FLUOROPHOSPHINE COMPLEXES OF RHODIUM

by

Terence William Turney

A Thesis submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

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Research School of Chemistry,
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Canberra, A.C.T.

January 1972
Corrigenda and Addenda

p4 Line 21 Read "acceptor and donor" not "donor and acceptor".

p7 PF\textsubscript{3} entry in Table 1 Read "E" not "M".

Interchange references 32 and 33.

p9 After 1st sentence add following footnote
"Phosphorus trifluoride complexes of π-cyclopentadienylrhodium(III) have recently been described. [cf. R.B. King, A. Efraty, J.Organometal.Chem., 36, 371 (1972)]."

p15 Last 2 lines Read "\(^2J_{pp}\)" not "\(^2J_{p\text{M}}\)".

p17 Last line Read "orbitals, 104", not "orbitals, 76".

p33 Line 17 Add footnote "Nixon\textsuperscript{11} has reported better resolved spectra in which \(^3J_{PF}\) is clearly discernible".

p34 Line 21 Add footnote "Nixon\textsuperscript{11} has also described the rapid exchange between free and coordinated ligands in trans-RhCl(PPh\textsubscript{3})F\textsubscript{3}\textsuperscript{PF}\".

p40 After 1st sentence Add footnote "The addition of sulphur dioxide does not involve oxidative addition to the metal but it is included in this section for convenience only".

p63 Line 2 Read "RhCl(PF\textsubscript{2}NMe\textsubscript{2})\textsubscript{3}\" not "RhCl(PF\textsubscript{2}NEt\textsubscript{2})\textsubscript{3}\".

p67 Line 22 Read "spectrum" not "spectra".

p92 Line 4 Read "paramagnetic" not "diamagnetic".

p95 Line 9 Read "burgundy" not "burgandy".

p107 Line 19 Read "intramolecular" not "intermolecular".
The work described in this Thesis is the candidate's own, except where otherwise stated. It was carried out in the Research School of Chemistry, The Australian National University from 1969 to 1971 during the tenure of a research scholarship from The Australian National University.

I would also like to thank the following people:

Dr. R.H. Adams for recording the variable temperature 1H NMR spectra,
Dr. P.J. Dwyer for carrying out the X-ray crystal structure analysis,
Dr. J. O'Kane and Dr. K. Beggio for recording the mass spectra,
Mr. E. Nowak for typing a draft manuscript and especially for her patience and assistance.
ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr M.A. Bennett for the guidance and encouragement given throughout the course of this work. The provision of laboratory facilities and of a research scholarship by The Australian National University is gratefully acknowledged.

I would also like to thank the following people:

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Dr P.O. Whimp for carrying out the X-ray crystal structure analyses,
Dr J. McCleod and Mr K. Goggin for recording the mass spectra,
Dr J. Saxby and Mr D. Radford for dipole moment measurements,
Miss B. Stevenson and Dr J. Fildes for most of the good analytical results,
Drs P.W. Clark, I.B. Tomkins and Messrs A.K. Smith and E.J. Hann who did most of the proofreading of this thesis,
Mrs J. Hinchey for her competent typing,
My wife, Sharyn, for typing a draft typescript but especially for her patience and encouragement.
ABSTRACT

This thesis is divided into four parts, each of which is concerned with a different aspect of the chemistry and properties of the fluorophosphine complexes of rhodium.

The first part describes mainly the reactions of the rhodium(I) complexes, \([\text{RhX(PF}_3\text{)}_2]_2\) (X = Cl, Br, I), with a variety of phosphines [phosphorus trifluoride, diphos, triphenylphosphite, tris(dimethylamino)phosphine and triphenylphosphine]. Treatment of \([\text{RhCl(PF}_3\text{)}_2]_2\) with triphenylphosphine initially leads to the formation of \([\text{RhCl(PPh}_3\text{)}(\text{PF}_3\text{)}_2]_2\), which in turn reacts with more triphenylphosphine to give trans-\(\text{RhCl(PPh}_3\text{)}_2\text{PF}_3\). The latter complex is also obtained from the reaction of \(\text{RhCl(PPh}_3\text{)}_3\) with phosphorus trifluoride. The oxidative addition reactions of trans-\(\text{RhCl(PPh}_3\text{)}_2\text{PF}_3\) are briefly examined. \(^{19}\text{F N.M.R.}\) techniques show that a rapid exchange occurs between free and coordinated phosphorus trifluoride or triphenylphosphine in \([\text{RhCl(PF}_3\text{)}_2]_2\) and in trans-\(\text{RhCl(PPh}_3\text{)}_2\text{PF}_3\).

The second part deals with aminofluorophosphine complexes of rhodium(I). The preparations of \([\text{RhCl(PF}_2\text{NR}_2\text{)}_2]_2\) (R = Me, Et) are described. These dimeric complexes react with an excess of fluorophosphine to form the five-coordinate, \(\text{RhCl(PF}_2\text{NR}_2\text{)}_4\), and in one case a four-coordinate intermediate may be prepared [\(\text{RhCl(PF}_2\text{NMe}_2\text{)}_3\)]. The chloride bridges in \([\text{RhCl(PF}_2\text{NMe}_2\text{)}_2]_2\) may be cleaved by treatment with \(\text{Tl(acac)}\) or \(\text{Tl(o-C}_5\text{H}_5\text{)}\) affording \(\text{Rh(acac)(PF}_2\text{NMe}_2\text{)}_2\) or \(\text{Rh(\pi-C}_5\text{H}_5\text{)(PF}_2\text{NMe}_2\text{)}_2\) respectively. Both \([\text{RhCl(PF}_2\text{NMe}_2\text{)}_2]_2\) and \(\text{Rh(acac)(PF}_2\text{NMe}_2\text{)}_2\) undergo rapid intermolecular exchange between free and coordinated \(\text{PF}_2\text{NMe}_2\), whereas \(\text{Rh(\pi-C}_5\text{H}_5\text{)(PF}_2\text{NMe}_2\text{)}_2\) does not. The reaction of \(\text{RhCl(PPh}_3\text{)}_3\) with \(\text{PF}_2\text{NMe}_2\) initially gives trans-\(\text{RhCl(PPh}_3\text{)}_2(\text{PF}_2\text{NMe}_2\text{)}_2\) and this reacts further to afford
cis-RhCl(PPh₃)(PF₂NEt₂)₂. The cis-stereochemistry was confirmed by an X-ray structural analysis.

The third part describes the reactions of rhodium(0) complex, Rh₂(PF₃)₈, with a variety of acetylenes (RC≡CR'). Monoacetylene complexes of the type, Rh₂(PF₃)₆ (RC≡CR'), are usually obtained. The crystal structure of a derivative, Rh₂(PF₃)₄(PPh₃)₂(PhC≡CPh)·Et₂O, shows that these complexes contain a coordinated acetylene unit above and normal to the rhodium-rhodium bond. Rhodium complexes incorporating two acetylenic units are formed only with RC≡CCO₂Me (R = CO₂Me, H), and are of the stoichiometry, Rh₂(PF₃)₅(RC₂R')₂. Each contains a rhodiacyclopentadiene moiety to which a second rhodium atom is π-bonded. Low temperature ¹⁹F N.M.R. studies show that Rh₂(PF₃)₆(RC≡CR') and Rh₂(PF₃)₅(RC₂R')₂ are stereochemically non-rigid. This is explained in terms of a rapid internal rotation of phosphorus trifluoride groups about the threefold axes of the -Rh(PF₃)₃ moieties. Preliminary results indicate that Rh₂(PF₃)₈ is also a fluxional molecule.

