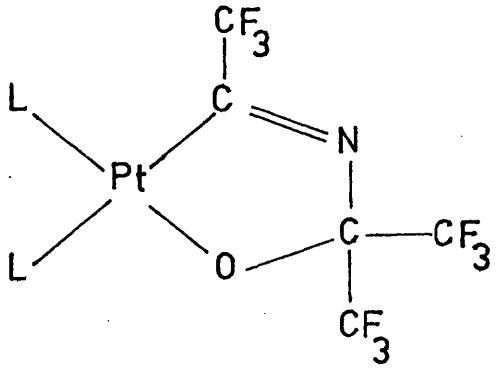


($L=MePPh_2$ or PPh_3).

FIGURE 1:6

$[(PPh_3)_2PtC(CF)_2NH]$ reacts slowly with hexafluoropropanone to give a ring expanded product [4] identical to that obtained from the reaction of $[(PPh_3)_2PtC(CF_3)_2O]$ with hexafluoroisopropylideneamine. (Figure 1:6).

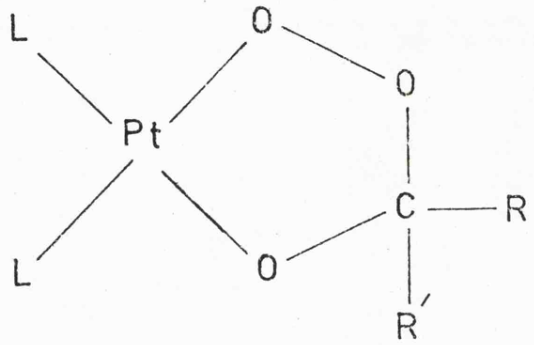
The reaction of hexafluoropropanone with $[(PPh_3)_2PtC(CF_3)_2NMe]$ yields the ligand displacement product $[(PPh_3)_2PtC(CF_3)_2O]$ This displacement also occurs when hexafluoropropanone reacts with $[(PPh_3)_2PtN{=}CCF_3]$.[1] However, a ring expansion product (Figure 1:7) is also produced in this reaction.



$(L{=}PPh_3)$

FIGURE 1:7

The treatment of peroxobis(triphenylphosphine)platinum(II) with some aldehydes and ketones [9,10,11,12,13] leads to reactions analogous to the ring expansion reactions of three membered ring complexes containing hexafluoropropanone and similar molecules.



($L=PPh_3$)

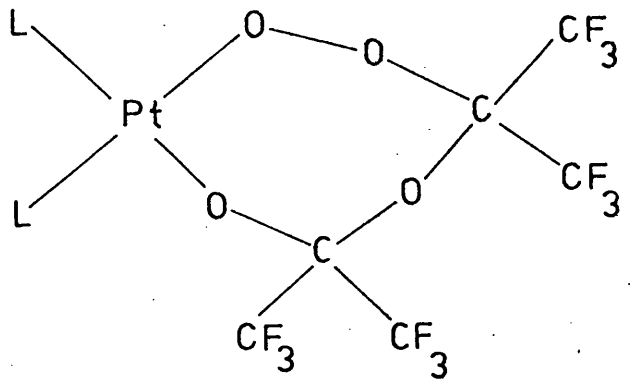
FIGURE 1:8

Some examples include: $R=R' = CH_3$;[10,11] $R=CH_3$, $R'=H$;[10] $R=CH_2CH_3$, $R'=H$;[10] $R=ClCH_2$, $R'=CH_3$;[10] $R=R' = CF_3$;[14] $R=CH_3$, $R' = CF_3$;[9] $R=CH_3$, $R'=COCH_3$;[13] $R=C_6H_5$, $R' = COC_6H_5$.[13]

An X-ray crystallographic study for the 1:1 adduct between peroxobis(triphenylphosphine)platinum(II) and propanone[11] confirmed the assigned structure and showed that the P-Pt-P plane is almost co-planar with the plane of the five membered ring.

Complexes containing the peroxo group show weak bands in the infra-red around $780 cm^{-1}$[9,10] assignable to the(O-O) stretch.

A seven membered ring complex (Figure 1:9) can be prepared by the reaction of excess hexafluoropropanone on peroxobis(triphenylphosphine) platinum(II) but not via the ring expansion of $[(PPh_3)_2PtOO(CF_3)_2CO]$ in the presence of hexafluoropropanone. This complex shows two signals in its ^{19}F n.m.r. spectrum.

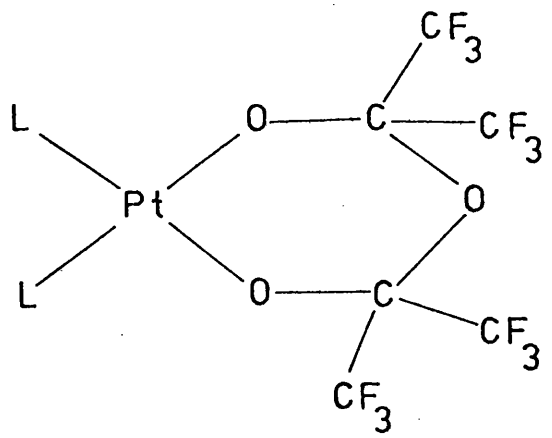


($L=PPh_3$)

FIGURE 1:9

These seven membered rings have also been prepared from zerovalent platinum complexes. $[PtL_4]$ ($L=PPh_3$, $PMePh_2$, or PMe_2Ph) react with organic azides or sulphonyl azides in dry solvents to give azadiene compounds $[\overline{Pt \cdot N(R)N:NN}(R)L_2]$ ($R=PH, pMeC_6H_4$ or $PhSO_2$ etc)[15] These products react with hexafluoropropanone (containing small amounts of its hydrate) to give azobenzeneplatinum complexes $[Pt(RN:NR)L_2]$ as well as compounds believed, on the basis of ^{19}F n.m.r. and other studies, to contain both six and seven membered ring systems.

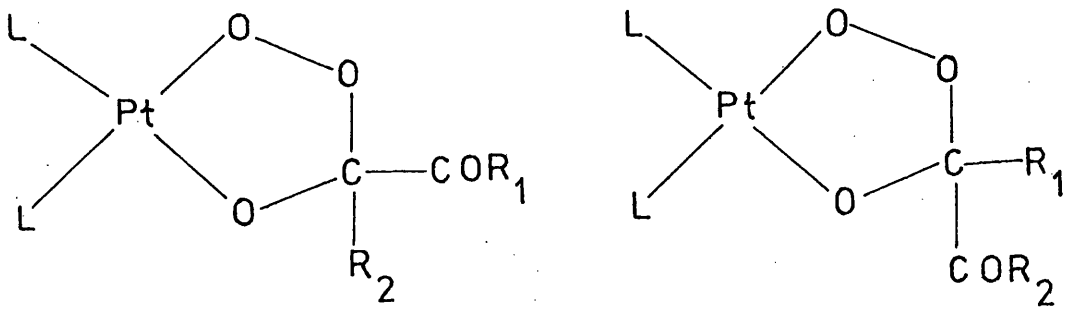
The presence of a six membered ring has recently been clearly demonstrated[16] by an X-ray crystallographic determination. The compound believed to be a seven membered ring with a peroxo linkage adjacent to the platinum atom decomposed in the X-ray beam, while a crystal of its presumed isomer with a peroxy linkage between the two $C(CF_3)_2$ groups proved also to contain the six membered ring. (Figure 1:10)



(L=$PMePh_2$, PPh_3)

FIGURE 1:10

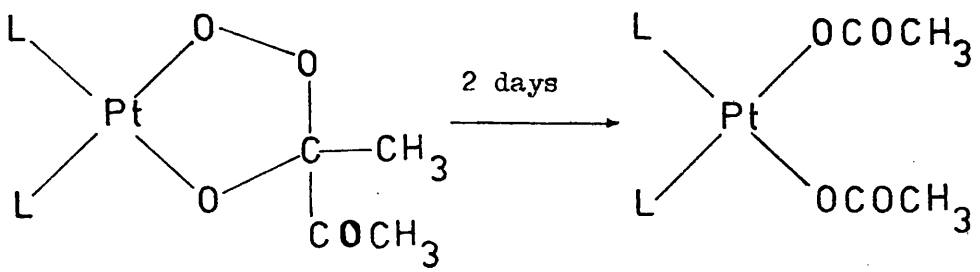
A variety of α-diketones (e.g. 2,3 pentanedione, $C_2H_5COCOCH_3$; 2,3 butanedione, $CH_3COCOCH_3$; 1-phenyl -1,2-propanedione, $C_6H_5COCOCH_3$; etc) react with peroxobis(triphenylphosphine)platinum(II) to give products in which just one of the carbonyl groups is incorporated into the cyclic part of the structure, the other remaining free.[13] (Figure 1:11).



(L=PPh_3)

FIGURE 1:11

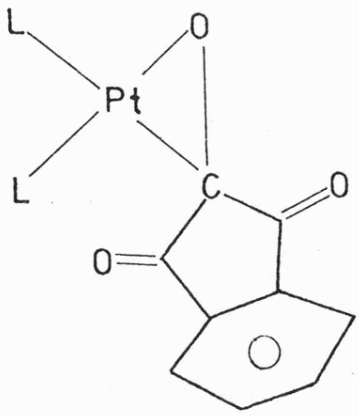
The initial adducts will then react with a further molecule of peroxobis(triphenylphosphine)platinum(II) to give a dinuclear species in which both carbonyl groups are co-ordinated. The 1:1 adducts undergo a novel rearrangement to give eventually a dicarboxylate complex (Figure 1:12). When the α -diketone is glyoxal (CHO-CHO), the rearrangement occurs rapidly and it is not possible to isolate the peroxy five membered ring complex.



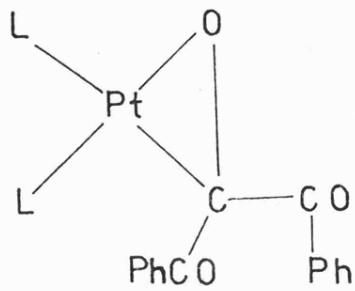
(L=PPh_3)

FIGURE 1:12

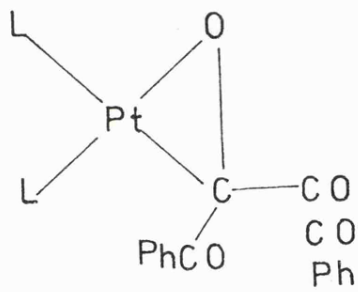
The four electrophilic ketones triketoindane,diphenyltriketone, diphenyltetraketone and alloxan each give crystalline compounds with the zerovalent platinum complexes tetrakis(triphenylphosphine)platinum(0), trans - stilbenebis(triphenylphosphine)platinum(0) and diphenylacetylenebis (triphenylphosphine)platinum(0).[17] The complexes have been assigned a structure in which the ketones are π -bonded by the central electrophilic carbonyl groups p π - p π orbitals to give the three membered ring systems shown in figure 1:13.



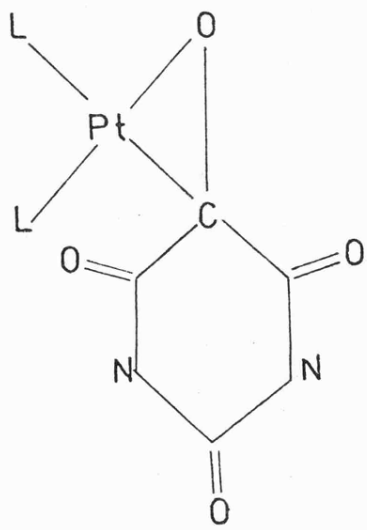
triketoindanebis-
(triphenylphosphine)platinum.



diphenyltriketonebis-
(triphenylphosphine)platinum.



diphenyltetraketonebis-
(triphenylphosphine)platinum.



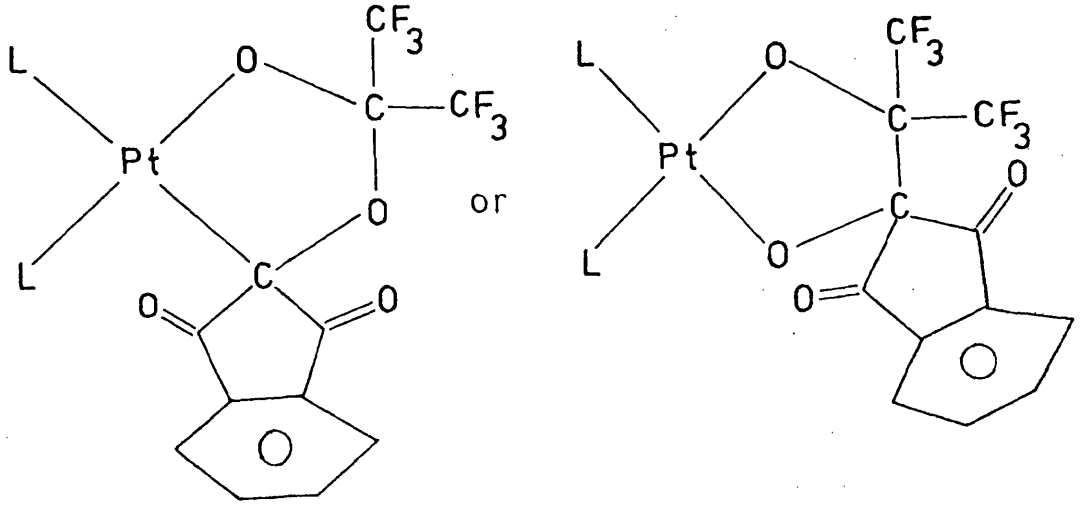
alloxabis(triphenylphosphine)
platinum.

($L=PPh_3$).

FIGURE 1:13

These four products react with molecular oxygen to form the 1:1 adducts.

Hexafluoropropanone reacts with the diphenyltriketone complex at room temperature to give the displacement product hexafluoropropanone-bis(triphenylphosphine)platinum(0) together with a ring expanded product. The reaction of hexafluoropropanone with the triketoindane complex also produces two products. The first was a 1:1 adduct between the triketoindane complex and hexafluoropropanone which had a single singlet signal in its ^{19}F n.m.r. indicating a five membered ring system between triketoindane and hexafluoropropanone. (Figure 1:14).

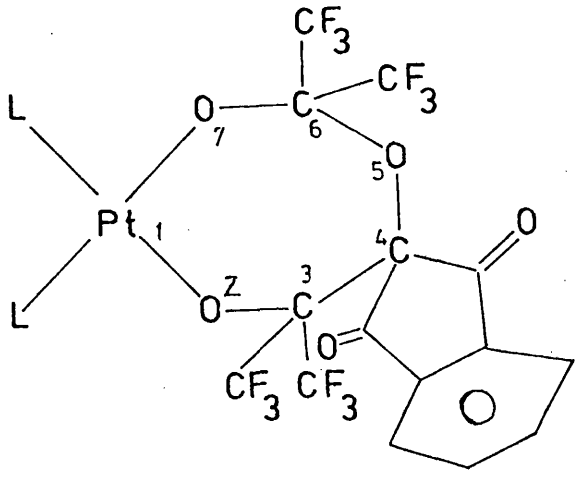


($L=PPh_3$)

FIGURE 1:14

Lack of ^{195}Pt or ^{31}P coupling on the signal due to the $C(CF_3)_2$ seemed to suggest that the hexafluoropropanone is bonded to platinum via the carbonyl oxygen rather than the carbon. From the chemical shift of the ^{19}F n.m.r. spectrum structure (b) seems the most likely arrangement.[18]

The second product was a 1:2 adduct between the triketoindane complex and hexafluoropropanone. The ^{19}F n.m.r. spectrum contained four quartets centred at 5·98, 7·98, 15.6 and 17·8 p.p.m. each showing the same $^{19}F - ^{19}F$ coupling constant of 10·5Hz. The probable structure for this complex is shown (Figure 1:15)



($L=PPh_3$)

FIGURE 1:15

The seven membered ring is puckered so each CF_3 group is inequivalent. Any other arrangement should result in coupling between the CF_3 groups on the 3 carbon and those on the 6 carbon.

1:2 RESULTS AND DISCUSSION

A. The reactions of chlorofluoropropanones with some Platinum(0) compounds

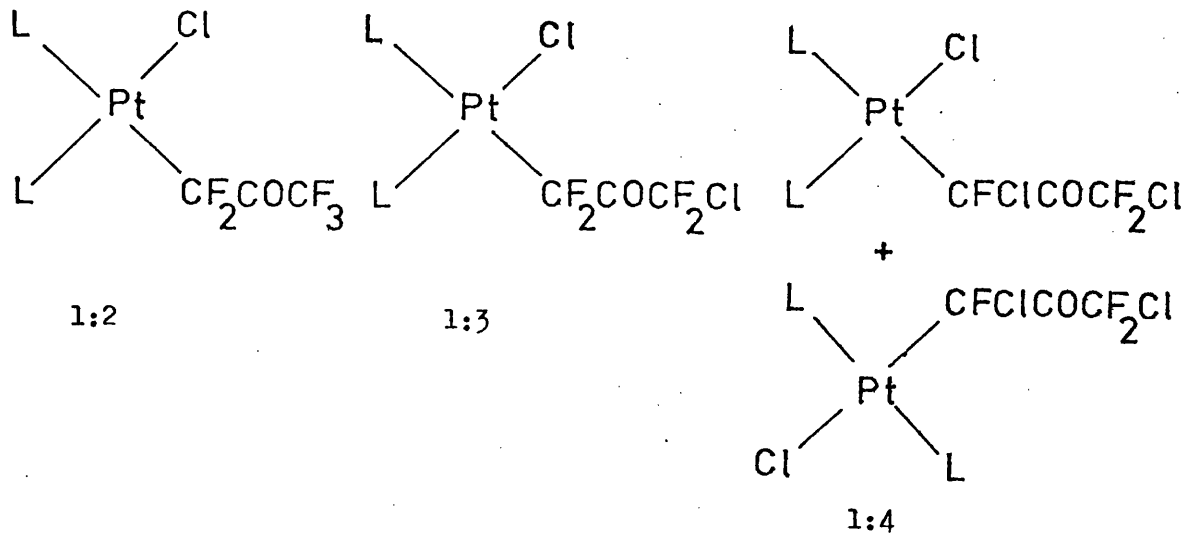
It was reported[1] that when 1,3-dichlorotetrafluoropropan-2-one was reacted at room temperature with tetrakis(triphenylphosphine)platinum(0) a complex formed where the carbonyl group of the ketone was π-bonded to the metal. It was thought worthwhile to repeat this reaction using tetrakis(triphenylphosphine)platinum(0) and tetrakis(triphenylphosphine) palladium(0) and extend the series by using other chloro-substituted fluoroketones, notably chloropentafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one.

On repeating the reaction with 1,3-dichlorotetrafluoropropan-2-one in benzene a white crystalline solid was obtained having a melting point of 310-312°C and no ν (C-F) bands visible in its infra-red spectrum. These results agreed well with the data given for the complex obtained previously.[1] However it appeared that this same compound was being formed when tetrakis(triphenylphosphine)platinum reacted with either chloropentafluoropropan-2-one, 1,3-dichlorotetrafluoropropan-2-one or 1,1,3-trichlorotrifluoropropan-2-one. Similarly if these ketones were reacted, in turn, with tetrakis(triphenylphosphine)palladium(0) a yellow compound melting at $\sim$280°C and having no ν (C-F) absorptions in its infra-red spectrum, was obtained each time. When different solvents were used in the reactions the same results were obtained.

No ^{19}F n.m.r. spectrum was obtainable for either the platinum or palladium compounds, and the conclusion reached was, that if chlorofluoropropan-2-ones were reacted with tetrakis(triphenylphosphine)

platinum(0) or tetrakis(triphenylphosphine)palladium(0) the only products of the reactions seemed to be either cis-dichlorobis (triphenylphosphine)platinum(II) or trans-dichlorobis(triphenylphosphine) palladium(II).

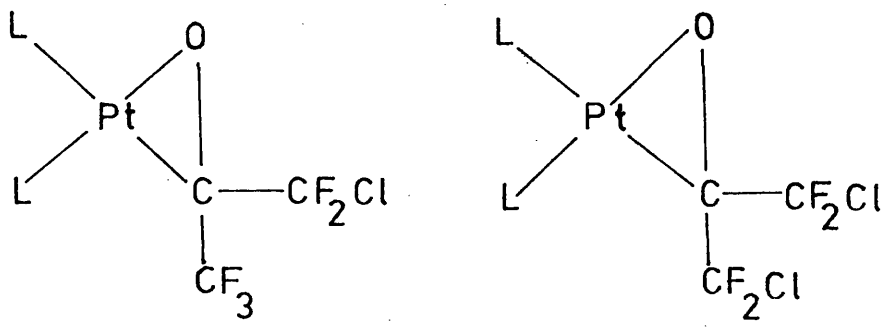
It seemed logical, as a final step, to repeat the reactions using other platinum(0) compounds. On reacting chloropentafluoropropan-2-one, 1,3 dichlorotetrafluoropropan-2-one or 1,1,3-trichlorotrifluoropropan-2-one with trans-stilbenebis(triphenylphosphine)platinum(0) in diethyl ether overnight, white crystalline compounds were produced each showing characteristics $\nu(C{=}O)$, $\nu(C{-}F)$ and $\nu(Pt{-}Cl)$ absorptions in their infra-red spectrum. The reactions involved the replacement of trans-stilbene by the chlorofluoropropan-2-ones to form complexes 1:2-1:4.



The reaction of trans-stilbenebis(triphenylphosphine)platinum(0) with chloropentafluoropropan-2-one and 1,3-dichlorotetrafluoropropan-2-one in benzene solution lead to the production of complexes 1:2 and 1:3 respectively,

but the reaction with 1,1,3-trichlorotrifluoropropan-2-one in benzene produced only cis-dichlorobis(triphenylphosphine)platinum(II).

On reacting the fluoropropanones hexafluoropropan-2-one, chloropentafluoropropan-2-one and 1,3-dichlorotetrafluoropropan-2-one, in turn with diphenylacetylenebis(triphenylphosphine)platinum(0) in diethyl ether, white crystalline compounds were again obtained. These complexes showed no evidence of ν(C=O) or ν(Pt-Cl) absorptions in their infra-red spectra, but there were many bands in the region 1100-1250cm^{-1} indicative of ν(C-F) stretching vibrations. When the complexes obtained in the reactions of chloropentafluoropropan-2-one and 1,3-dichlorotetrafluoropropan-2-one with diphenylacetylenebis-(triphenylphosphine)platinum(0) were recrystallised from dichloromethane-ethanol and their infra-red spectra rerun it was immediately evident that complexes 1:2 and 1:3 had been formed. It seemed likely therefore that the initial products from the reaction of these two chloro substituted fluoropropanones with diphenylacetylenebis(triphenylphosphine)platinum(0) had the ketones co-ordinated via their p π - p π orbitals (Figure 1:16)



(L=PPh$_3$)

FIGURE 1:16

These compounds, 1:5 and 1:6, are unstable in solution rapidly isomerising to the cis-oxidative addition products complexes 1:2 and 1:3 respectively.

The reaction of 1,1,3-trichlorotrifluoropropan-2-one with diphenylacetylenebis(triphenylphosphine)platinum(0) resulted in the isolation of the oxidative addition product mixture complex 1:4, in almost quantitative yield. Similarly the reaction in turn of all three chloro-substituted fluoropropan-2-ones with diphenylacetylenebis (triphenylphosphine)platinum(0) in benzene resulted in the formation of the oxidative addition complexes 1:2 - 1:4 respectively. Up to now the isolation of the π-bonded 1,1,3-trichlorotrifluoropropan-2-one complex of platinum has eluded us.

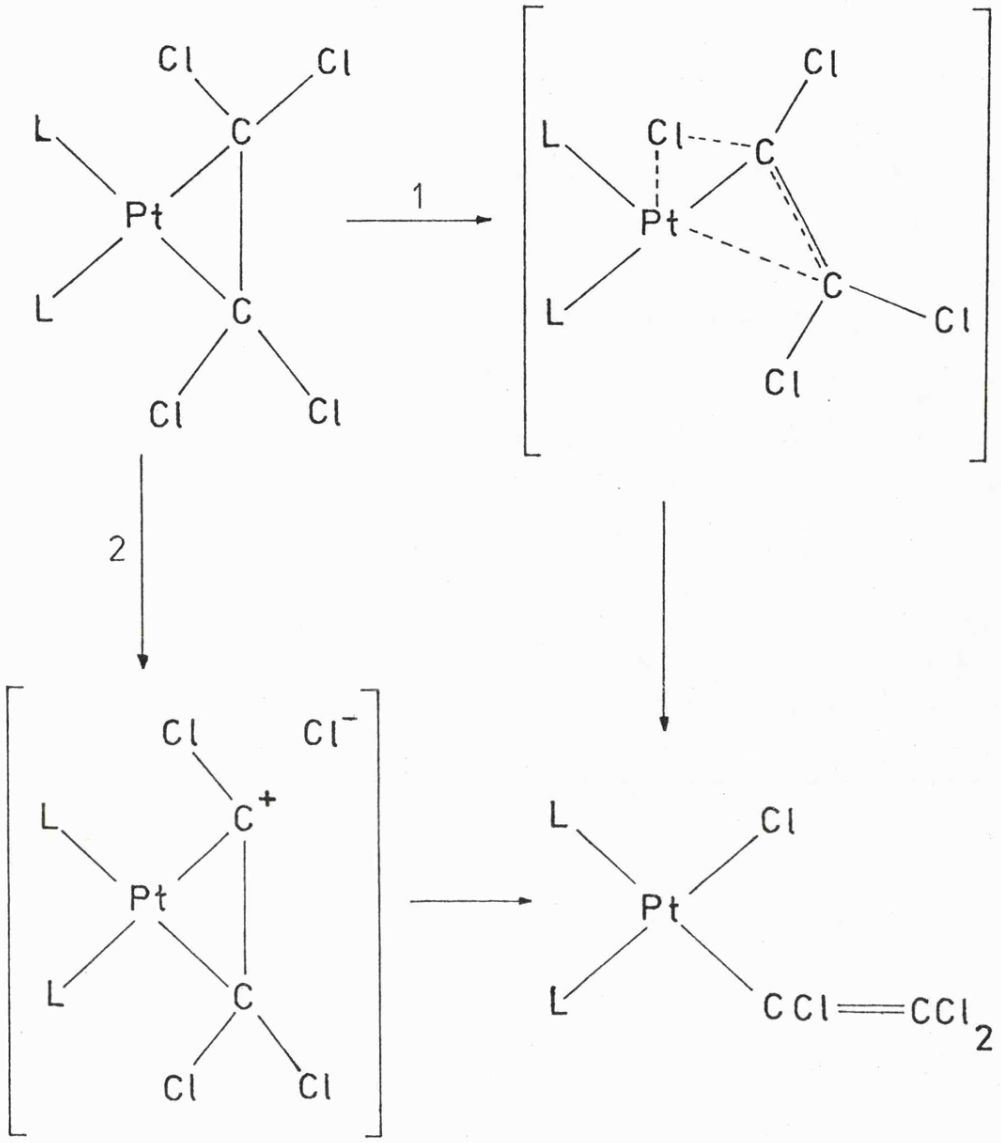
It is interesting to note that ethylenebis(triphenylphosphine) platinum(0) reacts with 1,3-dichlorotetrafluoropropan-2-one in diethyl ether to give the $p\pi$ - $p\pi$ co-ordinated complex 1:6.

These results seem to indicate that the C-Cl bond in chlorofluoropropan-2-ones is more readily broken than that in $CF_2{=}CFCl$ which is to be expected since the $O{=}C{-}CF_2Cl$ group is very similar to an allylic system. The reaction of chlorotrifluoroethylene with tetrakis (triphenylphosphine)platinum(0) in benzene results in the formation of $[(Ph_3P)_2Pt(C_2F_3Cl)]$ in 87% yield.[19] This complex appears to be stable in non-polar solvents and does not rearrange unless it is refluxed in n-butanol for several hours. The bromotrifluoroethylene complex $[(Ph_3P)_2Pt(C_2F_3Br)]$ rearranges much more rapidly and quantitatively in this solvent. Both compounds isomerise to the trans-vinyl complexes

$[(Ph_3P)_2Pt(CF:CF_2)Cl]$ and $[(Ph_2P)_2Pt(CF:CF_2)Br]$ respectively. The complex $[(Ph_3P)Pt(CCl_2CCl_2)]$[20] isomerises in refluxing ethanol to form the cis-$[(Ph_3P)_2PtCl(CCl:CCl_2)]$ compound, but this isomerisation does not occur in acetone, benzene or dichloromethane. Complexes 1:5 and 1:6, however, rearrange rapidly at room temperature in chloroform, benzene, and dichloromethane solution and even in a hexachlorobutadiene mull where the $\nu(C=O)$ stretching frequency can be seen appearing on running infra-red spectra in this mulling agent. Because the rate of isomerisation appeared to be much faster for compounds 1:5 and 1:6 when compared with substituted fluoro-olefin complexes of platinum, it was decided to investigate further the rate of this isomerisation for complex 1:5 (complex 1:5 seemed to be more stable than 1:6).

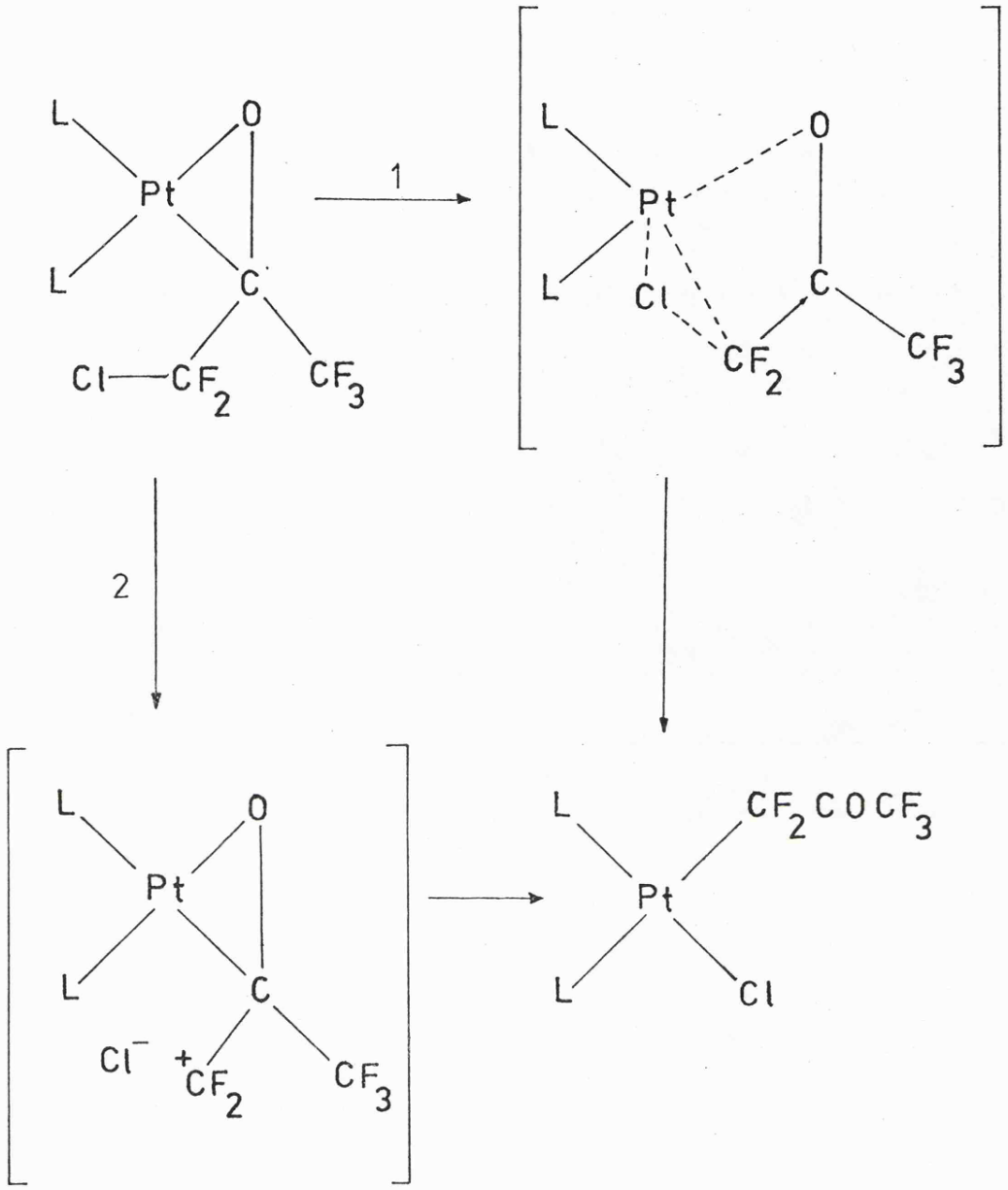
The solvents used for the kinetic runs on this compound were dichloromethane, chloroform and 1,2 dichloroethane. Results obtained[5] showed that complex 1:5 has a similar lack of solvent sensitivity to the platinum olefin compounds $[(Ph_3As)_2Pt(CF_2CFCl)]$ and $[(Ph_3As)_2Pt(CF_2CFBr)]$[17]

Several mechanisms have been proposed for the observed first order kineties of olefin-vinyl isomerisation[21] but only two seem plausible. These are shown in figure 1:17 for the tetrachloro-olefin compound which isomerises to a cis-vinylic system. Mechanism (1) involves a intramolecular rearrangement and mechanism (2) involves an ionic intermediate. By comparison with previously reported platinum halogeno-olefin isomerisations it would seem reasonable to propose similar mechanisms for the isomerisation of complex 1:5 - 1:2, (Figure 1:18). Because of the lack of solvent effects the intramolecular rearrangement seems most likely, although the limited range of solvents used must be taken into account.



(L=PPh_3)

FIGURE 1:17



(L=PPh_3)

FIGURE 1:18

Due to the extra carbon atom on the ketone group (i.e. CF_2Cl) compared with the olefin complexes, the ease of approach of the chloride to the platinum centre will be increased relative to the analogous olefin compounds. This may be responsible for the marked increase in the rate of isomerisation displayed by complex 1:5.

One other point that needs explaining is why, when complexes 1:5 and 1:6 isomerise they form the cis-oxidative addition compounds. The fact that they do form a cis-complex has been verified by an X-ray crystal structure determination on complex 1:3;[22] the results of which can be seen in figure 1:19.

Crystals of the complex $C_{39}H_{30}Cl_2F_4OP_2Pt$, (mol.wt.918.6) are monoclinic, space group $P2_1/a$ with a=20·45, b=18·66, c=10·43Å, β =114°, U=3635·5Å^3 and Z=4.

If the Pt-P bond lengths in complex 1:3 are compared with those of a similar complex $[(Ph_3P)_2PtF(CH(CF_3)_2)]$ [23] (Figure 1:20) then it can be seen that in both cases the Pt-P bond trans-to a fluoroalkyl group is long and that trans-to a halogen is short.

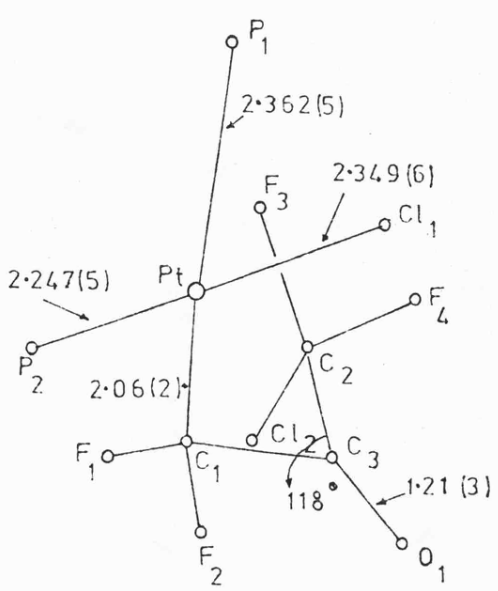


FIGURE 1:19

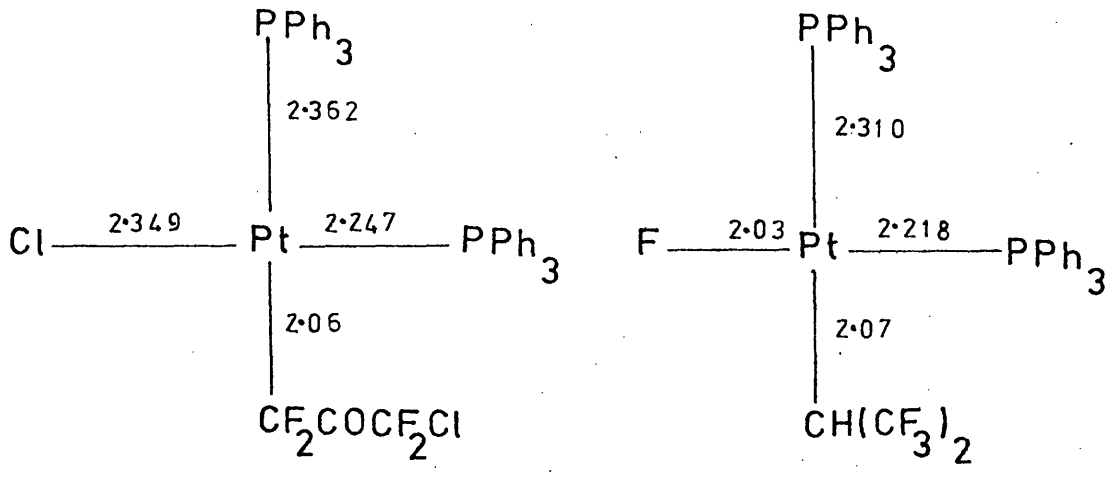


FIGURE 1:20

In complex 1:3 the Pt-P bond trans to the CF_2COCF_2Cl group is one of the longest reported.[24,25] The complex $[(Ph_3P)_2PtF(CH(CF_3)_2)]$ has the shortest known Pt-P bond trans-to fluorine and the Pt-P bond lengths in the two complexes are consistent with the increasing trans-influence of ligand (X) i.e. $F^- < Cl^- \leqslant$ Fluoroalkyl, which follows the increasing co-valent character of the trans-Pt-X bond; a correlation first suggested by Syrkin.[26] The CF_2COCF_2Cl group has a larger trans-influence than the $CH(CF_3)_2$ group.

Although the Pt-Cl bond is slightly shorter than that normally found when trans-to a phosphine ligand,[27] the Pt-P bond trans-to the Pt-Cl falls within the range of values normally found.[27]

It is possible to isolate the trans isomers of complexes 1:2 and 1:3. When the complexes cis - $[PtCl(CF_2COCF_3)(PPh_3)_2]$ and cis-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ are heated in benzene to 150°C in a sealed tube for 48 hours a pale yellow solution is produced. On evaporating this solution to small volume, off-white crystals of the trans-isomers complexes 1:7 and 1:8 are isolated. The cis complexes are less soluble in benzene compared with the trans, so any unisomerised cis-compound remains as a precipitate and can be filtered from the yellow solution before this is reduced in volume. This technique has been used previously to produce trans -$[PtCl(CCl{=}CCl_2)(PPh_3)_2]$ from its cis-isomer.[28] Attempts to isolate pure trans -$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$ using this process proved unsuccessful. When complex 1:4, a mixture of the cis- and trans- isomers, was treated in this manner the only isolable product was trans -$[PtCl_2(PPh_3)_2]$. Recently cis -$[PtCl_2(n\text{-}Bu_3P)_2]$[29] has been isomerised to the trans-adduct using CO in a cyclohexane solution, and this method might prove successful in isomerising cis -$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$ to trans -$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$

Infra-red Spectra.

The main features of the infra-red spectra of complexes 1:1 to 1:8 are given in Table 1:1. The most notable feature is the presence of a $\nu(C{=}O)$ absorption in complexes 1:2 to 1:4 and 1:7, 1:8 but the absence of them in the spectra of complexes 1:1, 1:5 and 1:6. A strong absorption band in the region of $550cm^{-1}$ in the infra-red spectra of complexes 1:1 to 1:6 strongly suggests a cis-configuration for these complexes.[30] The absence of this bond in complexes 1:7 and 1:8

has been used to lable them as the trans-isomer. The previously[28] reported correlation between the stereochemistry of the phosphines about the metal atoms and the relative intensities of two bonds observed at about 1586 and 1572cm^{-1} has proved to be rather uncertain in some of the complexes. In one or two of the cis complexes discussed above, the lower frequency bond has shown up as the stronger absorption, which contradicts the previous reports.

