

# THE ROLE OF FLUOROCARBONS IN OXIDATIVE-ADDITION AND -ELIMINATION REACTIONS

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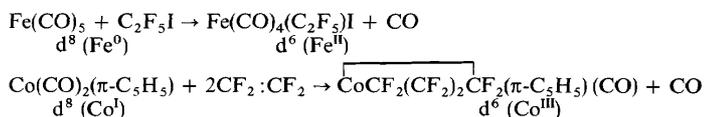
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## ABSTRACT

This lecture describes a comprehensive study of the reactions of unsaturated fluorocarbons with zero-valent complexes of nickel, palladium and platinum. Many stable complexes  $L_2M(AB)$ , where  $A:B = CF_2:CFX$  [ $X = F, Cl, CF_3$  etc],  $(CF_3)_2C:O$  and  $(CF_3)_2C:NR$  [ $R = H$  or  $Me$ ], have been prepared, as well as five-membered ring complexes  $L_2M\overline{A \cdot B \cdot A \cdot B}$ . The various factors which determine the nature of the products are discussed, and it is shown that several of the five-membered ring complexes are formed from the adducts  $L_2M\overline{A \cdot B}$ . The formation of azine metal complexes from  $(CF_3)_2CN_2$  is also described.

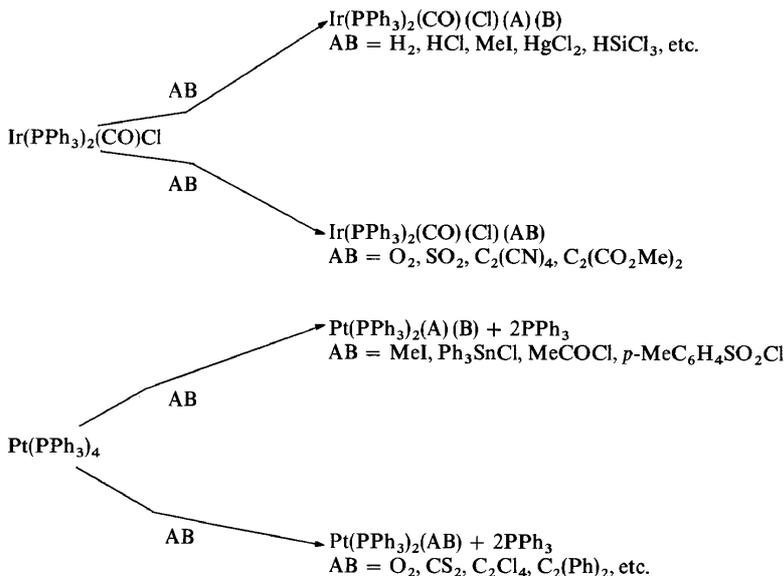
## INTRODUCTION

In 1960, at Harvard University, my research group discovered several methods for synthesizing fluorocarbon-transition metal complexes<sup>1-4</sup>. These included some reactions in which metal ions with a  $d^8$ -configuration are formally oxidized by a fluorocarbon, viz.



These syntheses are now known to be examples of a widespread class of reaction in which the metal's oxidation state and coordination number are both increased as a result of interaction with a substrate molecule<sup>5, 6</sup>. In this context reactions of Vaska's<sup>7</sup> iridium(I) complex,  $Ir(PPh_3)_2(CO)Cl$ , have been intensively studied, the term oxidative-addition being used to describe the over-all processes given in *Scheme 1*. Two types of product may be recognized according to whether in the reaction with a substrate molecule  $AB$  the reactant has been cleaved into two fragments forming distinct  $Ir-A$  and  $Ir-B$  bonds, or whether the reactant merely complexes with the iridium ion to form an adduct with a three-centre interaction  $Ir(AB)$ . In the former case the coordination number of the metal has clearly changed from four to six so that it is no longer coordinatively unsaturated and its oxidation number has increased from +I to +III, following the accepted convention<sup>6</sup>. In the latter case, a bond, albeit modified in character compared with that in

the free substrate<sup>8</sup>, remains between A and B in the product; so that the assignment of coordination number and oxidation state to the iridium atom cannot be settled with certainty. The complex will contain five or six coordinate iridium depending on whether the group AB is regarded as being a mono- or bidentate ligand. The extent of oxidation of the metal ion depends on the degree to which electrons are transferred to the antibonding orbitals of the reactant, which in turn depends on its electrophilic character. Since the latter varies for each reactant it becomes impossible to assign integral oxidation states to the metal, and as a working hypothesis it is necessary to qualitatively relate oxidation of the metal to some spectroscopic property of a ligand in the complex.



Scheme 1. Some examples of the oxidative-addition chemistry of  $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ ,<sup>7,10,11</sup> and the oxidative-elimination chemistry of  $\text{Pt}(\text{PPh}_3)_4$ .<sup>12-14</sup>

Complexes in which the metal has a  $d^{10}$ -configuration also undergo facile oxidative reactions with electrophilic reagents. A good example of this behaviour is shown by Malatesta's<sup>9</sup> platinum compound  $\text{Pt}(\text{PPh}_3)_4$  (see Scheme 1). Ostensibly the reactions shown appear to proceed without increase in the coordination number of the platinum atom. However, it is known<sup>15\*</sup> that  $\text{Pt}(\text{PPh}_3)_4$  dissociates in benzene giving  $\text{Pt}(\text{PPh}_3)_n$  [ $n=2$  or  $3$ ]. Reaction of the latter species with electrophiles does therefore involve an increase in the coordination number of the metal in the oxidative step, but the net loss of phosphine ligands leads to the term oxidative-elimination<sup>16</sup> being more properly applied to these processes, and equally to those, mentioned above, in which carbon monoxide is released.

\* More recent work (C. A. Tolman, W. C. Seidel and D. H. Gerlach, *Inorg. Chem.* in press) has established that dissociation stops at  $n = 3$ .

The electrophilic character of unsaturated organic fluorine-containing compounds is well known<sup>17,18</sup> and arises through withdrawal of electron density by fluorine atoms from C=C, C=O, C=S and C=N groups. We are carrying out a comprehensive study of reactions of fluorocarbons with d<sup>8</sup> and d<sup>10</sup> metal complexes; especially the latter. In this way it is hoped to gain a better understanding of the ability of low-valent transition metal complexes to activate unsaturated organic molecules in general. The bonding of a fluorocarbon such as tetrafluoroethylene to a transition metal ion would be similar to that of a hydrocarbon such as ethylene in that one can rationalize the attachment by invoking the customary idea of a synergic effect involving both the  $\sigma$ -donating and the  $\pi$ -acceptor characteristics of the ligand. With a fluoro-olefin, however, as discussed later, retro-dative bonding from the metal would be particularly important. Bonding of the two ligands (C<sub>2</sub>F<sub>4</sub> or C<sub>2</sub>H<sub>4</sub>) would thus differ only in degree rather than in kind. Hence a study of the interaction of unsaturated fluorocarbons with metal complexes could increase our knowledge of the mechanisms of certain catalytic reactions involving hydrocarbons such as, for example, ethylene or butadiene.

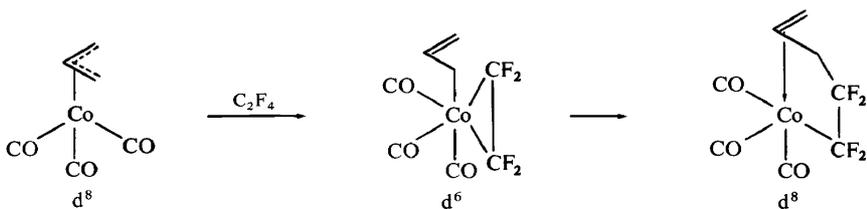
Such a connection between hydrocarbon- and fluorocarbon-metal chemistry is illustrated by some recent studies of reactions of tetrafluoroethylene with  $\pi$ -allylcobalt and -rhodium complexes.  $\pi$ -Allylcobalt tricarbonyl reacts with tetrafluoroethylene at room temperature almost quantitatively to give complex (I), formulated as an insertion product on the basis of its infrared and n.m.r. (<sup>1</sup>H and <sup>19</sup>F) spectra<sup>19</sup>. It seemed likely that (II) would be a precursor in the formation of (I) but no evidence for the former compound was obtained. In contrast, with  $\pi$ -allylrhodium compounds it has been possible to isolate and fully characterize both insertion products such as (IIIa) and complexes such as (IV)<sup>20</sup>. Thus if  $\pi$ -allylrhodium dicarbonyl, methyldiphenylphosphine, and tetrafluoroethylene are heated at 60°C the insertion product (IIIa) ( $\nu_{\text{CO}}$  1996 cm<sup>-1</sup>) is obtained, whereas if the reactants are mixed at room temperature compound (IV) is produced. In related studies,  $\pi$ -allylrhodium dicarbonyl reacts with triphenylarsine to give Rh( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(AsPh<sub>3</sub>)<sub>2</sub>(CO) [ $\nu_{\text{CO}}$  1945 cm<sup>-1</sup>] which will subsequently react with tetrafluoroethylene to give (IIIb).

