# Trifluorophosphine Complexes of the Platinum Metals

## A REVIEW OF RECENT DEVELOPMENTS

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*The chemistry of the trifluorophosphine complexes of the transition metals, and of the platinum metals in particular, is of increasing importance. This article describes some of the more recent developments in trifluorophosphine complexes of the platinum metals, including their syntheses, structures, reactions, and potential as homogeneous catalysts.*

The rapid development of transition metal carbonyl chemistry originated with the discovery of $Ni(CO)_4$ in 1890. About the same time the first trifluorophosphine coordination complex $[PtF_2(PF_3)]_2$ was synthesised by Moissan, but its true identity was not recognised at the time. It was only following the synthesis of the complexes cis-$PtCl_2$ $(PF_3)_2$ and $[PtCl_2(PF_3)]_2$ by Chatt and Williams in 1950 that attention was drawn to the similarity of trifluorophosphine and carbon monoxide as ligands towards transition metals. It was proposed that the dative sigma bond formed by donation of the lone-pair of electrons on phosphorus to the metal was supplemented by a symmetry allowed $\pi$-bond involving back donation of transition metal $d$-electrons into empty phosphorus $3d$-orbitals. The $\sigma$- and $\pi$-components were considered to operate in the same "synergic" fashion as that already suggested for the analogous metal carbonyls. The $\pi$-component was expected to be favoured in trifluorophosphine-metal complexes because of the presence of the highly electronegative fluorine atoms attached to phosphorus (1). A large number of trifluorophosphine-transition metal complexes are now known and their chemistry has been extensively studied (2, 3, 4).

## Binary Compounds

Platinum metal complexes in which trifluorophosphine is the only ligand present are listed in Table I. It is interesting to note that the corresponding carbonyl complexes $M(CO)_4$, (M =Pd, Pt) and $M'_2(CO)_8$, (M'= Rh, Ir) are unstable. As yet there is no

### Table I
### Platinum Metal – Trifluorophosphine Complexes

| | | |
|---|---|---|
| $Ru(PF_3)_5$ (colourless, m.p. 30°C) | $Rh_2(PF_3)_8$ (yellow, m.p. 92.5°C) <br><br> $[Rh(PF_3)_3]_x$ (x=3 or 4) (red crystals) | $Pd(PF_3)_4$ (colourless, m.p. −40°C, dec −20°C) |
| $Os(PF_3)_5$ (colourless crystals) | $Ir_2(PF_3)_8$ yellow, m.p. 113−116°C | $Pt(PF_3)_4$ (colourless, m.p. −15°C) b.p. 86°C/730 dec 130°C) |

extensive chemistry of polynuclear metal trifluorophosphine complexes.

## Methods of Preparation

The main synthetic route developed by Th. Kruck and co-workers in Germany involves "reductive fluorophosphination". In this method the platinum metal halide is heated in an autoclave with copper or zinc in the presence of high pressures (50–500 atm) of trifluorophosphine (2, 5, 6).
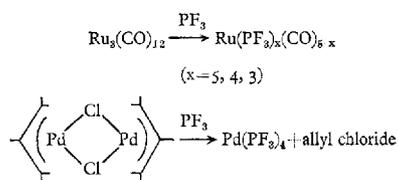
$$M''Cl_3 + 3Cu + 5PF_3 \xrightarrow[150-250°C]{>400\ atm} M''(PF_3)_5 + 3CuCl$$

$$(M'' = Ru, Os)$$

$$2RhCl_3 + 6Cu + 8PF_3 \xrightarrow[>150°C]{250\ atm} Rh_2(PF_3)_8 + 6CuCl$$
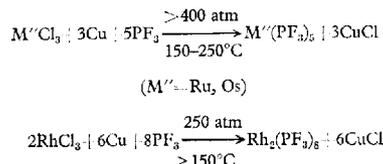
Interestingly, when $IrCl_3$ is heated with $PF_3$ and copper only small amounts of the orange red crystalline $\mu_3$-phosphido-nonakis-(trifluorophosphine)tri-iridium $Ir_3P(PF_3)_9$ are formed rather than $Ir_2(PF_3)_8$ (7). The latter can be obtained in good yield from the reaction between $K[Ir(PF_3)_4]$ and $IrCl(PF_3)_4$ (8) or by u.v. irradiation of $IrH(PF_3)_4$ (9). It is thermally stable up to 200°C. The rhodium analogue, on the other hand, evolves two moles of $PF_3$ per dimer at 170°C to afford a red volatile solid, $[Rh(PF_3)_3]_x$, whose identity is not yet fully established (8).