TABLE 1:1

Selected infra-red absorptions for the fluoropropan-2-one complexes 1:1 - 1:8.

COMPOUND	ν(C=O)	ν(C-F)	ν(Pt-Cl)
$[Pt(\eta-CF_3COCF_3)(PPh_3)_2]$		1190s,1175, 1135,1100,	
cis-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	1764	1233,1212, 1191,1167, 1155,1138, 1103,	320
cis-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	1759	1243,1191, 1171,1159, 1139,1103,	316
$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$(cis-& trans-)	1757	1229,1201, 1159,1131,	308
$[Pt(\eta-ClCF_2COCF_3)(PPh_3)_2]$		1343,1225, 1191,1171, 1159,1119,	
$[Pt(\eta-ClCF_2COCF_2Cl)(PPh_3)_2]$		1245,1236, 1191,1186, 1167,1160, 1147,1139, 1103,	
trans-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	1762	1215,1185 1162,1151, 1138,1110,	307
trans-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	1762	1219,1209, 1182,1167, 1156,1147, 1144,	311

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

Details of the ^{19}F n.m.r. spectra of complexes 1:1 - 1:4 and 1:7, 1:8 are given in Table 1:3. In the cis-complexes 1:2, 1:3 and 1:4 the fluorocarbon group bonded to the platinum appears to high field of the fluorocarbon group γ to the platinum. This is the reverse of most cases where a fluoroalkyl group is bonded to a transition metal[31]. (Table 1:2).

TABLE 1:2

COMPOUND TYPE	F.ATOM	p.p.m. (relative to benzotrifluoride)
CF_3CF_2M.	CF_2	-10→ +10
	CF_3	20→ 25
$CF_3CF_2CF_2M$	α-CF_2	-15→ +10
	β-CF_2	35→ 55
	CF_3	15→ 20

However, in the trans complexes 1:7 and 1:8 the $-CF_2$ group is now to low field of the γ-CF_3 or γ-CF_2 group, in agreement with previous reports. This downfield shift of the α-CF_2 group must be caused by the group trans to it i.e. the chloride ligand. H.C.Clark noticed the same effect in some trifluoromethyl complexes of platinum[32]. If the ligand trans to the perfluoroalkyl group is a weak σ-donor (Cl is a weaker σ-donor than PPh_3) then a; the electron density at the platinum will decrease, causing contraction of the d - orbitals resulting in an

upfield chemical shift; b; the electronegativity of the group bound to the fluoro group would increase, causing a downfield chemical shift; c; the chlorine ligand has a lower trans-influence than the phosphine, which tends to decrease the Pt-C bond length, increasing the orbital overlap and causing a downfield chemical shift and d; the ligand is probably low in the spectrochemical series so that the excitation energy at the platinum atom will be low and the fluorine resonance will shift downfield. Observations indicate that b, c and d outweigh a.

Complexes 1:2 and 1:3 appear to exist purely as the cis-isomer but the ^{19}F n.m.r. spectrum of complex 1:4 suggests that the compound is an equi-molar mixture of the cis- and trans- isomers. The low field signal consists of two sets of doublets, one centred at -3.86 p.p.m. and the other at -4.71 p.p.m. each with ^{195}Pt satellites. The high field signal appears as a triplet, each part of which is split into a multiplet, with ^{195}Pt satellites.

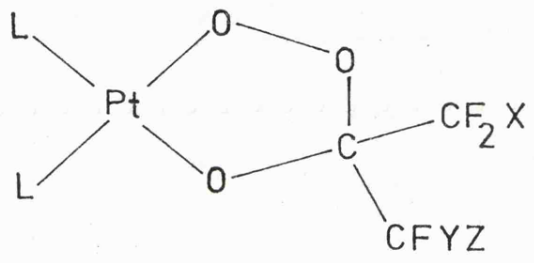
TABLE 1:3

Chemical shifts (p.p.m) and coupling constants (Hz) for the complexes 1:1 and 1:8

^{19}F n.m.r.	δCF	δCF_2	δCF_2	δCF_3	$J(P_{cis}-F)$	$J(P_{trans}-F)$	J(Pt-F)	J(F-F)
$[Pt(CF_3COCF_3)PPh_3)_2]$				3.71	0.97	11.85	75.44	
cis- $[PtCl(CF_2COCF_3)(PPh_3)_2]$		28.10m		11.73t	22.4	35.1	4.15	5.6
cis- $[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$		21.15m	-1.04t		26.65	37.30		7.8
trans- $[PtCl(CF_2COCF_3)(PPh_3)_2]$		-0.05m	8.94t					10.14
trans- $[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$		-2.20m	-1.17t				190.31	12.08
cis- $[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$	45.10m		-4.71d				10.94	6.03
trans- $[PtCl(CF_2ClCOCF_2Cl)(PPh_3)_2]$			-3.86d				17.72	12.82

B. Reaction of Peroxobis(triphenylphosphine)platinum(II) with fluoropropan-2-ones.

Peroxobis(triphenylphosphine)platinum(II) reacts with excess of the fluoropropan-2-ones, chloropentafluoropropan-2-one, 1,3-dichlorotetrafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one in diethyl ether to give the white crystalline complexes 1:10 - 1:12 respectively. (Figure 1:21).



($L=PPh_3$)

COMPLEX	X	Y	Z
1:10	Cl	F	F
1:11	Cl	Cl	F
1:12	Cl	Cl	Cl

FIGURE 1:21

No evidence of four or seven membered ring formation has been found in these reactions, and in this respect these chlorofluoropropan-2-ones resemble more closely trifluoropropan-2-one than hexafluoropropan-2-one.[9]

The complexes are assigned the structure shown in figure 1:21

on the basis of infra-red and ^{19}F n.m.r. spectra. The infra-red spectra of complexes 1:10 - 1:12 contain no absorptions attributable to $\nu(C=O)$ but do have a very weak band in the 780-810cm^{-1} region which can be assigned to an $\nu(O-O)$ absorption (Table 1:4). The fact that no $^{195}Pt-^{19}F$ or $^{31}P-^{19}F$ coupling are observable in the ^{19}F n.m.r. spectra of the complexes indicates that the $C(CF_2XCFYZ)$ group is not directly attached to the platinum (Table 1:4).

TABLE 1:4

COMPLEX	^{19}F n.m.r. spectrum[a] δCF	δCF_2	δCF_3	i.r. spectrum cm^{-1} $\nu(O-O)$	$\nu(C-F)$
$[Pt\overline{OOC(CF_2ClCF_3)O}(PPh_3)_2]$	J(F-F) = 11.1Hz	-2.92q	10.80t	784	1191,1175, 1159,1145, 1121,1107.
$[Pt\overline{OOC(CF_2Cl)_2O}(PPh_3)_2]$		-5.25s		803	1197,1187, 1163,1141, 1129,1105.
$[Pt\overline{OOC(CF_2ClCFCl)_2O}(PPh_3)]$	-3.25t J(F-F) = 13.95Hz	-7.07d		808	1192,1184, 1152,1128, 1120.

(a) - relative to external benzotrifluoride.

C. <u>The reaction of acetonedicarboxylic acid dimethyl ester with some complexes of platinum(0), platinum(II) and palladium(0).</u>

On stirring tetrakis(triphenylphosphine)platinum(0), <u>trans</u>-stilbenebis(triphenylphosphine)platinum(0), ethylenebis(triphenylphosphine) platinum(0) or peroxobis(triphenylphosphine)platinum(II) with acetonedicarboxylic acid dimethyl ester in diethyl ether in contact with the atmosphere, off-white microcrystals of complex 1:13 are produced.

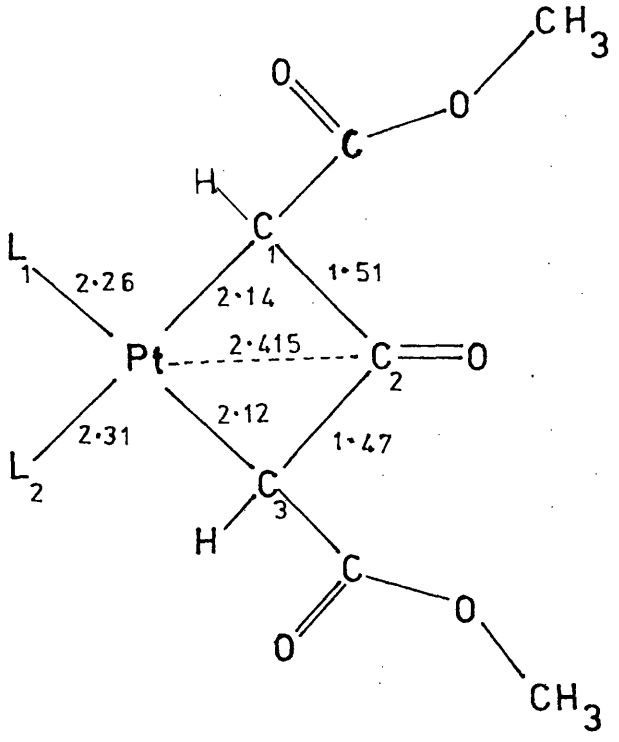
The i.r. spectrum of complex 1:13 contains two absorptions at 1725 and 1740cm^{-1} which can be assigned to carbonyl vibrations, and a strong bend at 557cm^{-1} is indicative of a <u>cis</u>-configuration for the triphenylphosphine ligands.

The ^{1}H n.m.r. spectrum consists of a singlet (6H) at 3.36 p.p.m due to the two methyl groups of the ester, and a quartet (2H) centred at 3.12 p.p.m.

In order to determine the structure of this compound a single crystal X-ray study was carried out. This has shown complex 1:13 to have the structure illustrated in figure 1:22

Crystals of the adduct $C_{43}H_{38}O_5P_2Pt$ (mol.wt.891.88) are triclinic, space group $\underline{P\bar{1}}$ with $\underline{a}$ = 17.5907, $\underline{b}$ = 12.7358, $\underline{c}$ = 10.2722Å, α = 118.19, β = 94.71° $\underline{U}$ = 1946.44Å^{3} and Z = 2

The crystallographic study clearly shows that complex 1:13 contains a four membered metallocyclobutane type ring, formed by two of the carbon atoms of the ADCADME ligand forming σ-bonds with the platinum. Two atoms of hydrogen have been lost in the reaction.



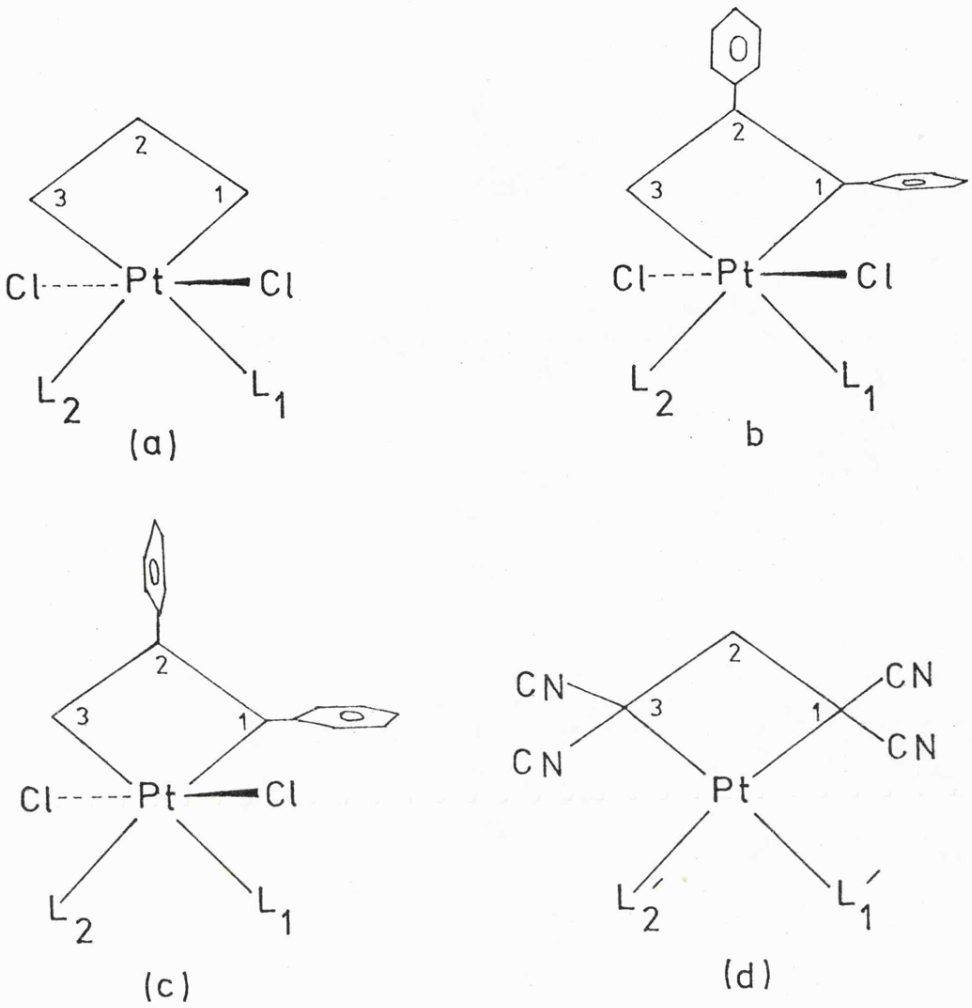
(L=PPh_3)

FIGURE 1:22

The structure of complex 1:13. Bond lengths in Å.

Comparisons can be made between the four co-ordinate complex 1:13 and other four co-ordinate platinum complexes containing a metallocyclobutane ring. If complex 1:13 is compared with the compound $[Pt(C_3H_2(CN)_4)(PPh_3)_2]$[33], $[PtCl_2(C_3H_6)(C_5H_5N)_2]$ and $[PtCl_2(C_3H_4)(C_6H_5)_2(C_5H_5N)_2]$ (two forms (b) and (c)) (Figure 1:23) some interesting points arise.

It should be remembered that the determinations on compounds (a),(b),and (c) are of limited accuracy because the crystals decomposed during data collection.



$(L_1'=L_2'=P(C_6H_5)_3;\quad L_1=L_2=C_5H_5N)$

FIGURE 1:23

The four complexes possess a puckered metallocyclobutane ring. Some noticeable differences can be seen when complex 1:13 is compared with the four previously known cyclobutane type compounds.

(1) The Pt-C_2 distance is much shorter (>0.2Å) for complex 1:13.

(2) The average value for the C_1-C_2, C_2-C_3 bond lengths at 1.49Å is also much shorter compared with the others.

These points might suggest that there is much more ring strain in complex 1:13 compared with the other complexes containing the cyclobutane type structured. Complex 1:13 also contains a much "flatter" cyclobutane

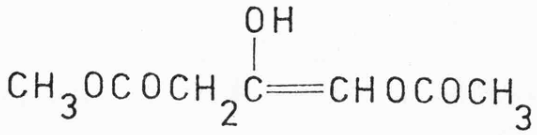
TABLE 1:5

Intramolecular distances Å	(a)	(b)	(c)	(d)	(e)
Pt - C_1	2.04(5)	2.06(3)	2.05(3)	2.137(6)	2.14
Pt - C_2	2.69(4)	2.60(4)	2.62(3)	2.712(6)	2.418
Pt - C_3	2.19(5)	2.11(5)	2.17(3)	2.139(6)	2.12
C_2 - C_3	1.82(9)	1.48(5)	1.71(4)	1.584(9)	1.47
C_2 - C_1	1.48(8)	1.59(7)	1.59(4)	1.545(9)	1.51
Bond angles (°)					
Pt - C_1 - C_2	99(4)	90(2)	91(2)	93.5(4)	80.8
Pt - C_3 - C_2	84(3)	91(3)	84(2)	92.3(4)	82.5
C_1 - C_2 - C_3	101(4)	102(3)	104(2)	100.4(5)	108.4
Dihedral angles					
C_3 - Pt - C_1 / C_1 - C_2 - C_3	12(5)	28(3)	22(2)	24.4(4)	50.13

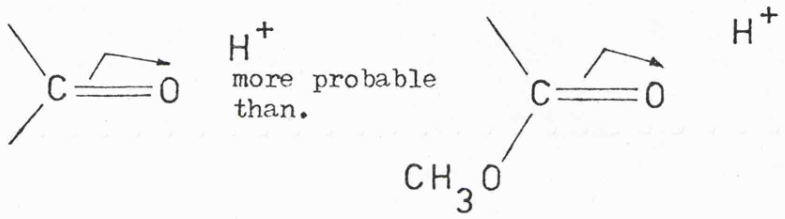
type ring as can be seen from the relatively low Pt-C_1-C_2 and Pt-C_3-C_2 angles and the high value of the C_1-C_2-C_3 angle.

The dihedral angle between the C_3-Pt-C_1 plane and the C_1-C_2-C_3 plane is also much greater in complex 1:13. This means that the metallocyclobutane type ring is more puckered compared with the other complexes, and explains why the Pt-C_2 distance is shorter in complex 1:13.

A suggested mechanism for the formation of complex 1:13 is shown in figure 1:24. It is suggested that the reaction goes via the enol form of the acetonedicarboxylic acid dimethyl ester -:

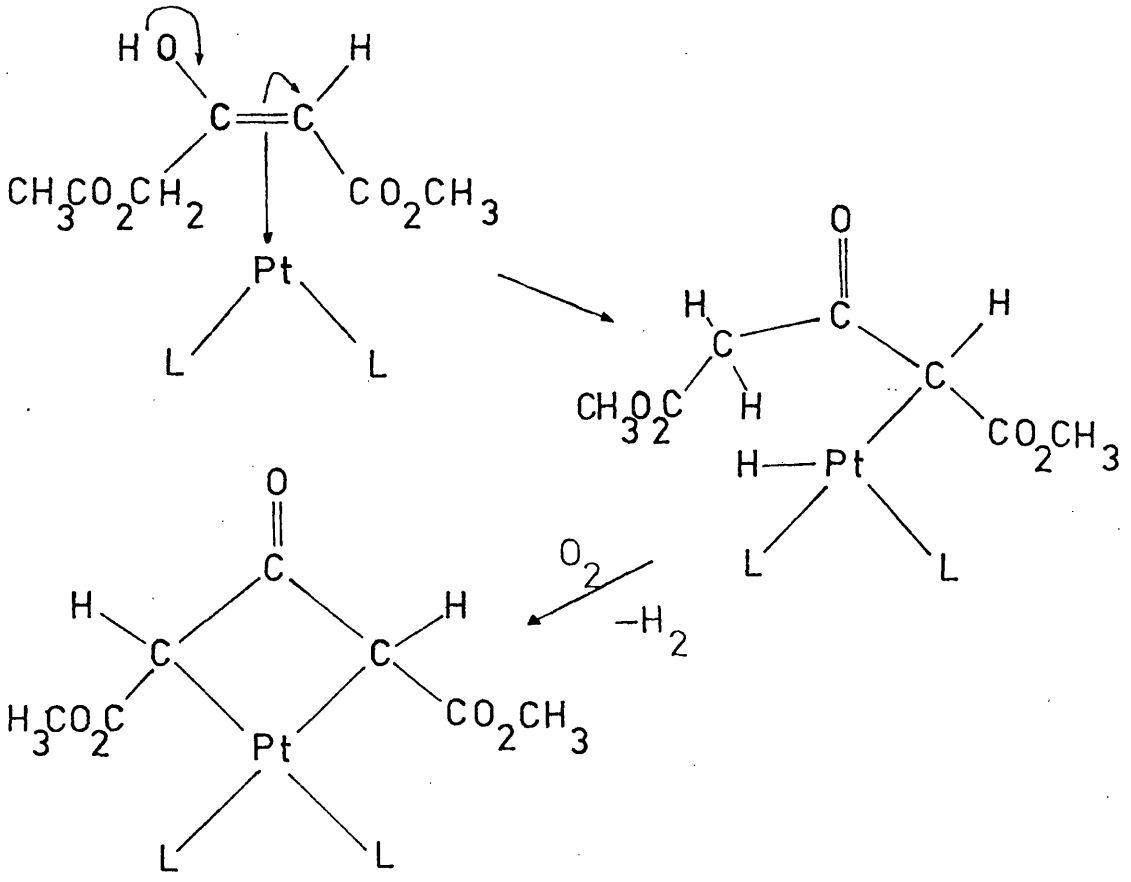


The enol form with the central carbonyl group protonated seems most likely because this carbonyl group is free of the electron withdrawing OCH_3 groups. These groups will inhibit the movement of electrons on to the oxygen atom of the ester groups i.e.



The first step in the mechanism could therefore be the formation of Pt-C and Pt-H σ bonds.

This type of mechanism has been previously postulated in the production of a β -oxoethyl complex from a π ethenol complex[34] (Figure 1:25).



(L=PPh_3)

FIGURE 1:24

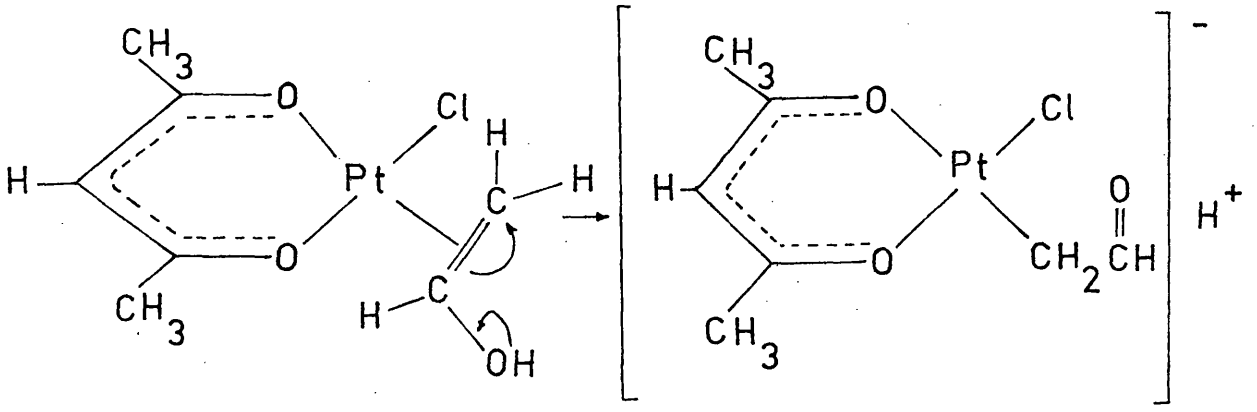
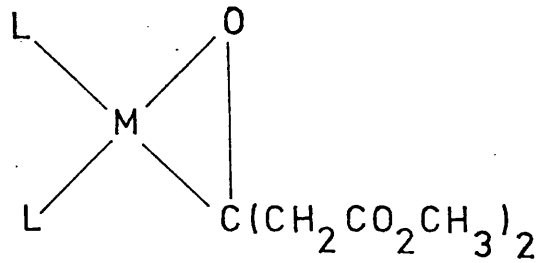


FIGURE 1:25

The metallocyclobutane system as found in complex 1:13 is only produced when ADCADME is treated with triphenylphosphine platinum complexes. The reactions of ADCADME with tetrakis(methyldiphenylphosphine)platinum(0), tetrakis(dimethylphenylphosphine)platinum(0) or tetrakis(triphenylphosphine) palladium(0) gives the complexes 1:14, 1:15, 1:17 respectively. These three complexes contain a three membered ring formed by the central carbonyl of the ADCADME ligand π-bonding to the metal (Figure 1:26).



(L=$MePh_2P$, Me_2PhP; M=Pt)

(L=Ph_3P; M=Pd)

FIGURE 1:26

Complexes 1:14, 1:15 and 1:17 are assigned the structure shown on the basis of micro-analytical, infra-red and ^1H n.m.r. data. The ^1H n.m.r. spectra of all three complexes are very similar (Table 1:6) Each has a singlet absorption around 3.00 p.p.m. due to equivalent methyl goups on the ADCADME ligand, plus a doublet absorption near 4.00 p.p.m. due to trans-phosphorous-hydrogen coupling on the equivalent

CH_2 groups on the ADCADME ligand. In the platinum complexes this doublet also has ^{195}Pt satellites.

TABLE 1:6

Selected ^1H n.m.r. absorptions for the complexes 1:14, 1:15 and 1:17

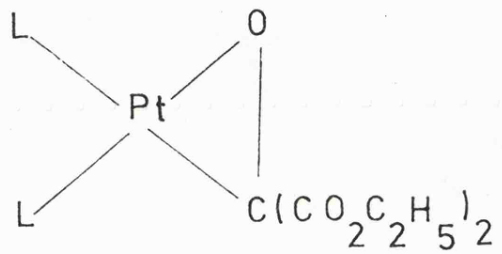
Compound	δCH_3	δCH_2	J trans P-H	J Pt-H
$[Pt(\eta\text{-}CO\{CH_2CO_2CH_3\}_2)(MePh_2P)_2]$	3.02s	4.00d	5.28	27.90
$[Pt(\eta\text{-}CO\{CH_2CO_2CH_3\}_2)(Me_2PhP)_2]$	3.50s	4.09d	5.73	28.66
$[Pd(\eta\text{-}CO\{CH_2CO_2CH_3\}_2)(Ph_3P)_2]$	2.97s	4.14d	3.30	

The infra-red spectra of complexes 1:14, 1:15 and 1:17 show three or four absorptions in the $\nu(C=O)$ stretching frequency region.

It is of interest to note that the reaction of ADCADME with tetrakis(methyldiphenylphosphine)platinum(0), tetrakis(dimethylphenylphosphine platinum(0), tetrakis(triphenylphosphine)platinum(0) or tetrakis (triphenylphosphine)palladium(0) only goes to completion in the presence of oxygen. One possible explanation is that in the absence of oxygen the phosphines displaced by the ADCADME are able to recombine in a reversible reaction. The presence of oxygen may cause the production of phosphine oxides which are less liable to co-ordinate to the metal. The reaction can therefore proceed to give either the cyclic complex 1:13, or the π-bonded ketone complexes 1:14, 1:15, 1:17 in high yield.

D. <u>The reaction of tetrakis(triphenylphosphine)platinum(0) with diethylketomalonate.</u>

The reaction between tetrakis(triphenylphosphine)platinum(0) and diethylketomalonate produces the white air stable complex 1:16 $[Pt\{\eta\text{-}CO(C_2H_5CO)_2\}(PPh_3)_2]$ in good yield. The complex is assigned the structure shown (Figure 1:27) on the basis of ^1H n.m.r. infra-red spectral and analytical data.



$(L=PPh_3)$

FIGURE 1:27

The ^1H n.m.r. spectrum contains a triplet at 1.04 p.p.m. and a multiplet at 3.94 p.p.m which arise from the ethyl groups. The multiplet at 3.94 does not appear as a quartet since there is probably a small Pt-H coupling on this signal which was not resolvable. Strong carbonyl absorptions are also visible in the infra-red spectrum.

The diethylketomalonate ligand is easily displaced from complex 1:16. The reaction between complex 1:16 and 1,3-dichlorotetrafluoropropan-2-one produces, after 24 hours, a good yield of complex 1:3 <u>cis-</u>

$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ in this respect the diethylketomalonate ligand is different from the π-bonded ADCADME ligand. The reactions of fluoropropanones with π-bonded carbonyl ADCADME complexes do not lead to displacement of the ADCADME ligand. Such an observation could indicate that the diethylketomalonate is less strongly bound to the metal, than is the ADCADME, when both are π-bonded through their central carbonyl group.

E. Reaction of 2-bis(triphenylphosphine)platinum-1,3-bis (methoxycarbonyl)but-3-one with fluoropropanones.

All the evidence obtained suggests that the fluoropropan-2-ones, hexafluoropropan-2-one, chloropentafluoropropan-2-one, 1,3-dichlorotetrafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one displace the 1,3-bis(methoxycarbonyl) but-3-one ligand from complex 1:13 to produce the five membered ring peroxy complexes 1:9, 1:10, 1:11 and 1:12 respectively. It is difficult to suggest a mechanism for such a reaction and further studies on these reactions are in progress.

F. <u>The reaction of 2-bis(methyldiphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan and 2-bis(triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium with fluoropropanones.</u>

2-bis(methyldiphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan reacts after 72 hours with hexafluoropropan-2-one in diethyl ether at room temperature to produce two compounds. The first complex is obtained as a white precipitate in the bottom of the Carius tube, and will be discussed later in context with the compound obtained from 2-bis(methyldiphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan and chloropentafluoropropan-2-one.

The second product is obtained when the solution from the reaction is evaporated to small volume and crystals of complex 1:19 allowed to crystallise. The white crystals obtained were shown to contain two molecules of hexafluoropropan-2-one per platinum atom.

The ^{19}F n.m.r. spectrum of complex 1:19 revealed little information that could be used to assign a structure to the compound. At room temperature in $CDCl_3$ solution the ^{1}H n.m.r. spectrum of the adduct contains a pair of overlapping doublets (3H) one centred at 1.64 p.p.m J(P-H)=5.20 Hz, J(P-H)=17.24Hz, J(Pt-H)=14.99Hz. These signals arise from the inequivalent methyl group on the phosphine ligands , the fact that they appear as doublets indicates a <u>cis</u>-configuration for these phosphine ligands. There are also two singlets at 3.60(3H) and 3.80 (3H) p.p.m which can be assigned to the two methyl groups on the co-ordinated bis(methoxycarbonylmethylene)groups. These also appear to be inequivalent. The remaining signals appear as a singlet (1H) at 4.50

p.p.m, a multiplet (20H) at 7.40 p.p.m, assignable to the phenyl groups on the phosphine ligands, and a singlet (1H) at 8.73 p.p.m.

It is not easy to assign the two singlets at 4.50 and 8.73 p.p.m The i.r. spectrum shows, in addition to strong C-F absorptions in the 1100-1399cm^{-1} region, many bands in the region 1669-1740cm^{-1} attributable to ν(C=O) vibrations.

The information obtained from these spectra did not enable us to assign a satisfactory structure to complex 1:19. A single crystal X-ray study was therefore undertaken and reveals that complex 1:19 has the structure illustrated in figure 1:28 Crystals of this complex, $C_{39}H_{34}F_{12}O_7P_2Pt$(mol.wt.1099.9) are triclinic, space group $\underline{P\bar{1}}$. with $\underline{a}$ = 16.437, $\underline{b}$=12.079, $\underline{c}$=13.944Å, α =116.66, β =121.17 and γ =84.94°, $\underline{U}$ = 2064.3Å^3 and Z = 2.

The crystallographic study clearly shows that complex 1:19 contains a six-membered ring and a possible reaction mechanism is shown in scheme 1:1. Two hydrogen atoms have again been lost in the reaction. The platinum atom is essentially four co-ordinate with two Pt-O bonds averaging 2.05 Å and two Pt-P bonds averaging 2.22Å in a <u>cis</u>-square-planar arrangement. The carbonyl of one of the ester groups is bent back towards the platinum, an affect that has been observed previously in the palladium compound $[Pd(acac)_2(C_4F_6)_2]$[35] where the Pd-O distances were shown to be 3.23 and 3.43Å . In complex 1:19 the Pt-O_3 distance of 2.95Å is much smaller than the corresponding distances in the palladium complex. This shorter distance may indicate some bonding between this carbonyl group and the metal, either in the form of π-bonding by the carbonyl, or from a lone pair on the oxygen atom.

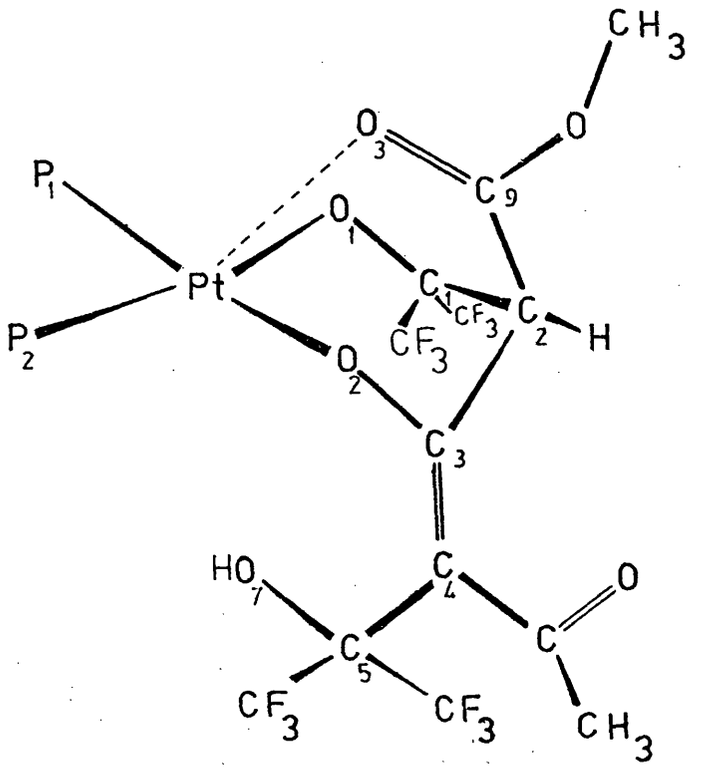


FIGURE 1:28

The fact that C_3 and C_4 lie in the same plane, and the distance of 1.33Å between them, confirms the presence of a double bond between these two carbon atoms. It also appears that O_7 is an hydroxyl group and there are indications that hydrogen bonding exists between the hydrogen on this oxygen and the atom O_2. If this were the case then there would be a six membered ring made up of the atoms O_2, C_3, C_4, C_5, O_7, and the hydrogen on O_7. An O_2-O_7 distance of 2.48Å supports this notion.

Using the information obtained from the crystal structure it is now possible to assign the remaining bands in the ^1H n.m.r. spectrum. The singlet (1H) at 4.50 p.p.m must arise from the hydrogen bonded to C_2 and the singlet (1H) at 8.73 p.p.m is due to the proton of the hydroxyl group on C_5.

Mechanism of Formation

A suggested mechanistic route for the formation of complex 1:19 is shown in Scheme 1:1. The first step probably involves an Aldol/Claisen condensation type reaction between one molecule of hexafluoropropan-one and complex 1:14 to produce an intermediate of the type shown, (b). This reaction is then repeated on the other methylenedicarboxylate group to produce a complex of the type shown in (C). This then rearranges as (d) indicates, losing one molecule of hydrogen to produce the final product, (e).

A similar type of reaction also seems to occur when 2-bis(triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium (complex 1:17) reacts with hexafluoropropan-2-one and chloropenta-fluoropropan-2-one to produce complexes 1:23 and 1:24 respectively. The ^{1}H n.m.r. spectra of both complexes are very similar to that of the crystal structure complex, 1:19 (Table 1:7). Each has a characteristic hydroxyl proton absorption above 8.00 p.p.m and a single proton absorption around 5.00 p.p.m.

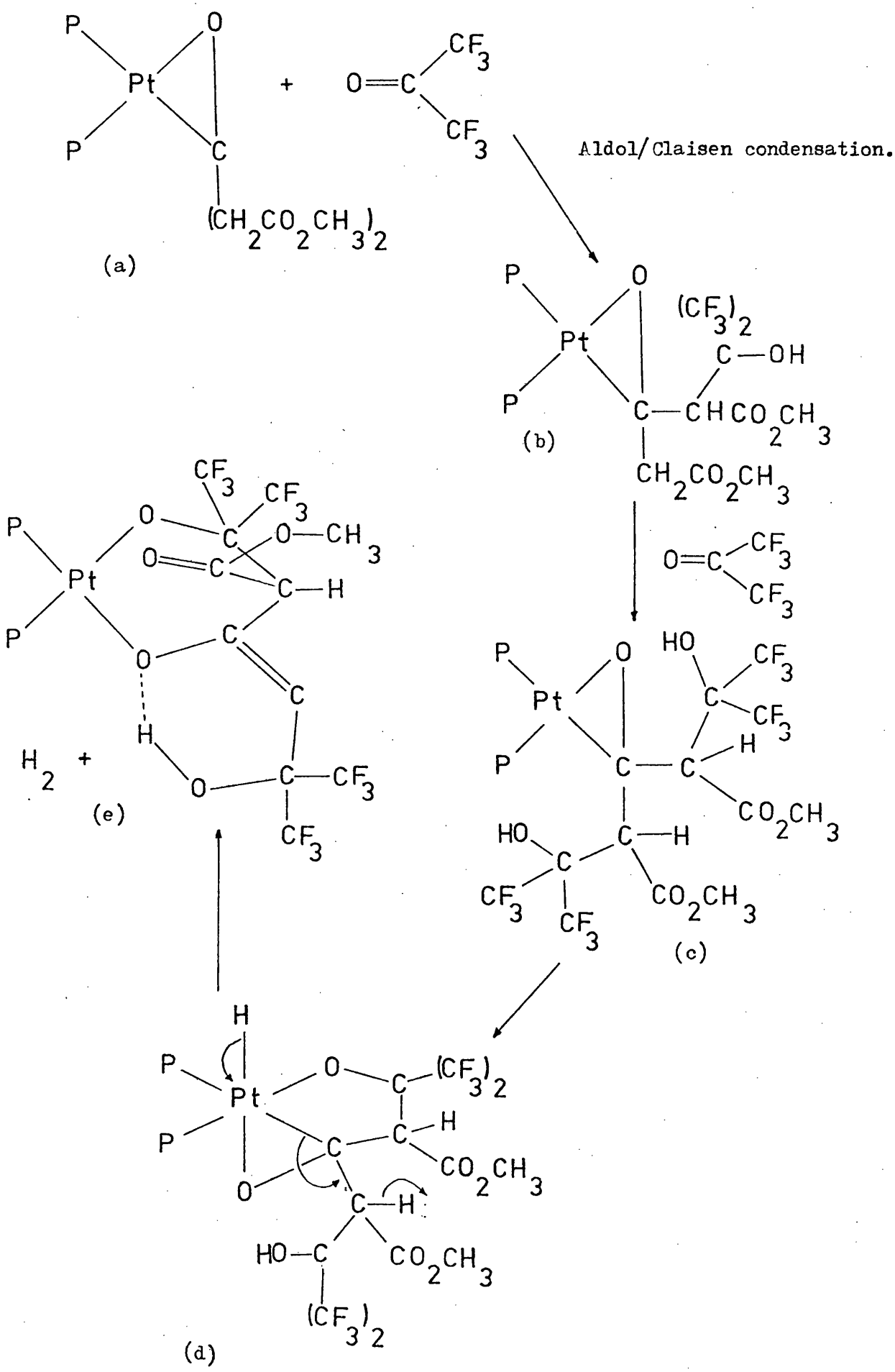
TABLE 1:7

^{1}H n.m.r. spectra of complexes 1:19, 1:23 and 1:24.

COMPLEX	δCH_3-	δCH_3-	δCH	δOH
1:19	3.60s	3.80s	4.50s	8.73s
1:23	3.59s	3.88s	4.70s	8.48s
1:24	3.54q	3.82d	4.72d	8.80s

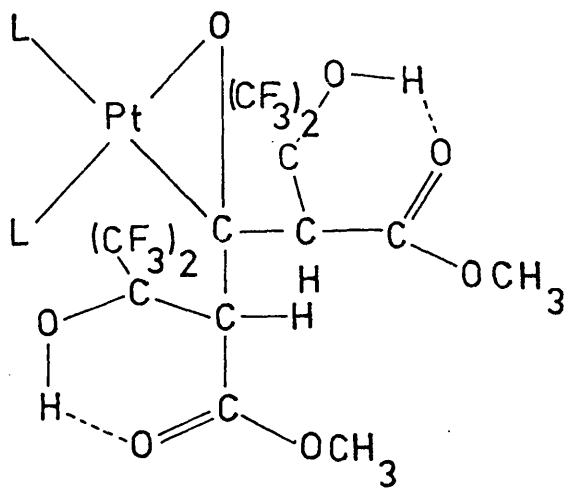
On the basis of this data complexes 1:23 and 1:24 are assigned structures analogous to that of complex 1:19.

SCHEME 1:1.