Complexes (III) and (IV) are structurally very similar to the intermediates [(V) and (VI)] postulated<sup>21</sup> in the rhodium-catalysed synthesis of 1,4-hexadiene from ethylene and butadiene where ( $\pi$ -crotyl) ( $\pi$ -ethylene)rhodium complexes have been implicated but not isolated\*.

If we assume that as a ligand tetrafluoroethylene behaves formally as a two electron acceptor (see below), formation of (IV) from Rh( $\pi$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> can be regarded as a d<sup>8</sup> to d<sup>6</sup> (Rh<sup>I</sup> to Rh<sup>III</sup>) transformation which is followed in the presence of CO by a reductive step (Rh<sup>III</sup> to Rh<sup>I</sup>) to give (IIIa).

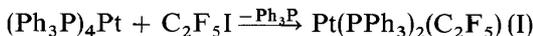
A similar mechanism of oxidative-addition followed by intramolecular reduction accounts for the ready insertion of fluoro-olefins into  $\pi$ -allyl- and methallylcobalt carbonyls<sup>19</sup> (Scheme 2).

\* Certain nickel complexes also catalyse the formation of hexadienes by the coupling of ethylene and 1,3-butadiene<sup>22</sup>.

Scheme 2. Possible mode of insertion of  $C_2F_4$  into  $\pi$ -allylcobalt bonds.REACTIONS OF  $d^{10}$ -COMPLEXES

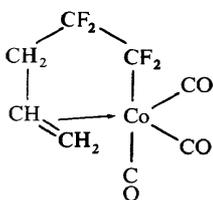
## 1. Fluoro-olefins

The observation that tetrakis(triphenylphosphine)platinum undergoes an oxidative-elimination reaction with perfluoroalkyl iodides<sup>23</sup>, e.g.

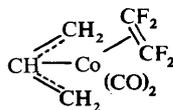


prompted a study of the corresponding reaction with tetrafluoroethylene<sup>24</sup>. The product  $(Ph_3P)_2Pt(C_2F_4)$  (VIIa) is air-stable, does not decompose below its melting point ( $218^\circ C$ ), and the tetrafluoroethylene moiety cannot be displaced by electron pair donor ligands. In contrast, the complex  $(Ph_3P)_2Pt(C_2H_4)$  [decomp.  $122^\circ C$ ] has not been made from  $Pt(PPh_3)_4$  but by reducing  $Pt(PPh_3)_2(O_2)$  in the presence of ethylene, and the latter is readily displaced from the platinum complex by other ligands<sup>25</sup>.

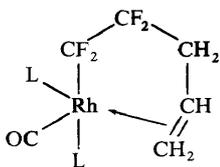
The reaction of fluoro-olefins with  $Pt(PPh_3)_4$  is general and a number of complexes of type (VII) have been prepared<sup>24</sup>, including the hexafluoro-bicyclo[2.2.0]hexa-2,5-diene ('Dewar' hexafluorobenzene) complex (VIII)<sup>26</sup>. The compounds  $PtL_4$  [ $L = PPh_2Me$  and  $L = PPhMe_2$ ] also form very stable adducts  $L_2Pt(C_2F_4)$  with tetrafluoroethylene<sup>27</sup>.



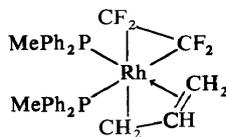
(I)



(II)

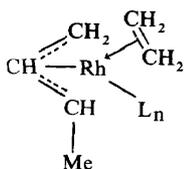


(III) (IIIa)  $L = PPh_2Me$   
(IIIb)  $L = AsPh_3$

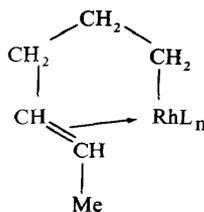


(IV)

## FLUOROCARBONS IN OXIDATIVE-ADDITION REACTIONS



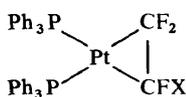
(V)



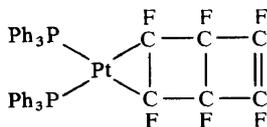
(VI)

The properties of the fluoro-olefin-platinum adducts  $L_2Pt$  (fluoro-olefin) are such that we believe that they are most satisfactorily formulated with metallocyclopropane ring structures (VII), rather than as conventional ' $\pi$ -complexes'.

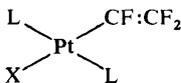
The  $^{19}F$  n.m.r. spectrum of (VIIa) is typical of the X resonance of an  $X_2AA'X'_2$  system and is invariant with temperature. The 'AB' resonance of the  $CF_2$  group in the spectrum of (VIIId) showed a coupling constant  $J_{FF} = 188$  Hz. This value is similar<sup>28</sup> to that observed for  $^2J(F,F)$  in substituted fluorocyclopropane systems and very much higher than that customarily found for a vinylic coupling constant. For example, from the spectrum of  $CF_3CF:CF_2$ , the coupling constant between the fluorine nuclei of the  $CF_2$  group is 57 Hz. These results imply not only a rigidity of the  $PtC_2$  interaction in (VII), but also a significant change in hybridization of the carbon atoms upon coordination. From a study of the  $^1H$  and  $^{19}F$  spectra of  $(\pi-C_5H_5)Rh(C_2F_4)(\pi-C_2H_4)$ , Cramer *et al.*<sup>29</sup> have similarly concluded that the bonding of the  $C_2F_4$  group is best pictured as occurring via two  $\sigma$ -bonds\*. Apparently the electronegative fluorine atoms induce an extensive transfer of electron density from the metal to the  $\pi^*$ -orbital of the  $C_2$  group, thereby perhaps even increasing by two the formal oxidation state of the metal. Thus in applying the Dewar, Chatt and Duncanson<sup>31,32</sup> scheme of



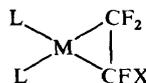
(VIIa) X = F  
 b X = Cl  
 c X = Br  
 d X =  $CF_3$   
 e X =  $CF:CF_2$



(VIII)



(IX) L =  $PPh_3$  or  $PPh_2Me$   
 X = Cl or Br



(X) M = Ni or Pd  
 X = Cl or Br

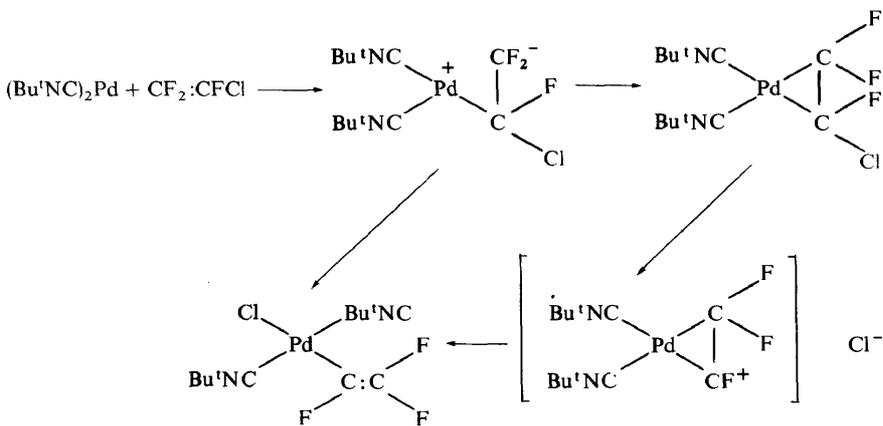
\* An analysis<sup>30</sup> of the  $^{19}F$  n.m.r. spectrum of *cis*- $[(MeO)_3P]_2Ru(C_2F_4)(CO)_2$  also reveals coupling constant changes as expected for  $sp^3$  hybridized carbon atoms of the  $C_2F_4$  group.