The fourth section deals with the far infra-red and Raman spectra of the rhodium(I) complexes, [RhX(PF₃)₂]₂ (X = Cl, Br, I), trans-RhX(MPh₃)₂L (X = Cl, M = P, As; X = Br, M = P) (L = CO, PF₃) and [RhX₂(PF₃)₂]⁻ (X = Cl, Br) together with their carbonyl analogues. The dimers, [RhX(CO)₂]₂, are shown to be non-planar in solution, whereas the structures in solution of [RhX(PF₃)₂]₂ cannot be unambiguously determined. There appears to be mixing of rhodium-chlorine stretching vibrations with the deformation modes of the coordinated phosphorus trifluoride groups. The spectra of both [RhX₂(PF₃)₂]⁻ and trans-RhX(PPh₃)₂PF₃ are consistent with C₂ᵥ local symmetry. In all cases, the rhodium-halogen bond orders of the phosphorus trifluoride complexes are less than those in the corresponding carbonyls.
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PHYSICAL MEASUREMENTS

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### ABBREVIATIONS

<table>
<thead>
<tr>
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<th>Full Name</th>
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<tbody>
<tr>
<td>acac</td>
<td>2,4-pentanedionato</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridyl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu&lt;sub&gt;n&lt;/sub&gt;</td>
<td>n-butyl</td>
</tr>
<tr>
<td>Bu&lt;sub&gt;t&lt;/sub&gt;</td>
<td>tert-butyl</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
<tr>
<td>δ(F-P-F) etc.</td>
<td>fluorine-phosphorus-fluorine bending vibrational mode etc.</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dp</td>
<td>depolarised</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>f&lt;sub&gt;6&lt;/sub&gt;fos</td>
<td>1,2-bis(diphenylphosphino)hexafluorocyclopentene</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>m</td>
<td>medium</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>m.p.</td>
<td>melting point</td>
</tr>
<tr>
<td>nbd</td>
<td>bicyclo[2,2,1]hepta-2,5-diene (norbornadiene)</td>
</tr>
<tr>
<td>n.m.</td>
<td>not measured</td>
</tr>
<tr>
<td>N.M.R.</td>
<td>nuclear magnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>ν(C-O) etc.</td>
<td>carbon-oxygen stretching vibrational mode etc.</td>
</tr>
<tr>
<td>P</td>
<td>polarised</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>p.p.m.</td>
<td>parts per million</td>
</tr>
<tr>
<td>Pr</td>
<td>n-propyl</td>
</tr>
<tr>
<td>s</td>
<td>strong (or singlet)</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>SP</td>
<td>o-styryldiphenylphosphine</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>v</td>
<td>very</td>
</tr>
<tr>
<td>w</td>
<td>weak</td>
</tr>
</tbody>
</table>

### Formulae

The chemical formulae of some of the compounds discussed in this thesis are used in place of their full names. This was deemed expedient in view of the length and often cumbersome nature of the latter. For example, [RhCl(CO)(PF<sub>2</sub>NEt<sub>2</sub>)<sub>2</sub>] is $\mu,\mu'$-dichlorodicarbonyl bisc(N,N-diethylphosphoramidous difluoride)dirhodium(I).
1. General

The ability of carbon monoxide to stabilize very low and negative oxidation states of metals was unique for many years. The chemical and physical properties of the resultant metal carbonyls were unparalleled until the discoveries of ferrocene, $^{1,2}$ Ni(PF$_3$)$_4$ $^{3,4}$ and PtCl$_2$(PF$_3$)$_2$ $^5$ in 1951. Intensive work since then has uncovered a very diverse range of molecules which form complexes with properties similar to those of the metal carbonyls. Ligands such as nitric oxide, phosphines, arsines, stibines, isonitriles, organic sulphides, 1,2-dithiolenes, olefins, acetylenes and carbenes form such compounds. The feature common to all of these molecules is that they not only possess a lone pair for donation to a metal but also have vacant orbitals of low energy capable of accepting electron density from filled metal d orbitals.

One class of ligands which have come into prominence recently is the fluorophosphines. These are compounds of trivalent phosphorus possessing at least one phosphorus-fluorine bond. Some examples are: PF$_3$, PF$_2$H, PF$_2$CCl$_3$, PF$_2$Bu', PF$_2$NMe$_2$, PF$_2$OPh, PF$_2$I, PF$_2$PH$_2$, EtN(PF$_2$)$_2$, PF(CF$_3$)$_2$, PFPhNMe$_2$, PF(NMe$_2$)$_2$, PF(OPr)$_2$, PFCl$_2$. The nature of the substituent markedly affects the donor-acceptor properties of the fluorophosphine. In principle, therefore, it is possible to design a fluorophosphine ligand to suit desired bonding requirements.

In addition to the well characterised metal(O)-phosphorus trifluoride complexes $^6$ many other fluorophosphine derivatives are known. Most of the complexes have carbonyl analogues. Examples of the various types of complex are given below.
<table>
<thead>
<tr>
<th>Metal (O) Complexes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(PF₃)₅]₂, Pd(PF₃)₄, Ni(PF₂Cl)₄.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydrides</th>
</tr>
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<tbody>
<tr>
<td>H₂Fe(PF₃)₄, HCo(PF₃)₃(PH₃).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(PF₃)₂⁻, Ir(PF₃)₄⁻.</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCo(PF₃)₄, RhCl(PF₃)(C₈F₁₂)(SbPh₃)₂, C₅F₇Co(PF₃)₄.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃COMn(CO)(PF₃)₂.</td>
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<table>
<thead>
<tr>
<th>Carbonyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(CO)(PF₃)₃, Ni(CO)(Bu⁺PF₂), Fe(CO)(PF₂NEt₂).</td>
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</table>

<table>
<thead>
<tr>
<th>Nitrosyls</th>
</tr>
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<tbody>
<tr>
<td>Fe(NO)(PF₃)₂, Rh(NO)(PF₃)₃.</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Olefins</th>
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<tr>
<td>(1,3-butadiene)Fe(PF₃)₃.</td>
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</table>

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Mo(π-C₆H₆)(PF₃)₃.</td>
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<th>Cyclopentadienyls</th>
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<tbody>
<tr>
<td>Rh(π-C₅H₅)(PF₃)₂, Mn(π-MeC₅H₄)(CO)(PF₃)₂.</td>
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</table>

<table>
<thead>
<tr>
<th>Allyls</th>
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<tbody>
<tr>
<td>Ta(π-C₃H₅)(PF₃)₅, Co(π-C₃H₅)(PF₃)₅.</td>
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</table>

<table>
<thead>
<tr>
<th>Metal-metal bonded</th>
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<tbody>
<tr>
<td>Rh₂(PF₃)₈, Ph₃SnIr(PF₃)₄, Ph₂BCo(PF₃)₄.</td>
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<table>
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<th>Halides</th>
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<tbody>
<tr>
<td>ReCl(PF₃)₅, cis-PtCl₂(PF₂NMe₂)₂, [RhCl(PF₃)₂]₂.</td>
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<table>
<thead>
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<td>Rh(SP)₂PF₃⁺, Ir(diphos)PF₃⁺.</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(CF₃PF₂)₂(PPh₃)₂, [Co(PF₃)₃PF₂]₂.</td>
</tr>
</tbody>
</table>

Several reviews have appeared on the preparation and chemistry of fluorophosphines and their complexes. ⁶, ⁷, ⁸, ⁹.

The present work is partly concerned with extending the chemistry of fluorophosphine complexes of rhodium(I) (Chapters 2, 3 and 5). The reactions of the rhodium(0) complex, Rh₂(PF₃)₈, with acetylenes have also been studied and the stereochemical non-rigidity of the products examined (Chapter 4). Wherever possible a comparison between the fluorophosphine complex and the analogous carbonyl has been made. The purpose of this is to illustrate how slight differences in the metal-ligand bond can alter the properties of the complex, and to also demonstrate some of the unique advantages in studying the metal fluorophosphines over the metal carbonyls.
2. Bonding in Fluorophosphines and their Complexes

As carbon monoxide and phosphorus trifluoride are structurally quite different it is remarkable that the complexes they form with a wide variety of acceptor molecules are so similar, not only in stoichiometry but in chemical and physical properties. The reasons for these similarities lie in the formally analogous bonding in the metal-phosphorus trifluoride and metal-carbon monoxide linkages.

In a complex of carbon monoxide with an acceptor molecule there is an electron donation from a filled σ-molecular orbital [which is essentially of C(2s) or C(2p) character] of the carbon monoxide. These electrons are donated into empty orbitals on the acceptor atom or molecule to form a σ-bond. A second overlap occurs between filled orbitals of the acceptor molecule (usually d or dp hybrids in transition metal complexes or p orbitals in boranes) and empty antibonding p orbitals of the carbon monoxide giving a π-bond. These two bonding processes act synergically since a σ-donation of electrons from the carbon monoxide makes this ligand positively charged. This results in an increase in the Lewis acidity of the carbon monoxide; enhancing the π-back-donation from the metal and promoting electroneutrality of the whole molecule. 10

Recently Hillier and co-workers have described ab initio self consistent field - molecular orbital calculations on phosphorus trifluoride, its borane adduct and related molecules. A comparison with data from photoelectron spectroscopy and dipole moment determinations showsthat these calculations are fairly accurate descriptions of the molecular bonding. 11,12,13,14.