The platinum and palladium complexes $M(PF_3)_4$, which are readily available by reductive fluorophosphination of the appropriate metal halide (10) can also be obtained in the absence of any reducing metal since $PF_3$ can act as its own reducing agent (11, 12), viz.

$$PtCl_2 + 5PF_3 \xrightarrow[100°C]{100-150\ atm} Pt(PF_3)_4 + PF_3Cl_2$$
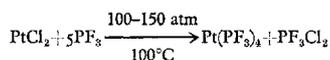
Other synthetic routes using milder reaction conditions involve displacement of ligands (e.g. CO, π-allyl) already coordinated to the platinum metal (13, 14), e.g.

$$Ru_3(CO)_{12} \xrightarrow{PF_3} Ru(PF_3)_x(CO)_{5-x}$$

$$(x = 5, 4, 3)$$

 $\xrightarrow{PF_3}$ Pd(PF_3)_4 + allyl chloride

$Pd(PF_3)_4$ can also be obtained by the direct reaction between palladium powder and trifluorophosphine at high temperature and pressure (15).

## Structures

Vibrational spectroscopic studies suggested that the $M(PF_3)_4$ complexes, (M = Pd, Pt), have perfectly tetrahedral structures and this has been subsequently confirmed in the case of the platinum complex (16). In contrast to the very short metal-phosphorus bond length found for $Ni(PF_3)_4$ (2.116 Å), the platinum-phosphorus distance in $Pt(PF_3)_4$ (2.230 Å) is not substantially different from that in other platinum-phosphine complexes. This may reflect the decreased importance of metal-phosphorus π-bonding for the heavier platinum metals.

The pentakis(trifluorophosphine)ruthenium and osmium complexes, $M''(PF_3)_5$, almost certainly have trigonal bipyramid structures. Detailed ^{19}F and ^{31}P nuclear magnetic resonance studies show that these molecules are "fluxional" even at temperatures as low as −160°C, the barrier to intramolecular ligand exchange between equatorial and axial positions being less than 5 kcal/mole (17) (Fig. 1).



Fig. 1 *Possible intramolecular ligand exchange mechanism in* $M''(PF_3)_5$ *complexes*
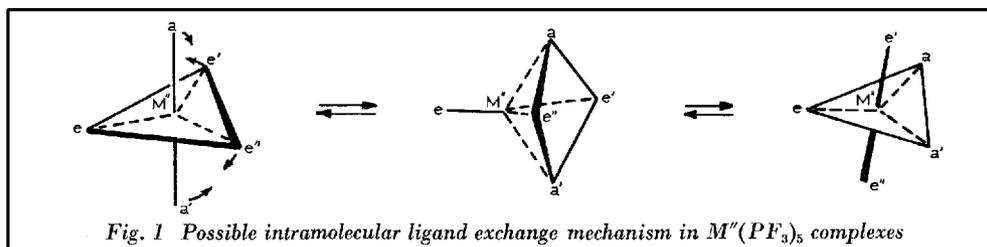
The structures of the $M'_2(PF_3)_8$ complexes ($M'$=Rh, Ir), are not yet known, but presumably consist of two staggered trigonal bipyramid $M'(PF_3)_4$ units held together by a metal-metal bond. $Ir_3P(PF_3)_9$ is thought to have the structure shown below (7).
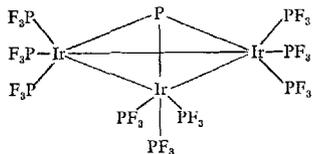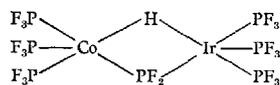
## Hydrides

The hydrides $M'H(PF_3)_4$ ($M'$=Rh, Ir) and $M''H_2(PF_3)_4$ ($M''$=Ru, Os) listed in Table II are obtained in high yields by heating a mixture of the metal chloride and copper under high pressures of trifluorophosphine and hydrogen (18, 19).