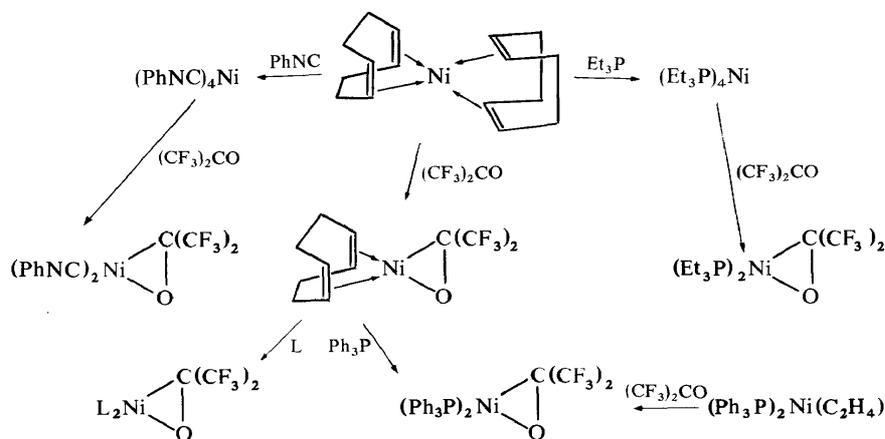
## FLUOROCARBONS IN OXIDATIVE-ADDITION REACTIONS

The perfluorovinylmetal compounds all show a strong band in their infrared spectra in the range  $1700\text{--}1730\text{ cm}^{-1}$  due to the double bond of the  $\text{CF}:\text{CF}_2$  group.

Our isolation of the platinum compounds (VIIb) and (VIIc) and their rearrangement into (IX), suggests that the complexes (XI) are formed via unstable three-membered ring compounds (X). However, an alternative pathway<sup>38</sup> could involve the direct elimination of  $\text{Cl}^-$  and  $\text{Br}^-$  from an intermediate ionic species (Scheme 4).



Scheme 4. Formation of a perfluorovinyl compound directly from a 1,3-dipolar intermediate or from a three-membered ring complex.



$\text{L} = \text{Ph}_2\text{PMe}, (\text{PhO})_3\text{P}, \text{EtC}(\text{CH}_2\text{O})_3\text{P}, \text{Bu}^t\text{NC}, \text{etc.}$

$\text{L}_2 = \text{diphos, diars and bipy.}$

Scheme 5. Some hexafluoroacetone complexes of nickel.

## 2. Hexafluoroacetone and hexafluoroisopropylideneamine complexes

Many hexafluoroacetone metal complexes<sup>42-46</sup> have been isolated from reactions between this electrophilic ketone<sup>18</sup> and low-valent transition metal compounds. In the earliest example of this behaviour hexafluoroacetone was found to react rapidly with tetrakis(triphenylphosphine)-platinum(0) in benzene to afford the air-stable complex (XII)<sup>42</sup>. Several hexafluoroacetone-nickel complexes have been prepared, some via ligand exchange from  $(1,5\text{-C}_8\text{H}_{12})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  (Scheme 5)<sup>36, 37, 43, 44</sup>.

Hexafluoroacetone shows a strong  $\nu_{\text{CO}}$  band in its infrared spectrum at  $1807\text{ cm}^{-1}$ <sup>47</sup>. No such band appears in the spectra of any of the hexafluoroacetone metal complexes. The <sup>19</sup>F n.m.r. spectra of the complexes all show signals at about 10 ppm to lower field than uncoordinated hexafluoroacetone (77.2 ppm)\*. The <sup>19</sup>F n.m.r. spectra of the complexes

$(\text{Ph}_2\text{MeP})_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  [double-doublet,  $J_{\text{PF}}$  (*cis*) 7.0;  $J_{\text{PF}}$  (*trans*) 11.0 Hz],

$(\text{Ph}_3\text{P})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  [doublet,  $J_{\text{PF}}$  (*trans*) 12.2 Hz], and  $(\text{Ph}_3\text{P})_2\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  (XII) [triplet of double-doublets,  $J_{\text{PF}}$  (*cis*) 1.3;  $J_{\text{PF}}$  (*trans*) 11.3;  $J_{\text{PF}}$  70.5 Hz] are informative concerning the structure and bonding in these compounds.

If the two phosphorus nuclei, the metal atom and the ketonic group are all coplanar then although the  $\text{CF}_3$  groups are magnetically equivalent they are *cis* and *trans* to two phosphorus nuclei, and this could give rise to two <sup>31</sup>P-<sup>19</sup>F couplings. In the case of spectra which show two doublets,

e.g.  $(\text{Ph}_2\text{MeP})_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , it is assumed that the larger coupling is due to <sup>31</sup>P- $\text{CF}_3$ (*trans*). In some spectra where only a doublet is observed, e.g.

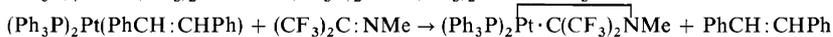
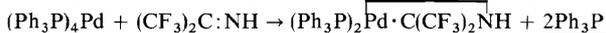
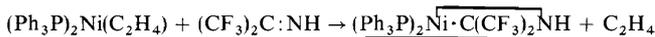
$(\text{Ph}_3\text{P})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , it is further assumed that the coupling  $J_{\text{P-CF}_3}$  (*cis*) has fallen below 1 Hz. The spectrum of (XII), which is invariant with temperature, appears as a triplet of double-doublets, the triplet arising through <sup>195</sup>Pt-<sup>19</sup>F coupling. The existence of doublets and double-doublets in the <sup>19</sup>F n.m.r. band patterns is in accord with a rigid three-membered ring structure as depicted for (XII). This could arise through strong back-bonding from the metal to the  $\pi^*$ -orbital of the CO group so that the metal ion approaches a formal oxidation state of +2, although the degree of oxidation will depend on the metal and the nature of the other ligands.

Very recently Penfold and Countryman<sup>50</sup> have carried out a single crystal x-ray diffraction study of the complex  $(\text{Ph}_3\text{P})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ . The two phosphorous atoms, the nickel atom and the C=O group are nearly coplanar, and the metal atom is equidistant from the C and O atoms. The three-membered ring structure for the hexafluoroacetone adducts is thus placed on a firm basis by this result.

A series of related three-membered ring complexes have been prepared from the imines  $(\text{CF}_3)_2\text{C}:\text{NH}$  and  $(\text{CF}_3)_2\text{C}:\text{NMe}$ , e.g.<sup>38, 44, 46, 51</sup>

\* A number of hexafluoroacetone adducts of d<sup>8</sup>-complexes have been described<sup>42, 48, 49</sup>, and in general the chemical shifts also fall below those of the free ligand, e.g.  $(\text{Ph}_2\text{MeP})_2(\text{OC})\overline{\text{Ir}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  (73.9 ppm),  $[\text{EtC}(\text{CH}_2\text{O})_3\text{P}]_2(\text{OC})_2\overline{\text{Ru}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  (68.6 ppm),  $(\text{Ph}_2\text{MeP})_2(\text{OC})_2\overline{\text{Ru}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  (75.7 ppm).

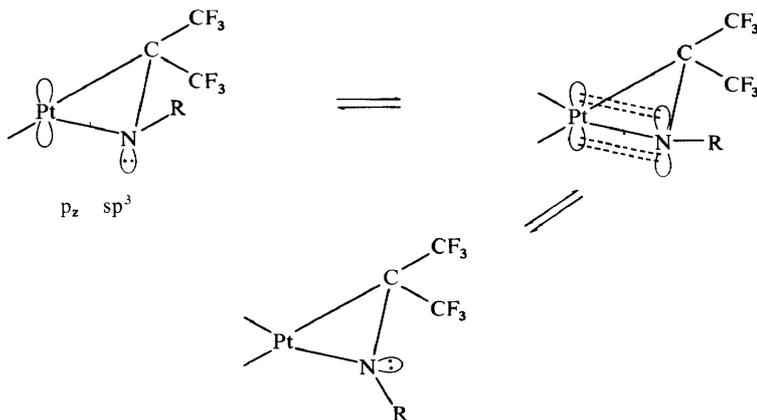
## FLUOROCARBONS IN OXIDATIVE-ADDITION REACTIONS



The  $^{19}\text{F}$  n.m.r. spectra of the hexafluoroisopropylideneamine and *N*-methylhexafluoroisopropylideneamine complexes are similar to those of their hexafluoroacetone analogues, and as with these compounds the resonance signal is centred at lower field than that of the free ligands [ $(\text{CF}_3)_2\text{C}:\text{NH}$ , 73.1 and 74.9 ppm,  $J_{\text{FF}}$  6 Hz;  $(\text{CF}_3)_2\text{C}:\text{NMe}$ , 66.9 and 73.4 ppm,

$J_{\text{FF}}$  8 Hz<sup>52</sup>]. Thus the spectrum<sup>46</sup> of  $(\text{diphos})\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2}\text{NH}$  appears as a double-doublet centred at 66.6 ppm with  $^{195}\text{Pt}$ - $^{19}\text{F}$  satellites ( $J_{\text{PF}}(\text{trans})$  11;  $J_{\text{PF}}(\text{cis})$  2;  $J_{\text{Pt-F}}$  72 Hz). The geminal  $\text{CF}_3$  groups are apparently equivalent but have different couplings with the *cis* and *trans*  $^{31}\text{P}$  nuclei.