In phosphorus trifluoride there is appreciable σ-bonding involving P(3p) and P(3d), and F(2s) and F(2p) orbitals [the P(3p)-F(2pσ) overlap is largest]. In this respect the bonding in phosphorus
trifluoride resembles that in trimethylphosphine and in phosphine itself.\textsuperscript{11,13}

However, in phosphorus trifluoride there is also significant $\pi$-bonding between P(3p) and P(3d), and F(2p$_\pi$) orbitals, the major interaction being P(3d$_\pi$)-F(2p$_\pi$). Such $\pi$-bonding is absent in both phosphine and trimethylphosphine, in which there are only small P(3d) orbital populations. The occupation of P(3d) orbitals may be correlated with the $\pi$-donor ability of the group bound to the phosphorus. Methyl and hydrogen are very poor $\pi$-donors, whereas fluorine is a relatively good one.\textsuperscript{6,11,15}

It is found that the phosphorus atom in phosphorus trifluoride is positively charged and that the phosphorus-fluorine bonds are strongly polar.\textsuperscript{11,13} The direction of the dipole in the molecule corresponds to P$^+\cdot F^-$ and arises from the strong electron accepting properties of the fluorine atom (i.e. its high electronegativity). The opposite situation is found in phosphine and trimethylphosphine, in which it is the phosphorus atom which is negatively charged.\textsuperscript{11,13} It would be expected, therefore, that the $\sigma$-donating ability of the phosphorus "lone-pair" in phosphorus trifluoride would be less than that in other phosphines.

The donor and acceptor properties of phosphorus trifluoride (and similar ligands) are determined by the energy and symmetry of the lowest unoccupied and highest occupied molecular orbitals (abbreviated to LUMO and HOMO respectively). These properties are also related to the various atomic orbitals which make up the LUMO and HOMO.

The HOMO (of $A_1$ symmetry) of phosphorus trifluoride is localised on the phosphorus and corresponds to the "lone pair"
orbital. It has equal amounts of P(3s) and P(3p) character as well as a little P(3d) character. An important feature of the HOMO is that it has a significant phosphorus-fluorine antibonding contribution involving the P(3s) and F(2p) orbitals.

The LUMO (of E symmetry) in phosphorus trifluoride is also largely localised on the phosphorus atom. It has both appreciable P(3p) and P(3d) character. This molecular orbital also is antibonding with respect to the phosphorus-fluorine bond, as the P(3p) and P(3d) atomic orbitals are already involved in the phosphorus-fluorine π-bonding. Occupation of the LUMO would compete with phosphorus-fluorine π-bonding for P(3p) and P(3d) orbitals. In addition the energy of the LUMO in phosphorus trifluoride is lower than either that of trimethylphosphine or phosphine and so it is more readily occupied.

The bonding in simple coordination complexes of these ligands has been examined. The general bonding scheme for the coordinated phosphines is similar to that found in the metal carbonyls; a σ-bond from donation of the phosphorus "lone pair" electrons and a π-bond from filled metal orbitals to an unoccupied molecular orbital essentially on the phosphorus (both processes acting synergically).

In the borane complex, BH$_3$PF$_3$, the phosphorus "lone pair" orbital is delocalised over the borane moiety. The "lone pair" orbital, which has 34% P(3s) character in the free ligand, possesses only 14% P(3s) character in the corresponding molecular orbital in the complex. This change has been ascribed to the electron donor properties of phosphorus trifluoride. Owing to the delocalisation of the "lone pair", the phosphorus-fluorine antibonding effects associated with the "lone pair" orbital are decreased. As the phosphorus-fluorine bonds are now stronger they might be expected to shorten on coordination.
The molecular orbital of \( \text{BH}_3\text{PF}_3 \) which corresponds to the LUMO of uncoordinated phosphorus trifluoride is localised mainly on the borane moiety with only a small phosphorus component.\(^{14}\) This indicates little \( \pi \)-back-donation on coordination and is reflected in the small increase in \( \text{P}(3\text{p}) \) and \( \text{P}(3\text{d}) \) orbital populations.\(^{17}\) However, any increase in these orbital populations arising from back-donation, results in a decrease in the phosphorus-fluorine \( \pi \)-bonding [which also employs \( \text{P}(3\text{p}) \) and \( \text{P}(3\text{d}) \) orbitals]. This should be reflected in an increase in the phosphorus-fluorine bond length. The result, that there is only a small \( \pi \)-contribution in the boron-ligand bond, is also found in \( \text{BH}_3\text{PH}_3 \) and in \( \text{BH}_3\text{CO} \).\(^{15,18}\) These conclusions are well supported by photoelectron spectra.\(^{15,17,18}\)

It has been suggested\(^{19}\) that this \( \pi \)-bonding in the adducts of borane arises from hyperconjugation in the borane. Recent N.M.R. results are not entirely consistent with this view, but do not exclude it.\(^{20,21}\)

Whatever the origin of the \( \pi \)-back-bonding in borane adducts, the presence of filled d orbitals in transition metals provides a ready mechanism for strong \( \pi \)-interaction with the LUMO of phosphorus trifluoride. This would synergically increase the metal-ligand \( \sigma \)-bond strength. The great stability of metal(0)-phosphorus trifluoride complexes\(^6\) as contrasted to the ease of dissociation of \( \text{BH}_3\text{PF}_3 \) supports this.

It can be seen in Table 1 that in all cases there is a significant decrease in the phosphorus-fluorine bond length on coordination, and in most cases an increase of bond angles. As expected, the decrease in phosphorus-fluorine bond length is greater in the borane adducts than in the transition metal complexes, \( \sigma \)-donation being the predominant bonding in the boranes. The small changes in phosphorus-fluorine
<table>
<thead>
<tr>
<th>Compound</th>
<th>r(P-F) ( (\text{Å}) )</th>
<th>F-P-F ( \text{(degrees)} )</th>
<th>Method(^a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF(_3)</td>
<td>1.5700(12)</td>
<td>97.8(2)</td>
<td>M</td>
<td>23</td>
</tr>
<tr>
<td>OPF(_3)</td>
<td>1.52(2)</td>
<td>102.5(20)</td>
<td>M</td>
<td>24</td>
</tr>
<tr>
<td>SPF(_3)</td>
<td>1.53(2)</td>
<td>100.3(20)</td>
<td>M</td>
<td>24</td>
</tr>
<tr>
<td>BH(_3)PF(_3)</td>
<td>1.538(8)</td>
<td>99.8(10)</td>
<td>M</td>
<td>25</td>
</tr>
<tr>
<td>B(_2)H(_4)(PF(_3))(_2)</td>
<td>1.539(3)</td>
<td>101</td>
<td>E</td>
<td>26</td>
</tr>
<tr>
<td>B(_4)F(_6)PF(_3)</td>
<td>1.511(15)</td>
<td>101.7(10)</td>
<td>X</td>
<td>27</td>
</tr>
<tr>
<td>Ni{(PF(_3))}_4</td>
<td>1.561(3)</td>
<td>99.3(3)</td>
<td>E</td>
<td>28</td>
</tr>
<tr>
<td>Ni{(PF(_3))}_4</td>
<td>1.561(5)</td>
<td>98.4(8)</td>
<td>E</td>
<td>16</td>
</tr>
<tr>
<td>Pt{(PF(_3))}_4</td>
<td>1.546(6)</td>
<td>98.9(7)</td>
<td>E</td>
<td>16</td>
</tr>
<tr>
<td>HCo{(PF(_3))}_4</td>
<td>1.549(12)</td>
<td>97.1(13)</td>
<td>X</td>
<td>29</td>
</tr>
<tr>
<td>Mo{(CO)}(_5)PF(_3)</td>
<td>1.557(4)</td>
<td>99.5(5)</td>
<td>E</td>
<td>30</td>
</tr>
<tr>
<td>PF(_2)H</td>
<td>1.582(2)</td>
<td>99.0(2)</td>
<td>M</td>
<td>31</td>
</tr>
<tr>
<td>OPF(_2)H</td>
<td>1.552(6)</td>
<td>100.0(5)</td>
<td>M</td>
<td>32</td>
</tr>
<tr>
<td>BH(_3)PF(_2)H</td>
<td>1.539(3)</td>
<td>99.8(5)</td>
<td>M</td>
<td>33</td>
</tr>
<tr>
<td>PF(_2)NMe(_2)</td>
<td>1.610(4)</td>
<td>91.5(3)</td>
<td>X</td>
<td>34</td>
</tr>
<tr>
<td>B(_4)H(_8)PF(_2)NMe(_2)</td>
<td>1.583(5)</td>
<td>96.4(3)</td>
<td>X</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^a\) M = Microwave spectroscopy, E = Electron diffraction, X = X-ray crystallography.
bond length in Ni(PF$_3$)$_4$ probably result from the partial cancellation of the effect of $\sigma$-bonding by the effect of $\pi$-bonding (one tending to decrease the phosphorus-fluorine bond length, the other increasing it). This interpretation is in accord with data from photoelectron spectroscopy, $^{36,37}$ which shows that the energy levels of phosphorus trifluoride are only slightly changed on coordination in Ni(PF$_3$)$_4$.