On reacting 2-bis(methyldiphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan (complex 1:14) with chloropentafluoropropan-2-one white microcrystals of complex 1:20 are obtained. The ^{1}H n.m.r. spectrum of this compound shows it to be similar to complex 1:18, obtained in the reaction of hexafluoropropanone with 2-bis(methyldiphenyl phosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan. Microanalytical data shows that both compounds contain two molecules of fluoropropan-2-one per platinum atom.

The ^{19}F n.m.r. spectrum of complex 1:18 contains only a singlet absorption at 18.31 p.p.m. which suggests that the four CF_3 groups are equivalent. The ^{1}H n.m.r. spectrum confirms a <u>cis</u> - configuration for this complex. The methyl groups of the ADCADME ligand appear as two singlets which show them to be inequivalent. A possible structure is shown in figure 1:29.



(L=$MePh_2P$)

FIGURE 1:29.

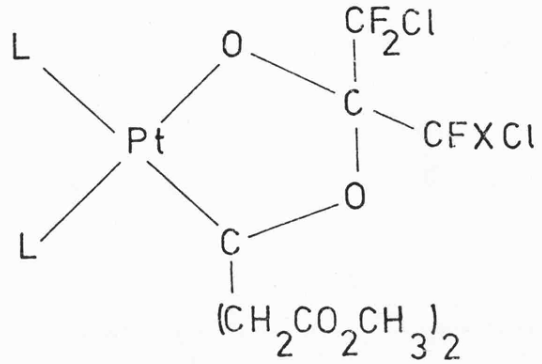
However no evidence for the presence of hydroxyl groups could be obtained from i.r. or ^{1}H n.m.r. studies, and confirmation of the structure must await a single crystal X-ray structure determination.

Complex 1:20 similarly shows no evidence of hydroxyl protons in its i.r. or ^{1}H n.m.r. spectra. The ^{19}F n.m.r. spectrum obtained for complex 1:20 consists of a quartet (4F) centred at 3.22 p.p.m. and a triplet (6F) centred at 16.33 p.p.m. This again seems to indicate two equivalent CF_2Cl groups and two equivalent CF_3 groups.

The proposed structures for complex 1:18 and 1:20 would result from an Aldol/Claisen condensation of the fluoroketone upon the co-ordinated ADCMDME ligand. Complex 1:18 could be an intermediate in the formation of the six membered metallocyclic complex 1:19.

The reaction between 2-bis(methyldiphenylphosphine)-3,3-bis-(methoxycarbonylmethylene)-1,2-oxaplatinan and 1,3-dichlorotetra-fluoropropan-2-one or 1,1,3-trichlorotrifluoropropan-2-one in diethyl ether over 72 hours produces good yields of the white microcrystalline adducts 1:21 and 1:22 respectively (Figure 1:30). Both compounds are air stable and can easily be recrystallised from dichloromethane/diethyl ether mixtures. The formulation of these as the illustrated adducts in which the fluoropropan-2-ones have inserted into the platinum-oxygen bond of the starting material, is substantiated by analytical, infra-red and n.m.r. spectroscopic data.

The i.r. spectra of both compounds contain a large number of intense bands in the 1100-1300cm^{-1} region which are due to either C-F or ester vibrations. In addition there are strong absorptions in the 1570 and 1590cm^{-1} region assignable to ν(C=O) stretching modes.



(L=$MePh_2P$)

Complex 1:21 X=F

Complex 1:22 X=Cl

FIGURE 1:30

Selected n.m.r. data for complexes 1:21 and 1:22 are shown in table 1:8. Complex 1:21 shows only one singlet resonance in its ^{19}F n.m.r. spectrum confirming the equivalence of the CF_2Cl groups. Complex 1:22 produces two ^{19}F n.m.r. absorptions; a triplet (1F) at 8.10 p.p.m. and a broad signal (2F) at 4.95 p.p.m. No ^{195}Pt satellites or evidence of phosphorous-flourine coupling is visible in either spectra. This suggests that the fluoropropan-2-one groups are bonded to platinum via the oxygen, and not via the carbon containing the fluoroalkyl groups.

The ^{1}H n.m.r. spectra of complexes 1:21 and 1:22 (Table 1:8) are very similar to the spectrum obtained from the complex 1:14, $[Pt\{\eta\text{-}CO(CH_2CO_2CH_3)_2\}(PMePh_2)_2]$. In all three spectra the CH_2 groups of the ADCADME ligand appear as doublets due to trans-phosphorous-fluorine coupling with additional ^{195}Pt satellites. The presence of these satellites indicates that the ADCADME ligand is bonded to the platinum

via the carbon atom of its central carbonyl group.

TABLE 1:8

n.m.r. spectra of Complexes 1:14, 1:21 and 1:22

COMPLEX	δCH_2	δCH_3	δCF	δCF_2
1:14	4.00d $J(P_{trans}-H)=5.28Hz$	3.02s		
1:21	3.96d $J(P_{trans}-H)=4.80Hz$	2.96s		0.82s
1:22	4.05d $J(P_{trans}-H)=5.25Hz$	3.04s	8.10t $J(F-F)=14.46Hz$	4.95m

The doublet arising from the methyl group on the phosphine ligand confirms the cis arrangement of the complexes.

All the available evidence suggests that similar reactions are occurring when 2-bis(triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium, complex 1:17, reacts with 1,3-dichlorotetrafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one. The pale yellow microcrystalline complexes 1:25 and 1:26 respectively are produced in reasonable yields.

On the evidence of microanalytical, infra-red and n.m.r. data the complexes are assigned structures analogous to those of the platinum complexes 1:21 and 1:22 (Figure 1:30).

As the number of the bulkier chlorine atoms is increased on the fluoropropan-2-ones the more difficult it becomes to arrange two of

these chloro substituted fluoropropan-2-ones about the platinum or palladium centres. This steric effect could be the reason why two molecules of hexafluoropropan-2-one and chloropentafluoropropan-2-one, but only one molecule of 1,3-dichlorotetrafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one react with the platinum and palladium complexes 1:14 and 1:17.

1:3 EXPERIMENTAL.

Analytical, melting point and spectroscopic data are shown in this section. Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd, 41, High Street, Teddington, Middlesex or by C.H.N. Analysis Ltd, Alpha House, South Wigston, Leicester. Melting points were recorded on a Reichart hot-stage apparatus and are uncorrected. Infra-red spectra were recorded as nujol or hexachlorobutadiene mulls on a Perkin-Elmer 225 spectrophotometer using CsI plates and were calibrated using a polystyrene film. ^{1}H n.m.r. spectra were recorded in $CDCl_3$ solution on a Jeol JNM-PS-100 spectrometer operating at 100 M.Hz, chemical shifts (p.p.m) being reported relative to internal T.M.S. ^{19}F n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer operating at 94.1 M.Hz chemical shifts (p.p.m) being reported relative to benzotrifluoride.

All reactions carried out in a Carius tube were done in 15mls of the appropriate solvent. All other reactions were performed under an atmosphere of dry nitrogen using previously dried and degassed solvents.

Ligands and reagents.

Hexafluoropropan-2-one, chloropentafluoropropan-2-one, 1,3-dichlorotetrafluoropropan-2-one and 1,1,3-trichlorotrifluoropropan-2-one were obtained from P.C.R. Inc. Acetonedicarboxylic acid dimethyl ester and diethylketomalonate were obtained from Koch-Light Laboratories Ltd.

Palladium dichloride and potassium tetrachloroplatinite were obtained on loan from Johnson Matthey Ltd.

Complexes:

$[Pt(PPh_3)_4]$,[36] $[Pt(MePh_2P)_4]$,[1] $[Pt(Me_2PhP)_4]$,[1] $[Pt(\underline{trans}\text{-stilbene})(PPh_3)_2]$,[37] $[Pt(tolan)(PPh_3)_2]$,[38] $[Pt(phenylacetylene)(PPh_3)_2]$,[38] $[Pt(O_2)(PPh_3)_2]$,[39] $[Pt(C_2H_4)(PPh_3)_2]$,[40] $[Pd(PPh_3)_4]$,[41] are prepared as described in the literature.

A. The reaction of fluoropropan-2-ones with tetrakis(triphenylphosphine) platinum(0)

1. With hexafluoropropan-2-one

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of tetrakis(triphenylphosphine)platinum(0) (0.7g 0.49m.mol) in diethyl ether contained in a Carius tube (150ml) After shaking for 24 hours the tube was opened and volatile material removed. The white suspension was filtered off and washed with diethyl ether to yield microcrystals of the previously prepared complex 1:1$[Pt(\eta\text{-}CF_3COCF_3)(PPh_3)_2]$(0·41g, 78%) identified by its melting point ^{19}F n.m.r. and infra-red spectra.

2. With chloropentafluoropropan-2-one

An excess of chloropentafluoropropan-2-one (1·0ml) was condensed (-196°) on to a suspension of tetrakis(triphenylphosphine)platinum(0) (1·0g, 0.60m.mol) in diethyl ether contained on a Carius tube (150ml) After shaking for 24 hours the tube was opened and volatile material removed. The white suspension was filtered off and washed with diethyl ether to yield crystals of the complex cis-dichlorobis(triphenylphosphine) platinum(II)(0.48g, 75%) identified by its melting point and infra-red spectrum.[20]

3. With 1,3-dichlorotetrafluoropropan-2-one

An excess of 1,3-dichlorotetrafluoropropan-2-one(1·0 ml) was added with stirring to a suspension of tetrakis(triphenylphosphine)

platinum(0) in diethyl ether contained in a round bottomed flask (100ml). After stirring for 24 hours the white suspension was filtered off and washed with diethyl ether to yield microcrystals of the complex cis-dichlorobis(triphenylphosphine)platinum(II) (0.50g, 78%) identified by its melting point and infra-red spectrum.[20]

4. With 1,1,3-trichlorotrifluoropropan-2-one

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1·0ml) was added with stirring to a suspension of tetrakis(triphenylphosphine) platinum(0)(1·0g, 0·69m.mol) in diethyl ether contained in a round-bottomed flask (100ml). After stirring for 24 hours the white suspension was filtered off and washed with diethyl ether to yield microcrystals of the complex cis-dichlorobis(triphenylphosphine) platinum(II) (0·51g, 80%) identified by its melting point and infra-red spectrum.

Similar results were obtained when using tetrakis(triphenylphosphine) palladium(0). On reacting tetrakis(triphenylphosphine)palladium(0) (0.5g, 0.43m.mol) with excess of any of the chloro-substituted fluoropropanones trans-dichlorobis(triphenylphosphine)palladium(II) was produced in almost quantitative yields.

On using different solvents the same results were obtained. Solvents used included light petroleum (40-60°), diethyl ether, benzene and propanone. In each case the only isolable products were cis-dichlorobis(triphenylphosphine)platinum(II) or trans-dichlorobis(triphenylphosphine)palladium(II).

B. The reaction of fluoropropan-2-one with trans-stilbenebis-(triphenylphosphine)platinum(0).

1. With hexafluoropropan-2-one

An excess of hexafluoropropan-2-one (1·0ml) was condensed (-196°) on to a suspension of trans-stilbenebis(triphenylphosphine) platinum(0) (0·58g, 0·64m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking for 24 hours at room temperature the tube was opened and volatile material removed. The white precipitate was filtered off and washed with diethyl ether to yield crystals of the previously prepared complex 1:1 $[Pt(\eta\text{-}CF_3COCF_3)(PPh_3)_2]$ (0.52g, 91%) identified by its melting point and infra-red spectrum.

2. With chloropentafluoropropan-2-one in diethyl ether

An excess of chloropentafluoropropan-2-one (1·0ml) was condensed (-196°) on to a suspension of trans-stilbenebis(triphenylphosphine)platinum(0) (0·50g. 0·56m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking for three hours at room temperature the tube was opened and volatile material removed. The white precipitate was filtered off and washed with diethyl ether to yield crystals of the complex 1:2 cis -$[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0·50g,99%)m.p. 222-224°C.

$C_{39}H_{30}ClF_5OP_2Pt$	requires	C, 51·92;	H, 3·35;	Cl, 3·90;	F,10·50%
	found	C, 50·59;	H, 3·12;	Cl, 3·83;	F, 9·64%

Infra-red; 1764 s, 1486 s, 1315 w, 1304 m, 1272 w, 1223 s, 1212 s, 1191 m, 1167 m, 1155 m, 1138 s, 1117 sh, 1103 s, 1098 s, 1031 w, 1003 s, 983 m, 871 m, 855 m, 757 s, 750 s, 743 s, 707 s, 707 sh, 698 s, 549 s, 527 s, 521 s, 505 m, 499 m, 320 m, 268 m.

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

Observed in dichloromethane solution: a triplet (3F) centred at 11·73p.p.m with ^{195}Pt satellites J(Pt-F)= 4·15Hz, J(F-F)=5·9Hz. Also four quartets with the centre two overlapping (2F) centred at 28·50 p.p.m. with ^{195}Pt satellites J(Pt-F)= 187.41 Hz; J(P-F) = 22·4Hz (cis-P); J(P-F) = 35.1 Hz (trans-P); J(F-F) = 5·6Hz (relative to internal benzotrifluoride)

3. With chloropentafluoropropan-2-one in benzene

An excess of chloropentafluoropropan-2-one (1·01ml) was condensed (-196°) on to a solution of trans-stilbenebis(triphenylphosphine) platinum(0)(0.50g, 0.56m.mol) in benzene contained in a Carius tube (150ml) After shaking at room temperature for three hours the tube was opened and volatile material removed. The benzene solution was slowly evaporated to small volume and the white crystalline precipitate, so obtained, was filtered, washed with diethyl ether and identified as complex 1:2 cis-$[PtCl(CF_2COCF_3)(PPh_3)_2]$(0.34g, 68%) m.p. 230-234°C.

$C_{39}H_{30}ClF_5OP_2Pt$	requires	C, 51·92;	H, 3·35;	Cl, 3·90;	F, 10·50%
	found	C, 51·70;	H, 3·36;	Cl, 4·03;	F, 9·93%

4. <u>With chloropentafluoropropan-2-one in propanone.</u>

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of <u>trans</u>-stilbenebis(triphenyl phosphine)platinum(0), (0.30g, 0.33m.mol) in propanone contained in a Carius tube (150ml). After standing overnight at room temperature the tube was opened and volatile material removed. The white precipitate was filtered off, washed with diethyl ether and identified as complex 1:5 $[Pt(\eta\text{-}ClCF_2COCF_3)(PPh_3)_2]$(0.07g, 23.3%)m.p. 178-180°C.

$C_{39}H_{30}ClF_5OP_2Pt$	required	C, 51.92;	H, 3.35%
	found	C, 51.78;	H, 3.36%

Infra-red; 1587 w, 1575 v.w, 1295 sh, 1279 s, 1243 s, 1225 m, 1191 sh, 1171 s, 1159 sh, 1119 s, 1095 s, 1031 w, 1003 m, 983 s, 939 w, 891 m, 855 m, 832 sh, 825 m, 751 s, 731 m, 717 sh, 701 s, 647 w, 555 s, 531 s, 523 s, 507 s, 499 s, 459 m, 427 m.

No ^{19}F n.m.r. obtainable for this compound.

The filtrate was slowly evaporated and diethyl ether added to give white crystals of a mixture of the oxidative addition complexes 1:2 and 1:7 <u>cis</u> and <u>trans</u>-$[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.20g, 66.5%) identified by the ^{19}F n.m.r. spectra.

^{19}F n.m.r. spectrum;

Observed in dichloromethane solution; two triplets one at 11.01 p.p.m. J (F-F)=9.83Hz, due to the CF_3 of the <u>trans</u> complex and one at 11.73 p.p.m. J(F-F) = 5.90Hz. J(Pt-F) = 4.15Hz due to the CF_3

of the cis complex. There is also the signal at 28.50 p.p.m. associated with the CF_2 group of the cis complex, and a small signal centred at 26.85 p.p.m. associated with the CF_2 group of the trans complex.

5. With chloropentafluoropropan-2-one in light petroleum (40-60°)

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of trans - stilbenebis(triphenylphosphine)platinum(0) (0.50g, 0.56m mol) in light petroleum (40-60°) contained in a Carius tube (150ml). After shaking at room temperature for three days the tube was opened and volatile material removed. The white product was filtered off and washed with diethyl ether to yield crystals of complex 1:2 cis -$[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.17g, 31%) identified by its melting point and ^{19}F n.m.r. and infra-red spectrum. From the filtrate crystals of cis -$[PtCl_2(PPh_3)_2]$ were isolated (0.15g, 32%)[20]

6. With 1,3-dichlorotetrafluoropropan-2-one in diethyl ether

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a suspension of trans - stilbenebis(triphenylphosphine)platinum(0) (0.50g, 0.56m.mol) in diethyl ether contained in a round bottomed flask (150ml). After stirring for two hours the white suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:3 cis -$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.40g, 80%) m.p. 230-234°C.

$C_{39}H_{30}Cl_2F_4OP_2Pt$ requires C, 50.99; H, 3.29; Cl, 7.72; F, 8.27%

found C, 50.91; H, 3.40; Cl, 7.81; F, 8.31%

Infra-red: 1759 s, 1590 w, 1571 w, 1483 s, 1438 s, 1335 w, 1317 m, 1243 s, 1215 w, 1191 m, 1171 m, 1159 m, 1139 m, 1103 s, 1096 s, 1039 sh, 1025 s, 989 m, 977 m, 947 w, 880 w, 863 m, 849 m, 784 m, 76o s, 751 s, 747 s, 723 w, 711 s, 695 s, 664 m, 647 w, 642 w, 554 s, 531 s, 515 s, 503 s, 477 w, 457 w, 443 w, 427 w, 316 m.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a triplet(2F) centred at -1.04p.p.m. with ^{195}Pt satellites, J(Pt-F)=8.99Hz, J(F-F) = 7.8Hz. Also four triplets (2F) with the centre two overlapping, centred at 21.15 p.p.m. with ^{195}Pt satellites, J(Pt-F)= 181.2Hz, J(P-F)=26.65Hz (cis-P), J(P-F) = 37.30Hz (trans-P), J(F-F)=7.8Hz (relative to internal benzotrifluoride.)

7. With 1,3-dichlorotetrafluoropropan-2-one in benzene

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.Cml) was added with stirring to a solution of trans - stilbenebis(triphenylphosphine)platinum(0) (0.50g, 0.56m.mol) in benzene. After stirring at room temperature for two hours the solution was evaporated to small volume and white crystals precipitated. The precipitate was filtered off, washed with diethyl ether and identified as complex 1:3 cis-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.33g, 68%) from its ^{19}F n.m.r. and infra-red spectra.

8. <u>With 1,3-dichlorotetrafluoropropan-2-one in light petroleum (40-60°)</u> .

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a suspension of <u>trans</u>-stilbenebis (triphenylphosphine)platinum(0) (0.50g, 0.56m.mol) in light petroleum (40-60°). After stirring for two hours at room temperature the suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:6 $[Pt(\eta\text{-}ClCF_2COCF_2Cl)(PPh_3)_2]$ (0.40g, 80%) m.p. 233-235°C.

$C_{39}H_{30}Cl_2F_4OP_2Pt$	requires	C, 50.99;	H, 3.29%
	found	C, 50.01;	H, 3.58%

Infra-red: 1590 w, 1573 w, 1485 s, 1442 s, 1319 m, 1245 s, 1236 s, 1191 m, 1186 m, 1167 w, 1160 s, 1147 s, 1139 s, 1103 s, 1093 s, 1075 w, 1028 m, 1003 m, 997 m, 944 s, 783 s, 755 s, 749 s, 733 s, 711 s, 695 s, 675 m, 621 m, 555 s, 527 s, 508 s, 491 m, 465 w, 455 w, 441 w, 430 m.

No ^{19}F n.m.r. spectrum obtainable.

9. <u>With 1,1,3-trichlorotrifluoropropan-2-one in diethyl ether</u>

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of <u>trans</u>-stilbenebis (triphenylphosphine)platinum(0) (0.50g, 0.56m.mol) in diethyl ether. After stirring for two hours at room temperature the suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:4 <u>cis</u> and <u>trans</u> -$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$ (0.30g, 61%) m.p. 269-271°dec.

$C_{39}H_{30}Cl_3F_3OP_2Pt$	requires	C,50.10;	H, 3.23;	Cl, 11.37;	F, 6.10%
	found	C,50.30;	H, 3.38;	Cl, 11.19;	F, 5.82%

Infra-red: 1753 s, 1740 m, 1483 s, 1437 s, 1336 w, 1315 m, 1229 s, 1201 m, 1159 s, 1131 m, 1095 s, 1075 m, 1031 m, 991 s, 903 s, 842 w, 830 w, 759 s, 749 s, 707 s, 697 s, 665 s, 639 m, 625 w, 551 s, 531 s, 519 s, 507 s, 503 sh, 471 m, 455 m, 423 m, 308 m.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution a doublet with ^{195}Pt satellites (2F) at - 3.86p.p.m J(F-F)=12.82Hz, J(Pt-F)=17.72Hz (trans-complex). A doublet at - 4.71 p.p.m (2F) with ^{195}Pt satellites J(F-F) = 6.03Hz, J(Pt-F)= 10.94Hz (cis-complex). Also four multiplets with the centre two overlapping centred at 45.00 p.p.m. again with ^{195}Pt satellites J(Pt-F) = 164.9Hz (relative to internal benzotrifluoride).

10. With 1,1,3-trichlorotrifluoropropan-2-one in benzene.

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring, to a solution of trans-stilbenebis(triphenyl phosphine)platinum(0) (0.50g, 0.56m.mol) in benzene. After stirring at room temperature for two hours the solution was evaporated to small volume and the white precipitate filtered and washed with diethyl ether to yield crystals of cis -$[PtCl_2(PPh_3)_2]$ identified by its melting point and infra-red spectrum.[20]

$C_{36}H_{30}Cl_2Pt$	requires	C,54.69;	H, 3.82;	Cl, 8.97%
	found	C,54.58;	H, 3.65;	Cl, 9.08%

11. With 1,1,3-trichlorotrifluoropropan-2-one in light petroleum (40-60°)

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of trans-stilbenebis (triphenylphosphine)platinum(0) (0.50g, 0.56m.mol) in light petroleum (40-60°). After stirring at room temperature for two hours the suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:4 cis-and trans -$[PtCl(CFCl_2COCFCl_2)(PPh_3)_2]$ (0.43g, 83%) identified from its melting point, infra-red and ^{19}F n.m.r. spectra.

C. The reaction of fluoropropan-2-ones with diphenylacetylenebis-(triphenylphosphine)platinum(0)

1. With hexafluoropropan-2-one in diethyl ether

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of diphenylacetylenebis(triphenylphosphine) platinum(0) (0.50g, 0.57m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The white crystalline material was filtered off and washed with diethyl ether to yield crystals of complex 1:1 $[Pt(\eta\text{-}CF_3COCF_3)(PPh_3)_2]$ (0.47g, 74%) identified by its melting point, infra-red and ^{19}F n.m.r. spectra.

2. With chloropentafluoropropan-2-one in diethyl

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of diphenylacetylenebis(triphenylphosphine)platinum(0) (0.50g, 0.57m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 4 hours

the tube was opened and volatile material removed. The white crystalline material was filtered off and washed with diethyl ether to yield complex 1:5, $[Pt(\eta\text{-}ClCF_2COCF_3)(PPh_3)_2]$ (0.33g, 65%) m.p. 179-182° dec.

$C_{39}H_{30}ClF_5OP_2Pt$	requires	C, 51.90;	H, 3.35;	F, 10.53%
	found	C,51.78;	H, 3.35;	F, 11.10%

Infra-red: 1587 w, 1575 w, 1295 sh,m, 1279 s, 1243 s, 1225 m, 1191 m, 1171 s, 1159 s, sh, 1119 s, 1095 s, 1031 m, 1003 m, 983 s, 939 w, 891 m, 855 s, 832 m, sh, 825 m, 759 s, 751 s, 731 m, 713 s, sh, 701s, 647 m, 555 s, 531 s, 523 s, 499 s, 459 m, 427 m.

No ^{19}F n.m.r. spectrum obtainable.

3. <u>With chloropentafluoropropan-2-one in benzene.</u>

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a solution of diphenylacetylenebis(triphenylphosphine)platinum(0) (0.50g, 0.57m.mol) in benzene contained in a Carius tube (150ml). After shaking for four hours the tube was opened and volatile material removed. The solution was evaporated to small volume and the white crystalline precipitate obtained was filtered off, washed with diethyl ether and identified as complex 1:2 $[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.48g, 95.5%) from its melting point, infra-red and ^{19}F n.m.r. spectra.

4. <u>With 1,3-dichlorotetrafluoropropan-2-one in diethyl ether.</u>

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a suspension of diphenylacetylenebis (triphenylphosphine)platinum(0) (0.50g, 0.57m.mol) in diethyl ether. After stirring at room temperature for four hours the white suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:6 $[Pt(\eta\text{-}ClCF_2COCF_2Cl)(PPh_3)_2]$ (0.49g, 96%) m.p. 234-236°C.

$C_{39}H_{30}Cl_2F_4OP_2Pt$	requires	C, 50.99;	H, 3.29;	Cl, 7.72;	F, 8.27%
	found	C, 50.77;	H, 3.32;	Cl, 8.13;	F, 7.77%

Infra-red: 1590 w, 1573 w, 1485 s, 1442 s, 1319 m, 1245 s, 1236 s, 1191 m, 1186 m, 1167 w, 1160 s, 1147 s, 1139 s, 1103 s, 1093 s, 1075 w, 1028 m, 1003 m, 997 m, 944 s, 783 s, 755 s, 749 s, 733 s, 711 s, 695 s, 675 m, 621 m, 555 s, 527 s, 508 s, 491 w, 465 w, 455 w, 441 w, 430 m.

No ^{19}F n.m.r. spectrum available.

5. <u>With 1,3-dichlorotetrafluoropropan-2-one in benzene</u>

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added, with stirring to a solution of diphenylacetylenebis-(triphenylphosphine)platinum(0) in benzene. After stirring for four hours the solution was evaporated to small volume and the white precipitate obtained filtered off, washed with diethyl ether and identified as complex 1:3 $[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.48g, 94%) from its melting point, infra-red and ^{19}F n.m.r. spectra.

6. With 1,1,3-trichlorotrifluoropropan-2-one in diethyl ether.

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of diphenylacetylenebis (triphenylphosphine)platinum(0) (0.50g, 0.57m.mol) in diethyl ether. After stirring for four hours the white suspension was filtered and washed with diethyl ether to yield microcrystals of complex cis-$[PtCl_2(PPh_3)_2]$(0.40g, 91 %) identified from its melting point, and infra-red spectrum.[20]

D. The reaction of fluoropropan-2-one with phenylacetylenebis (triphenylphosphine)platinum(0)

1. With hexafluoropropan-2-one.

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of phenylacetylenebis(triphenylphosphine) platinum(0) (0.66g, 0.80m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature overnight the tube was opened and volatile material removed. The white suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:1 $[Pt(\eta CF_3COCF_3)(PPh_3)_2]$ (0.45g, 64%) m.p. 179-183°C identified by its infra-red spectrum.

2. With chloropentafluoropropan-2-one

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of phenylacetylenebis-(triphenylphosphine)platinum(0) (0.30g, 0.37m.ml) in diethyl ether contained in a Carius tube (150ml).

After shaking at room temperature for three days the tube was opened and volatile material removed. The off-white suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:2 cis -$[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.17g, 52%) identified by its melting point and infra-red spectrum.

3. With 1,3-dichlorotetrafluoropropan-2-one in diethyl ether

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a suspension of phenylacetylenebis (triphenylphosphine)platinum(0) (0.50g, 0.61m.mol) in diethyl ether. After stirring at room temperature for three days the white precipitate was filtered and washed with diethyl ether to yield microcrystals of unreacted phenylacetylenebis(triphenylphosphine) platinum(0) identified by its melting point, and infra-red spectrum.

4. With 1,3-dichlorotetrafluoropropan-2-one in chloroform

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a solution of phenylacetylenebis (triphenylphosphine)platinum(0)(0.52g, 0.63m.mol) in chloroform. After refluxing for 1 hour the chloroform was evaporated to small volume under reduced pressure and off-white crystals obtained on addition of ethanol (2ml). These were identified as complex 1:3 cis- $[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.39g, 67%) by their infra-red and ^{19}F n.m.r. spectra.

5. With 1,1,3-trichlorotrifluoropropan-2-one in diethyl ether.

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of phenylacetylenebis (triphenylphosphine)platinum(0) (0.50g, 0.60m.mol) in diethyl ether. After stirring for 24 hours the white suspension was filtered off, washed with diethyl ether and identified as cis - $[PtCl_2(PPh_3)_2]$ from its melting point and infra-red spectrum.

E. The reaction of 1,3-dichlorotetrafluoropropan-2-one with ethylenebis(triphenylphosphine)platinum(0).

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added, with stirring, to a suspension of ethylenebis(triphenylphosphine)platinum(0) (0.50g, 0.67m.mol) in diethyl ether. After stirring for 24 hours the white suspension was filtered off, washed with diethyl ether and identified as complex 1:6 $[Pt(\eta-ClCF_2COCF_2Cl)(PPh_3)_2]$ from its infra-red and ^{19}F n.m.r. spectra.

F. Cis to trans isomerisation

1. cis -$[PtCl(CF_2COCF_3)(PPh_3)_2]$

cis-$[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.30g, 0.33m.moles) was placed in a Carius tube (150ml) and benzene (15ml) added. After heating at 150°C for 48 hours the tube was opened and the yellow solution filtered. The filtrate was evaporated to small volume and careful addition of ethanol resulted in the precipitation of off-white crystals of complex 1:7 trans- $[PtCl(CF_2COCF_3)(PPh_3)_2]$ (0.27g, 90%) m.p 218-220°C.

$C_{39}H_{30}ClF_5OP_2Pt$	requires	C, 51.92;	H, 3.35;	Cl, 3.90%
	found	C, 53.89;	H, 3.57;	Cl, 5.40%

Infra-red; 1762 m, 1586 v.w. 1569 w, 1315 w, 1289 w, 1245 w, 1215 m, 1185 w, 1162 m, 1151 m, 1138 m, 1110 w, 1098 m, 1070 w, 1034 m, 998 m, 975 w, 965 w, 934 m, 888 w, 875 m, 860 w, 807 m, 774 w, 755 m, 743 m, 711 m, 704 m, 690 s, 675 w, 635 w, 618 w, 542 w, 524 s, 512 s, 499m, 465 w, 455 w, 434 w, 421 w, 307 m.

^{19}F n.m.r. spectrum;

Observed in benzene solution; a triplet (3F) centred at 8.94 p.p.m J(F-F) = 10.14Hz and a multiplet (2F) centred at =0.05 p.p.m. (relative to external benzotrifluoride).

2. cis -$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$

cis-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.30g, 0.33m.mol) was placed in a Carius tube (150ml) and benzene (15ml) added. After heating at 150°C for 48 hours the tube was opened and the yellow solution filtered. The filtrate was evaporated to small volume and careful addition of ethanol

resulted in the precipitation of off-white crystals of complex 1:8 trans - $[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (0.28g,93%) m.p. 238-239°C.

$C_{39}H_{30}Cl_2F_4OP_2Pt$	requires	C, 50.99; H, 3.29%
	found	C, 48.05; H, 3.15%

Infra-red: 1762 m, 1584 w, 1568 w, 1363 s, 1304 w, 1270 m, 1219 w, 1209 w, 1182 m, 1167 s, 1156 s, 1149 m, 1144 m, 1096 s, 1000 w, 980 s, 974 s, 879 w, 772 w, 757 s, 750 s, 745 s, 736 s, 711 s, 704 s, 696 s, 668 m, 620 w, 548 w, 532 s, 520 s, 504 s, 468 w, 440 m, 430 m, 311 s, 306 m,sh.

^{19}F n.m.r. spectrum:

Observed in benzene solution: a triplet (2F) centred at -1.17 p.p.m J(F-F) = 12.08Hz, and a multiplet (2F) centred at -2.20 p.p.m. with ^{195}Pt satellites J(Pt-F) = 190.31Hz J(F-F) = 12.08Hz.

3. cis- and trans-$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$

cis- and trans-$[PtCl(CFClCOCF_2Cl)(PPh_3)_2]$ (0.30g, 0.33m.mol) was placed in a Carius tube (150ml) and benzene (15ml) added. After heating at 150°C for 24 hours the tube was opened and the yellow solution filtered. The filtrate was evaporated to small volume and yellow microcrystals of the complex trans-$[PtCl_2(PPh_3)_2]$ precipitated. These were identified from their melting point and infra-red spectrum.

C. The reaction of fluoropropan-2-ones with peroxobis(triphenylphosphine) platinum(II).

1. With hexafluoropropan-2-one.

An excess of hexafluoropropan-2-one(1.0ml) was condensed (-196°) on to a suspension of peroxobis(triphenylphosphine)platinum(I) (0.40g, 0.53m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The white microcrystalline product was filtered off and recrystallised from dichloromethane -diethyl ether to yield crystals of the previously prepared complex 1:9 $[\overline{PtOOC(CF_3)_2O}(PPh_3)_2]$ identified from its ^{19}F n.m.r. and i.r. spectra.

2. With chloropentafluoropropan-2-one

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of peroxobis(triphenylphosphine) platinum(II) (0.40g, 0.53m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The white microcrystalline product was filtered off, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to yield complex 1:10 $[\overline{PtOOC(CF_2ClCF_3)O}(PPh_3)_2]$ (0.41g, 84%) m.p 220-224°dec.

$C_{39}H_{30}ClF_5O_3P_2Pt$	requires	C,50.15;	H,3.24;	F,10.17%
	found	C,49.00;	H,3.28;	F,10.00%

Infra-red; 1587 w, 1575 w, 1279 m, 1235 sh, 1217 sh, 1191 sh, 1175 s, 1159 s, 1145 s, 1121 m, 1107 s, 1097 s, 1051 s, 1043 sh, 1011 sh, 1000 m, 991 m, 909 m, 869 sh, 853 m, 784 w, 779 w, 761 s, 751 s, 727 m, 713 s, 701 s, 693 m, 625 w, 561 s, 535 s, 517 s, 505 s, 471 w, 459 w, 427 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution a quartet (2F) centred at -2.92 p.p.m. J(F-F) = 11.1Hz and a triplet (3F) centred at 10.80 p.p.m J(F-F) = 11.1Hz (relative to external benzotrifluoride).

3. <u>With 1,3-dichlorotetrafluoropropan-2-one.</u>

An excess of 1,3-dichlorotetrafluoropropan-2-one-10ml) added with stirring to a suspension of peroxobis(triphenylphosphine) platinum(II) (0.50g, 0.67 m.mol) in diethyl ether (25ml). After stirring at room temperature for 24 hours the white suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:11 $\left[Pt\overline{OOC(CF_2Cl)_2O}(PPh_3)_2 \right]$ (0.53g, 84%) m.p. 207-210°C.

$C_{39}H_{30}Cl_2F_4O_3P_2Pt$	requires	C, 49.28;	H,3.18;	F,7.99%
	found	C, 49.57;	H,3.32;	F,7.95%

Infra-red: 1588 w, 1575 w, 1223 w, 1197 m, 1187 m, 1163 m, 1141 s, 1129 m, 1105 s, 1095 s, 1043 s, 1031 sh, 1000 m, 947 m, 939 m, 855 w, 839 w, 823 w, 803 w, 772 w, 759 s, 750 s, 725 m, 715 s, 701 s, 695 s, 561 s, 537 s, 523 s, 519 s, 507 s, 451 w, 427 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a singlet at - 5.25 p.p.m (relative to external benzotrifluoride).

4. <u>With 1,3-dichlorotetrafluoropropan-2-one.</u>

Peroxobis(triphenylphosphine)platinum(II) (0.40g, 0.53m.mol) and 1,3-dichlorotetrafluoropropan-2-one (0.106g, 0.53m.mol) were stirred together in diethyl ether overnight. The white suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:11 $[\overline{PtOOC(CF_2Cl)_2O}(PPh_3)_2]$ (0.42g, 83%) m.p. 208-210°C.

$C_{39}H_{30}Cl_2F_4O_3P_2Pt$	requires	C, 49.28;	H, 3.18%	
	found	C, 48.84;	H, 3.24%	

Infra-red: 1588 w, 1575 w, 1223 w, 1197 m, 1187 m, 1163 m, 1141 s, 1129 m, 1105 s, 1095 s, 1043 s, 1031 sh, 1000 m, 947 m, 939 m, 855 w, 839 w, 823 w, 803 w, 772 w, 759 s, 750 s, 725 m, 715 s, 701 s, 695 s, 561 s, 537 s, 523 s, 519 s, 507 s, 451 w, 427 w.

5. <u>With 1,1,3-trichlorotrifluoropropan-2-one.</u>

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of peroxobis(triphenylphosphine) platinum(II)(0.30g, 0.40m.mol) in diethyl ether. After stirring at room temperature for one hour the white suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:12 $[\overline{PtOOC(CF_2ClCFCl_2)O}(PPh_3)_2]$ (0.29g 75.1%) m.p. 194-196°C.

$C_{39}H_{30}Cl_3F_3O_3P_2Pt$	requires	C,48.42;	H,3.13;	Cl, 10.99%
	found	C,48.64;	H,3.27;	Cl, 11.84%

Infra-red: 1584w, 1570 w, 1308 w, 1260 w, 1200 m, 1192 m, 1184 m, 1152 s, 1128 s, 1120 s, 1094 s, 1039 m, 1032 m, 1026 m, 1000 m, 946 m, 936 m, 868 m, 860 m, 849 m, 808 w, 770 w, 756 s, 745 s, 706 s, 696 s, 690 s, 622 w, 557 s, 532 s, 520 s, 514 s, 503 s, 468 w, 448 w, 420 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a triplet (1F) centred at -3.25 p.p.m J(F-F) = 13.95Hz and a doublet (2F) at -7.07 p.p.m J(F-F) = 13.95Hz (relative to external benzotrifluoride).

H. The reaction of acetonedicarboxylic acid dimethyl ester with some complexes of platinum(0) and platinum(II).

1. With tetrakis(triphenylphosphine)platinum(0).

An excess of acetonedicarboxylic acid dimethyl ester (1.0ml) was added with stirring to a suspension of tetrakis(triphenylphosphine) platinum(0)(1.0g, 0.69 m.mol) in diethyl ether. After stirring at room temperature, in a stoppered flask, for 4 days the off white precipitate was filtered and washed with diethyl ether to yield microcrystals of complex 1:13 $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(PPh_3)_2]$ (0.48g, 75%) m.p. 157-160°C.

$C_{43}H_{38}O_5P_2Pt$	requires	C,57.90;	H,4.29;	O,8.96%
	found	C,55.25;	H,4.24;	O,10.65%

Infra-red: 1740 s, 1725 s, 1586 w, 1574 w, 1295 s, 1221 m, 1184 m, 1168 m, 1156 sh, 1097 s, 1069 m, 1040 w, 1025 w, 1016 w, 941 w, 873 w, 853 w, 801 v,w, 757 s, 747 s, 706 s, 696 s, 624 w, 578 m, 557 s, 533 s, 525 s, 517 s, 507 s, 453 w, 421 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution, a singlet (6H) at 3.36 p.p.m and a quartet (2H) centred at 3.12 p.p.m J(H-H)= 12.70Hz. Also a multiplet (30H) centred at 7.30 p.p.m.

2. <u>With peroxobis(triphenylphosphine)platinum(II)</u>

An excess of acetonedicarboxylic acid dimethyl ester (1.0ml) was added, with stirring to a suspension of peroxobis(triphenylphosphine) platinum(II)(0.30g, 0.40 m.mol) in diethyl ether. After stirring at room temperature overnight the white suspension was filtered off and washed with diethyl ether to yield microcrystals of complex 1:13

$[\overline{Pt\{CH(CO_2CH_3)C(:O)CH}(CO_2CH_3)\}(PPh_3)_2]$ (0.34g,92%) m.p. 163-164°C

$C_{43}H_{38}O_5P_2Pt$	requires	C,57.90; H,4.29; O,8.96%
	found	C,55.12; H,4.40; O,11.91%

Infra-red: 1740 s, 1725 s, 1586 w, 1574 w, 1295 s, 1221 m, 1184 m, 1168 m, 1156 sh, 1097 s, 1069 m, 1040 w, 1025 w, 1016 w, 941 w, 873 w, 853 w, 801 v w, 757 s, 747 s, 706 s, 696 s, 624 w, 578 m, 557 s, 533 s, 525 s, 517 s, 507 s, 453 w, 421 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet (6H) at 3.36 p.p.m and a quartet (2H) centred at 3.12 p.p.m. J(H-H) = 12.70Hz. Also a multiplet (30H) centred at 7.30 p.p.m.