The apparent equivalence of the  $\text{CF}_3$  groups in the imine complexes is surprising because one  $\text{CF}_3$  group is ostensibly *syn* to a hydrogen or methyl group and the other *syn* to a lone pair. On cooling solutions of the compounds only line broadening is observed in the spectra. Two explanations have been advanced: (i) back bonding from the metal to the imine might be sufficient to rehybridize the N atoms so that the N-bonded methyl group or proton is coplanar with the PtCN ring, or (ii) rapid inversion is occurring at the nitrogen atom; a possible mechanism for which could involve a vacant metal  $p_z$ -orbital (Scheme 6)<sup>51</sup>.



Scheme 6. Inversion of imine complexes via a symmetrical intermediate formed by  $\pi$ -bonding from a filled nitrogen  $2p\pi$  orbital and a vacant  $6p\pi$  orbital of platinum.

This problem has been resolved by an x-ray crystallographic study of complex (XIII) by Chan and Penfold<sup>53</sup>. The three-membered ring is symmetrical, and the coordination about the platinum closely planar. The methyl group projects from the  $\text{P}_2\text{PtNC}$  plane, with the  $\text{PtNC}(\text{H}_3)$  angle being  $110^\circ$ . The CN distance is 1.39 Å. This result is important both in establishing the previously postulated three-membered ring structures for

Table 1. Five-membered heterocyclic metallo-ring complexes.

Compound	Colour	m.p. °C	<sup>19</sup> F n.m.r.*	Reference
(Et <sub>3</sub> P) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	141	104.8 (tt, J <sub>FF</sub> 1.7; J <sub>PF</sub> 44), 138.9 (t, J <sub>FF</sub> 1.7).	56
(Ph <sub>2</sub> MeP) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow-brown	182†	101.5 (t, J <sub>PF</sub> 47), 138.8 (s).	56
(Bu <sub>3</sub> P) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	47	103.3 (t, J <sub>PF</sub> 44.8), 138.6 (s).	56
(Ph <sub>3</sub> P) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	182	99.3 (t, J <sub>PF</sub> 48.0), 137.0 (s).	56
(diphos)Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	268†	104.0 (tt, J <sub>FF</sub> 2.3; J <sub>PF</sub> 58.1), 138.8 (t, J <sub>FF</sub> 2.3).	56
[(MeO) <sub>3</sub> P] <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	89	103.6 (br.s), 138.9 (s).	56
(bipy)Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	320†	109.0 (t, J <sub>FF</sub> 1.5), 139.4 (t, J <sub>FF</sub> 1.5).	56
(γ-picoline)Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	White	204†	111.7 (s), 139.8 (s).	56
(1,5-C <sub>8</sub> H <sub>1,2</sub> )Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	133†	103.3 (t, J <sub>FF</sub> 2.5), 138.4 (t, J <sub>FF</sub> 2.5).	56
(PhMe <sub>3</sub> As) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Orange	165	99.0 (t, J <sub>FF</sub> ~ 1.0), 139.1 (t, J <sub>FF</sub> ~ 1.0).	37
(diars)Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	254	99.0 (t, J <sub>FF</sub> ~ 1.0), 137.5 (t, J <sub>FF</sub> ~ 1.0).	37
(Bu'NC) <sub>2</sub> Ni(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	Yellow	148	101.6 (s), 138.2 (s).	44
(1,5-C <sub>8</sub> H <sub>1,2</sub> )Pt(CF <sub>2</sub> (CF <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub>	White	164	98.92 (br.s, J <sub>PF</sub> 422), 137.8 (br.s, J <sub>PF</sub> 60).	58
(diphos)Ni(C(CF <sub>3</sub> ) <sub>2</sub> O-C(CF <sub>3</sub> ) <sub>2</sub> O)	Yellow	201	64.6 (m, J <sub>PF</sub> 7.0; J <sub>FF</sub> 3), 80.9 (m, J <sub>FF</sub> 3).	46
(diars)Ni(C(CF <sub>3</sub> ) <sub>2</sub> O-C(CF <sub>3</sub> ) <sub>2</sub> O)	Yellow	180	65.7 (s), 81.5 (s).	37
(Bu'NC) <sub>2</sub> Ni(C(CF <sub>3</sub> ) <sub>2</sub> O-C(CF <sub>3</sub> ) <sub>2</sub> O)	Yellow	160	64.3 (m), 80.7 (m).	44
(Bu'NC) <sub>2</sub> Ni(C(CF <sub>3</sub> ) <sub>2</sub> NH-C(CF <sub>3</sub> ) <sub>2</sub> NH)	Yellow	128†	66.1 (m), 80.6 (m).	44

## FLUOROCARBONS IN OXIDATIVE-ADDITION REACTIONS

White	92†	65.7 (m, $J_{PF}(trans)$ 9.0, $J_{PF}(cis)$ 5.0), 81.4 (m, $J_{FF}$ 3.0).	45
White	134†	64.8 (m, $J_{PF}(trans)$ 8.0, $J_{PF}(cis)$ 5.0), 80.9 (m, $J_{FF}$ 3.0).	45
White	134	64.1 (m, $J_{PF}$ 6.0), 80.4 (m, $J_{FF}$ 3.0).	45
White	193†	66.3 (m, $J_{PF}$ 6.0), 81.1 (m, $J_{FF}$ 3.0).	45
White	117†	66.4 (m, $J_{PF}$ 6.0), 81.1 (m, $J_{FF}$ 3.0).	45
Yellow	131†	65.5 (m, $J_{PF}$ 3.0), 80.4 (m, $J_{FF}$ 3.0).	45
White	218†	71.0 (s).	45
White	156	68.3 (m), 81.1 (m).	38
White	180†	65.7 (m), 80.5 (m).	38
Yellow	93	64.4 (m, $J_{FF}$ 3.0), 81.1 (m, $J_{FF}$ 3.0).	38
White	173	64.9 (m, $J_{PF}(trans)$ 6; $J_{PF}(cis)$ 1; $J_{FF}$ 3; $J_{PF}$ 76), 80.6 (m, $J_{FF}$ 3).	46
White	234	66.6 (m, $J_{PF}$ 4.5; $J_{FF}$ 3; $J_{PF}$ 72), 80.7 (m, $J_{FF}$ 3).	46
White	—	66.0 (m, $J_{PF}$ 80), 82.5 (m).	46
White	210	67.3 (m, $J_{PF}$ 6; $J_{FF}$ 3; $J_{PF}$ 86), 81.0 (m, $J_{FF}$ 3).	46
White	66	71.3 (s).	58
White	183	67.1 (m, $J_{FF}$ 3; $J_{PF}$ 68), 80.4 (m, $J_{FF}$ 3).	58, 59
White	249	66.1 (m, $J_{PF}(trans)$ 7; $J_{PF}(cis)$ 3; $J_{FF}$ 3; $J_{PF}$ 80), 81.7 (m, $J_{FF}$ 2).	46

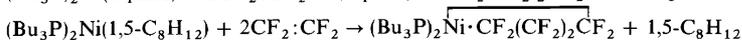
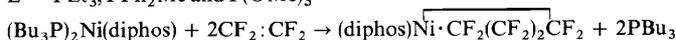
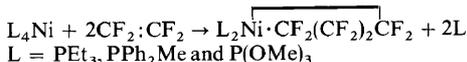
\* Chemical shifts are relative to  $CCl_4F$  (0.0) ppm; couplings are measured in Hz. For further details of the spectra, see original references.

† Decomposes.

the imine complexes, and strongly suggesting also that the n.m.r. equivalence of the  $\text{CF}_3$  groups is due to rapid inversion at the nitrogen atom in solution<sup>51</sup>.

### 3. Formation of five-membered ring complexes

Reference was made earlier to the octafluorometallocyclopentane complex  $(\pi\text{-C}_5\text{H}_5)(\text{OC})\overline{\text{Co}\cdot\text{CF}_2(\text{CF}_2)_2\text{CF}_2}$ , formed from  $\text{Co}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  and tetrafluoroethylene. Of early vintage also was the iron compound  $(\text{OC})_4\overline{\text{Fe}\cdot\text{CF}_2(\text{CF}_2)_2\text{CF}_2}$ ,<sup>1,54</sup> and a nickel complex  $(\text{diphos})\overline{\text{Ni}\cdot\text{CF}_2(\text{CF}_2)_2\text{CF}_2}$ .<sup>55</sup> No other complexes of this kind were discovered until the work of Cundy<sup>56</sup> who found that a variety of zero-valent nickel complexes having phosphine groups as ligands reacted with tetrafluoroethylene to give octafluoronickelacyclopentane complexes (XIV) (Table 1).