In contrast, coordination to borane or to platinum(0) substantially lowers the energy of the "lone pair" orbital in phosphorus trifluoride.$^{17,36}$ This reflects the delocalisation of the "lone pair" orbital over the acceptor moiety and is a measure of the increased $\sigma$-donation of the "lone pair"$^{36}$ The result of the increased $\sigma$-bonding is to increase the strength of the phosphorus-fluorine overlap. The extent of the $\pi$-back-bonding is not sufficient to compensate for the increased $\sigma$-bonding and so a shorter phosphorus-fluorine bond length is found in Pt(PF$_3$)$_4$ and in BH$_3$PF$_3$ than in Ni(PF$_3$)$_4$ (Table 1).

That there is also a decrease in the phosphorus-fluorine bond length in the substituted fluorophosphines on coordination, strongly suggests that the bonding scheme, outlined above for phosphorus trifluoride, holds equally well for the substituted fluorophosphines. There will be differences, however, in the relative $\sigma$- and $\pi$-bonding abilities of the substituted fluorophosphines depending upon the nature of the substituent. Some of the factors affecting the bonding in substituted fluorophosphines have been discussed by Nixon.$^{38,39}$

The importance of $\pi$-bonding in phosphine complexes has been the subject of some controversy.$^{40,41,42}$ However, apart from the photoelectron studies mentioned above, there is much evidence for the participation of metal d orbitals in $\pi$-bond formation in low valent metal-phosphorus trifluoride complexes. This has been reviewed.$^6,8,9$
Phosphorus trifluoride complexes have not been reported with transition metals in oxidation states higher than two or as cationic complexes (with the exceptions of [Ir(diphos)$_2$PF$_3$]$^+$ and [Rh(SP)$_2$PF$_3$]$^+$). This is probably due to the ability of fluorophosphines to stabilize only complexes in which $\pi$-back-bonding is maximized. This occurs in anionic complexes, in complexes with metals in a low oxidation state and with metals containing enough d electrons for $\pi$-bonding.

The availability of $\pi$-bonding electrons on the metal appears to be a relatively more important requirement for the stability of metal-phosphorus trifluoride complexes than for the carbonyls. Cationic metal carbonyls are well known, as are carbonyls in which the metal has an oxidation state of three.

The general similarity in the coordinating powers of phosphorus trifluoride and carbon monoxide is illustrated by the ability of phosphorus trifluoride to yield a mixture of every possible substitution product when reacted with Ni(CO)$_4$, Fe(CO)$_5$, Mo(CO)$_6$, or Co(NO)(CO)$_3$. No other pair of ligands can displace each other so unrestrictedly or reversibly in metal complexes. The complexes become progressively more stable as the degree of substitution of phosphorus trifluoride increases. The only exception to this observation is V(CO)$_5$PF$_3$, which is less stable than V(CO)$_6$. This can be ascribed to insufficient d electrons on the metal to provide strong $\pi$-bonding to the phosphorus trifluoride. That attempts to prepare the phosphorus trifluoride analogue of [Ta(CO)$_6$] have also failed, is probably attributable to the same cause.

The heats of formation and bond energies of the metal-ligand bonds have been shown to be about the same in phosphorus trifluoride and in carbon monoxide complexes.
It has been suggested that phosphorus trifluoride is a slightly better $\sigma$-donor and better $\pi$-acceptor than carbon monoxide, but considerable differences in opinion have been expressed.

It appears that no dependable order of relative $\sigma$- and $\pi$-bonding abilities can be given. The two effects are synergically interrelated in any one complex. They are also related to the bonding abilities of other ligands on the complex, as well as the charge, oxidation state and electronic configuration of the metal in any particular system.

In summary, the stability of the metal-phosphorus trifluoride linkage compared with the corresponding carbonyl is higher in negatively charged complexes, with metals containing the maximum number of d electrons and in low oxidation states. The complexes of the zero-valent second and third row transition elements are also much more stable with phosphorus trifluoride than with carbon monoxide, e.g. $\text{Rh}_2(\text{PF}_3)_8$ and $\text{Pd}(\text{PF}_3)_4$ exist whereas $\text{Rh}_2(\text{CO})_8$ is very unstable and $\text{Pd}(\text{CO})_4$ has not been reported.

...
3. Spectroscopic Properties

(a) Vibrational Spectroscopy

In metal carbonyls the vibrational spectrum in the $\nu$(C=O) region is by far the most widely used physical property of the complexes. The reason for this lies in the relative ease of observation and simplicity in interpreting the results. It is generally found that on coordination $\nu$(C=O) is lower than the free ligand value. The different spectra exhibited in this region may be readily related to structural and bonding differences in the various carbon monoxide complexes.

The corresponding bands in phosphorus trifluoride, $\nu$(P-F) have not been as widely used in the interpretation of the molecular properties of metal-phosphorus trifluoride complexes. The reasons for this are twofold. In phosphorus trifluoride there are two vibrations of different symmetry which involve essentially phosphorus-fluorine stretching - at 892 cm$^{-1}$ ($A_1$ symmetry) and at 860 cm$^{-1}$ (E symmetry). The ability of phosphorus trifluoride to give rise to two stretching vibrations (or three if the degeneracy of the E mode is removed), as compared with only one in carbon monoxide, makes spectral interpretation much more difficult than in the corresponding carbonyl. The second complication is that these $\nu$(P-F) bands lie in the "fingerprint" region of the spectrum and are thus often obscured by other vibrations. Although these difficulties usually preclude a quantitative interpretation of spectra they are still of use in determining the nature of the bonding and often the structure of many fluorophosphine complexes.

On coordination to boranes $\nu$(P-F) in phosphorus trifluoride increases in frequency (see Table 2). This shift is attributable to the predominance of $\sigma$-bonding in the boron-phosphorus linkage, resulting in a decrease in the phosphorus-fluorine antibonding component. An analogous mechanism may explain the increase in $\nu$(C=O) noted on
### TABLE 2