$$RhCl_3 + 3Cu + 4PF_3 + \tfrac{1}{2}H_2 \longrightarrow RhH(PF_3)_4 + 3CuCl$$
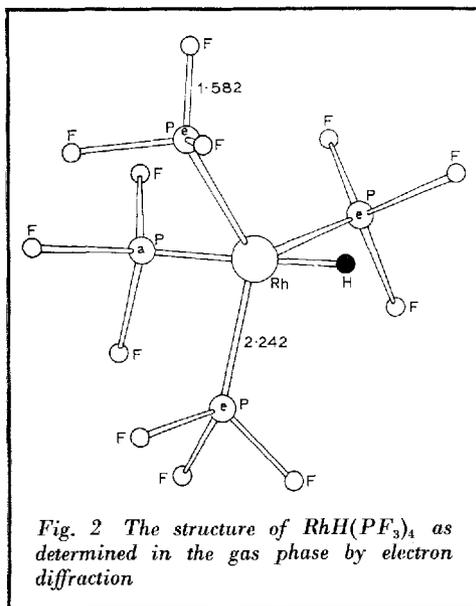
The rhodium and iridium hydrides can also be obtained by acidification of the metallates $[M'(PF_3)_4]^-$ which are available from alternative low pressure synthetic routes. All the hydrides are very volatile liquids and, except for $RhH(PF_3)_4$, exhibit considerable thermal stability.

The binuclear complex $Rh_2(PF_3)_8$ is readily cleaved by hydrogen gas to yield $RhH(PF_3)_4$ quantitatively, while $Ir_2(PF_3)_8$ forms $IrH(PF_3)_4$ in the presence of moisture (2). When a mixture of $HIr(PF_3)_4$ and $HCo(PF_3)_4$ is subjected to u.v. irradiation, the interesting bridged complex shown below is obtained as a red oil (7).

All the trifluorophosphine metal hydrides exhibit acidic properties, readily forming the metallates $[M'(PF_3)_4]^-$, ($M'$=Rh, Ir), $[M''H(PF_3)_4]^-$ and $[M''(PF_3)_4]^{2-}$, ($M''$=Ru, Os), with bases or potassium amalgam (18, 19).

The $M'H(PF_3)_4$ complexes react with triphenylphosphine to produce the salts $[Ph_3PH]^+[M'(PF_3)_4]^-$ while the substituted products $RhH(PF_3)(PPh_3)_3$ and $RhH(PF_3)_2(PPh_3)_2$ have recently been obtained by reaction of the stoichiometric quantities of $PF_3$ and $RhH(PPh_3)_4$ (20). The complexes $RhH(PF_3)(PPh_3)_3$ and $RhH(PF_3)_2(PPh_3)_2$ exhibit high activity as homogeneous catalysts. For example, $RhH(PF_3)(PPh_3)_3$ catalyses the hydrogenation of terminal olefins (at 25°C, 1 atm $H_2$) while $RhH(PF_3)_2(PPh_3)_2$ has been found to bring about rapid isomerisation of terminal olefins (20). The ruthenium complexes $RuH_2(PPh_3)_3$ ($PF_3$) and $RuH_2(PPh_3)_2(PF_3)_2$ have been obtained very recently from $RuH_4(PPh_3)_3$, but are not as catalytically active as their rhodium counterparts (21).



*Fig. 2 The structure of RhH(PF$_3$)$_4$ as determined in the gas phase by electron diffraction*

## Structures

The structure of $RhH(PF_3)_4$ (Fig. 2), which has recently been determined by electron diffraction (22), may be considered to be pseudo-tetrahedral, i.e. based on a distorted trigonal bipyramid in which the hydrogen atom occupies an axial position. The rhodium-phosphorus distance is shorter than that in $RhH(PPh_3)_4$ and of the same order of magnitude as that found for $Rh(NO)$ $(PF_3)_3$ (Rh–P = 2.245 Å) (23). It is not, however, the shortest rhodium-phosphorus bond length known. In the analogous cobalt complex, $CoH(PF_3)_4$, the cobalt-phosphorus bond is exceptionally short (24).

Variable temperature n.m.r. studies on $M'H(PF_3)_4$ (M' = Co, Rh, Ir) establish that all these complexes are stereochemically non-rigid (fluxional) and it has been proposed that the phosphorus environments are interchanged by a "tetrahedral tunnelling" rearrangement mechanism (17).