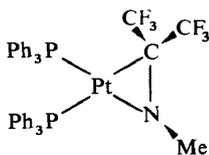
These results were in marked contrast with the corresponding reactions with tetrakis(phosphine)platinum complexes which afford three-membered ring complexes  $\text{L}_2\overline{\text{Pt}\cdot\text{CF}_2\text{CF}_2}$  (e.g. VIIa). Octafluorometallocyclopentane complexes all show a characteristic band pattern in their  $^{19}\text{F}$  n.m.r. spectra consisting of two multiplets of equal intensity; the signal at lower field being assigned<sup>57</sup> to the  $\text{CF}_2$  groups adjacent to the metal atoms. The two signals often appear as triplets, with splittings of  $\sim 2$  Hz. The apparent chemical shift equivalence of the fluorine nuclei of a given  $\text{CF}_2$  group suggests either a planar metallocyclopentane ring, or an envelope structure undergoing rapid conformational change. An x-ray crystallographic study should resolve this problem.

The isolation of several complexes of type (XIV) prompted a search for other compounds containing metal atoms in five-membered rings. It was noted that the nickel compounds  $\text{L}_2\overline{\text{Ni}\cdot\text{CF}_2\text{CFCF}_3}$  (L =  $\text{PEt}_3$  or  $\text{PPh}_3$ ) did not react further with perfluoropropene and also that in contrast to tetrafluoroethylene, hexafluoroacetone reacted with tetrakis(tertiary phosphine)nickel compounds to give three-membered ring compounds  $\text{L}_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , and not compounds of type  $\text{L}_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  \*. Nevertheless, the important observation was made that the imine complex  $(\text{Ph}_3\text{P})_2\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\text{NH}}$  reacted slowly with hexafluoroacetone to give the five-membered heterocyclic ring compound (XV)<sup>51</sup>.

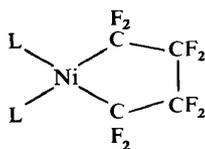
The  $^{19}\text{F}$  n.m.r. spectrum was in agreement with the structure proposed. Two resonances of equal intensity occurred at 64.1 and 81.0 ppm. Double irradiation of the high-field band collapsed the low-field band to a doublet having  $^{195}\text{Pt}$  satellites, which is therefore assigned to a  $(\text{CF}_3)_2\text{C}$  group

\* Interestingly  $(\text{diphos})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  can be prepared from  $(\text{diphos})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ .<sup>46</sup>

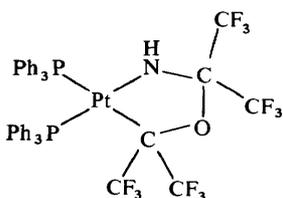
FLUOROCARBONS IN OXIDATIVE-ADDITION REACTIONS



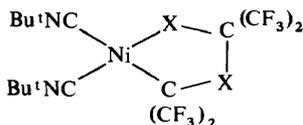
(XIII)



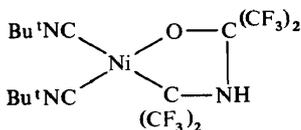
(XIV)



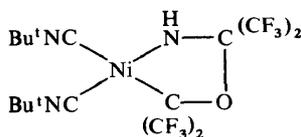
(XV)



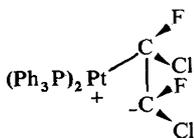
(XVI X = O or NH)



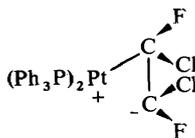
(XVIIa)



(XVIIb)



(XVIIIa)



(XVIIIb)

directly attached to platinum, the doublet arising owing to coupling with the  $^{31}\text{P}$  nucleus *trans* to the  $(\text{CF}_3)_2\text{C}$  group. Double irradiation of the low-field band collapsed the high-field band to a singlet, there being no evidence of  $^{195}\text{Pt}$ - $^{19}\text{F}$  spin-spin coupling; this was expected since this band is assigned to a  $\text{C}(\text{CF}_3)_2$  group not directly attached to platinum. These observations are consistent with structure (XV), or an isomer in which the O and NH groups exchange positions. However, because of results discussed later, structure (XV) is preferred, since it would be formed by insertion of  $(\text{CF}_3)_2\text{CO}$  into the  $\text{Pt}-\text{C}$  bond of  $(\text{Ph}_3\text{P})_2\text{Pt}\cdot\overline{\text{C}(\text{CF}_3)_2}\text{NH}$ .

It was also found<sup>44</sup> that the complex  $\text{Ni}(\text{Bu}'\text{NC})_4$ <sup>60</sup> was very reactive towards the fluorocarbon substrates readily forming  $(\text{Bu}'\text{NC})_2\text{-Ni}\cdot\overline{\text{CF}_2(\text{CF}_2)_2\text{CF}_2}$  with tetrafluoroethylene and ring compounds (XVI) with hexafluoro-acetone or -isopropylideneamine. These were the first

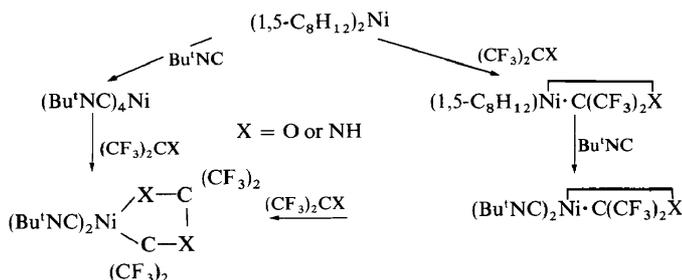
five-membered ring complexes to be prepared involving the direct reaction of  $(\text{CF}_3)_2\text{C}:\text{O}$  or  $(\text{CF}_3)_2\text{C}:\text{NH}$  with a  $d^{10}$ -metal complex, and their synthesis served to show the important role of the ligand  $(\text{Bu}^i\text{NC})$  in determining the course of the reaction, since as mentioned above, if tertiary phosphine groups are present on nickel, five-membered ring formation with  $(\text{CF}_3)_2\text{C}:\text{O}$  or  $(\text{CF}_3)_2\text{C}:\text{NH}$  does not generally occur. Another early observation which indicated the importance of the nature of the ligands present on the metal atom concerned the reaction of  $(1,5\text{-C}_8\text{H}_{12})_2\text{Ni}$  with  $\text{C}_2\text{F}_4$ <sup>56</sup>. The product of this reaction was not  $1,5\text{-C}_8\text{H}_{12}\overline{\text{Ni}\cdot\text{CF}_2(\text{CF}_2)_2\text{CF}_2}$ , but an unstable compound believed to be  $1,5\text{-C}_8\text{H}_{12}\overline{\text{Ni}\cdot\text{CF}_2\text{CF}_2}$ . Interestingly, when the latter was treated with triethylphosphine in the presence of tetrafluoroethylene a further molecule of this substrate was 'activated' by nickel and the stable five-membered ring compound (XIV) [ $\text{L} = \text{PEt}_3$ ] formed.

With a view to understanding the mechanism of three- and five-membered ring formation a series of experiments were undertaken to elucidate some of the factors involved.

(i) *Formation of five- from three-membered rings.*

Formation of (XV) from  $(\text{Ph}_3\text{P})_2\text{Pt}\cdot\overline{\text{C}(\text{CF}_3)_2\text{NH}}$  indicated that three-membered ring complexes were intermediates in the formation of five-membered ring compounds but it was necessary to establish the generality of this single observation.

As mentioned above, treatment of  $\text{Ni}(\text{Bu}^i\text{NC})_4$  with  $(\text{CF}_3)_2\text{CO}$  or  $(\text{CF}_3)_2\text{CNH}$  affords complexes (XVI). However, treatment of  $(1,5\text{-C}_8\text{H}_{12})\text{-Ni}\cdot\overline{\text{C}(\text{CF}_3)_2\text{X}}$  [ $\text{X} = \text{O}$  or  $\text{NH}$ ] with tertiary butylisocyanide yielded the three-membered ring compounds  $(\text{Bu}^i\text{NC})_2\text{Ni}\cdot\overline{\text{C}(\text{CF}_3)_2\text{X}}$ . These complexes were then shown to undergo facile ring expansion (Scheme 7)<sup>44</sup>. Moreover, treatment of  $(\text{Bu}^i\text{NC})_2\text{Ni}\cdot\overline{\text{C}(\text{CF}_3)_2\text{O}}$  with  $(\text{CF}_3)_2\text{CNH}$  affords a single product, the structure of which has been established by Penfold and Countryman<sup>50</sup> by a single crystal x-ray diffraction study as (XVIIa), rather than its isomer (XVIIb). When hexafluoroacetone reacts with  $(\text{Bu}^i\text{NC})_2\text{-Ni}\cdot\overline{\text{C}(\text{CF}_3)_2\text{NH}}$  isomer (XVIIb) is formed as a minor product, but (XVIIa) is the major product of this ring expansion reaction.