\( \nu(\text{P-F}) \) in some Fluorophosphines and their Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(\text{P-F}) ) (cm(^{-1}))(^a)</th>
<th>Phase</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF(_3)</td>
<td>892,860</td>
<td>gas</td>
<td>60</td>
</tr>
<tr>
<td>BH(_3)PF(_3)</td>
<td>957,944</td>
<td>liquid (-80°)</td>
<td>63</td>
</tr>
<tr>
<td>B(_4)F(_6)PF(_3)</td>
<td>995,974</td>
<td>gas</td>
<td>64</td>
</tr>
<tr>
<td>HRh(PF(_3))(_4)</td>
<td>949,912,904,863</td>
<td>gas</td>
<td>65</td>
</tr>
<tr>
<td>H(_2)Ru(PF(_3))(_4)</td>
<td>959,919,905,873</td>
<td>gas</td>
<td>66</td>
</tr>
<tr>
<td>Ni(PF(_3))(_4)</td>
<td>898,860</td>
<td>gas</td>
<td>60</td>
</tr>
<tr>
<td>Os(PF(_3))(_5)</td>
<td>930,912,880,862</td>
<td>gas</td>
<td>67</td>
</tr>
<tr>
<td>Fe(NO)(_2)(PF(_3))(_2)</td>
<td>907,887,864</td>
<td>gas</td>
<td>68</td>
</tr>
<tr>
<td>Pt(CNC(<em>6)(</em>{11}))(PF(_3))(_3)</td>
<td>878,838,815</td>
<td>n-heptane</td>
<td>69</td>
</tr>
<tr>
<td>Ni(bipy)(PF(_3))(_2)</td>
<td>856,815,773</td>
<td>KBr disc</td>
<td>70</td>
</tr>
<tr>
<td>K(_2)Ru(PF(_3))(_4)</td>
<td>818,778</td>
<td>acetone</td>
<td>71</td>
</tr>
<tr>
<td>KCo(PF(_3))(_3)(PPh(_3))</td>
<td>877,871,788,775,749</td>
<td>acetone</td>
<td>72</td>
</tr>
<tr>
<td>CF(_3)PF(_2)</td>
<td>863,859</td>
<td>gas</td>
<td>73</td>
</tr>
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<td>BH(_3)CF(_3)PF(_2)</td>
<td>928,921</td>
<td>gas</td>
<td>74</td>
</tr>
<tr>
<td>Ni(CF(_3)PF(_2))(_4)</td>
<td>894,863</td>
<td>gas</td>
<td>74</td>
</tr>
<tr>
<td>Pt(PPh(_3))(_2)(CF(_3)PF(_2))(_2)</td>
<td>836,802</td>
<td>Nujol</td>
<td>74</td>
</tr>
<tr>
<td>Ni(CO)(_2)(CF(_3)PF(_2))(_2)</td>
<td>887,857</td>
<td>gas</td>
<td>75</td>
</tr>
<tr>
<td>PF(_2)NMe(_2)</td>
<td>814,770</td>
<td>gas</td>
<td>76</td>
</tr>
<tr>
<td>BH(_3)PF(_2)NMe(_2)</td>
<td>873,763</td>
<td>gas</td>
<td>76</td>
</tr>
<tr>
<td>B(_3)H(_2)PF(_2)NMe(_2)</td>
<td>867,755</td>
<td>liquid</td>
<td>76</td>
</tr>
<tr>
<td>cis-Mo(CO)(_3)(PF(_2)NMe(_2))(_3)</td>
<td>826,808,777</td>
<td>KBr disc</td>
<td>77</td>
</tr>
<tr>
<td>Ni(PF(_2)NMe(_2))(_4)</td>
<td>799,760</td>
<td>KBr disc</td>
<td>77</td>
</tr>
</tbody>
</table>

\( ^a \) All bands medium to strong.
coordination of carbon monoxide to borane (an increase from 2155 \text{ cm}^{-1} \text{ to } 2169 \text{ cm}^{-1}).\text{61}

In metal carbonyls \nu(C=O) almost invariably appears at a lower frequency than in free carbon monoxide.\text{62} This is not the case with \nu(P-F) in the corresponding phosphorus trifluoride complexes. It is found that \nu(P-F) in neutral metal(0)-phosphorus trifluoride complexes [e.g. Mo(PF$_3$)$_6$] and in metal hydrides [e.g. HIr(PF$_3$)$_4$] occur at higher frequencies than free phosphorus trifluoride. In these complexes there is considerable delocalisation of the "lone pair" on complexation, significantly decreasing the phosphorus fluorine antibonding component.

In phosphorus trifluoride complexes containing a relatively strong \sigma-donor substituent (e.g. PPh$_3$, RNC) or in anionic complexes, the \sigma-donor function of the phosphorus trifluoride is reduced but the \pi-acceptor function is increased. Both factors result in an increased occupancy of phosphorus-fluorine antibonding orbitals and hence a lowering of \nu(P-F) from that in the free ligand.

In uncomplexed, substituted fluorophosphines it has been shown that there is a linear relationship between \nu(P-F) and the electronegativity of the substituent (-R), \nu(P-F) decreasing with decreasing electron withdrawing ability of -R.\text{80} If -R is capable of \pi-donation to the phosphorus (e.g. R = -NMe$_2$, -OMe, -C$_6$H$_5$) then this will compete with phosphorus-fluorine \pi-bonding, resulting in a lower \nu(P-F).

On coordination, \nu(P-F) in substituted fluorophosphines may shift to higher or lower frequencies depending on the nature of the metal, the other ligands present and the fluorophosphine. The borane adducts usually have higher \nu(P-F). With strongly \pi-accepting ligands,
such as CF$_3$PF$_2$ or PF$_2$Cl, ν(P-F) usually increases on coordination in complexes of the type NiL$_4$. With poor π-acceptors but relatively strong σ-donors (e.g. Me$_2$NPF$_2$, MePF$_2$), ν(P-F) remains unchanged or decreases on coordination in NiL$_4$. In mixed ligand complexes [e.g. cis-Mo(CO)$_3$L$_3$] the shifts in frequency are variable and there are insufficient series of complexes from which to draw conclusions.

(b) N.M.R. Spectroscopy

N.M.R. studies have played an important role in the development of the chemistry of fluorophosphines and their complexes. The reason for this is that both $^{31}$P and $^{19}$F have nuclear spins of $\frac{1}{2}$ and are present in 100% natural abundance. Correspondingly few $^{13}$C N.M.R. studies of the metal carbonyls have been reported as the technique is subject to experimental limitations.

Complete analysis of the N.M.R. spectra of fluorophosphine complexes is difficult due to the complicated spin systems involved. However a qualitative picture may be readily obtained from consideration of the chemical shifts and some coupling constants which are easily extracted from the spectra (mainly $^1J_{PF}$).

The $^{19}$F chemical shifts of the free fluorophosphines occur in the region +26 to +219 p.p.m. (relative to CFC$_3$). Compared with free ligand values, transition metal-fluorophosphine complexes have a resonance at a much lower field. In contrast borane adducts exhibit a shift to higher field, (e.g.).

In free fluorophosphines it is found that $^{31}$P chemical shifts occur in the region -97 to -255 p.p.m. (relative to 85% H$_3$PO$_4$), with the resonance of phosphorus trifluoride at the highest field. On complexation to transition metals there is a low field shift from the free ligand value. Borane complexes on the other hand usually have
resonances at higher fields than the free ligands.

The $^{19}\text{F}$ and $^{31}\text{P}$ N.M.R. shifts have been related to some changes in molecular structure and electronic populations by Schmutzler$^{84,86}$ and others.$^{8,87,88}$

Direct coupling between $^{31}\text{P}$ and $^{19}\text{F}$ in free fluorophosphines give rise to a $^{19}\text{F}$ spectrum which is a broadly spaced doublet. The magnitude of this coupling decreases with decreasing electronegativity of the substituents on the fluorophosphine and ranges from $J_{\text{PF}} = 1441$ Hz in phosphorus trifluoride to 823 Hz in $\text{Me}_2\text{PF}$.\(^{84}\)

On coordination of more than one fluorophosphine to a metal the spectra become more complicated due to additional inter-ligand coupling of the type $J_{\text{PF}}$, $J_{\text{pp}}$ and $J_{\text{FF}}$. In $^{19}\text{F}$ N.M.R. spectra the separation of the doublet in the coordinated ligand is due to both $J_{\text{PF}}$ and $J_{\text{FF}}$.\(^{89}\) However, the magnitude of $J_{\text{PF}}$ is usually much greater than that of $J_{\text{PF}}$, and so changes in the separation of this doublet on coordination generally reflect changes in $J_{\text{PF}}$. On coordination to either a transition metal or a borane, the absolute magnitude of $J_{\text{PF}}$ decreases (a few exceptions are known).\(^{90}\) Assuming Fermi contact to be the dominant factor in determining $J_{\text{PF}}$, this decrease on coordination may be partly understood in terms of a smaller P(3s) population compared with that in the free ligand. The decrease in P(3s) atomic population is predicted in the complex $\text{BH}_3\text{PF}_3$.\(^{14,17}\) The difference between $J_{\text{PF}}$ in the free ligand and $J_{\text{PF}}$ in metal(0) complexes has also been related to the energies of the molecular orbitals involved.\(^{88,91}\)

Other coupling constants to have been examined in some detail are $J_{\text{PMP}}$ in transition metal complexes and $J_{\text{PB}}$ in borane adducts. The magnitude of $J_{\text{PMP}}$ has been related to the electron withdrawing...
power of the substituent on the fluorophosphine. In recent studies of donor-acceptor strengths in borane adducts, it has been found that the magnitude of $J_{PB}$ can be correlated with the base strength of the phosphine towards borane.