3. <u>With trans-stilbenebis(triphenylphosphine)platinum(0)</u>

An excess of acetonedicarboxylic acid dimethyl ester (1.0ml) was added with stirring to a suspension of <u>trans</u>-stilbenebis(triphenylphosphin platinum(0) (0.65g,0.72 m.mol) in diethyl ether. After stirring at room temperature for 4 days the off white suspension was filtered and washed with diethyl ether to yield microcrystals of complex 1:13

$[\overline{Pt\{CH(CO_2CH_3)C(:O)CH}(CO_2CH_3)\}(PPh_3)_2]$ (0.36g, 52.3%) m.p. 162-164°C

4. <u>With ethylenebis(triphenylphosphine)platinum(0).</u>

An excess of acetonedicarboxylic acid dimethyl ester (0.50 ml) was added with stirring to a suspension of ethylenebis (triphenylphosphine)platinum(0)(0.50g, 0.67m.mol) in diethyl ether. After stirring at room temperature for 24 hours the white suspension was filtered off and washed with diethyl ether. Recrystallisation from dichloromethane-ethanol yielded crystals of complex 1:13 $[\overline{Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}}(PPh_3)_2]$ (0.43g, 70%) m.p. 158-160°C identified from its infra-red and ^1H n.m.r. spectra.

$C_{43}H_{38}O_5P_2Pt$	requires	C,57.90;	H,4.29;	O,8.96%
	found	C,56.42;	H,4.47;	O,11.32%

5. <u>With tetrakis(methyldiphenylphosphine)platinum(0).</u>

An excess of acetonedicarboxylic acid dimethyl ester (0.50ml) was added with stirring to a suspension of tetrakis(methyldiphenylphosphine) platinum(0) (1.0g, 1.29m.mol) in diethyl ether. After stirring for 72 hours under an atmosphere of nitrogen, the yellow suspension was filtered off, washed with diethyl ether and identified as unreacted tetrakis (methyldiphenylphosphine)platinum(0) (0.95g, 95%) from its infra-red spectrum.

The reaction was repeated in an oxygen atmosphere. This time a white precipitate was produced, which was filtered off, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to yield crystals of complex 1:14 $[Pt(\eta\text{-}CO(CH_2CO_2CH_3)_2)(PMePh_2)_2]$ (0.85g,85%) m.p. 229-231°C.

$C_{33}H_{36}O_5P_2Pt$	requires	C, 51.50;	H, 4.71;	O,10.38% M742
	found	C, 51.50;	H, 4.47;	O,10.38% M750

Infra-red: 1719 s, 1685 s, 1680 s, 1628 s, 1570 w, 1363 s, 1330 s, 1320 s, 1289 w, 1195 s, 1138 s, 1115 s, 1107 s, 1100 s, 1070 w, 1035 v w, 1025 w, 1014 m, 997 w, 955 m, 921 w, 907 s, 898 s, 886 m, 873 m, 846 w, 789 m, 759 s, 745 s, 732 s, 703 s, 695 s, 690 s, 615 v w, 576 w, 525 w, 513 s, 501 s, 491 s, 450 m, 432 m, 372 w, 360 w, 350 w.

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet (6H) centred at 1.88 p.p.m with ^{195}Pt satellites J(P-H) = 9.05Hz; J(Pt-H) = 16.59Hz. A singlet (6H) at 3.02 p.p.m and a doublet (4H) centred at 4.00 p.p.m with ^{195}Pt satellites; J(P-H)=5.28Hz J(Pt-H)=27.90Hz. Also a multiplet (20H) centred at 7.26 p.p.m.

6. <u>With tetrakis(dimethylphenylphosphine)platinum(0)</u>

An excess of acetonedicarboxylic acid dimethyl ester (0.50ml) was added with stirring to a suspension of tetrakis(dimethylphenylphosphine) platinum(0)(0.70g, 0.93m.mol) in diethyl ether. After stirring at room temperature, with exposure to the atmosphere, for 24 hours the solution was evaporated to small volume and a few drops of ethanol added. A small amount of a white complex precipitated, which was filtered, washed with diethyl ether and identified as complex 1:15,

$[Pt\{\eta\text{-}CO(CH_2CO_2CH_3)_2\}(PMe_2Ph)_2]$ (0.18g, 29%) m.p. 173-175°C.

$C_{23}H_{32}O_3P_2Pt$	requires	C,42.79; H,4.99%
	found	C,42.78; H,4.72%

Infra-red: 1725 s, br, 1570 m, 1373 m, 1296 s, 1256 m.br, 1168 s, 1152 s. 1112 m, 1080 w, 1060 m, 1016 m, 1000 m, 928 m, 908 m, 732 s, 689 s, 670 m,sh, 466 s.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a pair of doublets (12H) centred at 1.59 p.p.m. with ^{195}Pt satellites; J(P-H)=4.0Hz, J(Pt-H)=16.5Hz. A singlet (6H) at 3.50 p.p.m and a doublet (4H) centred at 4.09 p.p.m with ^{195}Pt satellites; J(P-H)=5.73Hz, J(Pt-H)=28.66Hz. Also a doublet (10H)centred at 7.31 p.p.m.

1. <u>The reaction of tetrakis(triphenylphosphine)platinum(0) with diethylketomalonate.</u>

An excess of diethylketomalonate (0.5ml) was added with stirring to a suspension of tetrakis(triphenylphosphine)platinum(0) (1.0g, 0.69m.mol) in diethyl ether. After stirring at room temperature for 24 hours (not under nitrogen) the white precipitate was filtered off and identified as complex 1:16 $[Pt\{\eta-CO(C_2H_5CO_2)_2\}(PPh_3)_2]$ (0.55g,89%) m.p. 159-161°C.

$C_{43}H_{40}O_5P_2Pt$	requires	C,57.78;	H,4.51;	O,8.50%
	found	C,57.02;	H,4.46;	O,8.99%

Infra-red: 1680 s, br, 1582 w, 1568 w, 1358 s, 1258 s, 1240 s, 1178 s, 1149 s, 1088 s, 1050 s, 1025 m, 996 m, 980 m, 920 w, 876 m, 855 m, 810 w, 758 s, 746 s, 738 s, 700 s, 692 s, 630 m, 622 m, 544 s, 522 s, 512 s, 495 s, 453 m, 420 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$solution: a triplet (6H) centred at 1.04 p.p.m. J(H-H)=6.62Hz and a multiplet (4H) at 3.94 p.p.m. J(H-H)=6.60Hz. Also a multiplet (30H) centred at 7.32 p.p.m.

When the complex $[Pt\{\eta CO(C_2H_5OO_2)_2\}(PPh_3)_2]$ (0.30g 0.34 m.mol) is stirred for 24 hours, in diethyl ether, with excess 1,3-dichlorotetrafluoropropan-2-one(0.5ml), white microcrystals of complex 1:3 $[PtCl(CF_2OOCF_2Cl)(PPh_3)_2]$ are produced (0.23 g, 75.0%) These were identified from their infra-red and ^{19}F n.m.r. spectra.

J. <u>The reaction of 2-bis(triphenylphosphine)platinum-1,3-bis(methoxycarbonyl)but-3-one with fluoropropan-2-ones.</u>

1. <u>With hexafluoropropan-2-one</u>

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(triphenylphosphone)platinum-1,3-bis(methoxycarbonyl)but-3-one (0.30g, 0.34m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 1 week the tube was opened and volatile material removed. The white precipitate was filtered, washed with diethyl ether and recrystallised from dichloromethane - light petroleum (40-60°) to give white crystals of complex 1:9 $[\overline{PtOOC(CF_3)_2O}(PPh_3)_2]$ (0.24g, 84%) m.p. 212 - 214°C.

$C_{39}H_{30}F_6O_3P_2Pt$	requires	C, 51.00;	H, 3.30;	F,12.40%
	found	C, 49.71;	H, 3.17;	F,10.70%

infra-red; 1586 w, 1574 w, 1361 s, 1350 s, 1300 s, 1280 s, 1223 s, 1201 s, 1182 s, 1154 s, 1136 s, 1096 s, 1070 s, 1050 s, 1026 s, 1000 s, 971 s, 960 s, 911 m, 874 m, 845 m, 790 w, 776 w, 753 s, 742 s, 735 s, 720 s, 705 s, 689 s, 648 w, 639 w, 616 w, 554 s, 529 s, 510 s, 500 s, 459 w, 446 w, 420 m, 390 m.

2. With chloropentafluoropropan-2-one.

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(triphenylphosphine)platinum-1,3-bis(methoxycarbonyl)but-3-one (0.40g, 0.45m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 3 days the tube was opened and volatile material removed. The white suspension was filtered and washed with diethyl ether. Recrystallisation from dichloromethane - light petroleum (40-60°) resulted in white crystals of complex 1:10 $[\overline{PtOOC(CF_2ClCF_3)O}(PPh_3)_2]$ (0.30g, 78%) m.p. 219 - 222°C.

$C_{39}H_{30}ClF_5O_3P_2Pt$	requires	C,50.15;	H,3.24;	F,10.17%
	found	C,50.92;	H,3.36;	F,10.00%

Infra-red: 1587 w, 1575 w, 1279 w, 1235 w, 1217 m, 1191 s, 1175 s, 1159 s, 1145 s, 1121 m, 1107 s, 1097 s, 1051 s, 1043 s,sh, 1011 m, 1000 m, 991 m, 909 m, 869 m, 853 m, 784 w, 779 w, 761 s, 751 s, 727 m, 713 s, 701 s, 693 s, 625 w, 561 s, 535 s, 523 s, 517 s, 505 s, 471 w, 459 w, 427 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a triplet (3F) centred at -2.92 p.p.m. J(F-F)=11.11Hz and a quartet (2F) at 10.80 p.p.m. J(F-F)= 11.11Hz (relative to external benzotrifluoride).

3. With 1,3-dichlorotetrafluoropropan-2-one.

An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0ml) was added with stirring to a suspension of 2-bis(triphenylphosphine)platinum-1,3-bis(methoxycarbonyl)but-3-one, (0.50g, 0.56m.mol) in diethyl ether (25ml). After stirring at room temperature for 3 days the white

suspension was filtered and recrystallised from dichloromethane-light petroleum (40-60°) to give white crystals of complex 1:11 $[\overline{PtOOC(CF_2Cl)_2O}(PPh_3)_2]$ (0.39g,78%) m.p. 199-202°C.

$C_{39}H_{30}Cl_2F_4O_3P_2Pt$	requires	C,49.28; H,3.18; F,7.99%
	found	C,48.78; H,3.19; F,6.65%

Infra-red: 1588 w, 1575 w, 1223 w, 1197 m, 1187 m, 1163 m, 1141 s, 1129 m, 1105 s, 1095 s, 1043 s, 1031 sh, 1000 m, 947 m, 939 m, 855 w, 839 w, 823 w, 803 w, 772 w, 759 s, 650 s, 725 m, 715 s, 701 s, 695 s, 561 s, 537 s, 523 s, 519 s, 507 s, 451 w, 427 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a singlet at -5.25 p.p.m (relative to external benzotrifluoride).

4. <u>With 1,1,3-trichlorotrifluoropropan-2-one.</u>

An excess of 1,1,3-trichlorotrifluoropropan-2-one (1.0ml) was added with stirring to a suspension of 2-bis(triphenylphosphine) platinum-1,3-bis(methoxycarbonyl)but-3-one (0.50g, 0.56 m.mol) in diethyl ether (25ml). After stirring at room temperature for three days the white suspension was filtered and recrystallised from dichloromethane - light petroleum (40-60°) to give white crystals of complex 1:12 $[\overline{PtOOC(CF_2ClCFCl_2)O}(PPh_3)_2]$ (0.48g,74%) m.p. 195-197°C.

$C_{39}H_{30}Cl_3F_3O_3P_2Pt$	requires	C,48.42; H,3.13; Cl,10.99%
	found	C,48.69; H,3.51; Cl,11.40%

Infra-red: 1584 w, 1570 w, 1308 w, 1260 w, 1200 m, 1192 m, 1184 m, 1152 s, 1128 s, 1120 s, 1094 s, 1039 m, 1032 m, 1026 m, 1000 m, 946 m, 936 m, 868 m, 860 m, 849 m, 808 w, 770 w, 756 s, 745 s, 706 s, 696 s, 690 s, 622 w, 557 s, 532 s, 520 s, 514 s, 503 s, 468 w, 448 w, 420 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a triplet (1F) centred at -3.25 p.p.m J(F-F)=13.95Hz and a doublet (2F) at 7.07 p.p.m. J(F-F)=13.95Hz (relative to external benzotrifluoride).

K. The reaction of acetonedicarboxylic acid dimethyl ester with tetrakis(triphenylphosphine)palladium.

1. An excess of acetonedicarboxylic acid dimethyl ester (0.5ml) was added with stirring to a suspension of tetrakis(triphenylphosphine) palladium(0) (1.0g, 0.87 m.mol) in dried degassed diethyl ether (25ml). After stirring under an atmosphere of nitrogen for 24 hours the yellow suspension was filtered and washed with diethyl ether to yield unreacted tetrakis(triphenylphosphine)palladium(0) (0.98g, 98%).

2. An excess of acetonedicarboxylic acid dimethyl ester (0.5ml) was added with stirring to a suspension of tetrakis(triphenylphosphine) palladium(0) (1.0g, 0.87 m.mol) in diethyl ether (25ml). After stirring for 1 hour under an atmosphere of carbon dioxide free oxygen the white precipitate was filtered off, washed with diethyl ether and the white microcrystals identified as complex 1:17 $[Pd\{\eta\text{-}CO(CH_2CO_2CH_3)_2\}(PPh_3)_2]$ (0.53g 76%) m.p. 172-175°dec.

$C_{43}H_{40}O_5P_2Pd$	requires	C,64.13;	H,5.01; O,9.93%
	found	C,64.43;	H,5.16; O,9.67%

Infra-red: 1705 s, 1684 s, 1664 m, 1590 s, 1566 s, 1556 s, 1362 s, 1328 s, 1256 m, 1233 s, 1188 m, 1180 w, 1160 m, 1144 s, 1130 s, 1103 s, 1092 s, 1086 s, 1072 w, 1038 m, 1022 s, 1001 m, 947 m, 906 m, 880 m, 800 w, 766 s, 758 s, 745 s, 708 s, 705 s, 697 s, 672 w, 597 w, 536 s, 527 s, 510 s, 498 s, 494 m, 464 w, 460 w, 424 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet (6H) at 2.97 p.p.m. and a doublet (4H) at 4.14 p.p.m J(P-H) = 3.30Hz. Also a multiplet (30H) centred at 7.24 p.p.m.

L. The reaction of 2-bis(methyldiphenylphosphine)-3,3-bis (methoxycarbonylmethylene)-1,2-oxaplatinan with fluoropropan-2-ones.

1. With hexafluoropropan-2-one.

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(methyldiphenylphosphine)-3,3-bis-(methoxylcarbonylmethylene)-1,2-oxaplatinan (0.50g, 0.65 m.mol) in diethyl ether (15ml) contained in a Carius tube (150ml). After shaking at room temperature for 72 hours the tube was opened and volatile material removed. The white microcrystals were filtered, washed with diethyl ether and identified as complex 1:18.

$\left[Pt\left[OC\{CH(CO_2CH_3)C(CF_3)_2OH\}_2\right](MePh_2P)_2\right]$ (0.10g,16.5%) m.p. 120-122°C.

$C_{39}H_{36}F_{12}O_7P_2Pt$	requires	C, 42.52; H, 3.30; F, 20.70%
	found	C, 42.92; H, 3.48, F, 21.79%

Infra-red: 1747 s, br, 1717 s, br, 1589 s, br, 1360 s, 1256 s, 1232 s, 1208 s, 1192 s, 1164 s, 1152 s, 1100 m, 1080 s, br, 1046 w, 996 m, 978 m, 936 m, 904 s, 888 s, 879 m, 788 w, 744 s, 730 s, 690 s, 596 w, 542 m, 528 s, 508 s, 496 m, 487 m, 456 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet at + 18.31 p.p.m. (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet (3H) centred at 1.76 p.p.m. with ^{195}Pt satellites $J(P_{\underline{trans}}-H)$ = 11.99Hz and a doublet (3H) at 1.87 p.p.m. with ^{195}Pt satellites $J(P_{\underline{cis}}-H)$ = 8.99Hz. J(Pt-H)=14.99Hz. There are also two singlets (6H) at 3.66 and 3.69 p.p.m, plus a multiplet (20H) centred at 7.40 p.p.m.

The filtrate was evaporated to dryness and the white powder obtained recrystallised from dichloromethane - diethyl ether/light petroleum (40-60°) to yield white crystals of complex 1:19 $\left[Pt\left[OC(CF_3)_2CH(CO_2CH_3)C\{:C(CO_2CH_3)C(CF_3)_2OH\}O\right](MePh_2P)_2\right]$ (0.36g, 50.5%) m.p. 188-189°C.

$C_{39}H_{34}F_{12}O_7P_2Pt$	requires	C,42.52; H,3.11; F,20.70; O,10.20%
	found	C,42.53; H,3.07; F,20.05; O,10.05%

Infra-red: 3160 m,br, 2945 m, 2920 m, 1740 s, 1730 s, 1692 s, 1679 m, 1669 s, 1573 m, 1557 m, 1480 m, 1436 s, 1430 s, 1385 s, 1361 s, 1346 s, 1310 s, 1292 s, 1277 s, 1259 s, 1216 s, 1199 s, 1160 s, 1146 s, 1105 s, 1070 s, 1045 m, 1013 m, 967 s, 946 s, 925 m, 905 m, 893 s, 885 s, sh, 876 m, 859 w, 840 w, 823 w, 802 m, 793 m, 734 s, 722 s, 706 m, 691 s, 665 m, 616 w, 605 w, 595 w, 543 w, 529 w, 515 m, 504 s, 490 m, 455 m, 430 w, 381 w, 359 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet centred at 11.15 p.p.m. (relative to external benzotrifluoride).

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet (3H) centred at 1.64 p.p.m. J(P-H)=5.20Hz and a doublet (3H) at 1.75 p.p.m. J(P-H)=5.20Hz. J(Pt-H)=14.99Hz. Two singlets at 3.60(3H) and 3.80(3H) p.p.m. a singlet (1H) at 4.50 p.p.m and a multiplet (20H) centred at 7.40 p.p.m. There is also a singlet (1H) at 8.73 p.p.m.

2. <u>With chloropentafluoropropan-2-one.</u>

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(methyldiphenylphosphine) -3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan(0) (0.40g, 0.52m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 48 hours the tube was opened and volatile material removed. The white precipitate was filtered off and recrystallised from dichloromethane-diethyl ether to yield microcrystals of complex 1:20 $\left[Pt\left[OC\{CH(CO_2CH_3)C(CF_2ClCF_3)OH\}_2\right](MePh_2P)_2\right]$ (0.49g, 86%) m.p. 105-107°C.

$C_{39}H_{36}Cl_2F_{10}O_7P_2Pt$	requires	C,41.28; H,3.20; Cl,6.25%
	found	C,41.50; H,3.44; Cl,7.08%

Infra-red: 1751 s, 1724 s, 1685 m,sh, 1590 s, 1362 s, 1330 s, 1294 s, 1280 s, 1259 s, 1230 s, 1204 s, 1191 s, 1180 s, 1165 s, 1155 s, 1118 s, 1105 s, 1079 s, 1050 m, 1029 m, 995 s, 988 s, 961 m, 945 m, 927 s, 900 s.

885 s, 875 s, 837 s, 801 m, 785 m, 755 s, 740 s, 730 s, 697 s, 687 s, 640 m, 597 m, 538 m, sh, 528 s, 509 s, 495 s, 459 m, 425 m.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a quartet (2F) centred at 3.22 p.p.m. J(F-F)=10.86Hz, and a triplet (3F) centred at 16.33 p.p.m. J(F-F)= 10.86Hz (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: A multiplet (6H) centred at 1.80 p.p.m. A multiplet (6H) centred at 3.60 p.p.m. and a multiplet (20H) centred at 7.39 p.p.m.

3. <u>With 1,3-dichlorotetrafluoropropan-2-one.</u>

An excess of 1,3-dichlorotetrafluoropan-2-one (0.50ml) was added with stirring to a suspension of 2-bis(methyldiphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan(0) (0.30g, 0.39 m.mol) in diethyl ether (25 ml). After stirring at room temperature for 72 hours the white precipitate was filtered off and recrystallised from dichloromethane-diethyl ether to yield microcrystals of complex 1:21 $[Pt\{OC(CF_2Cl)_2OC(CH_2CO_2CH_3)_2\}(MePh_2P)_2]$ (0.27g, 72%) m.p.143-145°C

$C_{36}H_{36}Cl_2F_4O_6P_2Pt$	requires	C,44.12;	H,3.71;	Cl, 7.31%
	found	C,39.86;	H,3.05;	Cl,11.94%

Infra-red: 1740 s, 1697 s, 1572 s,br, 1362 s, 1341 s, 1301 s, 1261 s, 1240 s, 1196 s, 1173 s, 1160 s, 1150 s, 1128 s, 1103 s, 1075 s, 1044 s, 1009 s, 998 s, 960 s, 955 s, 939 s, 922 s, 915 s, 906 s, 895 s, 886 s, 880 s, 873 s, 843 m, 820 m, 793 s, 768 s, 754 s,sh, 745 s, 731 s, 703 s, 690 s, 650 s, 622 m, 595 m, 536 w, 526 s, 508 s, 498 s, 484 s, 453 m, 446 m, 438 m.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet at 0.82 p.p.m (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet (6H) centred at 1.80 p.p.m. with ^{195}Pt satellites J(P-H)=8.69Hz J(Pt-H)=14.99Hz, a singlet (6H) at 2.96 p.p.m and a doublet (4H) centred at 3.96 with ^{195}Pt satellites J(P-H)=4.80Hz J(Pt-H)=22.49Hz. Also a multiplet (20H) centred at 7.08 p.p.m.

4. <u>With 1,1,3-trichlorotrifluoropropan-2-one</u>

An excess of 1,1,3-trichlorotrifluoropropan-2-one (0.5 ml) was added with stirring to a suspension of 2-bis(methyldiphenylphosphine)-3, 3-bis(methoxycarbonylmethylene)-1,2-oxaplatinan(0)(0.40g, 0.52m.mol) in diethyl ether. After stirring at room temperature for 72 hours the white precipitate was filtered off, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to yield microcrystals of complex 1:22 $[Pt\{OC(CF_2ClCFCl_2)OC(CH_2CO_2CH_3)_2\}(MePh_2P)_2]$ (0.38g, 74%) 74%) m.p. 216-218°C

$C_{36}H_{36}Cl_3F_3O_6P_2Pt$	requires	C 44.03; H,3.69; Cl, 10.83%
	found	C, 42.78; H,3.70; Cl, 11.44%

Infra-red: 1685 s, 1604 m,sh, 1580 s, 1482 m, 1460 s, 1435 s, 1383 s, 1361 s, 1328 s, 1288 m, 1234 s, 1209 m, 1194 s, 1187 s, 1143 s, 1135 s, 1102 s, 1067 s, 1047 s, 1007 m, 970 w, 950 s, 922 m, 909 s, 897 s, 889 s, 875 s, 802 s, 760 m, 750 s, 740 s, 726 s, 694 s, 677 m, 616 w, 586 m, 521 s, 508 s, 490 m, 478 m, 459 m, 444 w, 425 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a broad singlet (2F) centred at 4.95 p.p.m and a triplet (1F) centred at 8.10 p.p.m J(F-F)=14.46Hz (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet (6H) with ^{195}Pt satellites centred at 1.89p.p.m. J(P-H)=9.37Hz, J(Pt-H)=15.74Hz, a singlet (6H) at 3.04 p.p.m and a doublet (4H) with ^{195}Pt satellites centred at 4.05 p.p.m. J(P-H)=5.25Hz, J(Pt-H)=23.99Hz. Also a multiplet (20H) centred at 7.36 p.p.m. (relative to external benzotrifluoride).

M. The reaction of 2-bis(triphenylphosphine)-3,3-bis (methoxycarbonylmethylene)-1,2-oxapalladium with fluoropropan-2-ones.

1. With hexafluoropropan-2-one.

An excess of hexafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(triphenylphosphine)-3,3-bis (methoxycarbonylmethylene)-1,2-oxapalladium(0.50g, 0.62m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The yellow solution was filtered and the filtrate evaporated to small volume. The addition of a few drops of diethyl ether and light petroleum ($40-60^{o}$) lead to the production of fine yellow crystals of complex 1:23 $\left[Pd\left[OC(CF_3)_2.CH(CO_2CH_3)C\{:C(CO_2CH_3)C(CF_3)_2OH\}O\right](Ph_3P)_2\right]$ (0.54g, 77%)m.p 194-196°C.

$C_{49}H_{48}F_{12}O_7P_2Pd$	requires	C,51.74; H, 3.37%
	found	C,51.76; H, 3.35%

Infra-red: 1760 w, 3012 w, 3003 w, 2950 w, 2898 w, 1716 s,br, 1564 s,br, 1364 s, 1340 s, 1304 s, 1272 s, 1252 s, 1220 s, 1180 s, 1160 s, 1148 s, 1095 s, 1076 s, 1004 s, 972 s, 964 s, 912 w, 890 w, 856 m, 812 w, 792 m, 748 s, 732 m, 696 s, 676 m, 608 m, 528 s, 516 s, 504 s, 448 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a broad singlet (6F) centred at 11.14 p.p.m and a sharp singlet (6F) at 18.67 p.p.m (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet (3H) at 3.59 p.p.m and another (3H) at 3.88 p.p.m, a singlet (1H) at 4.70 p.p.m,a broad multiplet (30H) centred at 7.32 p.p.m. Also a singlet (1H) at 8.48 p.p.m.

2. <u>With chloropentafluoropropan-2-one.</u>

An excess of chloropentafluoropropan-2-one (1.0ml) was condensed (-196°) on to a suspension of 2-bis(triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium (0.50g, 0.62 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 96 hours the tube was opened and volatile material removed. The yellow precipitate was filtered off, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to yield microcrystals of complex 1:24 $\left[Pd[OC(CF_2ClCF_3)CH(CO_2CH_3)C\{:C(CO_2CH_3)C(CF_2ClCF_3)_2OH\}O]\ (Ph_3P)_2\right]$ (0.54g 74%) m.p. 183-185°C.

$C_{49}H_{40}Cl_2F_{10}O_7P_2Pd$ requires C,50.28; H,3.44%

found C,50.24; H,3.36%

Infra-red: 1726 s, 1718 s, 1584 m,sh, 1562 s, 1363 s, 1336 s, 1326 s, 1300 s, 1270 s, 1263 s, 1256 s, 1248 s, 1216 s, 1206 s, 1190 s, 1180 s, 1174 s, 1156 s, 1144 s, 1120 m, 1088 s, 1072 s, 1028 m, 1000 s, 980 s, 950 m, 924 s, 916 s, 910 s, 888 m, 872 s, 848 s, 806 m, 792 m, 757 s, 747 s, 726 s, 712 s, 700 s, 692 s, 646 m, 622m,sh, 615 m, 608 m, 546 s, 529 s, 519 s, 507 s, 50 2s, 446 m, 425 m.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a multiplet (3F) centred at 8.81p.p.m, a multiplet (1H) centred at -2.65 p.p.m and a multiplet

(1F) centred at -4.96 p.p.m (relative to external benzotrifluoride).

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a badly defined quartet (3H) centred at 3.54 p.p.m and a doublet (3H) centred at 4.82 p.p.m J(H-H)=2.25Hz. Also a doublet (1H) at 4.72 p.p.m J(H-H)=6.00Hz, a multiplet (30H) centred at 7.28 p.p.m and a broad singlet (1H) at 8.80 p.p.m.

3. <u>With 1,3-dichlorotetrafluoropropan-2-one.</u>

An excess of 1,3-dichlorotetrafluoropropan-2-one (0.50 ml) was added, with stirring, to a suspension of 2-bis (triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium (1.00g, 1.24 m.mol) in diethyl ether (25ml). After stirring at room temperature for 24 hours the bright yellow suspension was filtered and recrystallised from dichloromethane-diethyl ether and identified as complex 1:25 $[Pd\{OC(CF_2Cl)_2OC(CH_2CO_2CH_3)_2\}(Ph_3P)_2]$ (0.97g, 97 %)m.p. 165-166°C.

$C_{46}H_{40}Cl_2F_4O_6P_2Pd$	requires	C,55.03; H,4.02%
	found	C,52.14; H,3.71%

infra-red: 1716 s, 1664 s, 1530 s,br, 1360 s, 1340 s, 1312 s, 1256 s 1185 sm 1167 s, 1156 s, 1108 s, 1096 s, 1036 m, 998 m, 984 m, 953 s, 944 s, 912 m, 876 m, 848 m, 815 s, 806 s, 784 w, 762 m, 747 s, 740 s, 708 s, 688 s, 672 m, 634 w, 620 m, 573 m, 544 m, 518 s, 510 s, 500 s, 455 w, 424 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet at 0.63 p.p.m (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet (6H) at 3.32 p.p.m, a singlet (4H) at 3.60 p.p.m, and a multiplet (30H) centred at 6.98 p.p.m.

4. <u>With 1,1,3-trichlorotrifluoropropan-2-one.</u>

An excess of 1,1,3-trichlorotrifluoropropan-2-one (0.5ml) was added with stirring to a suspension of 2-bis(triphenylphosphine)-3,3-bis(methoxycarbonylmethylene)-1,2-oxapalladium (1.00g,1.24m.mol) in diethyl ether (25ml). After stirring at room temperature for 72 hours the bright yellow suspension was filtered, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to yield microcrystals of complex 1:26 $[Pd\{OC(CFCl_2CF_2Cl)OC(CH_2CO_2CH_3)_2\}(Ph_3P)_2]$ (1.11g,87.6%) m.p. 140-144°dec.

$C_{46}H_{40}Cl_3F_3O_6P_2Pd$	requires	C,54.12; H,3.95; Cl,10.42%
	found	C,52.88; H,3.73; Cl,10.32%

Infra-red: 1720 s, 1668 s, 1554 s, 1548 s, 1542 s, 1536 s, 1312 s, 1255 s, 1195 s, 1190 s, 1167 s, 1164 s, 1155 s, 1144 s, 1124 s, 1108 s, 1098 s, 1094 s, 1080 s, 1040 s, 1028 m, 1000 m, 981 w, 950 s, 918 w, 880 m, 848 m, 836 m, 816 m, 804 m, 785 m, 764 s, 751 s, 744 s, 714 s, 696 s, 656 w, 633 w, 624 m, 578 m, 548 s, 528 s, 514 s, 504 s, 460 m, 444 w, 424 m, 400 w, 376 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a singlet (6H) at 3.53 p.p.m, a singlet (4H) at 3.81 p.p.m. a multiplet (30H) centred at 7.24 p.p.m.

CHAPTER TWO

THE STRUCTURE OF DITHIO COMPLEXES.

The ability of dithiocarbamate ligands to form stable four membered rings with metal ions has long been known.[42] A valence bond representation of the structure of the dithio complexes is shown below (Figure 2:1)

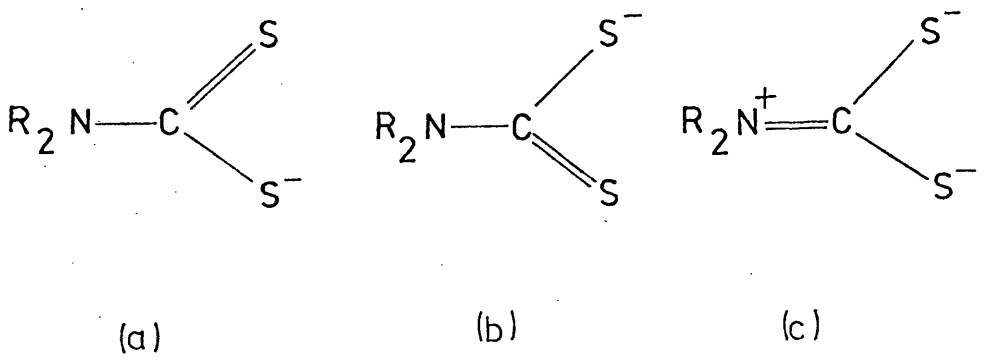


FIGURE 2:1

The extent to which resonance form (c) contributes to the structure, and its effects on physical and chemical properties, of the dithio complexes has been the subject of considerable study.

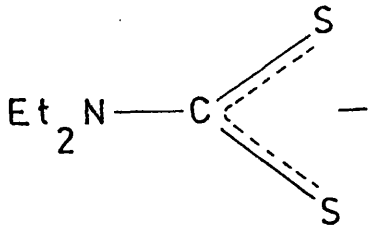
In 1956 Chatt and his co-workers conducted a detailed infra-red study on a number of dithiocarbamate compounds and concluded that (c) makes a large contribution to the structure. They based their conclusion on an infra-red band in the region 1480-1550cm^{-1}.

The energy of this band lies between the region assigned to the C-N stretch (1250-1350cm^{-1}) and the C=N stretch (1640-1690cm^{-1}) and can best be explained as a vibration of a polar C=N^{+} bond.[43,44] X-ray crystallographic data also confirms that the C-N bond length in metal dithiocarbamate complexes is between that of a C-N single bond (~ 1·46Å) and a C=N double bond (~ 1·27Å). A normal co-ordinate analysis of the $\left[Pt(S_2CNH_2)_2\right]$ complex by Nakamoto and co-workers confirmed the assignment of this band (at 1438cm^{-1}) to a C ⟹ N stretching mode. These authors also suggest that resonance form (c) contributes more to the structure than do (a) or (b).[45]

The C=N stretching frequencies of a series of N,N-diethyl-dithiocarbamate complexes vary with the probable arrangement of the sulphur atoms about the central metal atom, and decrease in the order: planar > tetrahedral > octahedral > distorted octahedral or pyramidal.[44] Nakamoto et al. also noticed that this C ⟹ N stretching frequency decreased as the hydrogen of a NH_2 group in a dithiocarbamate ligand was replaced by a methyl or an ethyl group. This agrees with the observations for a series of $\left[Cu(S_2CNR_2)_2\right]$ complexes, when a steady decrease in the C ⟹N frequency with increasing size of the R groups was noticed. A reduction in the electron releasing ability of the NR_2 group due to electron withdrawing R groups seems to be a plausible explanation.[46] Cotton and McCleverty[47] suggested that the very high C ⟹N frequencies in Nickel (II) derivatives of dithiocarbamates might be the result of electron donation by sulphur atoms into a non-bonding molecular orbital containing the $4p_z$ function of nickel. If this is so,

the ability of the ligand to mesomerically shift electron density on to the sulphur atoms should affect the ability of the nickel(II) ion to interact with Lewis bases to form base adducts. The C ⟝N stretching frequency of Nickel(II) dithiocarbamate complexes decreases on changing the R group in a manner which parallels the adduct forming ability of the complex; the greater the C-N bond order the less is the tendency for the nickel(II) complex to form a base adduct. Adducts, once prepared and isolated, show a considerably lower C-N frequency than do the planar Nickel(II) dithiocarbamate complexes, in accord with a decreased double bond character of the C-N bond.

Recently Evtushenko[48] re-examined the infra-red spectra of the Na(I), Pb(II), Bi(III), Cd(II), Zn(II) and Cu(II) dithiocarbamates and observed bands at 1477, 1483, 1490, 1494, 1499 and 1505 and at 1418, 1419, 1423, 1428, 1432 and 1437cm^{-1} respectively. The first set he attributed to the C=N^{+} of resonance form (c) and the second set he assigned to the 1·5 C-S bond of the resonance form shown below



These second bands may however belong to another C=N stretching mode.[45]

In 1968 B.J. McCormick prepared four dithiocarbamate compounds from the oxovanadium(IV) ion. He found that the structure of these complexes was quite similar to that of $[VO(acac)_2]$[49] and that as with $[VO(acac)_2]$ there was a distinct spectral change when the complexes were dissolved in co-ordinating solvents. This indicates that the co-ordinating position trans to the apical oxygen atom is open for co-ordination by a sixth ligand. This type of addition reaction has been extensively studied for $[VO(acac)_2]$.[50,51] The tendency however, to bond to a sixth ligand is lower in dithiocarbamate complexes than in acetylacetonate compounds. Again addition of the sixth ligand resulted in a general lowering in the frequency of the C ═ N bond.

The infra-red spectra of $[Au(III)(S_2CNR_2)_3]$[52] $[(CH_3)_2 Au(III)(S_2CNR_2)]$[53] and $[Br_2Au(III)(S_2CNR_2)]$[52] show the C ═N stretching frequencies at 1550, 1522 and 1565cm^{-1} respectively. This behaviour is consistant with the electron withdrawing character of the Br^- and the electron releasing nature of the CH_3group (R=^{n}Bu).

The double bond character of the C-N bond in dithiocarbamate complexes should result in hindered rotation of the NR_2 group. This effect was observed in the $[Mo(S_2CNR_2)_3(NO)]$ complex[54] (Figure 2:2), where the methyl groups a and a′ and b and b′ show different chemical shifts.

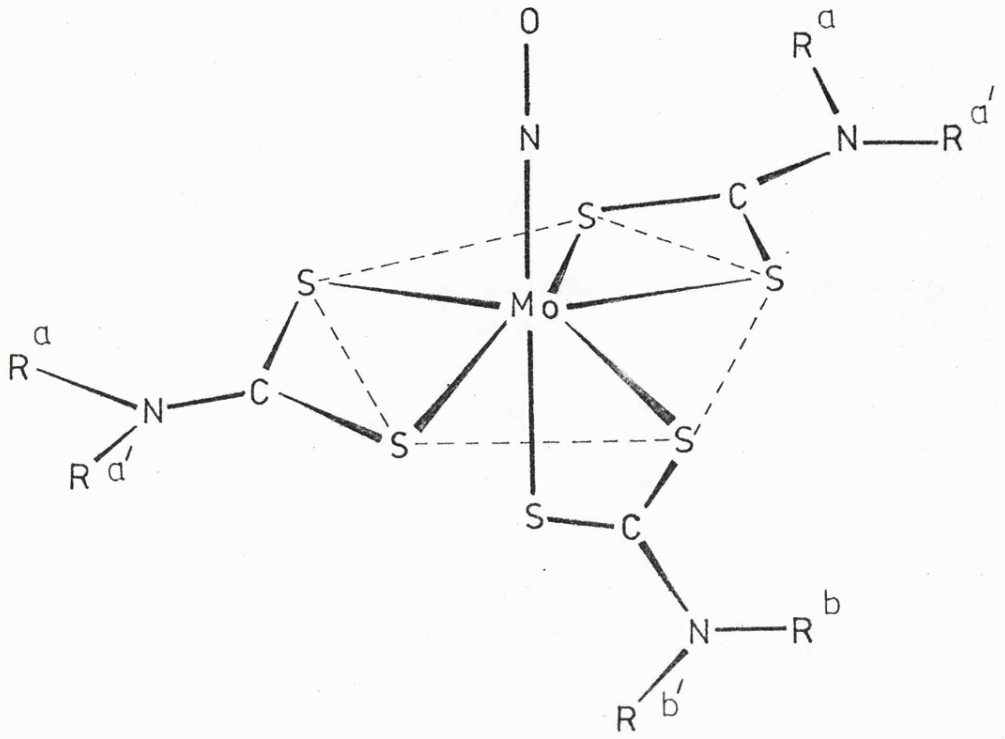
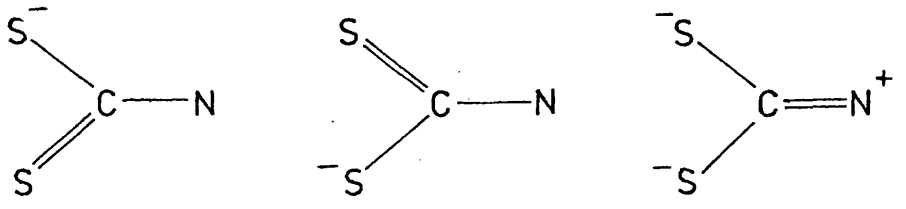


FIGURE 2:2

A crystal structure determination [55] of the $[Ru(dtc)_3(NO)]$ complex reveals that one of the dithiocarbamate ligands is unidentate. The infra-red spectrum of this compound contains C-N absorptions at $\sim$ 1460-1470cm^{-1} which have been assigned to the unidentate ligand. The absence of similar bands has been used to rule out the presence of unidentate ligands in the $[Mo(S_2CNR_2)_3(NO)]$ complexes.[54] The complexes $M(S\text{-}S)_2$(M=Pd or Pt; S-S$^-$ = $Ph_2PS_2^-$ or $(Eto)_2PS_2^-$) react with tertiary phosphines by stepwise cleavage of metal-sulphur bonds to give four co-ordinate adducts $[M(S\text{-}S)_2PR_3]$ and $[M(S\text{-}S)(PR_3)_2)(S\text{-}S)]$ with unidentate-bidentate and bidentate-ionic dithio-ligand

co-ordination respectively.[56,57,58]

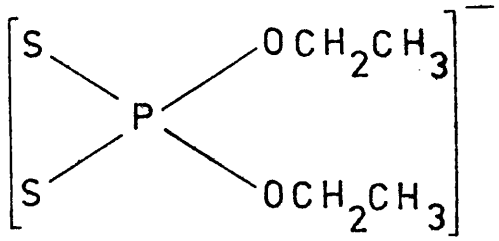
There have been many detailed reports in the literature of X-ray crystal structure determinations on metal dithiocarbamate compounds. For the $[Co(dtc)_3]$ complex the bond distances in the diethyldithiocarbamate ligand, calculated in terms of valence bond theory, agree very well with those observed,[59] assuming the following contribution of the resonance structures.