Scheme 7. Formation of three- and five-membered ring (isocyanide)nickel complexes.

As discussed later, it is significant that the x-ray diffraction study shows that (XVIIa) forms by insertion of the imine into the nickel-carbon bond of  $(\text{Bu}^t\text{NC})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ .

We have alluded earlier to the ready formation of the phosphine complexes (XIV) from  $\text{Ni}(\text{PR}_3)_4$  compounds and tetrafluoroethylene. In order to establish the mode of formation of the octafluoronickelacyclopentane complexes, *t,t,t*-cyclododeca-1,5,9-trienickel was treated with  $\text{C}_2\text{F}_4$  at  $-78^\circ\text{C}$  to give  $(\text{cdt})\overline{\text{Ni}\cdot\text{C}_2\text{F}_2}$ . Treatment of this compound with triphenylphosphine afforded the desired three-membered ring complex  $(\text{Ph}_3\text{P})_2\overline{\text{Ni}\cdot\text{C}_2\text{F}_2}$ , which although reasonably stable in the crystalline state (decomp.  $170^\circ\text{C}$ ) was unstable in solution<sup>61</sup>. Significantly it reacted rapidly with tetrafluoroethylene to afford (XIV) [ $\text{L} = \text{PPh}_3$ ], providing yet another example of the formation of a five- from a three-membered ring.

Several other examples of ring expansion reactions have been established. The compound  $(\text{diars})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , prepared from  $(1,5\text{-C}_8\text{H}_{12})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  and *o*-bis(dimethylarsino)benzene, reacts with  $(\text{CF}_3)_2\text{CO}$  to give  $(\text{diars})\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ <sup>37</sup>. Similarly,  $(\text{diphos})\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , prepared from  $[(\text{PhO})_3\text{P}]_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  and 1,2-bis(diphenylphosphino)ethane, reacts with  $(\text{CF}_3)_2\text{CNH}$  to give  $(\text{diphos})\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{NH}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ <sup>45</sup>.

(ii) *The role of the ligands in promoting reactions with fluorocarbon substrates.*

We have referred earlier to the activating effect of tertiary butylisocyanide, compared with tertiary phosphine, in promoting formation of five-membered ring complexes with nickel. Several observations have been made suggesting that ring expansion is delicately controlled by the relative  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands on the metal atoms. Only a few examples can be listed:

- Whereas  $(\text{Bu}^t\text{NC})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  undergoes ring expansion with hexafluoroacetone, the analogous complex  $(\text{PhNC})_2\overline{\text{Ni}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  does not<sup>44</sup>.
- Whereas  $(\text{Ph}_2\text{MeP})_2\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  reacts with hexafluoroacetone to give  $(\text{Ph}_2\text{MeP})_2\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , the complex  $(\text{Ph}_3\text{P})_2\overline{\text{Pt}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  does not react with excess of the ketone<sup>46</sup>.
- Although  $(\text{diphos})\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  reacts with hexafluoroacetone to give a five-membered ring complex, the compound  $[(\text{PhO})_3\text{P}]_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$  does not<sup>45</sup>.
- Whereas  $[(\text{MeO})_3\text{P}]_4\overline{\text{Pd}}$  reacts immediately with hexafluoroacetone to give  $[(\text{MeO})_3\text{P}]_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ ,  $(\text{Ph}_2\text{MeP})_4\overline{\text{Pd}}$  forms  $(\text{Ph}_2\text{MeP})_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ , which only on heating with excess of the ketone affords  $(\text{Ph}_2\text{MeP})_2\overline{\text{Pd}\cdot\text{C}(\text{CF}_3)_2\text{O}\cdot\text{C}(\text{CF}_3)_2\text{O}}$ <sup>45</sup>.

Observations (a)–(c) can be accounted for by assuming that replacement of a ligand by another which is a stronger  $\sigma$ -donor increases the nucleophilicity of the metal and permits insertion of a second molecule of substrate. With (d), however, a species  $(\text{Ph}_2\text{MeP})_n\text{Pd}^0$  would be expected to be more reactive in oxidative-elimination chemistry than  $[(\text{MeO})_3\text{P}]_n\text{Pd}^0$ . The strong  $\pi$ -acceptor properties of  $(\text{MeO})_3\text{P}$  should reduce electron density at palladium.

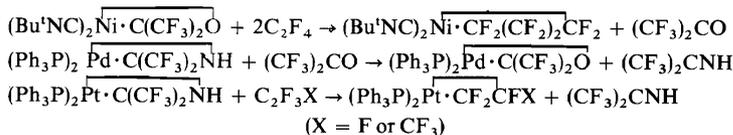
It is possible that steric factors in an intermediate (see below) are responsible for the order of reactivity  $\text{P}(\text{OMe})_3 > \text{PPh}_2\text{Me}$  with palladium but as discussed later electronic factors may be involved also. In the case of related nickel chemistry, it has been established that access of the fluorocarbon to the metal atom is a critical factor in ring expansions. Mention was made earlier that  $(\text{Ph}_3\text{P})_2\text{Ni}\cdot\overline{\text{CF}_2\text{CF}_2}$  reacts readily with tetrafluoroethylene. In contrast the complex  $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]\text{Ni}\cdot\overline{\text{CF}_2\text{CF}_2}$ , containing a tridentate ligand, is quite inert to  $\text{C}_2\text{F}_4$ <sup>27</sup>.

(iii) *The role of the fluorocarbon substrates.*

Interestingly, although the ligands  $\text{CF}_3\text{CF}:\text{CF}_2$ ,  $(\text{CF}_3)_2\text{C}:\text{C}(\text{CN})_2$  and  $(\text{CF}_3)_2\text{C}:\text{NMe}$  all readily form stable three-membered ring complexes with nickel, palladium and platinum, no five-membered ring complexes of these fluorocarbons have as yet been isolated.

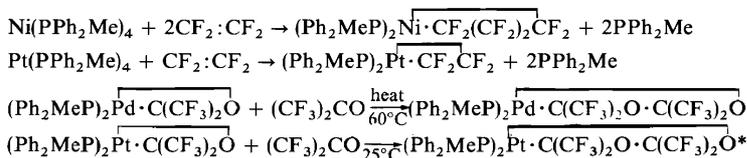
Although, as mentioned above,  $(\text{Ph}_3\text{P})_2\text{Pt}\cdot\overline{\text{C}(\text{CF}_3)_2\text{O}}$  does not react with excess of hexafluoroacetone, this complex does react with hexafluoroisopropylideneamine, to give (XV)<sup>46</sup>. Moreover, whereas  $\text{NiL}_4$  ( $\text{L} = \text{PR}_3$ ) compounds readily form octafluoronickelacyclopentane complexes with tetrafluoroethylene, hexafluoroacetone affords three-membered ring complexes  $\text{L}_2\text{Ni}\cdot\overline{\text{C}(\text{CF}_3)_2\text{O}}$ . Surprisingly, we have not isolated three- or five-membered ring complexes from reactions involving  $\text{PdL}_4$  compounds and tetrafluoroethylene, yet hexafluoroacetone and hexafluoroisopropylideneamine afford a variety of complexes with palladium.

Clearly the nature of the fluorocarbon reactant is critical in determining what kind of product, if any, is obtained. In this context we have observed several simple fluorocarbon displacement reactions, e.g.<sup>44, 58, 62</sup>

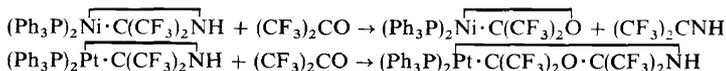


(iv) *The role of the metal atom*

This is well illustrated by comparing the following pairs of reactions.



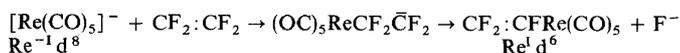
\* This ring expansion does not occur in the presence of  $\text{PPh}_2\text{Me}$ .