The $^{59}$Co N.M.R. spectra ($^{59}$Co: $I = 7/2$, 100% abundance) of the anions $[\text{Co(CO)}_4]^{-}$ and $[\text{Co(PF}_3)_4]^{-}$ have been measured. It was suggested that $\sigma$-bonding is more important in the Co-P bond than in Co-C bond. It was also proposed that $\pi$-bonding was greater in the carbonyl complex than in the phosphorus trifluoride complex. These conclusions were consistent with $^{55}$Mn N.M.R. data ($^{55}$Mn: $I = 5/2$, 100% abundance) for the series, $\text{HMn(CO)}_5\text{(PF}_3)_x$ ($x = 0$ to 5), which indicated that phosphorus trifluoride is a better $\sigma$-donor than carbon monoxide.

Several chemical and physical properties of coordination compounds have been examined by $^{19}$F and $^{31}$P N.M.R. These include confirmation of the existence of bridging $\text{-PF}_2^{-}$ and terminal $\text{-PF}_2$ groups, establishing the coordination site in $\text{R}_2\text{NPF}_2$ ligands, studying group and ligand redistribution reactions. One of the most interesting applications of $^{19}$F and $^{31}$P spectroscopy is in the study of stereochemical non-rigidity in fluorophosphines and their complexes. This will be discussed in Chapter 4.

(c) Mass Spectra

As transition metal-phosphorus trifluoride complexes are generally more volatile than the corresponding carbonyl complex and the metal-phosphorus bond is a stable one, these complexes may be readily studied by mass spectral techniques. However, very few studies have appeared in the literature on metal-phosphorus trifluoride complexes and none on substituted fluorophosphine complexes.
Mass spectra reported up the end of 1971 are for Ni(PF)$_4$, Fe(PF$_3$)$_5$, HCo(CO)$_{4-x}$(PF$_3$)$_x$ ($x = 0$ to 4), Mo(CO)$_{6-x}$(PF$_3$)$_x$ [RhX(PF$_3$)$_2$]$_2$ (X = Cl, Br, I), M$_2$(PF$_3$)$_8$ (M = Rh, Ir), and Ta($\pi$-C$_3$H$_5$)(PF$_3$)$_5$. They all exhibit strong parent molecular ions.

The fragmentation pattern of the above complexes always consists of consecutive loss of phosphorus trifluoride groups, and is similar to the carbonyls which progressively lose carbon monoxide. An additional breakdown pattern is found in phosphorus trifluoride complexes. There is a loss of a single fluorine atom which is followed by elimination of phosphorus trifluoride groups. This results in two series of ions in the mass spectra of these complexes, [M(PF$_3$)$_x$]$^+$ and [M(PF$_3$)$_y$PF$_2$]$^+$. An analogous situation is found in metal carbonyls (especially with second and third row metals), in which ions of the type [M(CO)$_x$C]$_y$$^+$ are fairly common. In some cases heats of formation of the metal complex have been estimated from mass spectrometry. They indicate that the metal-phosphorus and metal-carbon bonds are of comparable energy. Conclusions from appearance potentials suggest that the HOMO in phosphorus trifluoride complexes is constituted largely from the metal orbitals, supporting the results of photoelectron spectroscopy.
Chapter 2
The Preparation and Properties of Phosphorus Trifluoride Complexes of Rhodium(I)

1. Introduction

The preparation and chemical properties of the square-planar complexes of rhodium(I) have been the subject of intensive research, partly due to the ability of some of these compounds to act as catalysts in organic reactions. Although not of great catalytic interest, one of the most important compounds of rhodium and a convenient starting material for other rhodium(I) complexes is \([\text{RhCl(CO)}_2]_2\) (1a). This substance undergoes a variety of bridge splitting, bridge replacement and carbonyl replacement reactions.\(^{107}\) The reaction of (1a) with triphenylphosphine, for example, produces the mononuclear species, \(\text{trans-RhCl(PPh}_3)_2\text{CO}\) (2).\(^{108}\) The latter complex is an active hydroformylation catalyst\(^ {109}\) and undergoes a wide variety of oxidative addition reactions.\(^ {110}\)

In view of the similarity between carbon monoxide and phosphorus trifluoride as ligands, an examination of the properties of rhodium(I) complexes containing phosphorus trifluoride has been undertaken, with emphasis on the analogues of the two carbonyl complexes mentioned above. The preparation of these complexes was facilitated by the previous discovery of a convenient low pressure synthesis for phosphorus trifluoride complexes of rhodium(I).\(^ {57}\) The present research was contemporaneous with an entirely independent study of fluorophosphine complexes of rhodium(I) by Nixon and co-workers.\(^ {111}\)

Several complexes of rhodium(I) with phosphorus trifluoride had been reported previously. Kruck and co-workers\(^ {112}\) prepared the red, crystalline dimer, \([\text{RhCl(PF}_3)_2]_2\) (3a), in low yield by passing phosphorus trifluoride over a mixture of anhydrous rhodium trichloride and
1. $a, \ X = \text{Cl}$  
   $b, \ X = \text{Br}$  
   $c, \ X = \text{I}$

2. \[
\begin{array}{c}
\text{Cl} \\
\text{Rh} \\
\text{Ph}_3\text{P} \\
\text{CO}
\end{array}
\]

3. $a, \ X = \text{Cl}$  
   $b, \ X = \text{Br}$  
   $c, \ X = \text{I}$

4. \[
\begin{array}{c}
\text{PF}_3 \\
\text{Rh} \\
\text{PF}_3 \\
\text{Rh} \\
\text{PF}_3 \\
\text{PF}_3 \\
\text{PF}_3
\end{array}
\]

5. $a, \ X = \text{Cl}$  
   $b, \ X = \text{Br}$  
   $c, \ X = \text{I}$

6. \[
\begin{array}{c}
\text{Bu}^n\text{N} \\
\text{Rh} \\
\text{PF}_3
\end{array}
\]

7. \[
\begin{array}{c}
\text{Rh} \\
\text{F}_3\text{P} \\
\text{PF}_3
\end{array}
\]

8. \[
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{O} \\
\text{O} \\
\text{Rh} \\
\text{PF}_3 \\
\text{H}_3\text{C} \\
\text{H}_3\text{C}
\end{array}
\]
copper powder at 80° and one atmosphere pressure. They also obtained the latter complex as an inseparable mixture with Rh₂(PF₃)₈ (4), by a "reductive fluorophosphination" of rhodium trichloride at high temperatures and pressures. Reaction of this mixture with an excess of triphenylphosphine yielded the square-planar complex, trans-RhCl(PPH₃)₂PF₅ (5a).

Bennett and Patmore have prepared [RhCl(PF₃)₂]₂ (3a) in good yield by displacement of the coordinated cyclooctene from [RhCl(C₈H₁₄)₂]ₙ with phosphorus trifluoride. From complex (3a) they have prepared the bromo- and iodo- bridged dimers, (3b) and (3c) by metathetical reactions. The chlorine bridges were readily cleaved by chloride ion, affording the anion [cis-RhCl₂(PF₃)₂]⁻ (6a) and replaced by Tl(C₅H₅) or Tlacac, to produce Rh(C₅H₅)(PF₃)₂ (7) and Rh(acac)(PF₃)₂ (8) respectively. It was also found possible to reduce [RhCl(PF₃)₂]₂ in the presence of phosphorus trifluoride with potassium amalgam to produce K[Rh(PF₃)₄] and to react the latter with another equivalent of complex (3a), affording the previously reported binuclear, rhodium(0) complex (4).

Concurrently with this research, Nixon published the preparation of complex (3a) by displacement of olefin from either [RhCl(nbd)]₂ or [RhCl(C₂H₄)₂]₂, by phosphorus trifluoride. The reactions of complex (3a) with carbon monoxide, trichloromethylidifluorophosphine and triphenylphosphine were also noted. Fluorine N.M.R. techniques were used to examine the intermolecular ligand exchange of trans-RhCl(PPH₃)₂PF₅ (5a).
The Interconversion of Phosphorus Trifluoride Complexes of Rhodium(1)
2. Results and Discussion

The reactions discussed in this Chapter are summarised in Figure 1.