(a) (b) (c)

The mean value of the C-S bond distances in the $[Co(dtc)_3]$ complex is 1·704Å. In the $[Ni(S_2CNH_2)]$ complex the mean value of the C-S bond is 1·69Å.[60] These values are significantly shorter than the distance (1·76-1·78Å) which can be reasonably assumed for a C-S (sp^2) sigma bond. This again indicates that the canonical structures (a) and (b) are also important in describing the ground state of the ligand molecules.

Other metal dithio complexes include those containing dithiophosphate ligands e.g. (dtp)-diethyldithiophosphate.



Metal complexes of dithiophosphates were first reported in 1945 by Malatesta[61] who prepared $[Ni(dtp)_2]$. Since then a number of X-ray structures have been carried out e.g. $[Pb(dtp)_2]$[62], $[Co(dtp)_3]$[63] and $[Ni(dtp)_2]$.[64] The alkyl groups on the dithiophosphate ligand prevent the complexes from polymerising and the P-S bonds appear to have little double bond character.

Transition metal complexes having the ligands O,O′-dithiophosphate $(RO)_2PSS^-$ or P,P′-dithiophosphinate R_2PSS^- co-ordinated as bidentate ligands react with neutral ligands by stepwise cleavage of metal sulphur bonds to give products with unidentate co-ordinated or ionic dithio ligands. The nature of the neutral reactant influences the type of reaction.[56-58,65-70]

For platinum and palladium(II) diphenylphosphinodithioate complexes there appears to be an empirical i.r. method of distinguishing between bidentate, ionic and unidentate co-ordination of the Ph_2PSS^- group.[56] Bidentate-co-ordination seems to be characterised by two bands at 603, 570cm^{-1}; ionic, 650, 560cm^{-1}; and unidentate, 645 and 540cm^{-1}. Similar bands exist for the platinum and palladium(II) dimethylphosphinodithioates. These empirical methods for distinguishing between different types of R_2PSS^- co-ordination have been used to show the presence of bidentate and unidentate R_2PSS^- groups in ruthenium complexes.[68]

Until a few years ago iridium was hardly represented in metal dithiocarbamate chemistry,[71,72] and even then the complexes were mostly of iridium(III), e.g. $[Ir(dtp)_3]$[73], and an iridium dithiobenzoate prepared by Furlani and Luciani.[74] As far as iridium dithiocarbamate complexes in particular are concerned, the few reports which have appeared concern themselves mostly with analytical applications. Ravotsky et al.[75] did however study the formation and extraction of iridium as the diethyldithiocarbamate.

One of the first reports of iridium(I) dithiocarbamate complexes appeared in 1974, when de Croon and van Gaal[76] prepared a number of rhodium(I) and iridium(I) dialkyldithiocarbamate complexes containing cyclo-octene and 1,5-cyclo-octadiene. Shortly after this publication Faraone prepared dithiophosphato and dithiophosphinato complexes of rhodium(I)[77] and iridium(I)[78] Apart from these few results very little is known about the chemistry of iridium(I) dithio complexes. It was decided therefore that a study should be made, of the reactions of iridium(I) ditho complexes with electrophilic fluoro-olefins and acetylenes, in the hope that, perhaps, more olefin-acetylene complexes would be produced.

THE REACTIONS OF SOME IRIDIUM (I) - OLEFIN COMPLEXES WITH THE ELECTROPHILIC ACETYLENES HEXAFLUOROBUT-2-YNE AND DIMETHYLACETYLENEDICARBOXYLATE

2:1 INTRODUCTION.

On treating the complex $[RhCl(cod)]_2$ with hexafluorobut-2-yne in benzene solution at room temperature for 24 hours, the yellow air stable adduct $[RhCl(cod)(C_4F_6)\frac{1}{2}Et_2O]_n$ is formed,[79] (n=4). This complex readily reacts with sodium acetylacetonate in diethyl ether to give bright yellow crystals of the acetylacetonate adduct shown to be $[Rh(acac)(cod)(C_4F_6)H_2O]\frac{1}{2}H_2O$ from a single crystal X-ray structure determination. (Figure 2:3)

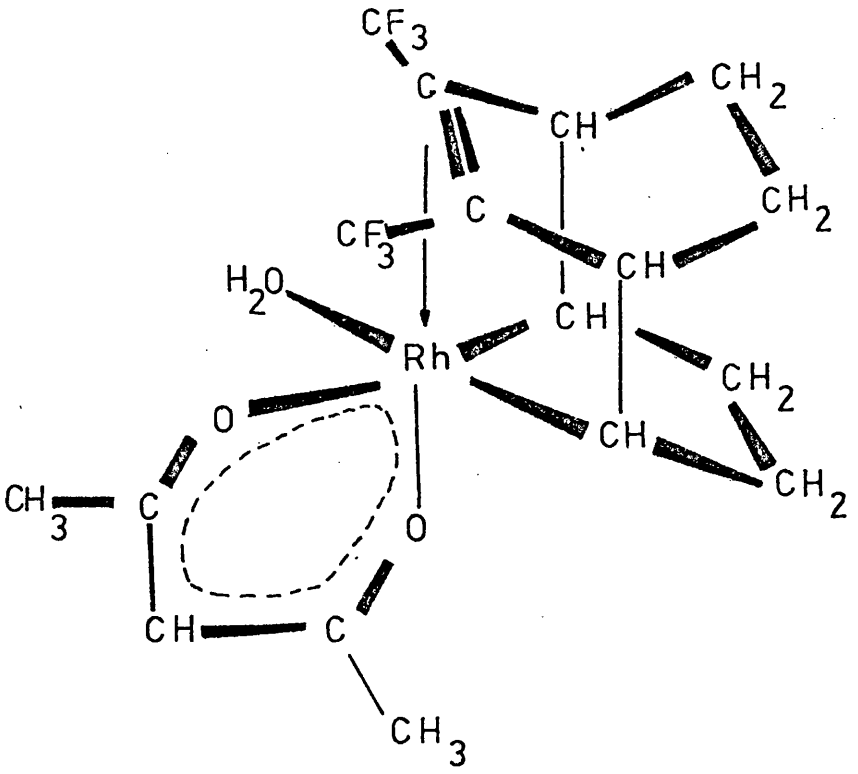


FIGURE 2:3

This structural determination shows quite clearly that the hexafluorobut-2-yne has added 1,4 across the co-ordinated cyclo-octadiene.

If the complex [Ir(acac)(cod)] is reacted at 60°C in diethyl ether with hexafluorobut-2-yne, then an alternative mode of addition is seen. In the complex so formed one mole of hexafluorobut-2-yne has inserted between the metal and one olefinic carbon atom to form an iridiacyclopentene ring, and a second molecule of the acetylene has added 1,4 to the iridium acetylacetonate ring. (Figure 2:4)

It was assumed that these addition reactions involved an intermediate metal acetylene complex and in the case of the reaction of hexafluorobut-2-yne with $[RhCl(cod)]_2$ the close proximity of the co-ordinated acetylene to cyclo-octadiene, held in the correct conformation by the metal, would then facilitate 1,4 addition to give the observed product.

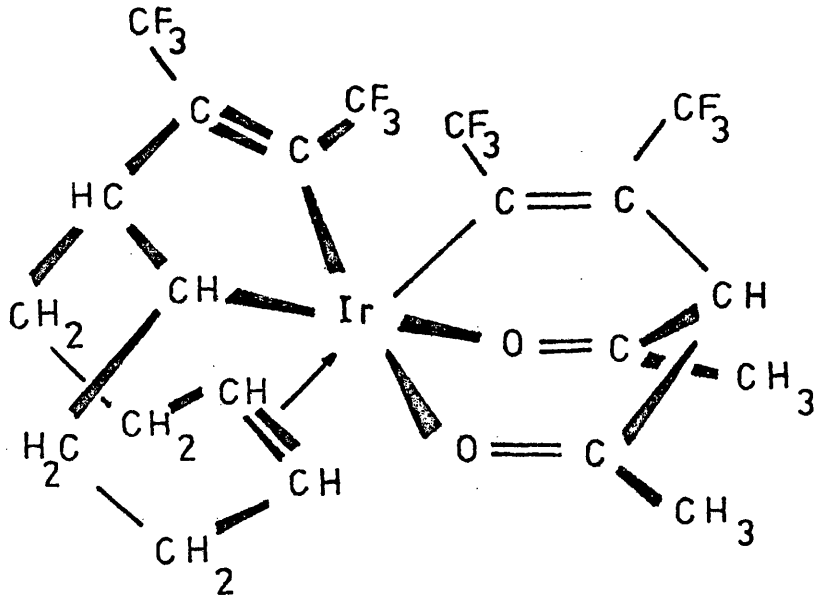


FIGURE 2:4

In the light of further investigations this hypothesis now seems less likely.

Following on from these results the next logical step seemed to be the reaction of hexafluorobut-2-yne with the complex $[IrCl(cod)]_2$.

2:2 RESULTS AND DISCUSSION

A. The reaction of hexafluorobut-2-yne with the complexes $[IrCl(cod)]_2$, $[Ir(bipy)(cod)]Cl$ and $[Ir(phen)(cod)]Cl$.

Hexafluorobut-2-yne reacts with $[IrCl(cod)]_2$ in diethyl ether or benzene solution at room temperature to give an orange air stable, microcrystalline product 2:1 which has been fully characterised by X-ray crystallographic, n.m.r. and i.r. spectroscopy. Crystals of complex 2:1 are sparingly soluble in benzene, dichloromethane and chloroform.

A single crystal X-ray study[80] has revealed that complex 2:1 has the structure shown in figure 2:5 Crystals of this complex $C_{24}H_{24}Cl_2F_{12}Ir_2$ (mol.wt.995.8), are monoclinic, space group $\underline{P2/n}$ with $\underline{a}$ = 9.58, $\underline{b}$=12.61, $\underline{c}$=12.59Å, β = 114.7°, $\underline{U}$=1376°Å^3, Z=2.

This determination shows that a molecule of hexafluorobut-2-yne has formed a rigidly bound π-complex with the metal, and the ^{19}F n.m.r. and i.r. spectra fit in with this structure. The ^{19}F n.m.r. spectrum exhibits two singlets at -6.45 and -11.45 p.p.m. (relative to internal benzotrifluoride) and the i.r. spectrum shows a strong absorption at 1860 cm^{-1}, ν(C≡C), and a weaker broad shoulder absorption at 1824cm^{-1}.

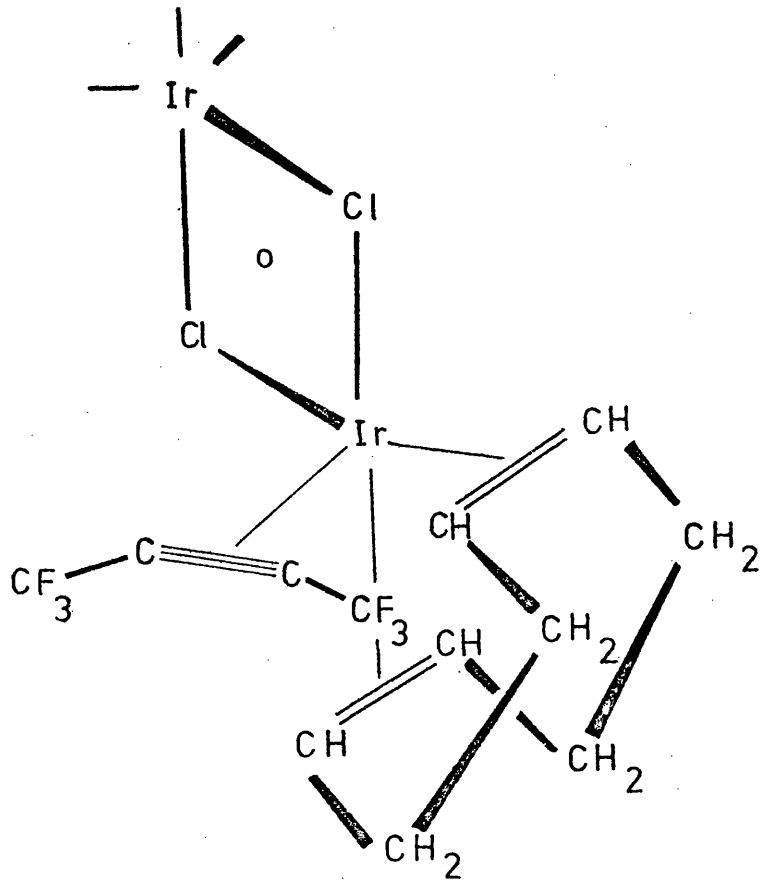


FIGURE 2:5

The dimer has a crystallographic centre of symmetry and the unique iridium atom exhibits approximate trigonal bipyramidal co-ordination. The detailed geometry of complex 2:1 is in excellent agreement with the conclusions of a theoretical treatment of penta co-ordination in transition metal complexes.[81] The acetylenic bond and one of the olefinic bonds of cyclo-octadiene lie approximately in the equatorial plane. The observed orientation of the cyclo-octadiene ligand is geometrically favoured and is similar to that in other complexes,[82] but there is no steric reason why the acetylene should lie in the equatorial plane. This orientation is however in agreement with the prediction [81] that, for trigonal

bipyramidal d^8 metal complexes the π interaction is strongest when the acceptor orbitals are in the equatorial plane (C_4F_6 is expected to be a good π- acceptor).

The axial Ir-Cl bond (2.438(3)Å) is shorter than the equatorial Ir-Cl bond (2.508(3)Å) following the predicted[81] greater strength of an axial σ bond for a d^8 metal complex. The distance Ir-M_1 and Ir-M_2 (where M_1 and M_2 are respectively the midpoints of the equatorial and axial olefinic bonds) are equal with values of 2.066 and 2.062 Å, because in the case of π-acceptor ligands the relative preferences for strong σ- or π-interactions for axial and equatorial sites oppose each other. However, the Ir-M_3 (where M_3 is the midpoint of the acetylenic bond) bond is shorter (2.017 Å) suggesting that the C_4F_6 is more strongly bound to the iridium than the olefin.

Complex 2:1 is the first definite example of a complex in which an alkene and an alkyne are co-ordinated to the same metal atom. The complex $[Ru_4(CO)_{11}C_8H_{10}]$ contains co-ordinated cyclo-octa-1-ene-5-yne but the acetylenic carbon atoms are bonded to four metal atoms.

Treatment of $[IrCl(cod)]_2$ with hexafluorobut-2-yne in diethyl ether at 90°C resulted in the formation of complex 2:2as a yellow air stable precipitate.

The infra-red spectrum of complex 2:2 shows that it does not contain a molecule of C_4F_6 π - bonded to the iridium. A strong absorption at 1611cm^{-1} indicates a vinylic system. The room temperature ^{19}F n.m.r. spectrum contains signals at -4.72 (m,3F) -10.31(q,1.5F) and -11.02p.p.m. (q,1.5F). At 73°C the ^{19}F.n.m.r. spectrum consists of

absorptions at -4.46(q,3F) and -10·97 p.p.m. (quin,3F).

As this spectral data does not allow a definite structure to be assigned to this complex a crystal was obtained from d_6 benzene solution, and a single crystal X-ray study carried out. This investigation revealed complex 2:2 to have the structure shown in figure 2:6

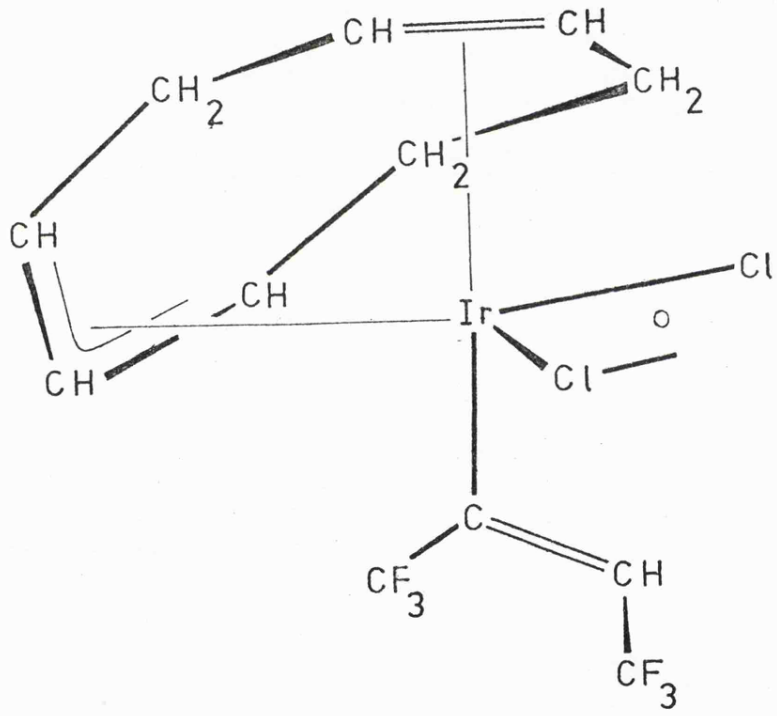


FIGURE 2:6

Crystals of 2:2, $IrC_{24}H_{24}Cl_2F_{12}2C_6D_6$ (mol.wt.1163·8) are monoclinic; space group $P2_1/n$ with a=10·97, b=17·96, c=11·63Å, β=127·4°, U=1820Å^3, Z=2.

The acetylene has abstracted a hydrogen atom, possibly from the cyclo-octadiene ligand, to form a cis-vinylic group σ -bonded to iridium. The original cyclo-octadiene, having lost a hydrogen atom, remains co-ordinated as the cyclo-octa-1,5-dienyl ligand. Mean bond lengths are Ir-Cl 2·467, Ir-C(allyl) 2·17, Ir-C(olefin) 2·36 and Ir-C(vinylic) 2·09Å.

Using the information obtained from the X-ray study it is now possible to interpret the ^{19}F n.m.r. data more precisely. At room temperature the spectrum appears as a multiplet and two quartets presumably because there is restricted rotation about the Ir-C σ – bond. The multiplet at -4·72p.p.m. (β-CF_3) arises from two overlapping quintets which coalesce to a single quintet as the temperature is raised and rotation about the Ir-C bond becomes faster. The quintet arises from the ^{1}H-^{19}F and ^{19}F-^{19}F coupling being of similar magnitude. The two quartets (α-CF_3) at -10·31 and -11·02 p.p.m. also become superimposed on raising the temperature.

The ^{19}Fn.m.r. spectrum in this case is very similar to that obtained for the complex $[MoHCp_2(\sigma$ -trans-$C(CF_3)=CHCF_3)]$[83] except that here the trans -^{19}F-^{19}F coupling is only 2Hz compared with11.28 Hz for the cis-complex 2:2. The spectra for the molybdenum complex is further complicated by the through space coupling of the hydride proton with the nearest three equivalent ^{19}F nuclei. (The nearest three equivalent ^{19}F nuclei can be either the α- or β-CF_3 group because the complex consists of conformational isomers -Figure 2:7).

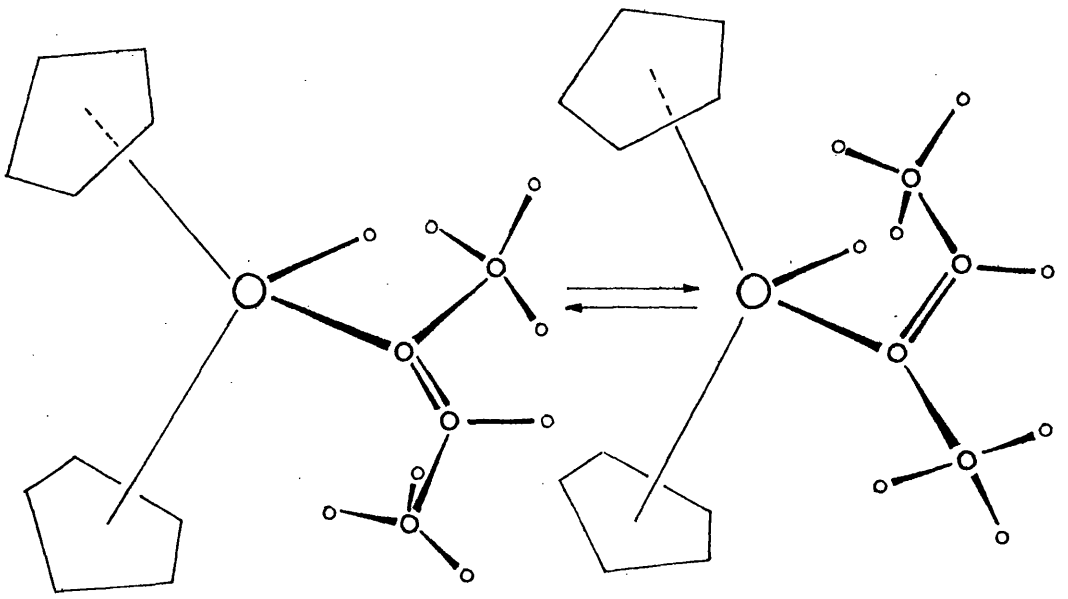


FIGURE 2:7

Further examples of this vinylic system have been obtained in the reactions of hexafluorobut-2-yne with [Ir(bipy)(cod)] Cl and [Ir(phen)(cod)] Cl.

Hexafluorobut-2-yne reacts over a period of six days with a suspension of [Ir(bipy)(cod)] Cl in diethyl ether to give a good yield of the orange microcrystalline complex 2:3 Elemental analysis suggests that one mole of C_4F_6 has reacted with one mole of [Ir(bipy)(cod)] Cl.

A strong absorption in the i.r. spectrum of complex 2:3 at 1600 cm^{-1} again seems to indicate that a vinylic group might be present. The ^{19}F n.m.r. spectrum of this complex is very similar to that obtained for complex 2:2 except that in this case there is no evidence of conformational isomerism at room temperature. The ^{19}F n.m.r.

spectrum consists of a quartet (α-CF_3) centred at -3·61 p.p.m, J(F-F)=11·11Hz and a quintet (β-CF_3) centred at -6·94p.p.m. J(F-F), = 12·36Hz. The quintet again being formed because the ^{1}H-^{19}F and ^{19}F-^{19}F coupling are of similar magnitude.

Under similar conditions a dark red microcrystalline adduct complex 2:4 can be isolated from the reaction of [Ir(phen)(cod)] Cl with hexafluorobut-2-yne. The spectroscopic data for this complex is very similar to that obtained for complexes 2:2 and 2:3 (Table 2:1) and so an analogous structure is proposed.

In addition to the signals shown in Table 2:1 complex 2:4 also had two other quartet absorptions in its ^{19}F n.m.r. spectrum. These appeared at -8·19 and -10·47 p.p.m. which together with an absorption in its i.r. spectrum at 1863cm^{-1}, could possible indicate the presence of an intermediate complex where the hexafluorobut-2-yne is π-bonded to the metal. It was not possible to isolate this intermediate, but if the mixture of products is removed from the n.m.r. solution, and the ^{19}F n.m.r. spectrum rerun six months later, no evidence of these quartets can be seen.

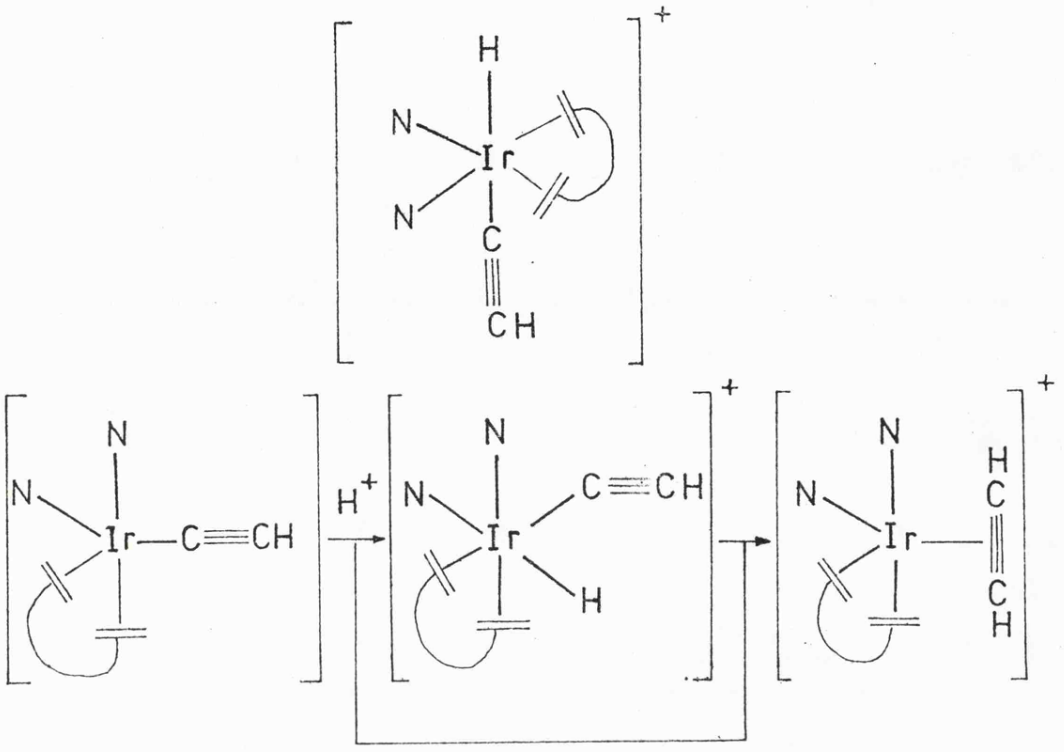
TABLE 2:1

Selected spectral absorptions for the vinylic complexes 2:2 - 2:4.

COMPOUND	^{19}F n.m.r. (p.p.m)	$\nu(C=C)cm^{-1}$
$[IrCl(CCF_3=CHCF_3)(C_8H_{11})]_2$	-4.46quin, -10.97q	1611
$[Ir(CCF_3=CHCF_3)(C_8H_{11})(bipy)]$	-3.61q, - 6.94quin	1600
$[Ir(CCF_3=CHCF_3)(C_8H_{11})(phen)]$	-3.29q, - 6.84quin	1602

There have been previous reports[84] of complexes with bidentate chelating N-containing ligands of the type $[Ir(chel)(L-L)]^+$ (chel=bipy, phen or substituted phen; L-L = cis, cis - cyclo-octa - 1,5-diene or norbornadiene) forming stable pentaco-ordinated adducts with acetylene, but no data has been published to substantiate these claims.

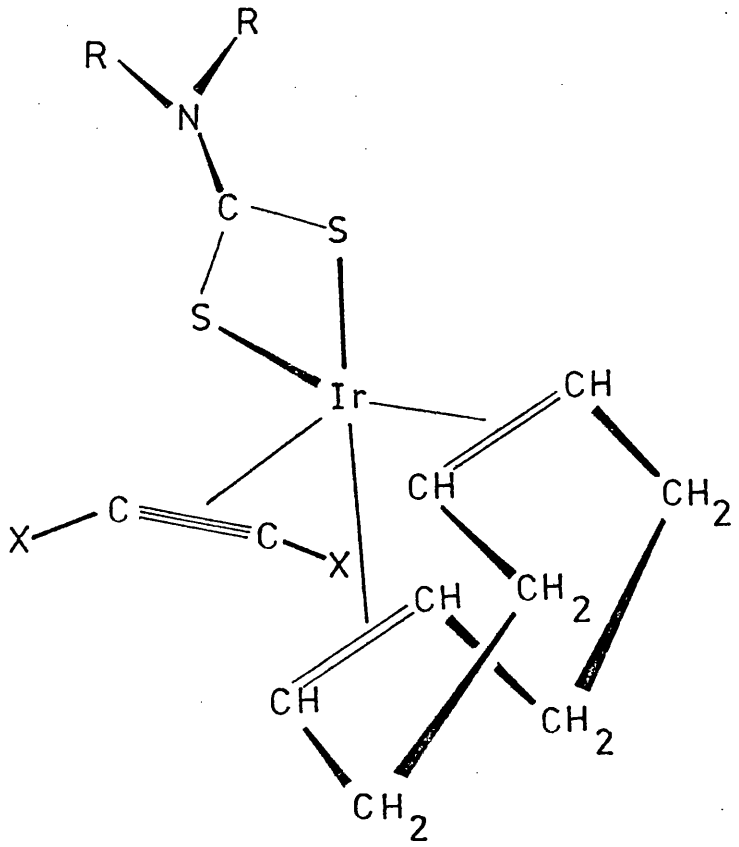
The same workers have also shown[85] that $[Ir(chel)(cod)]Cl$ reacts in methanol or ethanol with acetylene or phenylacetylene to give orange compounds of formula $[Ir(chel)(cod)(C\equiv CR)]$. These complexes reacted with dilute $HClO_4$ in methanol to regenerate the starting material, together with a trans-hydridic derivative, which is stable because it does not permit a reductive elimination of the acetylene. (Scheme 2:1).



SCHEME 2:1

It appears more probable therefore, from these results, that the complexes formed when hexafluorobut-2-yne is π-bonded to the metal, are intermediates in the formation of vinylic systems and not 1,4 addition products as has been previously stated.[79,80]

B. <u>The reaction of hexafluorobut-2-yne and dimethylacetylene dicarboxylate with the complexes [Ir(dithiocarbamate)(cod)] (dithiocarbamate = dmtc, dtc and dptc) and [Ir(dtp)(cod)]</u>



COMPLEX	R	X
2:6	CH_3	CF_3
2:7	C_2H_5	CF_3
2:8	phenyl	CF_3
2:10	C_2H_5	CO_2CH_3

The complexes [Ir(dithiocarbamate)(cod)], (dithiocarbamate=dmtc, dtc or dptc) readily react with hexafluorobut-2-yne in diethyl ether solution at room temperature to give the pale yellow air stable, crystalline complexes 2:6 - 2:8 respectively. Similarly the dithiophosphato complex [Ir(dtp)(cod)] reacts with C_4F_6 to give 2:9 in high yield. Dimethylacetylenedicarboxylate will also react with [Ir(dtc)(cod)] to form complex 2:10. In each of these compounds the acetylene is rigidly bound to the metal; the cyclo-octadiene remaining co-ordinated to the iridium as in complex 2:1.

These complexes are formulated as the illustrated olefin-acetylene compounds on the basis of microanalytical, X-ray crystallographic data and the similarity of their infra-red and ^{19}F n.m.r. spectra to those of the analogous compound, complex 2:1.

Infra-red spectra.

Selected i.r. absorptions of complexes 2:6 - 2:10 are given in table 2:2. A characteristic feature of the i.r. spectra of these compounds is a strong absorption in the 1845 - 1865 cm^{-1} region, assignable to the $\nu(C\equiv C)$ of the co-ordinated acetylene. In addition there is also a weaker shoulder on each of these absorptions. The splitting of this band has been noted previously in the infra-red spectra of nickel, palladium and platinum acetylene compounds.[86,87] No reasonable explanation can be given for this observation. Other characteristic bonds in the i.r. spectra of complexes 2:6, 2:7, 2:8 and 2:10 are those between 1500 and 1590 cm^{-1} which are typical of $\nu(C=N)$ values of co-ordinated dithiocarbamato groups.

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

The ^{19}F n.m.r. spectra of complexes 2:6 - 2:9 (Table 2:2) clearly show the presence of a rigidly bound hexafluorobut-2-yne ligand. Each spectrum consists of two quartet absorptions with J(F-F) values varying between 3.8 and 4.6 Hz.

The presence of ^{19}F - ^{19}F coupling in all the dithio complexes contrasts with complex 2:1 $[IrCl(cod)(C_4F_6)]_2$ which exhibits no discernible ^{19}F - ^{19}F coupling. The complexes $[IrX(CO)(PPh_3)_2(C_4F_6)]$[88,89] (X=F, Cl, Br, I) similarly exhibit no ^{19}F - ^{19}F coupling.

TABLE 2:2

Selected spectral absorptions for complexes containing an acetylenic system.

COMPOUND	^{19}F n.m.r.	J(F-F)Hz.	ν(C≡C)	ν(C=N)
$[IrCl(cod)(C_4F_6)]_2$	-11.54(s), - 6.45(s)		1860,1824	
$[Ir(dmtc)(cod)(C_4F_6)]$	-8.97(q), -8.00(q)	4.51	1851,1816	1527
$[Ir(dtc)(cod)(C_4F_6)]$	-7.79(q), -7.17(q)	4.15	1863,1815	1507
$[Ir(dptc)(cod)(C_4F_6)]$	-9.00(q), -8.29(q)	4.19	1860,1816	1589
$[Ir(dtp)(cod)(C_4F_6)]$	-8.41(q), -6.14(q)	3.84	1861,1817	
[Ir(dtc)(cod)(D.M.A.)]			1847	1506

^1H n.m.r. spectra

The data obtained for these complexes is given in Table 2:3. The information obtained fully supports the proposed structure of the compounds. The alkyl groups on the dithio ligand are inequivalent due to the hindered rotation of the NR_2 group about the C=N bond.[54]

TABLE 2:3

Selected ^1H n.m.r.[a] absorptions for complexes containing a dithio and an acetylenic system.

COMPOUND	Dithio Ligand: Pheryl	Dithio Ligand: CH_3	Dithio Ligand: CH_2	D.M.A.: CH_3	(cod)	Olefinic(2H)
$[Ir(dmtc)(cod)(C_4F_6)]$		2.97s,3.17s			1.0-3.5(10H)	4.59m,4.89m
$[Ir(dtc)(cod)(C_4F_6)]$		1.15t,1.28t J(H-H)=6.91Hz	3.47q,3.77w, J(H-H)=6.91Hz		2.00-4.00(10H)	4.60m,4.87m
$[Ir(dptc)(cod)(C_4F_6)]$	7.36s				1.52m(2H) 2.00-3.60(8H)	4.55m,4.90
$[Ir(dtp)(cod)(C_4F_6)]$		1.38t J(H-H)=7.13Hz	4.16m		2.20m(2H)2.60m(1H)[b] 2.84m(1H)3.42m(1H)	4.77m,5.08m
$[Ir(dtc)(cod)(DMA)]$		1.14t,1.26t J(H-H)=6.01Hz	3.38m	3.72s,3.85s	1.40-3.80(10H)	4.58m,4.82m

a) Measured in $CDCl_3$ solution at room temperature; chemical shifts (p.p.m) are relative to internal T.M.S.

b) There are absorptions due to the cod ligand beneath the signals at 1.38 and 4.16 p.p.m.

Structures and Bonding

Single crystal X-ray studies have been carried out on complexes 2:6 $[Ir(dmtc)(cod)(C_4F_6)]$ and 2:10 $[Ir(dtc)(cod)(D.M.A.)]$. The main reason for carrying out such a study on complex 2:6 was to determine whether there was a noticeable difference in the structure of this compound, compared to complex 2:1, that would account for the observed differences in their ^{19}F n.m.r. spectra.

Complexes 2:6 and 2:10 are based on a trigonal bipyramidally co-ordinated iridium with the acetylene lying in the equatorial plane. The iridium-carbon distances suggesting that the acetylene are more strongly bound to the metal than are the dienes. The olefinic bonds occupy one axial and one equatorial site in each compound. These positions of substitution are geometrically controlled because the bite at the metal atom is too large for the bidentate ligands, cyclo-octadiene and dimethyldithiocarbamate, to occupy two equatorial positions.

The acetylenic bond lengths of $[IrCl(cod)(C_4F_6)]_2$ and $[Ir(dmtc)(cod)(C_4F_6)]$, 1.23(2) and 1.27(2)Å respectively, compare favourably with values reported for the five co-ordinate Pt(II) complexes $[PtClMe(AsMe_3)(C_4F_6)]$[90] 1.292Å, and $[PtMeB(C_3H_3N_2)_3(C_4F_6)]$[91], 1.32Å. Similar acetylene geometry is found in the trigonal Pt(0) complex $[Pt(C_4F_6)(PPh_3)_2]$[92] and complex 2:10 (Figure 2:10) also has a similar acetylene geometry to the Pd(0) complex $[Pd(DMA)(PPh_3)_2]$[93].

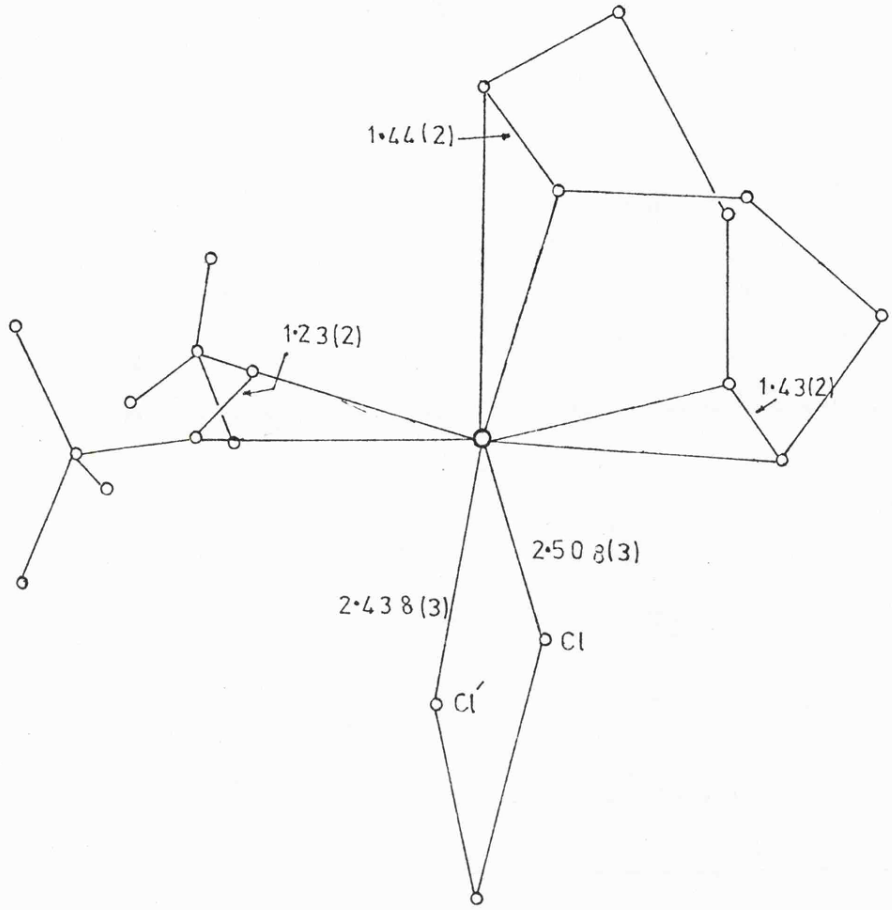


FIGURE 2:8

The molecular geometry of $[IrCl(cod)(C_4F_6)]_2$. Bond lengths in Å with e.s.d. of last figure in parentheses.