A recent X-ray crystallographic study (25) of the catalytically active complex RhH $(PF_3)(PPh_3)_3$ has confirmed the basic trigonal bipyramidal structure proposed earlier on the basis of its $^1H$, $^{19}F$, and $^{31}P$ n.m.r. spectra (20) (Fig. 3). The rhodium-trifluorophosphine distance (2.15 Å) is very much shorter than the rhodium-triphenylphosphine distances (average 2.33 Å), which is consistent with the stronger $\pi$-bonding ability of $PF_3$.

There is n.m.r. evidence that in complexes of the type $M''H_2(PF_3)_4$ (M'' = Ru, Os) (19), $RuH_2(PF_3)(PPh_3)_3$ and $RuH_2(PF_3)_2$ $(PPh_3)_2$ (21), the hydrides occupy cispositions in a distorted octahedron.

## Halides

The colourless complex cis-$PtCl_2(PF_3)_2$ and the orange dimeric compound [PtCl$_2$ $(PF_3)]_2$ mentioned above are both obtained by passing $PF_3$ through a plug of platinous chloride at 200–220°C.

Passage of $PF_3$ over heated rhodium trichloride in the presence of copper powder gives very low yields of the red crystalline, volatile, chlorine bridged dimer, $[RhCl(PF_3)_2]_2$ (2), but this complex has subsequently been conveniently synthesised in high yield by reaction of $PF_3$ with $[RhCl(L_2)]_2$ (L = ethylene, cyclo-octene, CO, etc.) under mild conditions (8, 26, 27).

*Fig. 3 The structure of $RhH(PF_3)(PPh_3)_3$ (inner coordination sphere only). The H position is not shown (Rh-H distance ~1.6 Å)*
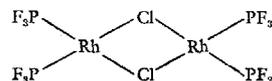
The complexes [RhX $(PF_3)_2]_2$ (X = Br, I) have been prepared similarly and are also obtained from halogen exchange reactions of $[RhCl(PF_3)_2]_2$ with LiBr or NaI (27). Treatment of $[IrCl(C_8H_{14})_2]_2$ ($C_8H_{14}$ = cyclo-octene) with trifluorophosphine yields the rather

$$Rh_2(PF_3)_6(acetylene)$$

$\pi-C_5H_5Rh(C_2H_4)_2$      $g$     $c$

$[RhCl(C_2H_4)_2]_2$    $trans$-RhCl(PPh$_3$)$_2$(PF$_3$)    $\pi-C_5H_5Rh(PF_3)_2$

$a$    $c$    $f$    $g$    $p$

RhCl$_3$.xH$_2$O   $s$   $[RhCl(PF_3)_2]_2$   $l$   Hg[Rh(PF$_3$)$_4$]$_2$ $\xrightarrow{m}$ KRh(PF$_3$)$_4$ $\xrightarrow{n}$ Rh$_2$(PF$_3$)$_8$

$b$   $b$   $c$   $d$   $e$   $t$   $r$   $o$   $q$

$[RhCl(CO)_2]_2$   $[RhCl_2(PF_3)_2]^-$   Rh($\pi$-allylic)(PF$_3$)$_3$   $j$ $\rightleftharpoons$ $k$   RhH(PF$_3$)$_4$   Ph$_3$SiRh(PF$_3$)$_4$

$i$   $h$   Rh(NO)(PF$_3$)$_3$

$^a$C$_2$H$_4$   $^b$CO   $^c$PF$_3$   $^d$Cl$^-$   $^e$HCl   $^f$Ph$_3$P   $^g$TlC$_5$H$_5$   $^h$NOCl   $^i$NO   $^j$H$_2$/PF$_3$   $^k$dienes   $^l$K/Hg + PF$_3$

$^m$K/Hg (excess)   $^n$[RhCl(PF$_3$)$_2$]$_2$+PF$_3$   $^o$H$_2$   $^p$acetylene   $^q$Ph$_3$SiH   $^r$H$^-$   $^s$PF$_3$/Cu   $^t$allyl chloride

*Fig. 4 Scheme showing some of the reactions of the halide compound* $[RhCl(PF_3)_2]_2$

unstable IrCl(PF$_3$)$_4$ which readily decomposes to the dimeric [IrCl(PF$_3$)$_2$]$_2$ on warming (8). It is interesting that the corresponding carbonyl complex has the composition IrCl(CO)$_3$. The very volatile IrI(PF$_3$)$_4$ has been made by treating the metallate salt KIr(PF$_3$)$_4$ with iodine at −80°C (28).