**Preparation of µ,µ'-dihalotetrakis(phosphorus trifluoride)dirhodium(I)**

Complexes of the type (3) may be conveniently synthesised by the reaction of \([\text{RhX(cod)}]_2\), with phosphorus trifluoride in n-pentane. On cooling the reaction mixture to -78°C, dark red or brown crystals of the product may be obtained. The substance so formed is usually contaminated by a 1,5-cyclooctadiene-containing material, which may be removed by recrystallisation from n-pentane saturated with PF₃ at -78°C. Complexes (3b) and (3c) are most conveniently prepared by this method as the corresponding cyclooctadiene dimers are readily accessible. The yield decreases in proceeding from \(X = \text{Cl}\) to \(X = \text{I}\), presumably because the thermal stability of complexes (3) also decreases in this order. An earlier preparation of (3b) and (3c) involving a metathetical reaction of lithium bromide or sodium iodide with (3a) in diethyl ether can be complicated by formation of stable anionic species of the type, \([\text{RhX}_2(\text{PF}_3)_2]^-\) (6), which are probably intermediates in the metathetical halide exchange process.

The complex, \([\text{RhCl(}\text{PF}_3)_2\]_2 (3a), is most readily synthesised by displacing volatile ligands such as carbon monoxide or ethylene from the dimers, \([\text{RhCl(CO)}]_2\) or \([\text{RhCl(C}_2\text{H}_4)]_2\), with phosphorus trifluoride. This is the preferred preparation of (3a), as the latter may be obtained in yields greater than 90% (based on RhCl₃·3H₂O) using \([\text{RhCl(CO)}]_2\), as an intermediate. This compares with 50% yield (based on RhCl₃·3H₂O) using \([\text{RhCl(C}_8\text{H}_{14})]_2\), as an intermediate, and 2.6% yield from the direct reaction of the hydrated trichloride with phosphorus trifluoride.
Phosphorus trifluoride will only displace carbon monoxide completely and rapidly from the complexes \([\text{RhX(CO)}_2]_2\) (1) in solution. In the solid state, carbon monoxide is only partially replaced to afford species which could not be adequately characterised (vide infra). Nixon\(^{11}\) has reported a complex, trans-RhCl(CO)(PF\(_3\))\(_2\) from the reaction of phosphorus trifluoride with complex (1a) in the solid state, but this result could not be confirmed in the present study. It is not clear as to why different products are obtained for the reaction of complex (1a) with phosphorus trifluoride in the solid state and in solution. Clark and co-workers have shown that phosphorus trifluoride can completely displace carbon monoxide from other carbonyl complexes, but often only with difficulty.\(^{47,48,49}\) In some cases [e.g. Mo(CO)\(_{6-x}(PF\(_3\))\(_x\)] all possible substitution products are formed and are in equilibrium with each other.

Reactions of \(\mu,\mu'-\text{dichlorotetraakis(phosphorus trifluoride)}\text{dirhodium(I)}\) (3a)

With \(\mu,\mu'-\text{dichlorotetracarbonyldirhodium(I)}\) (1a)

If \(n\)-pentane solutions of \([\text{RhCl}(PF\(_3\))_2]_2\) and \([\text{RhCl(CO)}_2]_2\) are mixed, a very rapid redistribution of the coordinated ligands occurs. This is evidenced by changes in the \(\nu(C-O)\) region of the IR spectrum. The spectrum varies with the proportions of (1a) and (3a) used. If the concentration of \([\text{RhCl(CO)}_2]_2\) (1a) is greater than that of \([\text{RhCl}(PF\(_3\))_2]_2\) (3a), then absorptions due to both unreacted complex (1a) and a new species are present. As more (3a) is added, the concentration of (1a) decreases and finally disappears when the ratio (1a):(3a) is less than 1:1. The new \(\nu(C-O)\) absorptions in the IR spectrum are observed at 2104\(\text{(m)}\), 2064\(\text{(vs)}\), 2039\(\text{(m)}\), 2023\(\text{(m)}\), \text{cm}^{-1}. Very moisture sensitive, orange-red crystals can be isolated from the reaction mixture [(1a):(3a) = 1:1] on cooling to -78\(^\circ\). The mass spectrum shows a major component of these crystals to be \([\text{RhCl(CO)}(PF\(_3\))]_2\) with lesser amounts of \(\text{Rh}_2\text{Cl}_2(CO)_4-x(PF\(_3\))_x\) \((x = 1, 3, 4)\) present.
On further addition of complex (3a) to the reaction mixture, one absorption \( \nu(C-O) = 2064 \text{ cm}^{-1} \) increases at the expense of the others. The absorption at 2064 cm\(^{-1}\) is coincident with that in the product of reaction of phosphorus trifluoride with complex (1a) in the solid state. Mass spectral data for the product of the reaction of PF\(_3\) with [RhCl(CO)]\(_2\)\(_2\) show that a mixture of complexes of the composition \( \text{Rh}_2\text{Cl}_2(\text{CO})_4-\chi(\text{PF}_3)_\chi \) (\( \chi = 0 \) to 4) is present. Mononuclear species of the type trans-RhCl(CO)(PF\(_3\))\(_2\) reported by Nixon\(^{111}\) could not be detected in the mass spectrum of either the reaction product of PF\(_3\) with the solid complex (1a) or from mixtures of complexes (3a) and (1a).

Owing to the complexity of the system, the nature of the products from either reaction could not be properly characterised, but it is believed they consist of the geometric isomers of [RhCl(CO)(PF\(_3\))]\(_2\), together with smaller amounts of the other mixed, carbonyl-phosphorus trifluoride binuclear species.

With \( \mu, \mu'\) -dichlorotetrakis(ethylene)rhodium(I)

When equivalent quantities of [RhCl(PF\(_3\))\(_2\)]\(_2\) and [RhCl(C\(_2\)H\(_4\))\(_2\)]\(_2\) are mixed in \( n\) -pentane and the clear solution cooled to -78°, an orange solid slowly crystallises. As the ethylene complex is only slightly soluble in \( n\) -pentane, it appears that a redistribution of ligands has occurred. The orange-red product is very moisture-sensitive and slowly decomposes at about 0°. Elemental analysis shows the product to contain both ethylene and phosphorus trifluoride. The proton N.M.R. of a freshly prepared solution shows a single, strong resonance at \( \delta_{\text{TMS}} = 3.23 \text{ p.p.m.} \) (in C\(_6\)D\(_6\)). This compares with \( \delta_{\text{TMS}} = 3.47 \text{ p.p.m.} \) for the mixed carbonyl-ethylene complex [RhCl(C\(_2\)H\(_4\))(CO)]\(_2\).\(^{114}\)

An intense molecular ion in the mass spectrum of the complex attributable to \( \text{[Rh}_2\text{Cl}_2(\text{PF}_3)_2(C_2\text{H}_4)_2]_+ \), is observed. Daughter ions due to the consecutive loss of two ethylene moieties and then two
phosphorus trifluoride moieties are also observed. Only relatively weak peaks which may be assigned to \([\text{Rh}_2\text{Cl}_2(\text{PF}_3)_x(\text{C}_2\text{H}_4)_{4-x}]^+\) (x = 1, 3, 4), are apparent. Thus it appears that the reaction of equimolar proportions of complex (3a) and \([\text{RhCl(C}_2\text{H}_4)_2]\) results in a redistribution of coordinated phosphorus trifluoride and ethylene, with the predominant species being \([\text{RhCl(PF}_3)(\text{C}_2\text{H}_4)]_2\).