Crystals of complex 2:6 $IrC_{15}H_{18}F_6NS_2$ (mol.wt.582.6) are monoclinic, space group $\underline{P2_1/n}$ with $\underline{a}$ = 13.659, $\underline{b}$=11.501, $\underline{c}$ = 12.173Å, β =101.1°, $\underline{U}$ = 1876.3Å^3 and Z = 4.

The crystal structure (Figure 2.9) clearly shows that once again we have a C_4F_6 molecule rigidly bound to the metal via its pπ- pπ orbitals. The structure has not helped to explain the differences in the ^{19}F n.m.r. spectra of complexes 2:1 and 2:6. On the basis of this work the difference in the Ir - M_3 bond distances (where M_3 is the midpoint of

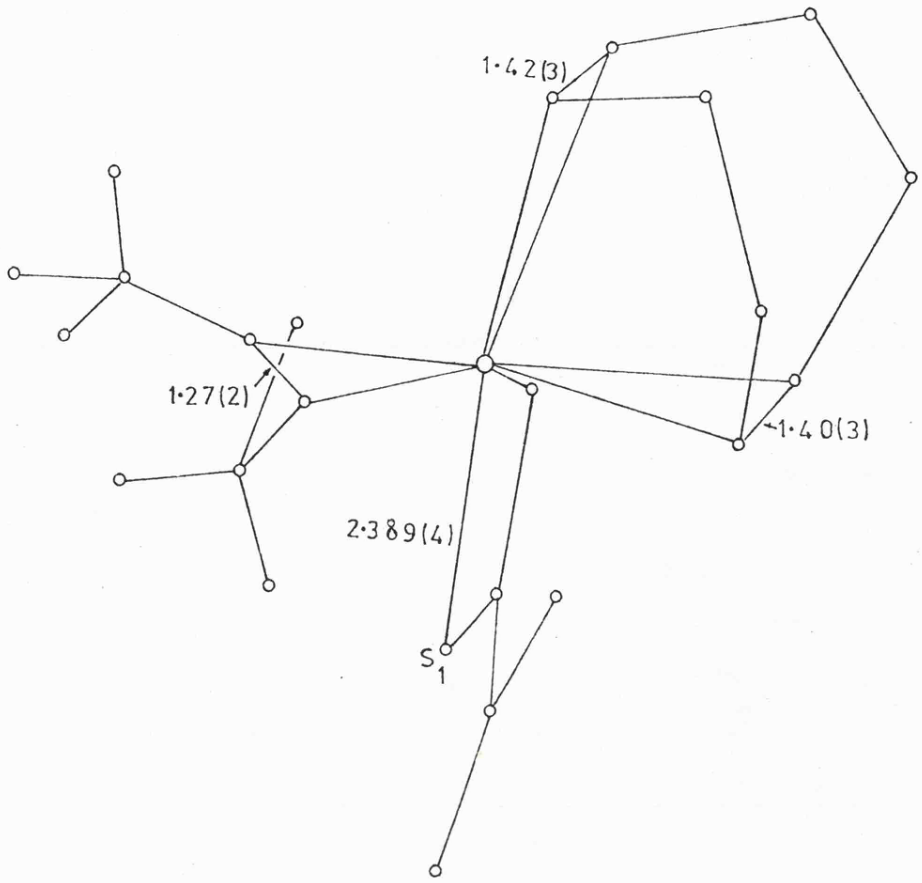


FIGURE 2:9

The molecular geometry of $[Ir(dmtc)(cod)(C_4F_6)]$. Bond lengths in Å with e.s.d. of last figure in parentheses.

the acetylenic bond) and the geometry about the acetylene, between complexes 2:1 and 2:6 are not significant.

The larger ^{19}F - ^{19}F coupling in complex 2:6 as compared to 2:1 may be related to suggestions that the axial Ir-M_2 bond (where M_2 is the midpoint of the axial olefin bond) is longer and the equatorial Ir-M_1 and Ir-M_3 bonds (where M_1 and M_3 are respectively the midpoints of the equatorial olefin and acetylene bonds) are shorter in complex

2:6 than in 2:1. Similarly in complex 2:10 the Ir-M_2 distance is longer, and the Ir-M_1 distance is shorter, than the corresponding distances in complex 2:1. A possible rationalisation for the shorter iridium-acetylene and iridium-olefin equatorial bonds in complex 2:6 is that since the covalent radius of sulphur is larger than chlorine, but the iridium-sulphur bonds are shorter than the iridium chlorine, the implication is that the dithio ligand acts as a better σ - donor than the dichloro bridge. In complex 2:6 therefore, the iridium has more σ - character, gained from the σ -donor dithio ligand. This being the case any bond normally strengthened by an increase in σ -donation (i.e. axial bonds[81]) will now be lengthened since the iridium already has enough σ -character, and any bond which is strengthened by an increase in π -acceptor ability (i.e. equatorial bonds) will be shortened. If the extent to which the acetylene accepts electrons into its π^* orbital is increased we expect to observe a lengthening of the C≡C bond and an increase in the C-C≡C angle. These differences are presumably smaller than experimental error.

In the three complexes the axial bond to the σ - donor ligand (Ir-Cl′ or Ir-S_1) is shorter than the equatorial bond and this follows the predicted[81] greater strength of an axial sigma bond for a d^8 metal complex.

Crystals of complex 2:10 $IrC_{20}H_{28}NOS_2$ (mol.wt.603.68) are triclinic, space group $\underline{P\bar{1}}$ with $\underline{a}$ = 12.693, $\underline{b}$ = 10.996, $\underline{c}$=8.364Å, α = 88.04°, β = 103.36°, $\underline{U}$ = 1102.98Å^3 and Z = 2. Here again we have the acetylene rigidly bound to the metal via its pπ -pπ orbitals, and the acetylenic C≡C bond length of 1.28Å is practically

identical to that found in the palladium complex $[Pd(DMA)(PPh_3)_2]$.[93] The Ir-M_3 distance is longer in complex 2:10 suggesting that the dimethylacetylenedicarboxylate ligand is less strongly bound to the iridium than is the C_4F_6 in complexes 2:1 and 2:6.

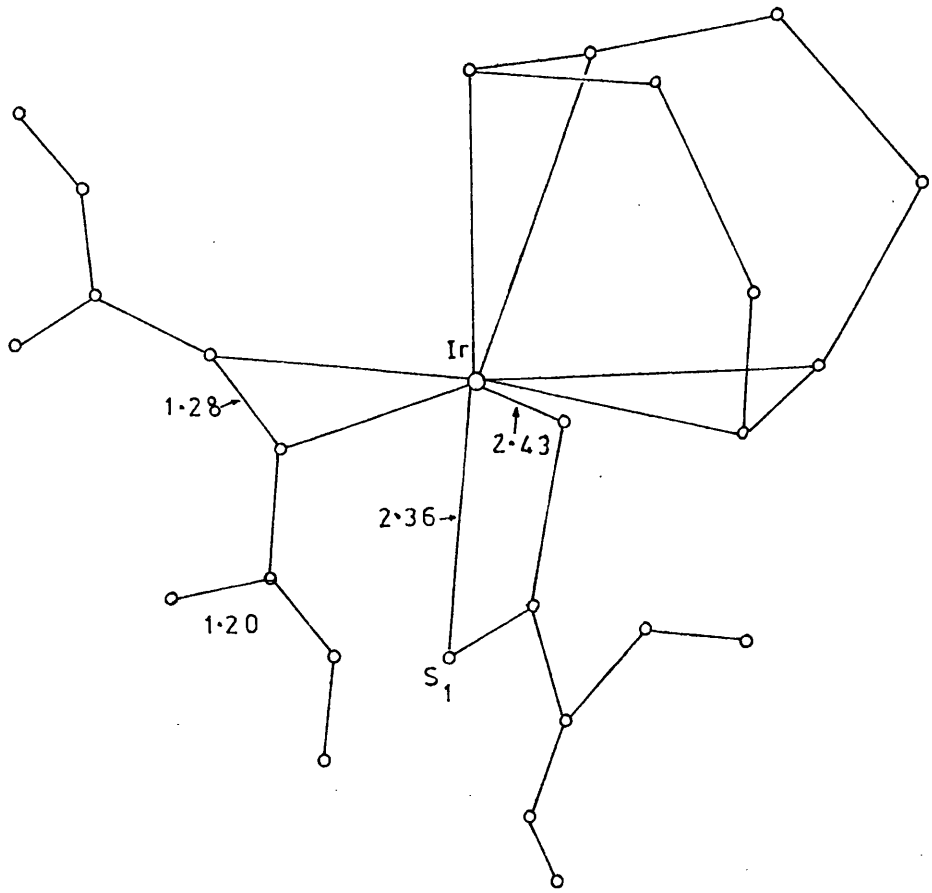


FIGURE 2:10.

The molecular geometry of $[Ir(dtc)(cod)(DMA)]$. Bond lengths in Å.

C. <u>The reaction of hexafluorobut-2-yne with complexes of the type $[Ir(dithiocarbamate)(C_8H_{14})_2]$ (dithiocarbamate = dmtc and dtc) or $[Ir(dtp)(C_8H_{14})_2]$</u>

The interaction of hexafluorobut-2-yne with the complexes $[Ir(dtc)(C_8H_{14})_2]$ $[Ir(dmtc)(C_8H_{14})_2]$ and $[Ir(dtp)(C_8H_{14})_2]$ in diethyl ether solution at room temperature results in the formation of complexes 2:11, 2:12, and 2:13 respectively. Microanalytical data shows that one mole of cyclo-octene has been displaced by two moles of hexafluorobut-2-yne.

The infra-red spectra of complexes 2:11 and 2:13 show bands at 1561 and 1610 and 1578 cm^{-1} respectively. Very little information can be obtained from the ^{19}F n.m.r. spectrum of either compound.

On the basis of the microanalytical and infra-red data complexes 2:11, 2:12 and 2:13 would seem to have one of two structures shown (Figure 2:11 (a) or (b)).

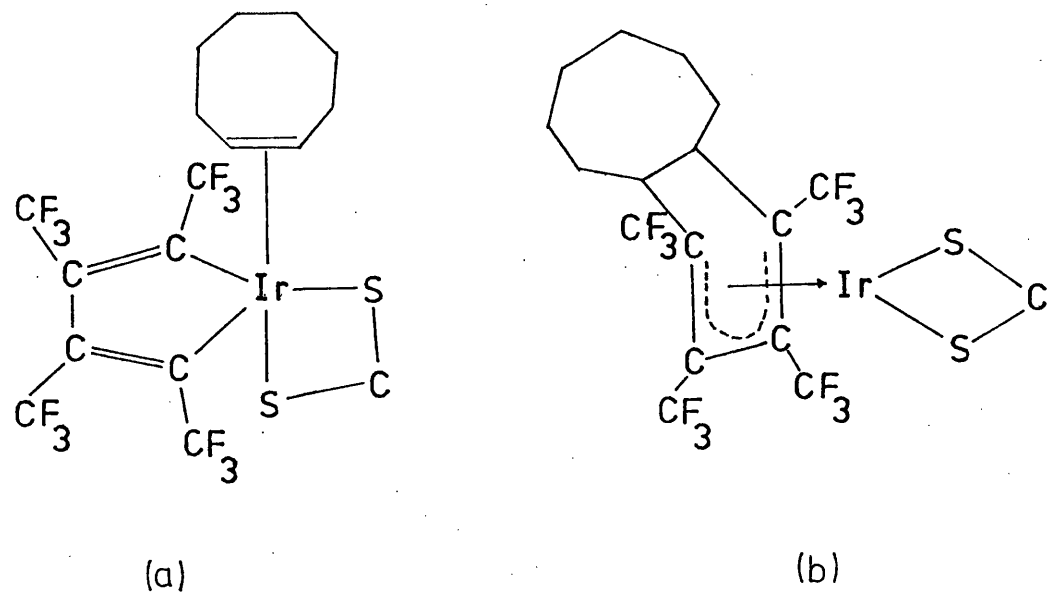


FIGURE 2:11

Compounds having structures similar to (a) and (b) have been prepared previously [94, 95, 96] Stone[95] has prepared the iridocyclopentadiene complex $[IrCl(CO)(CF_3C_2CF_3)_2(MePh_2P)]$ (Figure 2:12) The i.r. spectrum of this complex contains two weak bands at 1590 and 1570 cm^{-1} that are perhaps assignable to the double bonds in the iridocyclopentadiene ring.

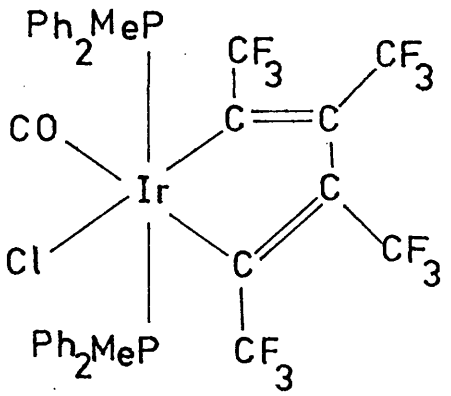
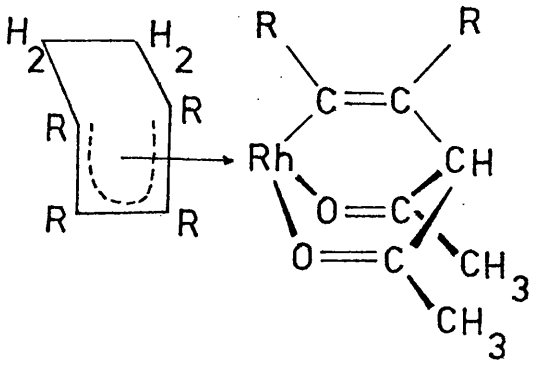


FIGURE 2:12.

Similar complexes have been prepared by Collman [94] who assigned two strong bands in the 1500 cm^{-1} region of the infra-red spectra as characteristic of the metallocyclopentadiene rings.

Rhodium complexes containing a system similar to that shown in Figure 2:11(b) have been prepared in this laboratory.[96] The reaction between acetylacetonatobis(ethylene)rhodium(I) and hexafluorobut-2-yne produces the complex shown in figure 2:13. As in the case of the iridium complexes one of the olefin ligands has been lost in the reaction and two molecules of hexafluorobut-2-yne have combined with the remaining olefin.



($R=CF_3$)

FIGURE 2:13

2:3 EXPERIMENTAL

Analytical, melting point and spectroscopic data are shown in this section. Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd, 41, High Street, Teddington, Middlesex, or by C.H.N. Analysis Ltd, Alpha House, South Wigston, Leicester. Melting points were recorded on a Reichart hot-stage apparatus and are uncorrected. Infra-red spectra were recorded as nujol mulls on a Perkin-Elmer 225 spectrophotometer using CsI plates and were calibrated using a polystyrene film. ^{1}H n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer operating at 100 M.Hz, chemical shifts (p.p.m) being reported relative to internal T.M.S. ^{19}F n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer operating at 94.1 M.Hz, chemical shifts (p.p.m) being reported relative to external benzotrifluoride.

All reactions carried out in a Carius tube were done in 15mls of the appropriate solvent. All other reactions were performed under an atmosphere of dry nitrogen using previously dried and degassed solvents. Reactions involving hexafluorobut-2-yne were carried out in thick walled pyrex tubes (150ml) which were made by Mr. D. Hopkins of this department.

Ligands and reagents.

Cyclo-octa-1,5-diene, and cyclo-octene were purchased from Koch-Light Laboratories Ltd, Hexafluorobut-2-yne was supplied by Bristol Organics Ltd and dimethylacetylenedicarboxylate by Eastman Kodak. Diethyldithiocarbamate was obtained from B.D.H. Ltd and

dimethyldithiocarbamate and diethyldithiophosphate from Aldrich Chemical Co.Inc. Diphenyldithiocarbamate was prepared as described in the literature.

Complexes.

$[IrCl(cod)]_2$,[97] $[IrCl(C_8H_{14})_2]_2$,[97] $[IrCl(C_4H_6)]_2$,[98] $[Ir(dtc)(cod)]$[76] $[Ir(dtc)(C_8H_{14})_2]$,[76] $[Ir(bipy)(cod)]Cl$,[84] $[Ir(phen)(cod)]Cl$[84] were prepared as described in the literature.

The following complexes were prepared via the general method outlined below: $[Ir(dmtc)(cod)]$, $[Ir(dptc)(cod)]$, $[Ir(dtp)(cod)]$, $[Ir(dmtc)(C_8H_{14})_2]$, $[Ir(dptc)(C_8H_{14})_2]$ and $[Ir(dtp)(C_8H_{14})_2]$

An excess of the appropriate dithiocarbamate or dithiophosphate was added to a suspension of the appropriate chloride dimer of the type $[Ir(olefin)_2Cl]_2$ in propanone. After stirring for 2 hours the propanone was evaporated to small volume and the product filtered off, washed with a little ethanol and then water. All the compounds made in this way gave the expected i.r. and ^1H n.m.r. spectra and their purity was confirmed by elemental analysis.

A. The reaction of hexafluorobut-2-yne with the complex $[IrCl(cod)]_2$

1. In diethyl ether at room temperature.

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of chloro(cyclo-octa -1,5-diene)iridium(I) dimer (0.50g, 0.75 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking overnight, the tube was opened and volatile material removed. The orange-yellow precipitate was filtered off and washed with diethyl ether to yield microcrystals of complex 2:1 $[IrCl(cod)(C_4F_6)]_2$ (0.52g, 70%) m.p. 142-144°C.

$C_{24}H_{24}Cl_2F_{12}Ir_2$	requires	C, 28.89;	H, 2.42;	F, 22.86%
	found	C, 28.56;	H, 2.49;	F, 21.72%

Infra-red: 1860 s, 1824 sh, 1335 s, 1310s, 1264 s, 1224 s, 1181 s, 1168 s, 1152 s, 1133 s, 1112 s, 1088 s, 1080 s, 1072 m, 1044 m, 1012 w, 1006 w, 976 w, 920 s, 910 s, 880 m, 848 m, 840 m, 821 m, 802 s, 788 m, 736 s, 705 w, 674 s, 670 s, 652 s, 602 w, 538 w, 527 w, 494 m, 473 m, 450 w, 350 m, 312 w, 278 s, 253 m.

^{19}F n.m.r. spectrum:

Observed in benzene solution: a singlet (3F) at - 6.45 p.p.m. and a singlet (3F) at - 11.54 p.p.m. (relative to benzotrifluoride).

2. <u>In diethyl ether at 90°C.</u>

An excess of hexafluorobut-2-yne (1.0ml.) was condensed (-196°) on to a suspension of chloro(cyclo-octa-1,5-diene)iridium(I) dimer (0.50g, 0.75m.mol.) in diethyl ether contained in a Carius tube (150ml.). After standing in an oven at 90°C for 2 days the tube was opened and volatile material removed. The yellow precipitate was filtered off and washed with diethyl ether to yield complex 2:2 $[IrCl(\sigma\text{-}\underline{cis}\text{-}CCF_3{=}CHCF_3)(C_8H_{11})]_2$(0.51g, 69%) m.p. 226-228° dec.

$C_{24}H_{24}Cl_2F_{12}Ir_2$	requires	C, 28.89;	H, 2.42;	F, 22.86%
	found	C, 28.94;	H, 2.67;	F, 23.28%

Infra-red: 1611 s, 1436 m, 1350 s, 1318 w, 1264 s, 1210 s, 1167 s, 1144 s, 1136 s, 1116 s, 1104 s, 1081 s, 1025 m, 967 w, 918 m, 874 m, 847 m, 833 m, 825 m, 796 m, 772 w, 700 w, 652 s, 626 s, 600 m, 501 m, 388 w, 333 m.

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

Observed in benzene solution: at room temperature a multiplet (3F) centred at - 4.72p.p.m. and two quartets (3F) centred at - 10.31 and -11.02 p.p.m. At 73°C the ^{19}F n.m.r. consists of a quintet (3F) centred at -4.46p.p.m. and a quartet (3F) centred at -10.97 p.p.m. J(F-F) = 11.28Hz (relative to internal benzotrifluoride).

This compound was too insoluble for a molecular weight determination.

3. In benzene at room temperature.

An excess of hexafluorobut-2-yne (0.7 ml) was condensed (-196°) on to a solution of chloro(cyclo-octa -1,5-diene)iridium(I) dimer (0.30g, 0.45m.mol) in benzene contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The orange solution was evaporated to small volume and 2 ml of diethyl ether added. The orange precipitate was filtered and washed with diethyl ether to yield complex 2:1 $[IrCl(cod)(C_4F_6)]_2$(0.30g 67%) m.p. 147-150°C.

$C_{24}H_{24}Cl_2F_{12}Ir_2$	requires	C, 28.89; H, 2.42;	F,22.86%
	found	C, 26.87; H, 2.41;	F,19.47%

Infra-red: 1861 s, 1823 sh, 1335 s, 1310s, 1264 s, 1224 s, 1181 s, 1168 s, 1152 s, 1133 s, 1112 s, 1088 s, 1080 s, 1072 s, 1044 m, 1012 w, 1006 w, 976 w, 920 m, 910 m, 880 w, 848 m, 840 m, 821 m, 802 s, 788 w, 736 s, 705 w, 674 s, 670 s, 652 s, 602 m, 538 w, 527 w, 494 m, 473 m, 450 w, 350 m, 312 w, 278 s, 253 m.

^{19}F n.m.r. spectrum:

Observed in benzene solution: two singlets, one at - 6.45 p.p.m (3F) and one at - 11.54 p.p.m. (3F) (relative to internal benzotrifluoride).

B. The reaction of hexafluorobut-2-yne with the complexes $[Ir(bipy)(cod)]Cl$ and $[Ir(phen)(cod)]Cl$

1. With $[Ir(bipy)(cod)]Cl$

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°)

on to a suspension of $[Ir(bipy)(cod)]Cl$ (0.20g, 0.40 m.mol.) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for six days an orange-red product was present. The tube was opened, volatile material removed, and the product filtered. The filtrate was evaporated to small volume to yield more orange precipitate. The product was washed with diethyl ether and ethanol to yield orange microcrystals of complex 2:3 $[Ir(\underline{cis}\text{-}CCF_3{=}CHCF_3)(C_8H_{11})(bipy)]Cl$ (0.22g, 82.9%) m.p. 246-248°C.

$C_{22}H_{22}ClF_6IrN_2$	requires	C, 40.22;	H, 3.38%
	found	C, 39.73;	H, 3.03%

Infra-red: 1670 m, 1600 s, 1578 w, 1360 s, 1347 s, 1332 s, 1313 m, 1284 s, 1273 s, 1247 m, 1229 m, 1165 s, 1141 s, 1122 s, 1110 m, sh, 1100 w, sh, 1080 m, 1052 w, 1030 m, 1005 v.w. 970 w, 874 m, 853 w, 802 v.w, 769 s, 751 w, 730 m, 720 w, sh, 681 w, 648 w, 601 m, 575 v.w. 531 w, 490 w, 370 w, 348 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a quartet (3F) centred at - 3.61p.p.m. with J(F-F) = 11.11Hz and a quintet (3F) centred at - 6.94 p.p.m. with J(F-F) = 12.36Hz (relative to external benzotrifluoride).

^{1}H.n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet at 0.65p.p.m, a singlet at 1.04 p.p.m. and broad multiplets at 1.32, 1.76, 4.60, 5.64, 7.28, 7.80, 7.96 and 9.28 p.p.m.

2. <u>With [Ir(phen)(cod)]Cl.</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196) on to a suspension of [Ir(phen)(cod)]Cl (0.50g, 0.97 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for seven weeks the tube was opened and volatile material removed. The product filtered and the precipitate washed with dichloromethane. Unreacted starting material remained in the filter. The dark red filtrate was evaporated to dryness and pumped overnight on a vacuum line to give dark red crystals of complex 2:4 [Ir(<u>cis</u>-CCF_3=$CHCF_3$)(C_8H_{11})(phen)]Cl (0.49g, 75%) m.p. 170-175°C.

$C_{24}H_{20}ClF_6IrN_2$	requires	C, 42 45;	H, 2.97%
	found	C, 40 67;	H, 2.50%

Infra-red: 1730 m, 1668 s, 1626 m,br, 1603 s, 1557 m, 1510 m, 1360 s, 1344 s, 1330 s, 1314 s, 1304 s, 1288 s, 1270 s, 1242 s,br 1208 s, br, 1192 s, 1176 s, 1144 s, br, 1105 s, 1083 s, 1056 m, 1033 m, 1000 m, 985 m, 947 m, 905 m, 879 m, 868 s, 800 m, 776 m, 724 s, 673 m, 649 m, 620 w, 610 w, 602 w, 546 w, 536 w, 520 m, 512 m, 496 m, 456 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a quartet (3F) centred at -3.29 p.p.m. with J(F-F) = 12.65Hz and a quintet (3F) at -6.84 p.p.m. with J(F-F) = 11.75Hz (relative to external benzofluoride.)

C. The reaction of $[Ir(cis = CCF_3{=}CHCF_3)(C_8H_{11})(bipy)]Cl$ with silver hexafluorophosphate.

Silver hexafluorophosphate was dissolved in ethanol (2mls) and added to a solution of $[Ir(CCF_3{=}CHCF_3)(C_8H_{11})(bipy)]Cl$ in dichloromethane (5ml.). The orange solution immediately turned yellow and silver chloride precipitated. The solution was filtered and the filtrate evaporated to give yellow crystals of complex 2:5 $[Ir(cis - CCF_3{=}CHCF_3)(C_8H_{11})(bipy)]PF_6$

D. The reaction of hexafluorobut-2-yne with $[IrCl(C_8H_{14})_2]_2$ and $[IrCl(C_4H_6)]_2$

1. With chlorobis(cyclo-octene)iridium(I)dimer.

An excess of hexafluorobut-2-yne (1.0ml.) was condensed (-196°) on to a suspension of chlorobis(cyclo-octene)iridium(I)dimer (0.40g,0.22 m.mol.) in diethyl ether contained in a Carius tube (150ml.). After shaking at room temperature for 24 hours the tube was opened and the brown solution filtered. The filtrate was evaporated to small volume but attempts to obtain a crystalline product resulted in only a brown intractable oil being produced.

2. With chloro(buta-1,3-diene)iridium(I)dimer

An excess of hexafluorobut-2-yne (1.0ml.) was condensed (-196°) on to a suspension of chloro(buta-1,3-diene)iridium(I)dimer (0.3g,0.35m.mol.) in diethyl ether contained in a Carius tube, (150ml.). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The brown solution was filtered and the

filtrate evaporated to small volume but attempts to obtain a crystalline produce resulted in only a brown intractable oil being produced.

E. The reaction of hexafluorobut-2-yne with some dithiocarbamato and dithiophosphatoalkene complexes of iridium(I).

1. With dimethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I).

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of dimethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I) (0.20g, 0.47 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for one hour the tube was opened and volatile material removed. The solution was filtered and the filtrate evaporated almost to dryness. On addition of three drops of light petroleum (40-60°C) large pale yellow crystals formed. These were filtered, washed with light petroleum and identified as complex 2:6 $[Ir(dmtc)(cod)(C_4F_6)]$ (0.24g, 87%) m.p. 82 -84°C.

$C_{15}H_{18}F_6IrNS_2$	requires	C,30.87;	H, 3.11%
	found	C,31.21;	H, 3.17%

Infra-red: 1851 s, 1816 sh, 1529 m, br, 1336 w, 1264 s, 1248 m, 1224 s, 1120 s,br, 1108 s, 1028 w, 992 w, 908 w, 848 w, 800 m, 678 m, 672 m, 652 m, 601 w, 584 w, 557 w, 534 w, 495 w, 444 w, 424 w.

^{19}F n.m.r. spectrum:

Observed in d_6 acetone solution: two quartets at -8.00 and -8.97 p.p.m (3F each) J(F-F) = 4.51Hz (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum.

Observed in $CDCl_3$ solution: two singlets at 2.97(3H) and 3.17(3H) p.p.m. There are also two multiplets at 4.59(1H) and 4.89(1H) p.p.m. arising from the olefinic protons of the cyclo-octadiene ligand. The other 10 protons from this ligand occur as broad absorptions in the region of 1.0 and 3.5 p.p.m.

2. <u>With diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I)</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I) (0.20g, 0.44m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for one hour the tube was opened and volatile material removed. The solution was filtered and the filtrate evaporated to a small volume and large pale yellow crystals formed on standing. These were filtered, washed with light petroleum ($<40°$) and identified as complex 2:7;[Ir(dtc)(cod)(C_4F_6) (0.25g, 92%) m.p 80-82°C.

$C_{17}H_{22}F_6IrNS_2$	requires	C, 33.38;	H, 3.63%
	found	C, 33.36;	H, 3.65%

Infra-red: 1863 s, 1815 sh, 1513 s, 1507 s, 1359 s, 1335 s, 1303 s, 1281 s, 1267 s, 1249 s, 1229 s, 1213 s, 1179 m, 1167 s, 1143 s, 1121 s, 1107 s, 1081 s, 1029 w, 1008 m, 1000 m, 977 w, 925 s, 911 s, 905 s, 873 w, 857 s, 843 m, 799 s, 787 s, 731 m, 711 w, 675 s, 653 s, 605 w, 593 w, 583 m, 539 w, 527 w, 495 m, 471 m, 459 w.

^{19}F n.m.r. spectrum:

Observed in d_6 acetone solution: two quartets centred at - 7.71(3F) and - 7.79 p.p.m. (relative to external benzotrifluoride)

^{1}H.n.m.r. spectrum:

Observed in $CDCl_3$ solution: two overlapping triplets centred at 1.15 p.p.m (3H) and 1.28 p.p.m. J(H-H)=6.9lHz. Two quartets centred at 3.47(2H) and 3.77 p.p.m. J(H-H) = 6.9lHz. There is a multiplet centred at 1.70 p.p.m. (2H) and another eight protons from the cyclo-octadiene ligand are in a broad band between 2.00 and 4.00 p.p.m. There are also two multiplets at 4.60(1H) and 4.87 p.p.m. (1H).

3. <u>With diphenyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I)</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of diphenyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I) (0.30g, 0.55 m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 1 hour the tube was opened and volatile material removed. The solution was filtered and the filtrate evaporated to small volume to yield yellow microcrystals of complex 2:8[Ir(dptc)(cod)(C_4F_6)] (0.36g 92.5%) m.p. 189-191°dec.

$C_{25}H_{22}F_6IrNS_2$ requires C,42.43; H,3.13%

found C,42.96; H,3.34%

Infra-red: 1860 s, 1816 sh, 1589 m, 1350 m, 1310 m, 1265 s, 1248 s, 1224 s, 1162 m, 1154 s, 1126 s, 1102 s, 1078 m, 1058 m, 1000 m, 980 w, 905 m, 883 w, 846 m, 798 m, 790 m, 761 s, 732 w, 704 s, 696 s, 679 s, 662 m, 654 m, 622 s, 531 m, 496 m, 472 w, 442 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: two quartets centred at -8.29(3F) and - 9.00(3F) p.p.m. J(F-F) = 4.19Hz (relative to external benzotrifluoride)

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a broad multiplet at 1.52 p.p.m. (2H) a very broad multiplet between 3.00 and 3.60 p.p.m (8H) and two multiplets centred at 4.55(1H) and 4.90 p.p.m(1H). The phenyl groups appear as a singlet at 7.36 p.p.m (10H).

4. <u>With diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of diethyldithiophosphato(cyclo-octa-1,5-diene) iridium(I)(0.50g,1.03m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for three days the tube was opened and volatile material removed. The solution was filtered and the filtrate evaporated to small volume. No crystalline solid

could be obtained from this reaction, only a yellow oil. This was identified as complex 2:9 $[Ir(dtp)(cod)(C_4F_6)]$ (0.60g,90%) from its infra-red and n.m.r. spectra.

Infra-red: 1861 s, 1817 m, br, 1474 m, 1452 m, 1442 m, 1434 m, 1389 m, 1334 m, 1263 s, 1155 s, br, 1119 s, 1043 m, 1016 m, 1000 m, 968 s, 962 s, 924 w, 907 m, 874 w, 850 w, 844 m, 796 s, 784 s, 730 m, 673 s, 652 s, 552 m, 540 m, 492 m, 468 w, 452 w.

^{19}F n.m.r. spectrum:

Observed in diethyl ether solution: two quartets centred at -6.14(3F) and -8.41p.p.m(3F) J(F-F)=3.84Hz (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a triplet centred at 1.38p.p.m. (6H), J(H-H)=7.13Hz. There are also absorptions due to the cyclo-octadiene ligand beneath this signal. Multiplets at 2.20 (2H), 2.60 (1H), 2.84(1H), 3.42 (1H) and 3.65 p.p.m. (1H). The CH_2 groups of the dithiophosphato ligand appear at 4.16 p.p.m. (4H) as a multiplet and there are also two other multiplets at 4.77(1H) and 5.08p.p.m. (1H).

5. <u>With diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I) at 90°C.</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°)

on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I) (0.20g, 0.44m. moles.) in diethyl ether contained in a Carius tube (150ml). After standing in an oven at 90°C for 18 hours the tube was opened and volatile material removed. The solution was filtered and the filtrate evaporated to small volume to produce pale yellow crystals of complex 2:7[Ir(dtc)(cod)(C_4F_6)] (0.24g 89%) identified from its melting point, infra-red and ^{19}F n.m.r. spectra.

F. <u>The reaction of diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I) with dimethylacetylenedicarboxylate.</u>

Dimethylacetylenedicarboxylate (0.5ml.) was added with stirring to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I) (0.3g, 0.67m.mol.) in diethyl ether. After stirring, at room temperature, for one hour the yellow solution was evaporated to a yellow oil which was pumped under vacuum overnight. Two drops of diethyl ether and ten drops of light petroleum (40-60°) caused lemon yellow crystals to form. These were identified as complex 2:10[Ir(dtc)(cod)(D.M.A.)](0.31g, 77 %) m.p. 79-81°C.

$C_{20}H_{28}IrNO_4S_2$	requires	C,39.80;	H, 4.68%
	found	C,38.79;	H, 4.80%

Infra-red: 1938 w, br, 1847 s, br, 1700 sh, 1684 s, 1666 s, br, 1650 sh, 1632 sh, 1506 sh, 1490 s, 1352 s, 1322 s, 1300 s, 1264 s, 1240 s, 1226 s, 1210 s, 1184 s, 1170 s, 1151 s, 1094 w, 1066 s, 1040s, 1000 s, 980 m, 916 m, 902 s, 876 w, 856 s, 848 s, 832 m, 784 s, 776 s, 710 m, 648 s, 575 m, 486 m, 468 m.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a triplet (3H) centred at 1.14 p.p.m. J(H-H)=6.01Hz, and a triplet (3H) centred at 1.26 p.p.m. J(H-H)=6.01Hz. A multiplet centred at 3.40 p.p.m. (4H) J(H-H)=6.00Hz and two singlets at 3.72 p.p.m. (3H) and 3.86 p.p.m. (3H). There are also 10H of the cod ligand between 1.40 and 3.80 p.p.m, plus a multiplet (1H) at 4.58 p.p.m and another (1H) centred at 4.82 p.p.m.

The reaction of $[IrCl(cod)(C_4F_6)]_2$ with sodium diethyldithiocarbamate.

An excess of sodium diethyldithiocarbamate (0.5g) was added, with stirring to a suspension of $IrCl(cod)(C_4F_6)_2$ (0.20g, 0.20m.mol) in diethyl ether (25ml). After stirring at room temperature for 2 hours the solution was filtered and the filtrate evaporated to small volume whereupon crystals of complex 2:7 $[Ir(dtc)(cod)(C_4F_6)]$(0.19g,77.0%) formed. These were identified from their melting point and ^{19}F n.m.r. spectrum.

C. The reaction of hexafluorobut-2-yne with complexes of the type $[Ir(dithiocarbamate)(C_8H_{14})_2]$ (dithiocarbamate=dmtc and dtc) or $[Ir(dtp)(C_8H_{14})_2]$

1. With diethyldithiocarbamatobis(cyclo-octene)iridium(I).

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of diethyldithiocarbamatobis(cyclo-octene)iridium(I) (0.30g, 0.54 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The brown suspension was filtered and the filtrate evaporated to small volume. The addition of light petroleum (40-60°) resulted in a further crop of the brown precipitate. This was filtered, washed with diethyl ether and identified as complex 2:11 $[Ir(dtc)(CF_3C_2CF_3)_2(C_8H_{14})]$ (0.28g, 67 %) m.p. > 270° dec.

$C_{21}H_{24}F_{12}IrNS_2$	requires	C, 32.51; H, 3.11; N, 1.93%
	found	C, 32.08; H, 3.09; N, 1.80%

Infra-red: 1561 m, 1529 s, 1575 s, 1505 m, 1363 m, 1351 m, 1319 s, 1227 s, 1259 s, 1219 s, 1191 s, 1167 s, 1143 s, 1113 s, 1083 s, 1009 w, 995 w, 985 m, 915 m, 907 m, 873 w, 843 w, 833 w, 805 w, 783 w, 743 m, 725 s, 693 w, 655 s, 647 s, 603 w, 559 w, 527 m, 513 w, 483 w.

^{19}F n.m.r. spectrum:

Observed in propanone solution: a multiplet centred at -8.73 p.p.m. (relative to external benzotrifluoride).

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet (6H) centred at 1.24 p.p.m. and a multiplet (4H) centred at 3.40 p.p.m. The absorptions due to the cyclo-octene ligand are also visible between 1.30 and 2.20 p.p.m and between 3.40 and 3.90 p.p.m.

2. <u>With dimethyldithiocarbamatobis(cyclo-octene)iridium(I).</u>

An excess of hexafluorobut-2-yne(1.0ml) was condensed (-196°) on to a suspension of dimethyldithiocarbamatobis(cyclo-octene)iridium(I) (0.30g,0.56m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The brown suspension was filtered and the filtrate evaporated to small volume. The addition of light petroleum (40-60°) resulted in a further crop of the brown/orange precipitate. This was filtered, washed with diethyl ether and identified as complex 2:12 $[Ir(dmtc)(CF_3C_2CF_3)_2(C_8H_{14})]$ (0.26g, 66%) m.p. > 270°dec.

3. <u>With diethyldithiophosphatobis(cyclo-octene)iridium(I).</u>

An excess of hexafluorobut-2-yne (1.0ml) was condensed (-196°) on to a suspension of diethyldithiophosphatobis(cyclo-octene)iridium(I) (0.25g, 0.51m.mol) in eithyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The orange-red solution was filtered and the

filtrate evaporated to small volume. Orange crystals formed on addition of ethanol (1.0ml). These were filtered and identified as complex 2:13 $[Ir(dtp)(CF_3C_2CF_3)_2(C_8H_{14})]$ (0.31g, 87%) m.p. 138-140°C.

$C_{20}H_{24}F_{12}IrO_2PS_2$	requires	C,29.56;	H,2.97;	P,3.81%
	found	C,29.21;	H,2.93;	P,5.10%

Infra-red: 1610 w, 1578 s, 1522 br,m, 1384 s, 1370 m, 1330 s, 1260 s, 1247 s, 1230 s, 1218 s, 1200 s, 1155 s, 1111 s, 1050 s, 1032 s, 1013 s, 973 s, 950 s, 913 m, 878 m, 836 m, 809 m, 790 m, 769 m, 723 s, 714 w, 692 w, 655 s, 645 s.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet (6F) centred at -8.10 p.p.m and a multiplet (6F) centred at -12.52 p.p.m. (relative to external benzotrifluoride).

No ^1H n.m.r. spectrum obtainable.

CHAPTER THREE

THE PREPARATION AND ^{19}F n.m.r. SPECTRA OF SOME FLUORO-OLEFIN COMPLEXES OF IRIDIUM(I)

3:1 INTRODUCTION.