The yellow crystalline complexes RhX(PF$_3$)$_4$ (X = Cl, Br, I) are stable at room temperature only under a pressure of PF$_3$, rapidly reverting to the red [RhX(PF$_3$)$_2$]$_2$ compounds on removal of the trifluorophosphine pressure (27).

$$RhX(PF_3)_4 \underset{+PF_3}{\overset{-PF_3}{\rightleftharpoons}} [RhX(PF_3)_2]_2$$
$$\text{yellow} \qquad\qquad \text{red}$$

The synthetic utility of the dimeric [RhCl(PF$_3$)$_2$]$_2$ complex is summarised in Fig. 4. The complex *trans*-RhCl(PPh$_3$)$_2$(PF$_3$)

formed by treating the dimer with an excess of triphenylphosphine has been shown to undergo fast ligand exchange reactions with traces of trifluorophosphine or triphenylphosphine (26).

No structural data are available at present on any of the above halide complexes, but [RhCl(PF$_3$)$_2$]$_2$ probably has a similar structure to that found for [RhCl(CO)$_2$]$_2$ with two chlorine bridges between the metal atoms and possibly some degree of metal-metal interaction in the solid state.

## Organometallic Compounds

Some typical complexes are listed in Table III. Rh$_2$(PF$_3$)$_8$ reacts with a variety of acetylenes to give volatile compounds of the type Rh$_2$(PF$_3$)$_6$(acetylene). The structural

## Table III
### Some Organometallic Compounds of the Platinum Metals Containing Trifluorophosphine

| | | |
|---|---|---|
| Ru(CO)$_x$(PF$_3$)$_{5-x}$ | Rh($\pi$-C$_5$H$_5$)(PF$_3$)$_2$ | |
| Ru(C$_7$H$_8$)(C$_8$H$_8$)PF$_3$ | Rh($\pi$-C$_4$H$_7$)(PF$_3$)$_3$ | |
| RuCl$_2$(C$_{10}$H$_{16}$)PF$_3$ | Rh(NO)(PF$_3$)$_3$ | |
| Ru(C$_8$H$_8$)(PF$_3$)$_3$ | Rh$_2$(PF$_3$)$_6$(C$_2$Ph$_2$) | |
| | [RhCl(CO)(PF$_3$)]$_2$ | |
| | Ir(SnPh$_3$)(PF$_3$)$_4$ | Pt(CO)$_x$(PF$_3$)$_{4-x}$ |
| | Ir($\pi$-C$_5$H$_5$)(PF$_3$)$_2$ | |

analogy between these compounds and the better known, related $Co_2(CO)_6$(acetylene) complexes has been confirmed by an X-ray diffraction study of $Rh_2(PF_3)_4(PPh_3)_2(PhC$ $\equiv CPh)$ (29) (Fig. 5). The rhodium-trifluorophosphine distances (average 2.216 Å) are again significantly shorter than the rhodium triphenylphosphine distances (average 2.391 Å).

A series of volatile, π-allylic complexes $Rh(\pi\text{-allylic})(PF_3)_3$ have been obtained by insertion of various dienes into the metal-hydride bond of $RhH(PF_3)_4$ (30, 31). These complexes react with hydrogen chloride to produce ultimately $[RhCl(PF_3)_2]_2$ and an olefin, e.g.



Fig. 5 The structure of $Rh_2(PF_3)_4(PPh_3)_2(PhC\equiv CPh)$. The $Ph_3P$ ligands have been deleted for clarity



The intermediate π-allyl rhodium(III) hydride complex has been detected by a low temperature n.m.r. study and this observation is important in providing support for the involvement of this type of intermediate during the isomerisation of olefins catalysed by transition metal complexes (32). A novel thermal isomerisation of $Rh(\pi\text{-}1,1\text{-dimethylallyl})(PF_3)_3$ to the 1,2-isomer has been observed (33) and a diene metal-hydride intermediate postulated (Fig. 6).