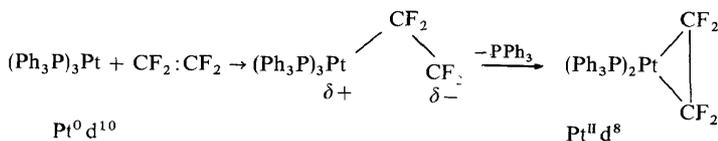
Interestingly, nickel is more reactive towards tetrafluoroethylene than platinum in the sense that octafluoronickelacyclopentane complexes readily form. This reactivity appears to be reversed, however, with  $(\text{CF}_3)_2\text{CO}$  or  $(\text{CF}_3)_2\text{CNH}$  when ring expansion reactions occur more readily in the sequence  $\text{Ni} < \text{Pd} < \text{Pt}$ .

#### 4. Mechanism of three- and five-membered ring formation

Some years ago it was shown<sup>63, 64</sup> that  $[\text{Re}(\text{CO})_5]^-$  and related carbonyl anions displaced fluoride ion from fluoro-olefins, and it was suggested that carbanions are involved as intermediates. It seems possible therefore that



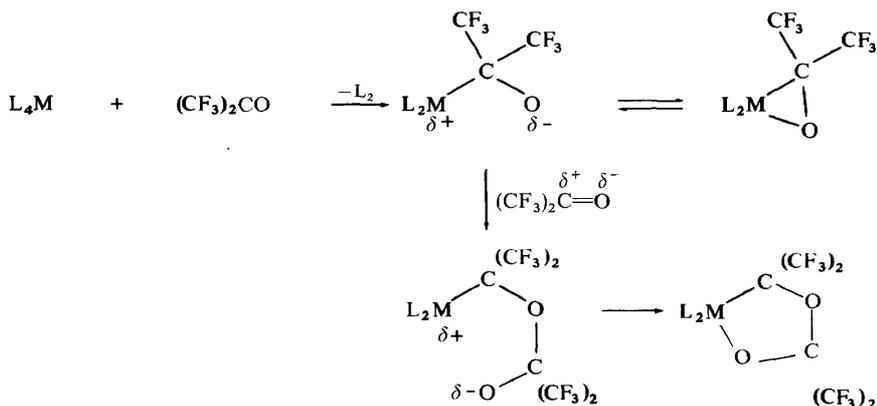
ionic intermediates are involved also in the formation of the three-membered ring complexes, viz.



Indeed studies on the reaction of  $(\text{Ph}_3\text{P})_4\text{Pt}$  with a 1:1 *cis/trans* mixture of  $\text{CFCl}:\text{CFCl}$  have revealed that the *trans* isomer predominates in the mixture of the complexes  $(\text{Ph}_3\text{P})_2\overline{\text{Pt}\cdot\text{CFClCFCl}}$  produced, whereas the unreacted gas retains its isomeric composition<sup>65</sup>. This result strongly suggests that ionic intermediates (XVIII), which permit isomerization by C—C bond rotation, are involved in formation of the three-membered rings  $\overline{\text{Pt}\cdot\text{CFClCFCl}}$ .

Just as three-membered ring complexes could form by ring closure of an ionic intermediate so five-membered ring complexes might also form (Scheme 8) from these 1,3-dipolar intermediates following the well established pattern of organic chemistry<sup>66</sup>. Although the mechanism of Scheme 8 accounts very satisfactorily for the 'head-to-tail' arrangement of the  $(\text{CF}_3)_2\text{-CX}[\text{X} = \text{O} \text{ or } \text{NH}]$  moieties in the five-membered ring complexes formed from hexafluoro-acetone and -isopropylideneamine, we do not favour this mechanism of five-membered ring formation for the following reasons.

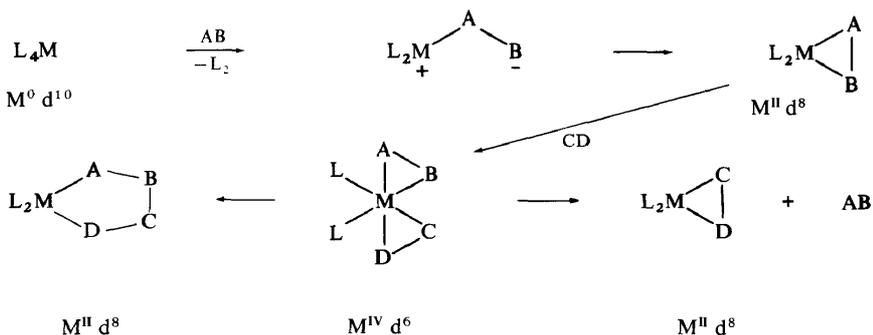
The mechanism does not involve coordination of a second molecule of fluorocarbon substrate to the metal ions yet, as mentioned in (iii) above, simple ligand exchange reactions  $\text{L}_2\text{M}(\text{AB}) + \text{CD} \rightleftharpoons \text{L}_2\text{M}(\text{CD}) + \text{AB}$  are observed, implying six-coordinate metal intermediates in a transition state. A more fundamental criticism of the 1,3-dipolar intermediate mechanism



Scheme 8. Formation of both three- and five-membered ring hexafluoroacetone complexes via ionic intermediates.

for five-membered ring formation comes from a consideration of the formation of (XVIIa) from  $(Bu^tNC)_2\overline{Ni} \cdot \overline{C(CF_3)_2O}$ <sup>44</sup>. Penfold and Countryman's<sup>50</sup> x-ray result shows that the oxygen atom remains bonded to the nickel atom and that the imine molecule has inserted into the carbon-nickel bond. On the basis of the most likely 1,3-dipolar intermediate  $(Bu^tNC)_2-Ni^+ \cdot C(CF_3)_2O^-$  one would not expect this result, but instead formation of isomer (XVIIb). While it is true that both (XVIIa) and (XVIIb) form from  $(Bu^tNC)_2\overline{Ni} \cdot \overline{C(CF_3)_2NH}$  and  $(CF_3)_2CO$  this can be accounted for on the basis of an octahedral intermediate with a long enough lifetime to allow free rotation of the coordinated ligands  $(CF_3)_2CX$  [ $X = O$  or  $NH$ ].

We believe that all the experimental results are best rationalized in terms of formation of the three-membered ring complexes via 1,3-dipolar intermediates and formation of the five-membered ring complexes via coordination of a second molecule of substrate giving rise to a six-coordinate intermediate (Scheme 9).



Scheme 9. A possible route to five-membered ring complexes. AB and CD are fluorocarbon substrate molecules, and in many instances (see text) AB and CD are the same compound.

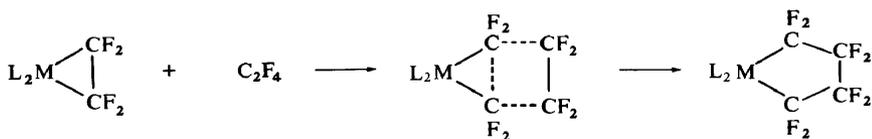
In the case of a substrate such as  $(CF_3)_2CO$  or  $(CF_3)_2CNH$  one might expect polarization in the sense  $\overset{+}{C}-\bar{O}$  and  $\overset{+}{C}-\bar{N}$  in the octahedral intermediate, which would then be expected to collapse in such a way as to give rise to a head-to-tail arrangement of the  $(CF_3)_2CX$  units.

From *Scheme 9* it should not be inferred that in the six-coordinate intermediate the metal ion is necessarily in as high a formal oxidation state as (+IV). Indeed, during coordination to a second molecule of substrate (CD) the metal ion in  $L_2M(AB)$  may need to withdraw electrons both from AB, so that the latter becomes more 'π-complexed', and also from the ligands L in order to interact with CD.

From this mechanism one might expect at first sight that five-membered ring formation would always be favoured in the sequence  $Ni < Pd < Pt$ , and also favoured by increasing the base strengths of the ligands L. As discussed earlier, there are several examples where these principles are followed but exceptions have also been noted. These exceptions can also be accommodated in terms of *Scheme 9* if it is recognized that the function of the ligands is very delicate and that they thereby 'fine tune' the nature of the final product. Thus steric effects could be important in the six-coordinate intermediate, inhibiting its formation in some cases. Moreover, the intermediate may not form because its precursor  $L_2M(AB)$  is too stable in the sense that the metal ion has become so oxidized by transfer of electrons to AB that it has no residual nucleophilicity to bond a second molecule (AB or CD).