Within the area of organometallic chemistry there have, in the past, been many studies of metal-olefin complexes. These complexes are of interest since many are thought to be intermediates in catalytic reactions, and much study has been concentrated on the description of this stable metal-olefin bond. It was originally described by Dewar, Chatt and Duncanson[99,100] as a bond involving the donation of an electron pair from filled d orbitals of the metal atom, (a π - bond) in addition to the normal σ - bond formed by a filled 2p π orbital of the olefin donating charge to an empty hybrid orbital on the metal. There are many known cases where the olefin freely rotates about the metal -olefin bond. This occurs when little back bonding takes place between the metal and the olefin.

Cramer was able to show[101] that two possible modes of rotation (Figure 3:1 (a) and (b)) satisfy the variable temperature n.m.r. data obtained on olefin complexes.

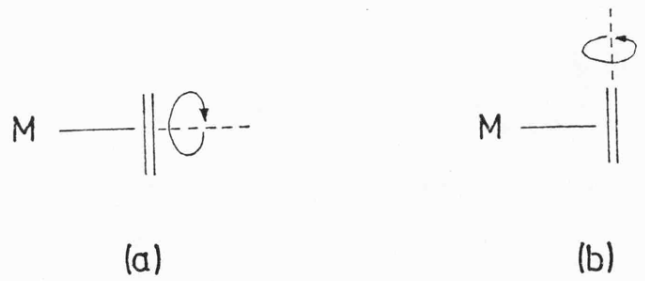


FIGURE 3:1

Johnson has since demonstrated [102] using the olefin complex $[Os(CO)NO(C_2H_4)(PPh_3)_2]PF_6$ that the olefin rotates about the metal along the axis shown in Figure 3:1(a).

In the complex $[(\pi-C_5H_5)Rh(C_2H_4)_2]$ [103] the ^1H n.m.r. spectrum of the ethylene ligands consists of two broad featureless peaks centred at approximately 1:23 and 3.12 p.p.m. These arise from pairs of nonequivalent co-ordinated ethylene protons which are undergoing rotation at an intermediate rate on the n.m.r. time scale. At -25^oC the fine structure in these peaks can be seen because at this temperature the olefin rotation is slow. Similarly in the complex $[(\pi-C_5H_5)Rh(C_2F_4)(C_2H_4)]$ [103] the ethylene ligand rotates quite freely about the metal centre. The complexes $[Pt(acac)Cl(olefin)]$[104] (olefin = trans-but-2-ene, propylene, cis-but-2-ene, ethylene or tetramethylethylene) also show olefin rotation about the metal olefin bond. The ^1H n.m.r. spectrum of the ethylene complex, run at 35^oC, consists of one line with ^{195}Pt satellites. When the solution is cooled down this signal becomes more complicated as the rotation of the ethylene slows down.

In the compounds mentioned if the ethylene is replaced by an olefin containing electron withdrawing groups e.g. $CF_2=CF_2$ then back bonding between the olefin and the metal is increased. This strengthens the metal olefin bond and it is then much more difficult for rotation of the olefin to take place. ^{19}F n.m.r. studies on the complex $[(\pi-C_5H_5)Rh(C_2F_4)(C_2H_4)]$[103] have shown that no rotation of the C_2F_4 molecule occurs.

Kaneshima et al[105] have prepared a series of new d^8 transition metal cyano-olefin complexes containing isocyanide ligands. They have shown that the dynamic behaviour of the complexes is dependant on the nature of the other ligands bonded to the metal centre. In some instances the cyano-olefin is undergoing hindered rotation about the co-ordination bond. The complex $[Rh(acac)(RNC)_2(TCNE)]$ $[R={}^tBu$, p $CH_3OC_6H_4$, p $CH_3C_6H_4$, p ClC_6H_4, $2,4,6(CH_3)_3C_6H_2]$ gives a temperature dependant ^1H n.m.r. spectrum which can be interpreted in terms of the tetracyanoethylene rotating about the Rh-TCNE bond.

The complexes $[Rh(RNC)_4(TCNE)]^+X^-$[106] where $X=ClO_4^-$, and $R=$p $CH_3OC_6H_4$ or o and p $CH_3C_6H_5$; $X=BPh_4$, $R=CH_3$; give temperature dependant ^1H n.m.r. spectra which may be interpreted in terms of the cyano-olefin rotation in time averaged square-pyramidal configurations. When two isocyanide groups are replaced by two triphenylphosphine ligands there is a change in the bonding behaviour of the tetracyanoethylene toward the rhodium atom from non-rigid to rigid. This can be explained by the fact that tertiary phosphines have more σ-donor and less π acceptor capacity as compared with the isocyanide ligands. An increase in electron density of the rhodium in the tertiary phosphine complexes will thus cause stronger back bonding from the metal to the tetracyanoethylene ligand which will consequently hinder rotation of the olefin system.

The relative importance therefore of the σ and π components can be shown to be influenced by 1) the nature of the olefin and 2) the nature of the other ligands present.[107] Similarly the fact that olefins freely rotate about platinum in the oxidation state (II) but not when it is in the oxidation state (0) also shows that the relative importance of the σ and π components is influenced by the oxidation state of the metal.

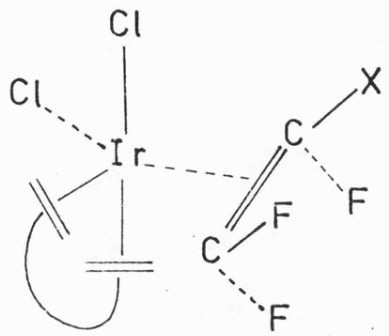
Tetrafluoroethylene is known to form 1:1 adducts with complexes of the type trans - $[IrX(CO)(PR_3)_2]$[88,89,95] (X=Cl,F), the stability of the adducts being dependant upon the nature of the phosphine ligand and the halogen. If the fluoro-olefin is regarded as a unidentate ligand then these adducts may be described as five co-ordinate complexes of iridium(I) and can be contrasted with the four co-ordinate tetrafluoroethylene complexes $[IrCl(C_2F_4)(PR_3)_2]$ and $[IrCl(C_2H_4)(C_2F_4)]_2$ which have been shown to be co-ordinately unsaturated. The observation that hexafluorobut-2-yne readily reacts with chloro(cyclo-octa-1,5-diene)iridium(I)dimer to give a dimeric trigonal bipyramidal complex of iridium(I), complex 2:1, prompted the investigation of the reactions of fluoro-olefins with $[IrCl(cod)]_2$ and other cyclo-octa-1,5-diene iridium(I) complexes.

3:2 RESULTS AND DISCUSSIONS.

The complex $[IrCl(cod)(C_2F_4)]_2$[108] has been prepared previously by the action of cyclo-octa-diene on the cyclo-octene complex $[IrCl(C_8H_{14})(C_2F_4)]_n$. The reaction of complex 3:1 $[IrCl(cod)(C_2F_4)]_2$ with sodium diethyldithiocarbamate produces the iridium(I) olefin complex 3:5 $[Ir(dtc)(cod)(C_2F_4)]$.

The fluoro-olefins, tetrafluoroethylene, hexafluoropropene, chlorotrifluoroethylene, and bromotrifluoroethylene readily react with $[IrCl(cod)]_2$ to form the stable insoluble complexes 3:1 - 3:4 respectively. (Figure 3:2). Their structures may be described as trigonal bipyramidal, as in the analogous complex $[IrCl(cod)(C_4F_6)]_2$, with a unidentate fluoro-olefin ligand. Again, if this description

is used, it seems likely that one of the olefinic bonds lies in the equatorial plane and one in the axial plane, with the fluoro-olefin occupying an equatorial position (Figure 3:2).



COMPOUND	X
3:1	F
3:2	CF_3
3:3	Cl
3:4	Br.

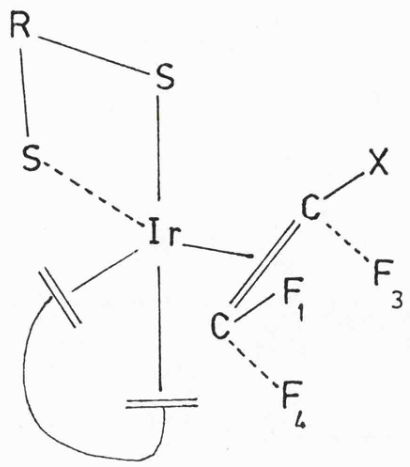
FIGURE 3:2

If the fluoro-olefin is rigidly bound to the metal atom, it can be seen that when X = Cl, Br, CF_3 there is a possibility of obtaining four isomeric products. The compounds 3:1 - 3:4 were too insoluble for ^{19}F n.m.r. spectra to be obtained so it is difficult to determine whether the fluorine atoms on the olefin are all

inequivalent, thus signifying a rigidly bound structure. The fact that the fluoro-olefin comes off when the complexes are refluxed in ethanol for 30 minutes, would suggest that perhaps they are not rigidly bound but rotate freely about the metal-olefin bond as is possibly the case for the complexes $[Rh(acac)(C_2H_4)(C_2F_4)]$[88] $[Rh(dpm)(C_2H_4)(C_2F_4)]$[109] and $[IrCl(AsPh_3)_2(C_2F_4)]$[108]. The dimeric structure assigned to complexes 3:1 to 3:4 is based on a molecular weight determination carried out by van Gaal and van der Ent on the complex $[IrCl(cod)(C_2F_4)]_2$[108], and on the Ir-Cl stretching frequencies occuring in the region 300-320cm^{-1}, which can be associated with a bridged chlorine system.

It would appear that hexafluorobut-2-yne is more strongly co-ordinated to iridium(I) than are the fluoro-olefins since the hexafluorobut-2-yne in complex 2:1 is not lost when the complex is refluxed in ethanol. Indeed the Ir-Cl stretching frequency of complex 2:1 occurs 30-40cm^{-1} higher than is observed in the fluoro-olefin complexes, a difference which may be correlated with the greater π-accepting nature of the acetylene.

On reacting the fluoro-olefins tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, trifluoroethylene, hexafluoropropene and hexafluorocyclobutene with selected compounds of the type [Ir(dithiocarbamato)(cod)] (where dithiocarbamato = dtc, dptc) and [Ir(dtp)(cod)], very soluble yellow compounds, complexes 3:5 - 3:14 (Figure 3:3) are produced. These complexes are stable in the solid state but decompose fairly rapidly in solution. In view of the structure of complex 2:1, complexes 3:5 - 3:14 are probably best formulated as analogous trigonal bipyramidal structures (Figure 3:3)



COMPOUND	R	X	COMPOUND	R	X
3:5	$CNEt_2$	F	3:10	$P(OEt)_2$	Cl
3:6	$P(OEt)_2$	F	3:11	$CNPh_2$	Cl
3:7	$CNEt_2$	Cl	3:12	$P(OEt)_2$	CF_3
3:8	$CNEt_2$	Br	3:13	$P(OEt)_2$	H
3:9	$CNEt_2$	H			

FIGURE 3:3

Complexes derived from the unsymmetrical fluoro-olefins $CF_2{=}CFX$ (X = Cl, Br, H, CF_3) can exist in four possible geometrical forms A, A′, B and B′ (Figure 3:4) each one of which can exist as two optical forms. The ^{19}F n.m.r. spectra of complexes 3:5 - 3:14 clearly show that the fluoro-olefins are rigidly bound to the metal. The ^{19}F n.m.r. spectrum of $[Ir(dtp)(cod)(CF_2{=}CFCl)]$ (Table 3:1), shows the presence of three inequivalent fluorine environments, in agreement with the proposed structure type, and on close examination

TABLE 3:1

^{19}F n.m.r. Chemical shifts[a] (p.p.m) for the complexes [Ir(dithio)(cod)(fluoro-olefin)]

COMPOUND	δF_1	δF_2	δF_3	δF_4	δCF_3	% isomer
$[Ir(dtc)(cod)(CF_2{=}CF_2)]$	61.28	62.57	68.37	50.05		
$[Ir(dtp)(cod)(CF_2{=}CF_2)]$[b]	59.47	67.10	67.88	48.36		
A) $[Ir(dtc)(cod)(CF_2{=}CFCl)]$	51.23		72.63	42.51		60
B) $[Ir(dtc)(cod)(CF_2{=}CFCl)]$	53.98	65.90		39.91		40
A) $[Ir(dtp)(cod)(CF_2{=}CFCl)]$	47.68		70.27	38.27		70
B) $[Ir(dtp)(cod)(CF_2{=}CFCl)]$[b]	49.88	69.64		34.45		30
A) $[Ir(dtc)(cod)(CF_2{=}CFBr)]$	47.22		67.01	42.13		75
B) $[Ir(dtc)(cod)(CF_2{=}CFBr)]$	53.42	63.95		35.87		25
A) $[Ir(dptc)(cod)(CF_2{=}CFCl)]$	50.76		71.59	41.35		70
B) $[Ir(dptc)(cod)(CF_2{=}CFCl)]$	52.92	68.57		38.73		30
$[Ir(dtc)(cod)(CF_2{=}CFH)]$	50.52	58.83		37.58		
$[Ir(dtp)(cod)(CF_2{=}CF{-}CF_3)]$[c]	42.59		135.70	31.10	3.94	
$[Ir(dtc)(cod)(F_2{=}F_2)]$ (F=F)						

a) Measured in $CDCl_3$ solution relative to external benzotrifluoride unless otherwise stated

b) Measured in diethyl ether solution.

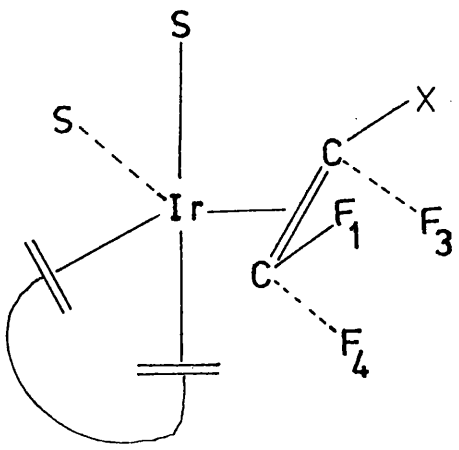
c) Measured in CH_2Cl_2 solution.

TABLE 3:2

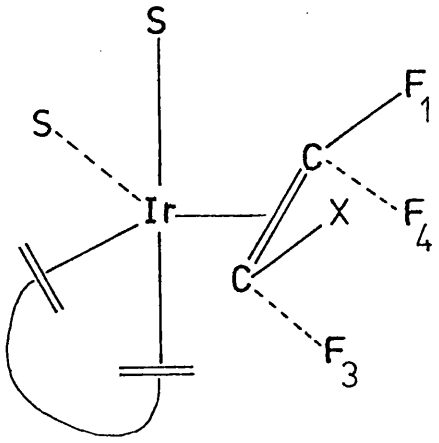
^{19}F n.m.r. Coupling constant(Hz) for Co-ordinated and free fluoro-olefins.

COMPOUND	JF_2-F_3	JF_1-F_3	JF_1-F_2	JF_2-F_4	JF_1-F_4	JF_3-F_4	J P-F_3	J P-F_4
[Ir(dtc)(cod)($CF_2=CF_2$)]	187.69	34.59		36.85	152.40	4.51		
[Ir(dtp)(cod)($CF_2=CF_2$)]		32.23	9.75	33.28	144.68	10.49	2.70	4.49
A) [Ir(dtc)(cod)($CF_2=CFCl$)]		41.79			141.79			
B) [Ir(dtc)(cod)($CF_2=CFCl$)]				44.78	137.31			
A) [Ir(dtp)(cod)($CF_2=CFCl$)]		41.38			130.43	8.25		4.50
B) [Ir(dtp)(cod)($CF_2=CFCl$)]			8.40	43.48	131.93			4.80
A) [Ir(dtc)(cod)($CF_2=CFBr$)]		44.38			145.43	9.00		
B) [Ir(dtc)(cod)($CF_2=CFBr$)]			8.99	45.58	137.93			
A) [Ir(dptc)(cod)($CF_2=CFCl$)]		38.98			146.93	8.99		
B) [Ir(dptc)(cod)($CF_2=CFCl$)]			7.50	44.98	146.93			
[Ir(dtc)(cod)($CF_2=CFH$)]				50.97	145.43	12.89		
[Ir(dtp)(cod)($CF_2=CF-CF_3$)]					157.42	14.99		
[Ir(dtc)(cod)(F_2—F_2, F=F)]			197.90			124.44		
$CF_2=CF_2$			74.3	111.7	123.8[a]			
$CF_2=CFCl$			58.0	115.0	78.0[a]			
$CF_2=CFBr$			58.0	115.0	78.0[b]			
$CF_2=CFCF_3$			40.0	120.0	57.0[c]			

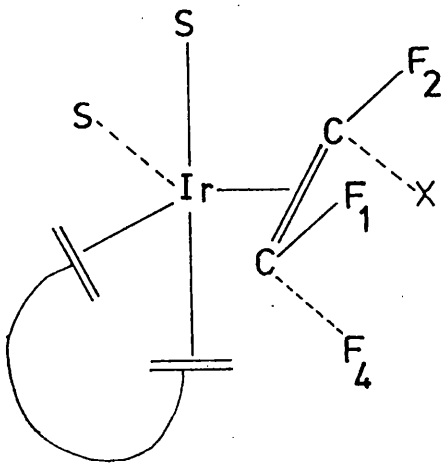
a - Ref. 115 b - Ref. 116 c - Ref. 117



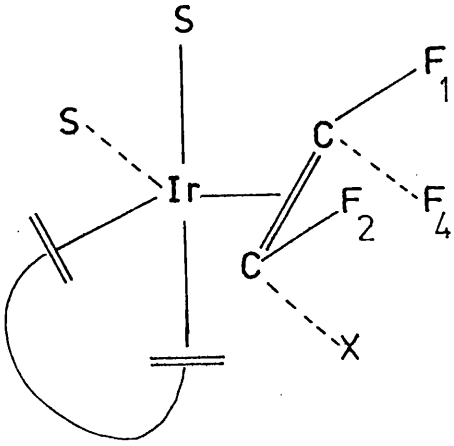
A



A′



B



B′

FIGURE 3:4

of the spectrum it is apparent that there are two isomers present. The resonance at 38.27 p.p.m. (relative to benzotrifluoride), which arises from the major isomer, consists of a double doublet arising from coupling to two inequivalent fluorines. Each of these four lines shows a further splitting which must arise from long range coupling of the phosphorous atom of the dithiophosphate ligand since this feature is absent in the corresponding dithiocarbamate complexes. The mechanism of this $^{31}P - ^{19}F$ coupling is not clear, but since the atom F_4 in, for example isomer A, forms part of a W arrangement with the phosphorous this could be an example of W coupling similar to that observed in long range $^{1}H - ^{1}H$ couplings.[110,111] In co-ordinated fluoro-olefins it is found that the magnitude of the $^{19}F - ^{19}F$ couplings follows the order JFF gem > JFF trans- > JFF cis. Thus since the resonance at 38.27 p.p.m. possesses, in addition to $^{31}P - ^{19}F$ coupling, both a large and a small $^{19}F - ^{19}F$ coupling, it is proposed that this resonance must arise from either the isomer A or A′ However since in A, F_4 forms a better W arrangement than it does in A′ it is suggested that the most abundant isomer has the structure shown in A. In agreement with this interpretation the resonance at 70.27 p.p.m is assigned to F_3 in A since this signal contains medium (trans-) and small (cis-) $^{19}F - ^{19}F$ couplings and exhibits a slight broadening possibly associated with an unresolved $^{31}P - ^{19}F$ coupling. The third resonance at 47.68 p.p.m. contains a large and medium $^{19}F - ^{19}F$ coupling but no $^{31}P - ^{19}F$ coupling is observed and consequently this resonance is assigned to F_1 in A. By similar reasoning the less abundant isomer

present in the ^{19}F n.m.r. spectrum of the complex $[Ir(dtp)(cod)(CF_2=CFCl)]$ is assigned structure B, the fluorine F_4 again exhibiting long range ^{31}P - ^{19}F coupling.

It is thus apparent that this chlorotrifluoroethylene complex is formed predominantly as a mixture of two isomers A and B with relative abundances A, 70% B, 30%. No resonances which could be associated with the isomers A′ or B′ were observable. The examination of molecular models of the various isomers suggests that isomer A is sterically more favourable than A′ since in A′ the chlorine is closer to the hydrogens of the equatorially bound double bond. In isomer A this position is occupied by the smaller fluorine atom. Similarly steric reasons favour isomer A rather than B since in B the chlorine will feel some replusion from the hydrogens of the axially co-ordinated double bond.

The ^{19}F n.m.r. spectra of the other chlorotrifluoroethylene complexes and the bromotrifluoroethylene complexes clearly show the presence of two isomers which are assigned structures A and B, (Table 3:1) on the basis of chemical shift and coupling constant data; isomer A always being the more abundant.

In contrast the ^{19}F n.m.r. spectrum of the complex $[Ir(dtc)(cod)(CF_2=CFH)]$ (Table 3:1) shows the presence of only one isomer. Furthermore this isomer appears to be B which is the minority product when complexes containing other substituted fluoro-olefins are prepared. This observation fits in very well with the steric

arguments used above. Since the hydrogen atom is much smaller than the fluorine atoms on the olefin, this would be expected to occupy the most sterically hindered position, which seems to be that occupied by X in isomer B. Actually the most sterically hindered position is probably that occupied by X in isomer B , and so it might be expected that the product obtained when trifluoroethylene is reacted with [Ir(dtc)(cod)] would be isomer B. The complex [Ir(dtp)(cod)(CF_2=CFH)] has been prepared and a reasonable analysis obtained but attempts to obtain a ^{19}F n.m.r. spectrum have, so far, proved unsuccessful. It still seems logical however, to suppose that the isomer obtained on reacting [Ir(dtc)(cod)] with trifluoroethylene is B .

The ^{19}F n.m.r. spectrum of the complex [Ir(dtc)(cod)(CF_2=CFBr)] (Figure 3:5) is very similar to that obtained for the complex [Ir(dtp)(cod)(CF_2=CFCl)] and clearly shows the presence of the two isomers A and B.

If one looks at the ^{19}F n.m.r. spectrum of the complex [Ir(dtp)(cod)(CF_2=CF_2)] it is evident that the F_2 and F_3 atoms are appearing as an AB pair. The ^{19}F n.m.r. spectrum of these two fluorine atoms is a typical AB pattern (Figure 3:6). Similarly, on close examination of the ^{19}F n.m.r. spectrum of the complex [Ir(dtc)(cod)(CF_2=CF_2)] (Figure 3:7) the resonances due to F_2 and F_3 appear to have some AB pair characteristics in this case the two outside groups of signals are of lower intensity than are the central pair. These observations only apply to the complexes containing tetrafluoroethylene. All other complexes prepared appear to show first order ^{19}F n.m.r. spectra.

FIGURE 3:5

^{19}F n.m.r. spectrum of $[Ir(dtc)(cod)(CF_2:CFBr)]$ showing two isomers A and B.

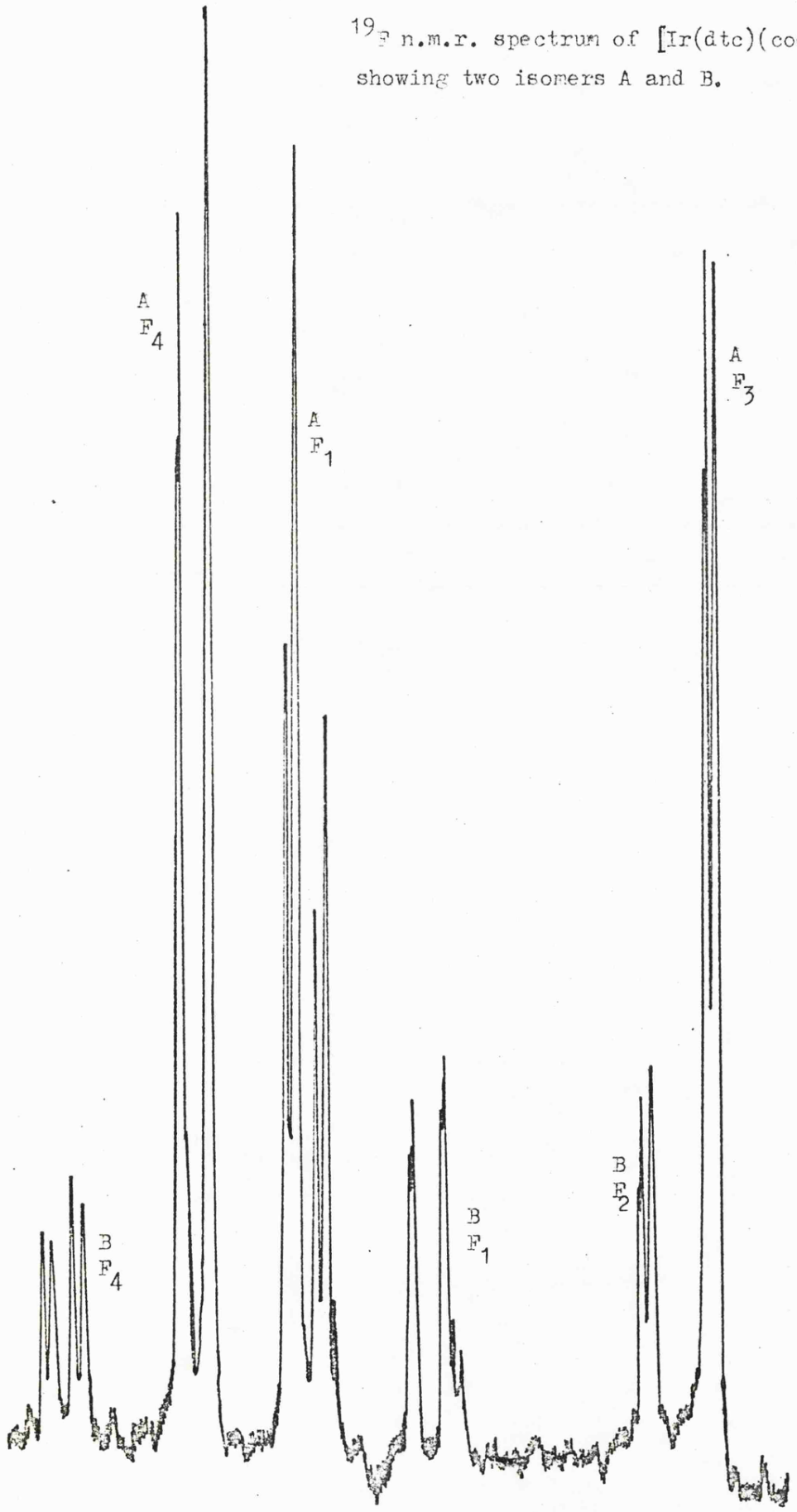


FIGURE 3.6

^{19}F n.m.r. Spectrum of $[Ir(dtp)(cod)(CF_2{=}CF_2)]$

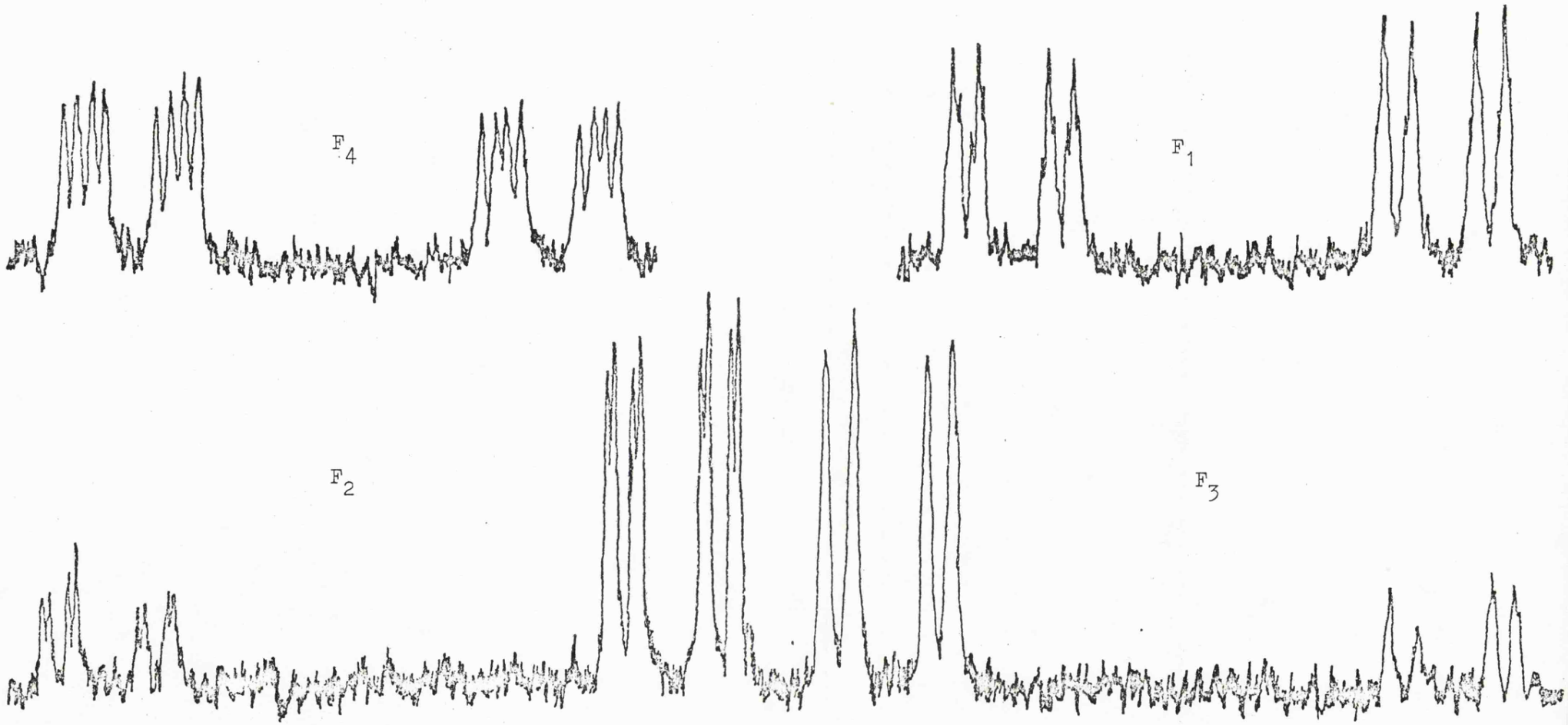
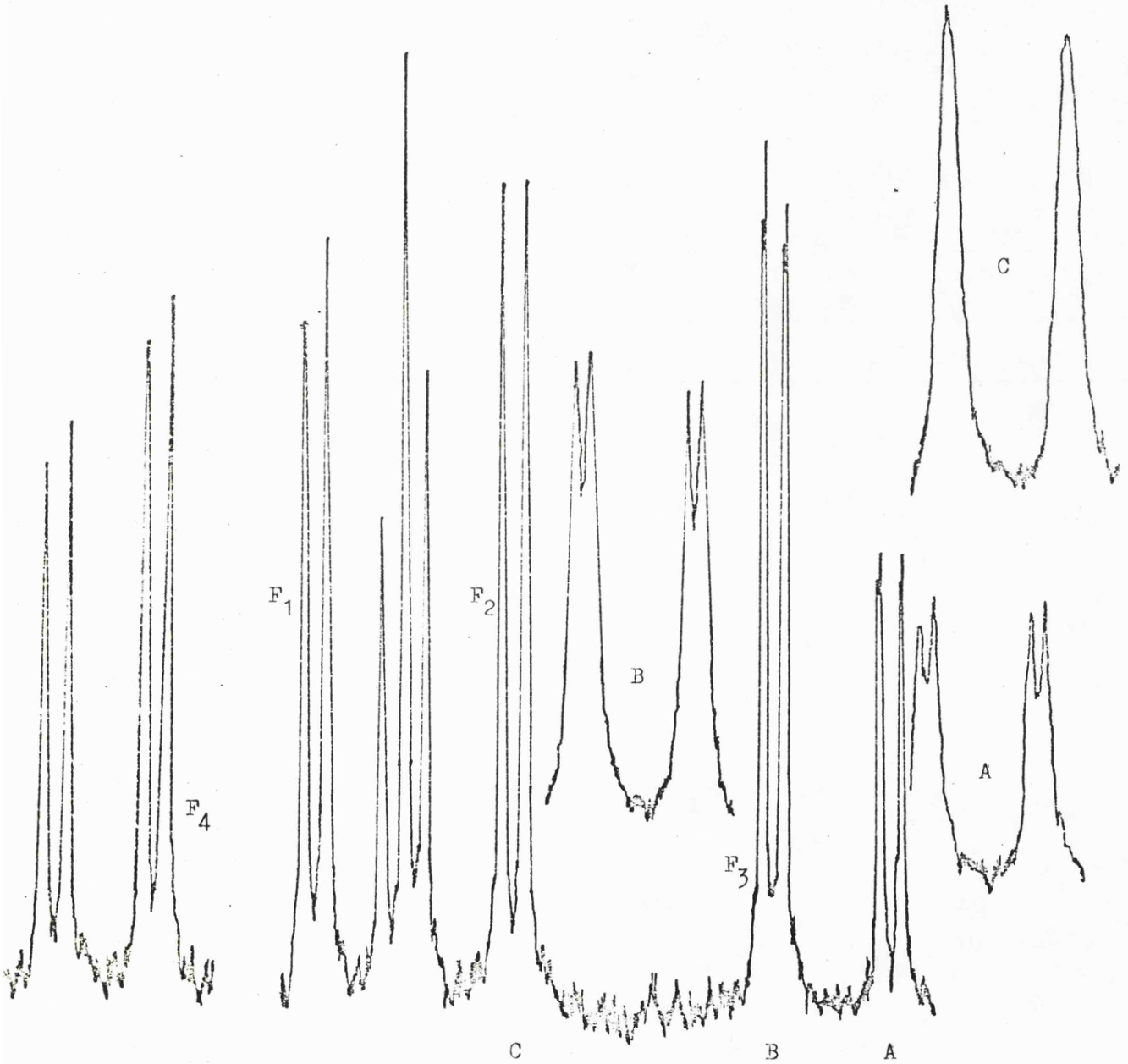


FIGURE 3:7

^{19}F n.m.r. spectrum of $[Ir(dtc)(cod)(CF_2:CF_2)]$



The ^{19}F n.m.r. spectrum of the complex $\left[Ir(dtc)(cod)(\begin{smallmatrix} F_2 & & F_2 \\ & & \\ F & & F \end{smallmatrix})\right]$ exhibits fluorine resonances at 38.44, 42.41 p.p.m 50.80 and 52.78 p.p.m each of which essentially appears as a doublet of multiplets.

Unlike complexes 3:5 - 3:13 complex 3:14 has the possibility of existing in only two isomeric forms: Figure 3:8 A or B, and on the basis of the steric reasons used before B seems the most probable structure for this complex.

The ^{1}H n.m.r. data for all the complexes are given in Table 3:3 and confirm the proposed structures for the compounds. The NR_2 groups of the dithiocarbamate ligands are inequivalent because of the hindered rotation about the C---N bond. The protons of the cod ligand are difficult to assign and no attempt has been made to distinguish between them.

A comparison of the ^{19}F-^{19}F coupling constants of free and co-ordinated fluoro-olefins [19,103] shows a decrease in the size of the vicinal $J(F_1-F_2)$ and $J(F_1-F_3)$ coupling and a corresponding increase in the size of the germinal $J(F_1-F_4)$ coupling upon co-ordination. Such changes can be interpreted in terms of a change in hybridisation of the olefinic carbon atoms from Sp^2 to Sp^3 hybridisation.

Similar trends are observed in the present iridium(1) complexes, where large changes in the coupling constants are observed for all three couplings. In general, these iridium(I) fluoro-olefins show much larger changes in the couplings constants on co-ordination than do some rhodium(I) fluoro-olefins prepared previously in this department.

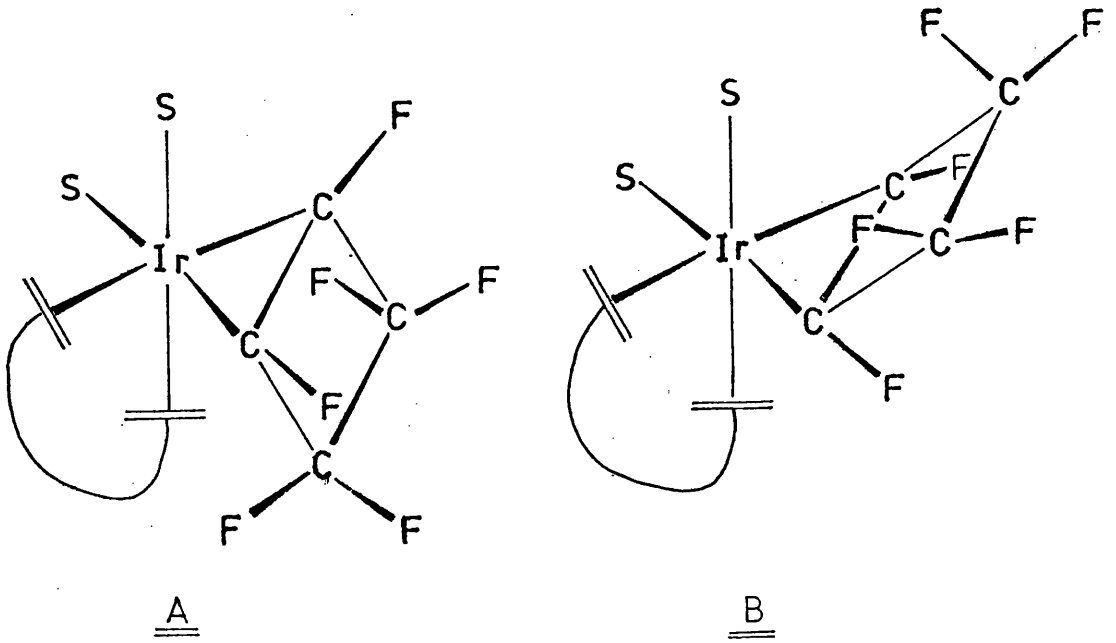
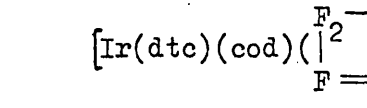


FIGURE 3:8.

TABLE 3:3

^{1}H n.m.r. spectra for the complexes [Ir(dithio)(cod)(fluoro-olefin)]

COMPOUND	Phenyl	CH_3	CH_2	H	cod	olefinic
[Ir(dtc)(cod)(CF_2=CFCl)]		1.20t,1.30t	3.48q,3.70q. J(H-H)=7.46Hz		1.40-4.60(10H)	4.66m,4.88m
[Ir(dtp)(cod)(CF_2=CFCl)]		1.36t J(H-H)=6.76Hz	4.04m		1.40m,2.18m, 4.05m.	
[Ir(dtc)(cod)(CF_2=CFBr)]		1.20t,1.29t J(H-H)=7.76Hz	3.45q, 3.69q		1.40-4.00(10H)	4.56m,4.84m
[Ir(dptc)(cod)(CF_2=CFCl)]	7.48s				0.80-4.20(10H)	4.64m,4.88m
[Ir(dtc)(cod)(CF_2=CFH)]		7.28m	3.62m	4.04s	1.40-4.00(11H)	4.58m
[Ir(dtp)(cod)(CF_2=CF-CF_3)]		1.36t J(H-H)=6.91Hz	4.10m		1.45-4.30(11H)	5.00m
[Ir(dtc)(cod)()]		1.16t,1.28t J(H-H)=6.31Hz	3.36q,3.60q		1.40-3.08(10H)	4.18m,4.67m

a) Measured in $CDCl_3$ solution at room temperature; chemical shifts (p.p.m) are relative to internal T.M.S.

3:3 The reaction of fluoro-olefins with the complex diethyldithiocarbamatobis(cyclo-octene)iridium(I).