The π-allyl group in $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ is readily displaced by hydrogen and trifluorophosphine to yield $RhH(PF_3)_4$ quantitatively
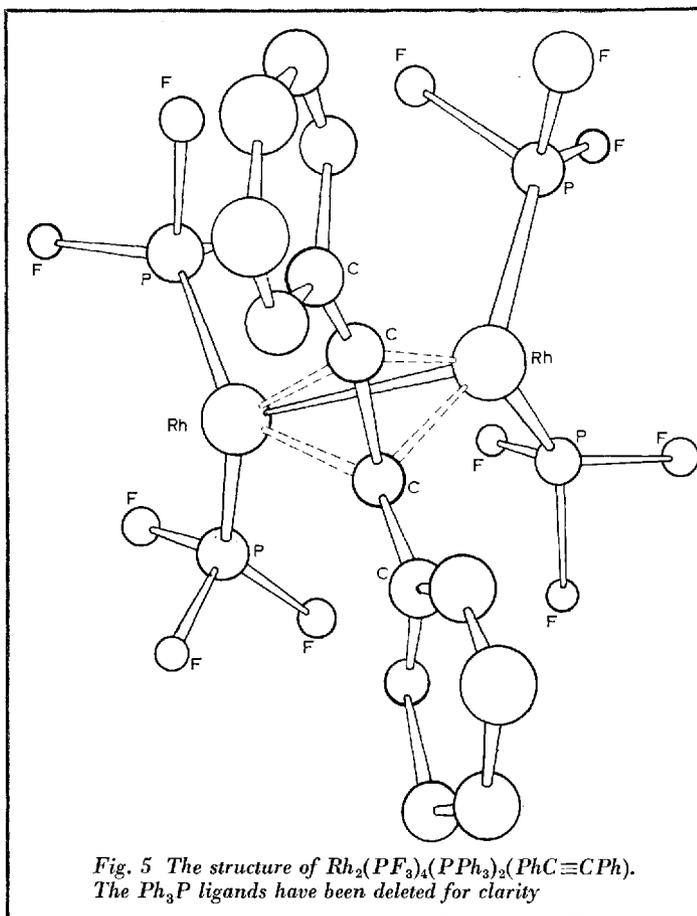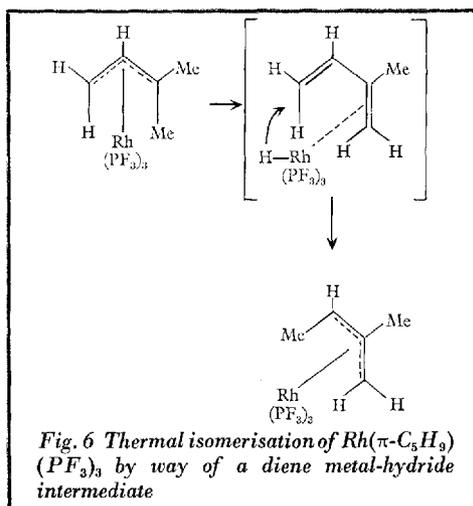


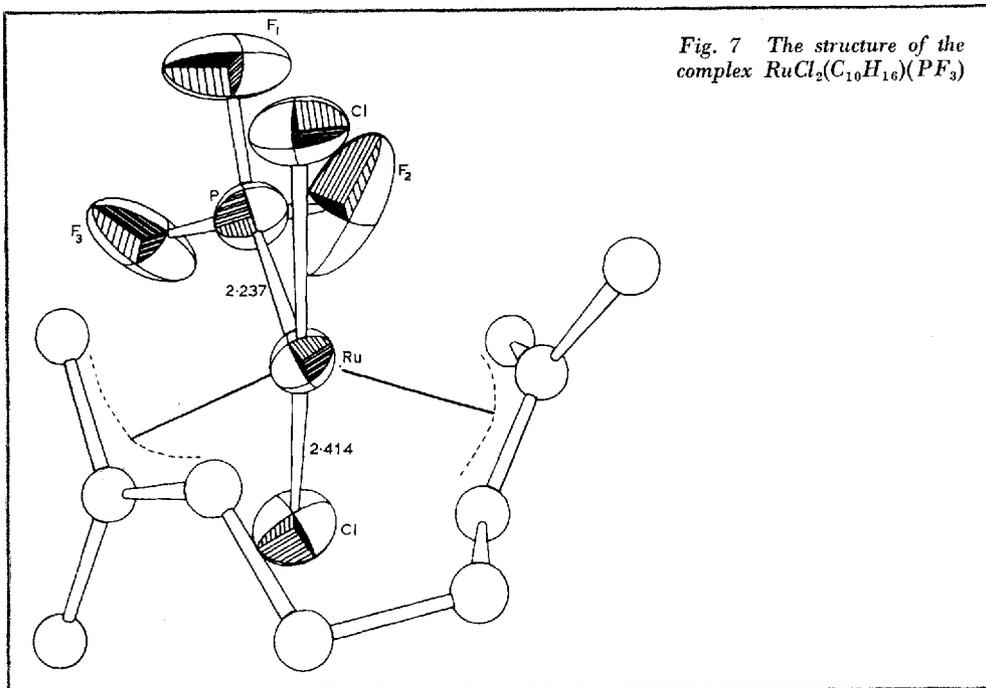Fig. 6 Thermal isomerisation of $Rh(\pi\text{-}C_5H_9)$ $(PF_3)_3$ by way of a diene metal-hydride intermediate