Indeed, the formation of  $L_2\overline{Pt \cdot CF_2CF_2}$  rather than  $L_2\overline{Pt \cdot CF_2(CF_2)_2CF_2}$  (L = phosphine) can be explained in this way. In  $L_2\overline{Pt \cdot CF_2CF_2}$  the platinum atom may be closer to  $Pt^{II}$  than is nickel to  $Ni^{II}$  in the analogous but more reactive  $L_2\overline{Ni \cdot CF_2CF_2}$ . It could be argued that if the ligands on platinum were less strong as σ-donors than phosphines, octafluoroplatinacyclopentane rings might form. Model compounds are difficult to prepare but a most interesting observation has been made by Empsall<sup>58</sup>. He found that the complex  $(1,5-C_8H_{12})\overline{Pt \cdot CF_2(CF_2)_2CF_2}$  forms when  $(1,5-C_8H_{12})Pt(i-C_3H_7)_2$  is u.v. irradiated in the presence of tetrafluoroethylene. If it is assumed that  $(C_8H_{12})Pt^0$  is formed *in situ* then apparently the platinum atom is able to activate two molecules of  $C_2F_4$ . It is well established that cycloocta-1,5-diene is much less basic as a ligand than tertiary phosphines. If  $(C_8H_{12})\overline{Pt \cdot CF_2CF_2}$  is an intermediate in this reaction then the back bonding from platinum to tetrafluoroethylene would not be so extensive and hence coordination of a second molecule of fluoro-olefin to give  $(C_8H_{12})\overline{Pt \cdot CF_2(CF_2)_2CF_2}$  might be possible.

In considering the formation of five- from three-membered rings we have discarded a mechanism of the type illustrated in *Scheme 10*. Firstly, it does not readily account for the simple fluorocarbon-fluorocarbon displacement reactions. Secondly, we have studied the reaction of  $Ni(AsMe_2Ph)_4$  with trifluoroethylene and obtained a single complex which on the basis of its n.m.r. spectra is formulated as (XIX). This isomer of the system  $Ni(CFHCF_2)_2$  would not be expected if the compound were formed by insertion of a  $CF_2CFH$  group into the C—C bond of  $L_2\overline{Ni \cdot CF_2CFH}$ .



Scheme 10. Formation of five-membered ring complexes by a pseudo (2 + 2)  $\pi$ -addition.

The  $^{19}\text{F}$  spectrum of (XIX) showed only two groups of bands, one with an AB pattern corresponding to four F nuclei centred at 90.3 ppm ( $J_{\text{AB}}$  262 Hz), and the other centred at 211.7 ppm of relative intensity corresponding to two F nuclei. The low-field band can be assigned to a  $\text{Ni}\cdot\text{CF}_2$  group<sup>56, 57</sup>. The signal for the CFH groups corresponds very closely to that observed in the spectrum of the structurally related cyclic compound  $\overline{\text{CF}_2\text{CF}_2\text{CFHCFHCF}_2}$  ( $\delta$ , 224 ppm)<sup>67</sup>.

### 5. Reactions of bis(trifluoromethyl)diazomethane

We have shown<sup>68, 69</sup> that  $(\text{CF}_3)_2\text{CN}_2$ <sup>70</sup> reacts with a variety of transition metal complexes to give products, e.g. (XX)–(XXII), in which the  $(\text{CF}_3)_2\text{C}$  group has inserted into metal–halogen, metal–hydrogen and metal–metal bonds. We have continued our studies with this reactive diazo compound by investigating reactions with zero-valent complexes of Ni, Pd and Pt<sup>71</sup>.

Reaction occurs at room temperature between  $(\text{CF}_3)_2\text{CN}_2$  and  $\text{Ni}(\text{Bu}^i\text{NC})_4$ ,  $\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ ,  $\text{Ni}(1,5\text{-C}_8\text{H}_{12})_2$ ,  $\text{Pd}(\text{Bu}^i\text{NC})_2$ ,  $\text{Pd}(\text{C}_6\text{H}_{11}\text{NC})_2$ ,  $\text{Pt}(\text{PPh}_3)_4$  and  $\text{Pt}(\text{PPh}_3)_2(\text{PhCH}:\text{CHPh})$  to form respectively complexes (XXIIIa–XXIIIf). The infrared,  $^1\text{H}$  and  $^{19}\text{F}$  n.m.r. spectra of the compounds showed that they were all isostructural. A strong band appears in the infrared near  $1560\text{ cm}^{-1}$  corresponding to an uncoordinated  $(\text{CF}_3)_2\text{C}=\text{N}$  group.

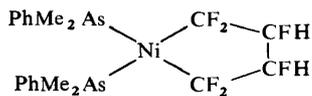
Surprisingly for the formulation shown (XXIII) the  $^{19}\text{F}$  n.m.r. spectra consisted of three multiplets of relative intensity 6:3:3, increasing to high field, implying that the  $\text{CF}_3$  groups attached to the carbon adjacent to the metal atom are in identical environments. In a stereochemically rigid structure in which the nitrogen atom bonded to the metal is  $\text{sp}^3$  hybridized all the  $\text{CF}_3$  groups should be non-equivalent. Even at low temperatures the spectra do not change their pattern.

In order to establish with certainty the nature of the complexes (XXIII) a single crystal x-ray diffraction study of (XXIII f)\* has been made by Davis and Oliver<sup>72</sup>. The 1,1,4,4-tetrakis(trifluoromethyl)buta-1,3-azine-metal structure has been confirmed. Moreover, the two phosphorus atoms, the platinum atom and the attached CN group are all coplanar. The CN distance is very similar to that found in the cyclic compound  $\overline{\text{N}(\text{H})\text{CH}_2\text{CH}_2}$ . Interestingly, the bond angles about the coordinated N atom imply that it is  $\text{sp}^3$  hybridized. The equivalence of the  $\text{CF}_3$  groups in the n.m.r. spectra must thus arise in solution through rapid inversion at the nitrogen atom bonded to the platinum.

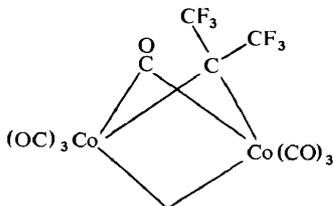
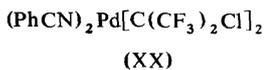
The mode of formation of the azine complexes is not clear but it is possible that the diazo-compound reacts as a 1,3-dipolarophile to form a four-

\* This complex has also been made by Lappert *et al.*<sup>73</sup>.

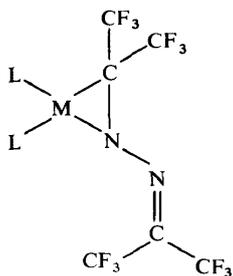
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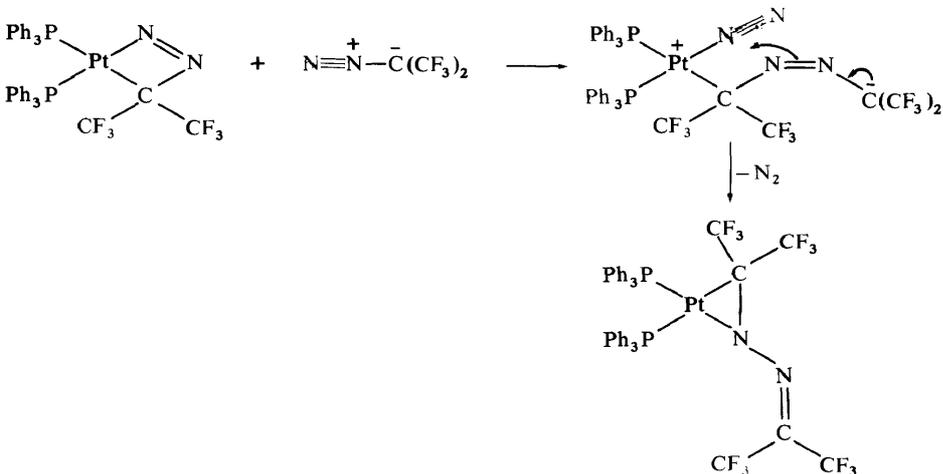
(XIX)



(XXII)



- (XXIIIa) M = Ni L = Bu<sup>t</sup>NC  
 b M = Ni L = PPh<sub>3</sub>  
 c M = Ni L<sub>2</sub> = C<sub>8</sub>H<sub>12</sub>  
 d M = Pd L = Bu<sup>t</sup>NC  
 e M = Pd L = cyclo-C<sub>6</sub>H<sub>11</sub>NC  
 f M = Pt L = PPh<sub>3</sub>)



Scheme 11. Possible mode of formation of azine metal complexes.

membered ring compound (*Scheme 11*). Cleavage of the carbon–nitrogen bond with concomitant attack on a further  $(\text{CF}_3)_2\text{CN}_2$  molecule is then facilitated by stabilization of the coordinated nitrogen.

### ACKNOWLEDGEMENTS

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