It has been noted previously[112] that when the complexes chlorotris(triphenylphosphine)rhodium(I) or chlorobis[tri(pentafluorophenylphosphine)] rhodium(I) dimer reacted with tetrafluoroethylene in benzene at 120°C, quantitive yields were produced of the carbonyl complexes trans-$[RhCl(CO)L_2]$ ($L=PPh_3, P(C_6F_5)_3$). Under similar conditions tetrafluoroethylene and trans-$[PtHCl(PEt_3)_2]$ give small yields of a carbonyl cation,[113] trans-$[PtCl(CO)(PEt_3)_2]$ and the complex $[Rh(acac)(C_2F_4)(C_2H_4)]$ catalyses the acetic acid solvolysis of tetrafluoroethylene to give carbon monoxide.[88]

It is now known that a variety of fluoro-olefins and phosphine-rhodium(I) complexes react under varying conditions in sealed vessels to give the carbonyl-rhodium complexes trans-$[RhCl(CO)L_2]$ ($L=(C_6F_5)_3P$, $(C_6F_5)_2PhP$, $(C_6F_5)Ph_2P$ or Ph_3P).[114] Since no carbonyl complex is formed under extremely anhydrous conditions the formation of the carbonyl appears to involve the hydrolysis of the intermediate olefin complex $[RhCl(C_2F_3X)L_2]$ (X=F or Cl), and the following mechanism has been proposed.[114]

$$Rh + C_2F_4 \longrightarrow Rh(\pi\text{-}C_2F_4)$$

$$Rh(\pi\text{-}C_2F_4) + H^+ \longrightarrow RhCF_2.CF_2H^+$$

$$RhCF_2.CF_2H^+ \longrightarrow RhCF{=}CF_2^+ + HF$$

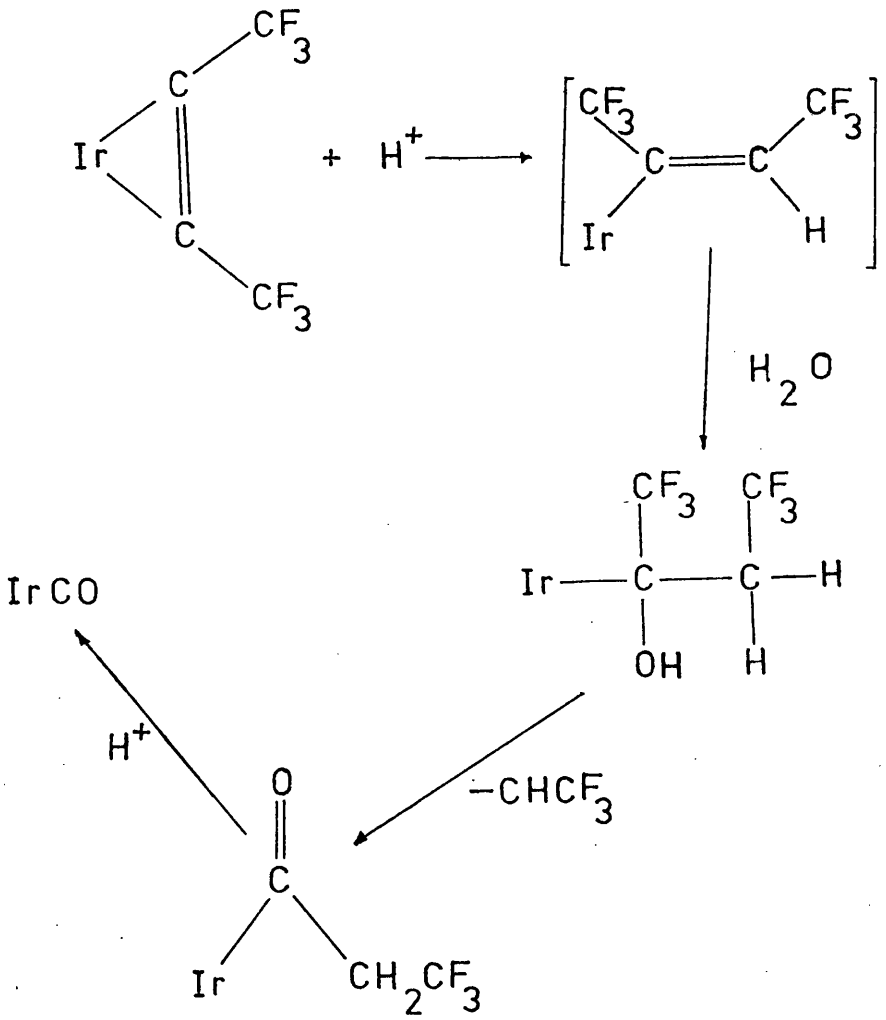
$$RhCF{=}CF_2^+ + H_2O \longrightarrow RhCF(OH)CF_2H$$

$$RhCF(OH)CF_2H^+ \longrightarrow RhCOCF_2H^+ + HF$$

$$RhCO.CF_2H^+ \longrightarrow Rh(CO).CF_2H^+$$

$$Rh(CO).CF_2H^+ \longrightarrow RhCO + \tfrac{1}{2}(CF_2H.CF_2H)$$

A similar degredation sequence has been proposed by Stone,[95] who noticed that if the complexes $[IrCl(CF_3C_2CF_3)(Ph_3P)_2]$ or $[IrCl(CF_2{:}CF_2)(Ph_3P)_2]$ were heated overnight in benzene in a sealed tube, with water present, Vaskas complex $[IrCl(CO)(Ph_3P)_2]$ was prepared each time. This was the first hydrolytic transformation of hexafluorobut-2-yne metal complexes to carbonyl compounds.



Very little work has been carried out on the reactions of fluoro-olefins with cyclo-octene iridium(I) compounds and it seemed worthwhile to carry out investigations into some of these reactions.

When the fluoro-olefins tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene and trifluoroethylene are reacted with diethyldithiocarbamatobis(cyclo-octene)iridium(I) in diethyl ether overnight an orange-brown, relatively insoluble, precipitate is produced each time.

The i.r. spectrum of each compound has a characteristic strong absorption in the region of 2050cm^{-1} which seems to indicate the presence of a terminal metal carbonyl group. The high value of this absorption is good evidence for the iridium being in the oxidation state +3. In addition to this the absorptions due to the dithiocarbamate ligand are still present, and also a broad medium strength absorption just above 1600cm^{-1}, which may be assignable to an hydroxyl group, is clearly visible.

On the basis of this spectroscopic evidence and analytical data the complexes 3:15, 3:16, 3:17, and 3:18 are tentatively assigned the trigonal bipyramidal structure shown in figure 3:9.

These carbonyl compounds are of interest since only mild conditions were necessary for their production. Previous cases[95,112,113] of carbonyl production from fluoro-olefins have required prolonged heating in benzene.

The ^{1}H n.m.r. spectra of complexes 3:16 to 3:18 show absorptions due to the dithiocarbamate ligand but no evidence of a hydroxyl proton is visible. Attempts to confirm the presence of an hydroxyl group has so far proved unsuccessful. The band in the i.r. spectrum above 1600cm^{-1} was still present after shaking complex 3:16 with D_2O.

The low solubility of the complexes may be the reason why the D_2O experiment proved unsuccessful.

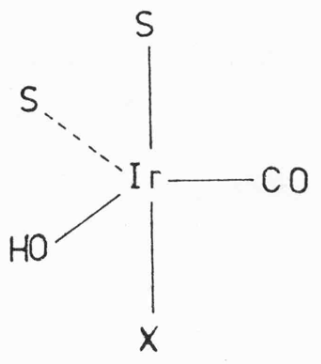


FIGURE 3:9

COMPLEX	X
3:15	F
3:16	Cl
3:17	Br
3:18	H

More work is necessary before definite structures can be assigned to complexes 3:15 - 3:18. It is of interest to note that no reaction appeared to take place when $[Ir(dtp)(cyclo\text{-}octene)_2]$ was shaken overnight in diethyl ether with tetrafluoroethylene. The dithiophosphate ligand must prevent the initial π-bond between the tetrafluoroethylene and the metal centre.

3:3 EXPERIMENTAL

Analytical melting point and spectroscopic data are shown in this section. Microanalysis were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd, 41 High Street, Teddington, Middlesex, Melting points were recorded on a Reichart hot-stage apparatus and are uncorrected. Infra-red spectra were recorded as nujol mulls on a Perkin-Elmer 225 spectrophotometer using CsI plates. ^{1}H n.m.r. spectra were recorded in $CDCl_3$ solution at room temperature on a Jeol JNM-PS-100 spectrometer operating at 100 M.Hz, chemical shifts (p.p.m) being reported relative to internal T.M.S. ^{19}F n.m.r. spectra were recorded at room temperature on a Jeol JNM-PS-100 spectrometer operating at 94.1 M.Hz, chemical shifts (p.p.m) being reported relative to external benzotrifluoride.

All reactions carried out in a Carius tube were done in 15mls of the appropriate solvent. The solvents were previously dried and degassed.

Ligands and reagents.

Tetrafluoroethylene was prepared by thermal decomposition of polytetrafluoroethylene (supplied by I.C.I Ltd) under vacuum in a silica tube and no further purification was performed after trapping out the olefin in liquid nitrogen. Hexafluoropropene and hexafluorocyclobutene were purchased from Peninsular Chemresearch Inc. Bromotrifluoroethylene and trifluoroethylene were supplied by Pierce Chemical Co and chlorotrifluoethylene was obtained from Pfaltz Bauer Inc. The iridium trichloride was obtained on loan from Johnson Matthey Ltd.

Complexes.

$[IrCl(cod)]_2$,[97] $[Ir(dtc)(cod)]$ [76] and $[Ir(dtc)(C_8H_{14})_2]$,[76] were prepared as described in the literature.

The complexes $[Ir(dptc)(cod)]$ and $[Ir(dtp)(cod)]$ were prepared as described in the experimental for Chapter two.

A. The reaction of fluoro-olefins with the complex $[IrCl(cod)]_2$.

1. With tetrafluoroethylene.

An excess of tetrafluoroethylene (1.0ml) was condensed (-196°) on to a suspension of chloro(cyclo-octa-1,5-diene)iridium(I) dimer (0.30g, 0.45 m.mol.) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature overnight, the tube was opened and volatile material removed. The lemon yellow precipitate was filtered and washed with diethyl ether to yield microcrystals of complex 3:1 $[IrCl(cod)(C_2F_4)]_2$ (0.30g, 77%) m.p. 138-141° dec.

$C_{20}H_{24}Cl_2F_8Ir_2$	requires	C, 27.80;	H, 2.76%
	found	C, 27.42;	H, 2.74%

Infra-red; 1616 w, 1494 w, 1370 m, 1340 s, 1315 m, 1309 m, 1191 m, 1170 m, 1140 s, 1132 s, 1096 m, 1050 m, 1037 s, 1015 m, 1008 m, 920 s, br, 880 w, 872 w, 842 s, 822 w, 790 m, 702 s, 717 sh, 704 s, 574 s, 485 m, 482 m, 450 s, 336 w, 318 s, 270 s, 254 w.

2. With hexafluoropropene.

An excess of hexafluoropropene (1.0ml) was condensed (-196°) on to a suspension of chloro(cyclo-octa -1,5-diene)iridium(I) dimer (0.30g, 0.45 m.mol.) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The lemon yellow precipitate was filtered off and washed with diethyl ether to yield

microcrystals of complex 3:2 $\left[IrCl(cod)(C_3F_6)\right]_2$ (0.32g, 75%) m.p. 115° dec.

$C_{22}H_{24}Cl_2F_{12}Ir_2$	requires	C, 27.14;	H, 2.48%
	found	C, 26.92;	H, 2.47%

Infra-red: 1356 s, 1336 s, 1280 s, 1177s, 1168 s, 1134 s, 1112 s, 1050 s, 1040 s, 1020 m, 978 s, 874 m, 852 m, 843 m, 822 w, 784 s, 776 s, 680 s, 616 m, 584 w, 528 w, 484 m, 450 m, 330 w, 308 m, 296 sh,w, 264 w.

When the complex $\left[IrCl(cod)(C_3F_6)\right]_2$ (0.20g, 0.41m.mol.) was refluxed in ethyl alcohol for 30 minutes a red/orange solution was produced. On evaporating the solution to small volume (2.0ml) a red microcrystalline complex precipitated. This was identified as $\left[IrCl(cod)\right]_2$ from its infra-red spectrum and melting point.

3. <u>With chlorotrifluoroethylene.</u>

An excess of chlorotrifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of chloro(cyclo-octa-1,5-diene) iridium(I) dimer (0.30g, 0.45 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The yellow precipitate was filtered off and washed with diethyl ether to yield microcrystals of complex 3:3 $\left[IrCl(cod)(ClCF{:}CF_2)\right]_2$ (0.37g, 92%) m.p. 139-143° dec.

$C_{20}H_{24}Cl_2F_6Ir_2$	requires	C, 26.50;	H, 2.67%
	found	C, 26.43;	H, 2.69%

Infra-red: 1612 w, 1494 w, 1368 m, 1340 s, 1332 s, 1308 m, 1191 m, 1170 m, 1140 s, 1132 s, 1096 m, 1050 m, 1037 s, 1015 m, 1008 m, 920 s, br, 880 w, 872 w, 842 s, 822 w, 790 m, 702 s, 717 sh, 704 s, 584 s, 520 w, 486 m, 450 s, 336 w, 313 s, 288 s, 252 w.

When the complex $[IrCl(cod)(ClCF:CF_2)]_2$ (0.20g, 0.44m. mol) was refluxed in ethyl alcohol for 30 minutes a red-orange solution was produced. Evaporation of this solution led to the precipitation of orange crystals which were identified as $[IrCl(cod)]_2$ from their infra-red spectrum and melting point.

4. <u>With bromotrifluoroethylene.</u>

An excess of bromotrifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of chloro(cyclo-octa-1,5-diene) iridium(I) dimer (0.20g, 0.30 m.mol) in diethyl ether contained in a Carius tube. After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The yellow precipitate was filtered, washed with diethyl ether and identified as complex 3:4 $[IrCl(cod)(BrCF:CF_2)]_2$ (0.26g, 88%) m.p. 140-144°dec.

$C_{20}H_{24}Br_2Cl_2F_6Ir_2$	requires	C, 24.13;	H, 2.43;	Br, 16.06%
	found	C, 24.34;	H, 2.50;	Br, 15.19%

Infra-red; 1359 s, 1343 s, 1168 w, 1148 w, 1111 m, 1076 sh, 1010 m, 975 s, 965 sh, 900 m, 876 s, 860 sh, 850 sh, 821 m, 807 w, 768 m, 732 s, 656 sh, 644 s, 557 m, 432 w, 325 s, 308 s, 302 s, 290 m, 263 m, 235 w.

5. With perfluorocyclobutene, vinyl fluoride, 1,2,difluoroethylene and trifluoroethylene.

When an excess of any one of these fluoro-olefins was shaken for 48 hours at room temperature with chloro(cyclo-octa-1, 5-diene)iridium(I) dimer no observable reaction took place. Unreacted chloro(cyclo-octa-1,5-diene)iridium(I) dimer was reclaimed at the end of the experiment.

B. The reaction of fluoro-olefins with some dithiocarbamato and dithiophosphatoalkene-iridium(I) complexes.

1. Tetrafluoroethylene with diethyldithiocarbamato(cyclo-octa-1, 5-diene)iridium(I).

An excess of tetrafluoroethylene (0.75 ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1, 5-diene)iridium(I) (0.5g, 1.11m.mol), in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The pale solution was filtered and the filtrate evaporated to small volume to give pale yellow microcrystals of complex 3:5[Ir(dtc)(cod)(C_2F_4)] (0.45g, 73.3%) m.p. 135-137°C.

$C_{15}H_{22}F_4IrNS_2$	requires	C, 32.78;	H, 4.06%
	found	C, 32.50;	H, 4.01%

Infra-red;1511 s, 1399 s, 1339 m, 1309 w, 1301 w, 1277 s, 1215 s, 1155 s, 1117 s, 1103 s, 1077 s, 1039 s, 1031 s,sh, 1015 m, 927 m, 905 w, 895 m, 859 m, 845 s, 823 m, 801 s, 783 s, 603 s, 595 sh, 579 m, 559 w, 519 w, 495 w, 481 w, 451 m.

^{19}F n.m.r. spectrum;

Observed in $CDCl_3$ solution; a doublet of doublets (IF) centred at 50.05 p.p.m. $J(F_1-F_4)$ = 152.40Hz, $J(F_2-F_4)$ = 36.85Hz, also a doublet of doublets (IF) centred at 61.28 p.p.m. $J(F_1-F_4)$=152.40Hz, $J(F_1-F_3)$=34.59Hz and a doublet of doublets (IF) centred at 62.52 p.p.m, $J(F_2-F_3)$ = 187.69Hz, J (F_2-F_4) = 36.85Hz. There is also a doublet of doublets (IF) at 68.37 p.p.m. with $J(F_2-F_3)$ = 187.69Hz, $J(F_1-F_3)$ = 34.59Hz, $J(F_3-F_4)$ = 4.51Hz (relative to external benzotrifluoride).

2. <u>Tetrafluoroethylene with diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of tetrafluoroethylene (0.5ml) was condensed (-196°) on to a suspension of diethyldithiophosphato(cyclo-octa -1,5-diene(iridium(I) (0.50g, 1.03 m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The pale yellow solution was filtered and the filtrate evaporated to small volume, to produce a pale yellow oil identified as complex 3:6[Ir(dtp)(cod)(CF_2:CF_2)](0.49g,81%).

^{19}F n.m.r. spectrum:

Observed in diethyl ether solution: a signal (1F) centred at 48.36 p.p.m. which consists of four sets of double doublets $J(F_2-F_4)=33.28Hz$, $J(F_1-F_4)=144.68Hz$, $J(F_3-F_4)=10.49Hz$, $J(P-F_4)=4.49Hz$. Also a signal (1F) centred at 54.47 p.p.m. consisting of two sets of double doublets $J(F_1-F_4)=144.68Hz$, $J(F_1-F_3)=32.23Hz$, $J(F_1-F_2)=9.75Hz$. There is also a signal that appears as an AB pair (2F) centred at 67.50 p.p.m.

3. Chlorotrifluoroethylene with diethyldithiocarbamato (cyclo-octa-1,5-diene)iridium(I).

An excess of chlorotrifluoroethylene (0.75ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I) (0.50g,1.11m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The pale yellow solution was filtered, and the filtrate evaporated to small volume to produce off-white microcrystals of complex 3:7. $[Ir(dtc)(cod)(CF_2=CFCl)]$ (0.51g,81%) m.p. 120-122°C.

$C_{15}H_{22}ClF_3IrNS_2$	requires	C,31.83; H,3.92; Cl,6.26%
	found	C,32.02; H,3.96; Cl,6.12%

Infra-red, 1506 s, 1488 s, 1352 s, 1314 s, 1304 s, 1272 s, 1210 s, 1183 m, 1148 s, 1088 s, 1072 s, 1020 s, 1008 s, 920 s, 904 s, 854 s, 842 s, 784 s, 756 s, 712 s, 698 s, 580 m, 454 w, 376 m, 342 m, 326 m, 314 m.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: Isomer (A) a doublet of doublets (1F) centred at 42.51 p.p.m. $J(F_1-F_4)$=141.79Hz, and a doublet of doublets (1F) centred at 51.23 p.p.m. $J(F_1-F_4)$=141.79Hz, $J(F_1-F_3)$=41.79Hz and a doublet of doublets (1F) centred at 72.63 p.p.m $J(F_1-F_3)$=41.79Hz (relative to external benzotrifluoride).

Isomer (B) a doublet of doublets (1F) centred at 39.91 p.p.m $J(F_1-F_4)$=137.31Hz, $J(F_2=F_4)$=44.78Hz, a doublet of doublets (1F) centred at 53.98 p.p.m $J(F_1-F_4)$=137.31Hz and a doublet of doublets centred at 65.90 p.p.m $J(F_2-F_4)$=44.78Hz, (relative to external benzotrifluoride). Ratio of isomers 60:40.

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: two badly defined triplets centred at 1.20(3H) and 1.30(3H) p.p.m, two quartets centred at 3.48(2H) and 3.70(2H) p.p.m, J(H-H)=7.46Hz. There are also two multiplets centred at 4.66(1H) and 4.88(1H) p.p.m. The remaining (10H) of the (cod) ligand occur in a broad band between 1.40 and 4.60 p.p.m.

4. <u>Bromotrifluoroethylene with diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of bromotrifluoroethylene (0.70ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I) (0.30g,0.67 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking for 24 hours at room temperature the tube was opened and volatile material removed. The pale yellow solution.

was filtered and evaporated to an oil. The oil was pumped under reduced pressure overnight and then a few drops of diethyl ether added. The off-white microcrystals, so obtained, were filtered and washed with light petroleum (40-60°) and identified as complex 3:8 [Ir(dtc)(cod)(CF_2=CFBr)] (0.29g, 71%) m.p. 107-110°C.

$C_{15}H_{22}BrF_3IrNS_2$	requires	C,29.51;	H,3.63;	Br,13.10%
	found	C,29.58;	H,3.61;	Br,12.90%

Infra-red: 1512 s, 1500 s, 1354 m, 1316 s, 1274 s, 1212 s, 1152 m, 1100 s, 1080 m, 1026 s, 896 m, 880 s, 858 m, 844 m, 796 m, 752 m, 698 m, 676 s, 672 s, 580 m, 532 w, 520 w, 484 w, 445 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: Isomer (A) a doublet of doublets (1F) centred at 42.13 p.p.m $J(F_1-F_4)$= 145.43Hz, $J(F_3-F_4)$=9.00Hz, a doublet of doublets (1F) centred at 47.22 p.p.m $J(F_1-F_4)$=145.43Hz, $J(F_1-F_3)$=44.38Hz, a doublet of doublets (1F) centred at 67.01 p.p.m $J(F_1-F_3)$=44.38Hz, $J(F_3-F_4)$=9.00Hz (relative to external benzotrifluoride).

Isomer (B) a doublet of doublets (1F) centred at 35.89 p.p.m $J(F_1-F_4)$=137.93Hz, $J(F_2-F_4)$=45.58Hz, a doublet of doublets (1F) centred at 53.42Hz, $J(F_1-F_4)$=137.93Hz, $J(F_1-F_2)$=8.99Hz, a doublet of doublets (1f) centred at 73.95 p.p.m $J(F_2-F_4)$=45.58Hz, $J(F_1-F_2)$=8.99Hz (relative to external benzotrifluoride) Ratio of isomers 75.25.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: two triplets centred at 1.20(3H) and 1.29(3H) p.p.m J(H-H)=7.76Hz, two quartets centred at 3.45(2H) and 3.69(2H)

p.p.m. J(H-H)=7.76Hz. There are also two multiplets centred at 4.56 (1H) and 4.84 p.p.m (1H). The remaining 10H of the (cod) ligand occur in a broad band between 1.40 and 4.00 p.p.m.

5. Trifluoroethylene with diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I).

An excess of trifluoroethylene (0.70ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I) (0.40g, 0.89 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The pale yellow solution was filtered and the filtrate evaporated to an oil. On adding a few drops of diethyl ether pale orange microcrystals were produced. These were filtered, washed with light petroleum (40-60°) and identified as complex 3:9 [Ir(dtc)(cod) (CF_2=CFH)] (0.15g,31%) m.p. 158-162°C.

$C_{15}H_{23}F_3IrNS_2$	requires	C, 33.89;	H, 4.36;	F, 10.72%
	found	C, 29.49;	H, 4.17;	F, 12.36%

Infra-red: 1512 s,br, 1352 m, 1320 m, 1296 m, 1278 s, 1206 s, 1152 m, 1096 m, 1088 m, 1080 m, 1068 m, 1000 m, 975 m, 910 m, 898 s, 865 m, 852 m, 829 m, 796w, 782 m, 740 w, 700 w, 616 w, 606 w, 568 w, 560 w, 532 w, 510 w, 498 w, 458 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: a doublet of doublets (1F) centred at 37.58 p.p.m. J(F_1-F_4)=145.43Hz, J(F_4-F_2)=50.97Hz a doublet of doublets (1F) centred at 50.52 p.p.m. J(F_1-F_4)=145.43Hz J(F_1-F_2)=12.89Hz, and what

appears to be a triplet (1F) centred at 58.83 p.p.m. probably arising because $J(F_2-F_4)$ and $J(F_2-H)$ are of the same magnitude (relative to external benzotrifluoride).

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a pair of overlapping triplets (6H) centred at 1.28 p.p.m and a multiplet (4H) centred at 3.62 p.p.m. There is also a broad singlet (1H) centred at 4.04 p.p.m and a multiplet (1H) at 4.58 p.p.m. The remaining protons of the cyclo-octadiene ligand absorb between 1.40 and 4.00 p.p.m.

6. <u>Chlorotrifluoroethylene with diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of chlorotrifluoroethylene (0.75 ml) was condensed (-196°) on to a suspension of diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I) (0.30g, 0.62 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The pale yellow solution was filtered and the filtrate evaporated to a yellow oil. On addition of a few drops of light petroleum (40-60°) and pumping on a vacuum line for several hours, yellow oily crystals of complex 3:10 $[Ir(dtp)(cod)(CF_2=CFCl)]$ (0.31g, 89.0%) m.p. 100-101°C. were produced.

$C_{14}H_{22}ClF_3IrO_2PS_2$	requires	C,27.89;	H, 3.68%
	found	C,30.17;	H, 4.57%

Infra-red: 1346 s, 1326 m, 1296 w, 1238 w, 1208 w, 1161 m, 1130 m, 1104 w, 1055 s, 1042 s, 1034 s, 1016 s, 1000 s, 972 s, 966 s, 936 m, 899 m, 880 m, 870 w, 820 s, 800 s, 784 s, 756 m, 726 w, 699 s, 656 s, 632 s, 585 w, 550 w, 533 m, 504 w, 451 w, 406 m, 310 m.

^{19}F n.m.r. spectrum:

Observed in diethyl ether solution: Isomer(A) a doublet of doublets (1F) centred at 48.27 p.p.m $J(F_4-F_1)$=130.43Hz, $J(F_4-F_3)$=8 25Hz, $J(P-F_4)$=3.15Hz, a doublet of doublets (1F) centred at 47.68 p.p.m. $J(F_1-F_4)$=130.43Hz, $J(F_1-F_3)$=41.38Hz, and a doublet of doublets (1F) centred at 70.27 p.p.m $J(F_3-F_1)$=41.38Hz, $J(F_3-F_4)$=8.25Hz (relative to external benzotrifluoride).

Isomer (B) a doublet of doublets (1F) centred at 35.45 p.p.m $J(F_4-F_1)$=131.93Hz, $J(F_4-F_2)$=43.48Hz, $J(P-F_4)$=4.80Hz, a doublet of doublets (1F) centred at 49.88 p.p.m. $J(F_1-F_4)$=131.93Hz, $J(F_1-F_2)$-8.40Hz, and a doublet of doublets (1F) centred at 69.64 p.p.m $J(F_2-F_4)$=43.48Hz, $J(F_2-F_1)$=8.40Hz (relative to external benzotrifluoride). Ratio of isomers 70-30.

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a triplet (6H) centred at 1.36 p.p.m. J(H-H)=6.76Hz and a multiplet (4H) centred at 4.04 p.p.m. The protons of the cyclo-octadiene ligand occurs as multiplets at 1.40, 2.18 and 4.05 p.p.m.

7. <u>Chlorotrifluoroethylene with diphenyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of chlorotrifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diphenyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I)

(0.30g, 0.55 m.mol) in diethyl ether contained in a Carius tube (150ml). After standing at room temperature for 24 hours the tube was opened and volatile material removed. The orange solution was filtered and the filtrate evaporated to small volume. Addition of light petroleum (40-60°) resulted in the production of yellow microcrystals of complex 3:11 [Ir(dptc)(cod)(CF_2:CFCl)] (0.31g,89%) m.p. 135-140°C.

$C_{23}H_{22}ClF_3IrNS_2$	requires	C,41.72;	H,3.35;	Cl, 5.36%
	found	C,42.04;	H,3.59;	Cl, 5.53%

Infra-red: 1588 m, 1568 w, 1364 s, 1328 s, 1312 m, 1305 m, 1296 w, 1272 w, 1164 w, 1104 m, 1073 w, 1060 m, 1028 m, 1004 m, 926 m, 914 s, 883 m, 844 m, 790 w, 762 s, 758 s, 728 m, 713 m, 700 s, 666 m, 622 m, 588 m, 532 w, 460 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: Isomer (A) a doublet of doublets (1F) centred at 41.35 p.p.m, $J(F_4-F_1)$=146.93Hz, $J(F_4-F_3)$=8.99Hz, a doublet of doublets (1F) at 50.76 p.p.m. $J(F_1-F_4)$=146.93Hz, $J(F_1-F_3)$=38.93Hz and a doublet of doublets (1F) centred at 71.59 p.p.m $J(F_3-F_1)$=38.98Hz $J(F_3-F_4)$=8.99Hz (relative to external benzotrifluoride)

Isomer (B) a doublet of doublets (1F) centred at 38.73 p.p.m $J(F_4-F_1)$=146.93Hz, $J(F_4-F_2)$=44.98Hz, a doublet of doublets (1F) centred at 52.92 p.p.m. $J(F_1-F_4)$=146.93Hz $J(F_1-F_2)$=7.50Hz and a doublet of doublets (1F) at 68.57 p.p.m.

$J(F_2-F_4)$=44.98Hz, $J(F_2-F_1)$=7.50Hz, (relative to external benzotrifluoride) Ratio of isomers 70:30.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet (4H) between 0.80 and 2.04 p.p.m a multiplet (4H) between 2.04 and 3.20 p.p.m, a multiplet (1H) centred at 3.48 p.p.m, a multiplet (1H) centred at 4.00 p.p.m, a multiplet (1H) centre at 4.64 p.p.m and a multiplet (1H) at 4.88 p.p.m. Also a broad singlet (10H) at 7.48 p.p.m.

8. <u>Hexafluoropropene with diethyldithiophosphato(cyclo-octa-1,5-diene) iridium(I).</u>

An excess of hexafluoropropene(1.0ml) was condensed (-196°) on to a suspension of diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I) (0.20g, 0.41 m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 2 hours the tube was opened and volatile material removed. The pale yellow solution was filtered and the filtrate evaporated to a yellow oil. The addition of light petroleum (40-60°) (5ml) and pumping under reduced pressure for 30 minutes resulted in the production of yellow microcrystals of complex 3:12 $[Ir(dtp)(cod)(CF_2:CFCF_3)]$ (0.13g, 50%).

$C_{15}H_{22}F_6IrO_2PS_2$	requires	C,28.30;	H,3.48;	F,17.91%
	found	C,28.67;	H,3.68;	F,17.62%

Infra-red: 1360 s, 1281 s, 1176 s, 1160 m, 1144 s, 1108 w, 1096 w, 1032 s, sh, 1012 s, 974 s, 964 s, 960 s, sh, 899 w, 880 w, 820 m, 792 s, 772 s, 727 m, 684 s, 656 m, 640 m, 612 w, 552 m, 532 m, 498 w, 456 w, 420 w, 404 w, 308 w.

^{19}F n.m.r. spectrum:

Observed in dichloromethane solution: a broad singlet (3F) at 3.94 p.p.m, a doublet of doublets (1F) at 31.10 p.p.m $J(F_1-F_4)$=157.42Hz, $J(F_2-F_4)$=14.99Hz and a doublet of doublets (1F) centred at 42.59 p.p.m $J(F_1-F_4)$=157.42Hz. There is also a broad singlet (1F) at 135.70 p.p.m. (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a triplet (6H) centred at 1.36 p.p.m J(H-H)=6.91Hz and a multiplet (4H) centred at 4.10 p.p.m. There is also a multiplet (1H) centred at 5.00 p.p.m. and the remaining cyclo-octadiene protons appear between 1.45 and 4.30 p.p.m.

9. <u>Trifluoroethylene with diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I).</u>

An excess of trifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diethyldithiophosphato(cyclo-octa-1,5-diene)iridium(I) (0.30g, 0.62 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 3 days the tube was opened and volatile material removed. The yellow solution was filtered and the filtrate evaporated to small volume. Yellow crystals of complex 3:13 $[Ir(dtp)(cod)(CF_2:CFH)]$ (0.30g, 84.5%) m.p. 102-104°C formed on standing.

$C_{14}H_{23}F_3IrO_2P$	requires	C, 29.58;	H,4.08;	F,10.03%
	found	C, 31.15;	H,4.67;	F,8.36%

Infra-red: 1325 m, 1296 m, 1234 m, 1207 m, 1163 m, 1159 m, 1104 m, 1057 s, 1035 s, 1018 sm 1009 s, 962 s,br, 892 s, 875 s, 864 m, 819 s, 779 s, 650 m, 627 s, 544 w, 526 m, 498 m, 398 s, 350 w, 301 s.

No ^{19}F or ^{1}H n.m.r. spectrum obtainable.

10. Perfluorocyclobutene with diethyldithiocarbamato(cyclo-octa-1,5-diene)iridium(I).

An excess of perfluorocyclobutane (0.5 ml) was condensed (-196°) on to a suspension of diethyldithiocarbamato(cyclo-octa-1,5-diene) iridium(I)(0.30g,0.67m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 72 hours the tube was opened and volatile material removed. The pale yellow solution was filtered and the filtrate evaporated to oily crystals of complex 3:14 $[Ir(dtc)(cod)(F_2C{=}CF_2)]$ (0.32g, 84 %) m.p. 56-60°C.

Infra-red: 1508 m,br, 1362 s, 1302 w, 1275 m, 1250 m,sh, 1208 m, 1150 m, 1113 m, 1096 m, 1073 m, 1013 w, 950 m, 915 w, 890 w, 875 m, 848 m, 780 m, 736 s, 722 s, 675 w, 665 w, 608 m, 483 w, 460 w.

^{19}F n.m.r. spectrum:

Observed in $CDCl_3$ solution: four fluorine resonances at 38.44(1F), 42.41(1F), 50.80(2F), and 52.78(2F) p.p.m. each of which appears as a doublet of multiplets with $J(F_1-F_2)$=197.90Hz and $J(F_3-F_4)$=124.44Hz (relative to external benzotrifluoride).

^{1}H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a triplet(3H) centred at 1.16 p.p.m.

and another centred at 1.28 p.p.m. J(H-H)=6.31Hz. Two quartets centred at 3.36(2H) and 3.60(2H) p.p.m. The protons of the cyclo-octadiene ligand appear as multiplet signals between 1.40 and 3.08 (10H) p.p.m. plus two multiplets at 4.18(1H) and 4.67(1H) p.p.m.

C. The reaction of fluoro-olefins with the complex diethyldithiocarbamatobis(cyclo-octene)iridium(I).

1. With tetrafluoroethylene.

An excess of tetrafluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diethyldithiocarbamatobis(cyclo-octene)iridium(I) (0.50g, 0.88 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 48 hours the tube was opened and volatile material removed. The dark orange precipitate was filtered off, washed with diethyl ether and identified as complex 3:15 [Ir(dtc)(CH)F(CO)] (0.32g,89%) m.p.220-270° dec without melting.

$C_6H_{11}FIrNO_2S_2$ requires C,17.77; H,2.73%

found C,19.16; H,2.52%

Infra-red: 2055 s, 1624 m,br, 1520 s, sh, 1501 s, 1351 s, 1279 m, 1268 m, 1199 m, 1192 m, 1186 w, 1150 m, 1140 m, 1088 m,br, 1068 m, 1040 w, 999 w, 960 m, 913 m, 880 w, 844 m, 788 s, 772 s, 748 s,br, 730 s, 560 m, 550 m, 498 m.

No n.m.r. spectra obtainable.

2. With chlorotrifluoroethylene.

An excess of chlorotrifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diethyldithiocarbamatobis(cyclo-octene) iridium(I) (0.50g, 0.88 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The brown-orange precipitate was filtered, washed and diethyl ether and identified as complex 3:15

$[Ir(dtc)(OH)Cl(CO)]$ (0.315g, 84%) m.p. 280° dec without melting.

$C_6H_{11}ClIrNO_2S_2$	requires	C,17.08; H,2.62; Cl,8.41%
	found	C,19.53; H,2.62; Cl,8.21%

Infra-red: 2045 s, 1643 m,br, 1531 s, br, 1356 m, 1280 s, 1200 m, 1152 m, 1090 m, 1076 m, 988 m, 940 m, 915 m, 847 m, 780 m, 756 s, 736 s, 610 w, 596 w, 556 w, 500 w, 484 w, 424 w.

^1H n.m.r. spectrum:

Observed in $CDCl_3$ solution: a multiplet (6H) centred at 1.36 p.p.m. and a multiplet (4H) centred at 3.60 p.p.m.

3. <u>With bromotrifluoroethylene.</u>

An excess of bromotrifluoroethylene (1.0 ml) was condensed (-196°) on to a suspension of diethyldithiocarbamatobis(cyclo-octene) iridium(I) (0.40g, 0.71 m.mol) in diethyl ether contained in a Carius tube (150 ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The orange-brown precipitate was filtered, washed with diethyl ether and identified as complex 3:17 $[Ir(dtc)(OH)Br(CO)]$ (0.25g, 75%) m.p. 280° dec without melting.

$C_6H_{11}BrIrNO_2S_2$	requires	C,15.45; H,2.37; Br.17.14%
	found	C,18.52; H,2.54; Br,13.96%

Infra-red: 2060 s, 1619 m,br, 1527 s,br, 1356 s, 1280 s, 1200 m, 1152 m, 1096 m, 1076 m, 1064 m, 988 m, 854 w, 847 w, 820 w, 782 m, 783 s,br, 530 m, 500 w, 480 w.

^{1}H n.m.r. Spectrum:

Observed in $CDCl_3$ solution: a multiplet (6H) centred at 1.40 p.p.m, and a multiplet (4H) centred at 3.56 p.p.m.

4. With trifluoroethylene.

An excess of trifluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diethyldithiocarbamatobis(cyclo-octene)iridium(I) (0.40g, 0.71 m.mol) in diethyl ether contained in a Carius tube (150ml). After shaking at room temperature for 24 hours the tube was opened and volatile material removed. The orange-brown precipitate was filtered off, washed with diethyl ether and identified as complex 3:18 [Ir(dtc)(OH)H(CO)] (0.23g, 83%) m.p. 280° dec without melting.

$C_6H_{12}IrNO_2S_2$	requires	C,18.60; H,3.12%
	found	C,18.93; H,2.80%

Infra-red: 2040 m, 1807 m,br, 1631 m,br, 1544 s, 1530 s, 1524 s, 1512 s, 1360 s, 1278 s, 1208 s, 1152 m, 1096 m, 1077 m, 1000 m, 982 m, 936 w, 917 m, 866 m, 856 m, 832 w, 793 m, 754 m, 748 m, 697 w, 608 w, 602 w, 587 w, 500 w.

D. The reaction of tetrafluoroethylene with diethyldithiophosphatobis (cyclo-octene)iridium(I).

An excess of tetrafluoroethylene (1.0ml) was condensed (-196°) on to a suspension of diethyldithiophosphatobis(cyclo-octene)iridium(I) (0.50g, 1.03 m.mol) in diethyl ether (15ml) contained in a Carius tube (150ml). After shaking for 5 days at room temperature, the tube was opened and volatile material removed. The orange precipitate was filtered, washed with diethyl ether and identified as unreacted diethyldithiophosphato(cyclo-octene)iridium(I), (0.45g, 90%) from its melting point, infra-red and ^{1}H n.m.r. spectra.

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SUMMARY

Chapter 1 presents a review on the reactions of electrophilic ketones with palladium and platinum compounds. Further reactions of various palladium(0) platinum(0) and platinum(II) complexes with the electrophilic ketones hexafluoropropan-2-one, chloropentafluoropropan-2-one 1,3-dichlorotetrafluoropropan-2-one, 1,1,3-trichlorotrifluoropropan-2-one, acetonedicarboxylic acid dimethyl ester and diethyl ketomalonate are described.

Chapter 2 contains the results of some investigations into the reactivity of some iridium(I) olefin complexes towards hexafluorobut-2-yne and dimethylacetylenedicarboxylate; hexafluorobut-2-yne reacts with complexes of the type $[IrCl(cod)]_2$ and $[Ir(dithio)(cod)]$ to produce previously unknown olefin-acetylene complexes.

Chapter 3 discusses the preparation of the fluoro-olefin complexes $[IrCl(cod)(CF_2{=}CFX)]$ and $[Ir(dithio)(cod)(CF_2{=}CFX)]$ where X=F, Cl, Br, H, CF_3. Studies of their ^{19}F n.m.r. spectra indicates the presence of two isomers in many of these fluoro-olefin complexes.