*Fig. 7    The structure of the complex $RuCl_2(C_{10}H_{16})(PF_3)$*

(34), and treatment with nitric oxide affords the volatile liquid nitrosyl $Rh(NO)(PF_3)_3$, (2, 34), whose structure has been determined by electron diffraction (23).

The structure of the unusual bis-π-allylic ruthenium complex dichloro-2,7-dimethyl-octa-2,6-diene-1,8-diyl(trifluorophosphine) ruthenium, $RuCl_2(C_{10}H_{16})(PF_3)$, (35) is shown in Fig. 7. This represents the first structural study of a trifluorophosphine complex of a metal in an oxidation state greater than one (25). It is interesting to note that the ruthenium-phosphorus bond length (2.237 Å) is still considerably shorter than in other ruthenium phosphine complexes (typically 2.30–2.37 Å).

A new synthetic method which promises to have considerable general application involves transfer of $PF_3$ initially coordinated to nickel to other transition metals. Thus treatment of the pentamethylcyclopentadienyl complexes $(Me_5C_5MCl_2)_2$ (M=Rh, Ir) with an excess of the commercially available complex $Ni(PF_3)_4$ in boiling toluene gives good yields of the complexes π-$(Me_5C_5)$ $M(PF_3)_2$ (36).

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# An Age-hardenable Palladium Based Spring Alloy

Strong, light and rigid structural components are frequently produced by incorporating strong fibres of high elastic modulus into a lighter and weaker matrix. Glass or graphite fibres can thus be used to reinforce synthetic resin matrices, while other types of glass fibres are being employed to strengthen fine concrete mixes. With metals, however, fibre reinforcement has met with little success because at high temperatures the matrix tends inevitably to react with the strengthening phase, which is either dissolved or seriously weakened.

Dr K. H. Reiff of the Carl Haas spring factory has recently described (*Metall*, 1974, **28**, (7), 686–690) an attempt to develop a fibre-strengthened spring alloy in which no degradation of the strengthening phase occurs because it is always in thermodynamic equilibrium with its weaker matrix. With this object in mind he selected eutectic alloys based on the ternary system palladium-copper-gallium, in which the lamellar phase was an intermetallic compound, strong but ductile enough to allow the alloy as a whole to be heavily cold worked. The working and annealing procedure adopted produced a highly aligned fibre structure in the wires drawn from chill cast ingots. The proportion of the reinforcing fibres appeared to vary with the copper rather than with the gallium content of the alloys, and similar considerations applied to the hardness and tensile strength.

Wires having an initial diameter of 1.75 mm were cold drawn without annealing to a diameter of 50 μm, the area reduction ratio being approximately 1000:1. The heavily cold worked wires were then aged, and tensile values peaking at 260 kp/mm² or) rather more than 165 ton/in²) were obtained after one hour at 425°C. Such tensile values are remarkably high for a ductile non-ferrous alloy and are comparable to those of maraging steels or of hard drawn wires of tungsten or rhenium. The high tensile strength was, however, due simply to age-hardening, and over-ageing reduced strength values catastrophically to the 80 ton/in² level, which was much below that of the hard drawn, un-aged wire.

These results, coupled with the fact that the elastic modulus of the fibrous wires was only marginally higher than that of pure palladium, show that the high strengths attained were a consequence of precipitation hardening alone and could not be attributed to fibre strengthening. Whatever the mechanism involved, however, a tensile strength approximately twice that of fully heat treated beryllium-copper is still impressive, and the heat treatment procedures required would seem well suited to the setting of hair springs. Certain applications might therefore be envisaged where economic justification could be found for the use of this strong but expensive palladium-based spring alloy.

A. S. D.