**With phosphorus trifluoride**

When phosphorus trifluoride is bubbled into a solution of \([\text{RhCl(PF}_3)_2]\) (3a) a rapid exchange between coordinated and free phosphorus trifluoride occurs. Evidence of this is obtained from the \(^{19}\text{F N.M.R. spectrum of complex (3a)} in the presence of free phosphorus trifluoride. The \(^{19}\text{F N.M.R. of [RhCl(PF}_3)_2}\) (3a) by itself consists of a doublet, mainly due to coupling of fluorine with directly bonded phosphorus \(^{1}J_{PF}\), with further fine structure (due to \(^2J_{RhF}, ^2J_{pp}\) and \(^4J_{PF}\)). When there is a small concentration of free phosphorus trifluoride in the solution all couplings of fluorine to every atom except the directly bound phosphorus \(^{1}J_{PF}\) are lost and the spectrum collapses into a sharp doublet. When the phosphorus trifluoride is driven off in a stream of nitrogen the spectrum reverts to its original complexity. Thus the intermolecular exchange between free and coordinated phosphorus trifluoride is rapid on the N.M.R. time scale. The resulting spectrum of (3a) in the presence of free phosphorus trifluoride depends only on the mean magnetic environment of the fluorine nuclei.

When an excess of phosphorus trifluoride is condensed onto the deep-red complex (3a) at -120° and the mixture then allowed to warm to -78°, a pale yellow solid remains. On further warming to about -20° this product decomposes to the original dimeric material (3a) with the liberation of phosphorus trifluoride. On complete
decomposition by warming to room temperature, two moles of phosphorus trifluoride gas are liberated per gram atom of rhodium. Thus, contrary to an earlier report, phosphorus trifluoride reacts with complex (3a) and apparently the species, RhCl(PF$_3$)$_4$ (9a), is formed.

The equilibrium,

$$[\text{RhCl(PF}_3\text{)}_2]_2 + 4 \text{PF}_3 \rightleftharpoons 2 \text{RhCl(PF}_3\text{)}_4,$$

lies to the right only at low temperatures, and the decomposition of (9a) is depressed by the presence of phosphorus trifluoride [in an atmosphere of phosphorus trifluoride the decomposition temperature of (9a) is increased to about $+7\degree$]. On passing a stream of nitrogen through a toluene slurry of complex (9a) at $-90\degree$ PF$_3$ is displaced and [RhCl(PF$_3$)$_2$]$_2$ (3a) results. However, RhCl(PF$_3$)$_4$ may be crystallised from n-pentane at low temperatures in the presence of phosphorus trifluoride. The analogous bromo- and iodo-complexes, (9b) and (9c), are prepared by the reaction of phosphorus trifluoride with

[RhX(PF$_3$)$_2$]$_2$ (X = Br, I). They are orange solids which are thermally more stable than the corresponding chloride complex; (9b) decomposes at about $-5\degree$ and (9c) decomposes at about $+10\degree$.

Both iridium and cobalt form five-coordinate analogues of complex (9). Treatment of the iridium complex, [IrCl(PF$_3$)$_2$]$_2$ with an excess of phosphorus trifluoride affords the pale yellow, IrCl(PF$_3$)$_4$. This iridium analogue is also found to be in equilibrium with the dimeric species, however, the equilibrium lies more to the right and the five coordinate complex may be isolated as a solid at room temperature. It is usually found that five-coordinate iridium(I) complexes are more stable than their rhodium(I) analogues.

A corresponding cobalt compound, CoI(PF$_3$)$_4$, has been synthesised and decomposes at about $+7\degree$ to free PF$_3$ and "cobalt mono-
This cobalt complex appears to be approximately as stable as \( \text{RhI(PF}_3\text{)}_4 \) \(^9\text{c} \), which is unusual, as five-coordinate cobalt complexes are generally much more stable than their rhodium analogues. For example, \( \text{HCo(PF}_3\text{)}_4 \) decomposes only above 250\(^\circ\text{C} \), whereas \( \text{HRh(PF}_3\text{)}_4 \) decomposes rapidly when heated to only 140\(^\circ\text{C} \), and slowly even at room temperature.\(^6\) Cobalt halocarbonyl species of the type, \( \text{CoX(CO)}_4 \), are known, but they are very unstable, decomposing at -40\(^\circ\text{C} \) (\( X = \text{I} \)) or even lower temperatures (\( X = \text{Br,Cl} \)).\(^116\)

The rapid intermolecular ligand exchange of \( \text{[RhCl(PF}_3\text{)}_2\text{]}_2 \) with free phosphorus trifluoride mentioned earlier, probably proceeds through the intermediacy of the five-coordinate \( \text{RhCl(PF}_3\text{)}_4 \). It has been shown that \( \text{[RhCl(CO)}_2\text{]}_2 \) exchanges rapidly with \(^{14}\text{CO} \) through a bimolecular process, the exchange being essentially complete at -20\(^\circ\text{C} \) within one minute.\(^117\) Moreover, the existence of five-coordinate complexes such as \( \text{RhCl(PF}_3\text{)}_4 \) offers a mechanism for the reduction of complex \( \text{[RhCl(PF}_3\text{)}_2\text{]}_2 \) by potassium amalgam in the presence of phosphorus trifluoride, the product being the ionic, \( \text{K[Rh(PF}_3\text{)}_4\text{]} \).\(^57\)

With tetrabutylammonium bromide

The reaction of \( \text{[RhCl(PF}_3\text{)}_2\text{]}_2 \) with \( \text{Bu}_4\text{NBr} \) and a large excess of lithium bromide in diethyl ether produces the salt, \( \text{Bu}_4\text{N}^+ \text{[cis-RhBr}_2\text{(PF}_3\text{)}_2\text{]}^- \) \(^{6b} \). The product crystallises as a lemon-yellow solid, soluble in chloroform but insoluble in aliphatic hydrocarbons. The starting material \( \text{(3a)} \), has undergone both a meta-thetical replacement of chloride and a cleavage of the bridging halogen. Similar reactions have been shown to occur with the carbonyl complex \( \text{[RhCl(CO)}_2\text{]}_2 \) \(^{118}\).

The IR spectra of the anions \( \text{(6a)} \) and \( \text{(6b)} \) and of the dimers \( \text{(3a)} \) and \( \text{(3b)} \) in the \( \nu(P-F) \) region are given in Table 3.
<table>
<thead>
<tr>
<th>Complex</th>
<th>X = Cl</th>
<th>X = Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RhX(PF₃)₂]₂</td>
<td>945 (m), 926 (m), 918 (s),</td>
<td>941 (m), 922 (m), 913 (s),</td>
</tr>
<tr>
<td>(3)</td>
<td>907 (s), 871 (s).</td>
<td>904 (s), 870 (s).</td>
</tr>
<tr>
<td>Bu⁴N[cis-RhX₂(PF₃)₂]</td>
<td>918 (s), 890 (m), 873 (vs),</td>
<td>914 (vs), 896 (s), 873 (vs),</td>
</tr>
<tr>
<td>(6)</td>
<td>866 (s, sh), 843 (s).</td>
<td>861 (vs), 839 (vs).</td>
</tr>
</tbody>
</table>

a All spectra in Nujol

The ν(P-F) of the anionic complexes (6a) and (6b) are approximately 30 cm⁻¹ lower than those observed for the bridging complexes (3a) and (3b). This is interpreted as being due to an increased electron density at the rhodium atom of the anionic complexes (6) which results in an increased donation of charge from the metal into the phosphorus-fluorine anti-bonding orbitals and hence a lowering in the value of ν(P-F). A similar lowering of ν(C-O) is observed in the analogous carbonyl complexes.¹¹⁸,¹¹⁹

The ¹⁹F N.M.R. of Bu⁴N[cis-RhX₂(PF₃)₂] (X = Cl, Br) have been analysed as AA'MX₃X₃ systems, following the treatment of Harris and Woodman.⁸⁹ The values of the coupling constants derived by this method are given in Table 4.

Changing the halogen from chloride to bromide has negligible effect on most of the coupling constants. ¹JPF or ²JRhf vary only slightly in comparison with other rhodium(I) complexes.⁵⁷ ²Jpp or ³JPF are very sensitive to the stereochemistry, electronic configuration, and charge of rhodium(I) complexes (for example, ²Jpp in Rh(acac)(PF₃)₂ is 160 Hz and ³JPF is only 4 Hz).⁵⁷ Some of the factors affecting these parameters have been discussed by Nixon and Pidcock.⁸⁸
TABLE 4

Coupling Constants and Chemical Shifts of
$\text{Bu}_4\text{N}[\text{cis-Rh}_2\text{X}_2(\text{PF}_3)_2] (\text{X} = \text{Cl}, \text{Br}).^a$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>X = Cl</th>
<th>X = Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1J_{\text{PF}}$</td>
<td>1311.5±1</td>
<td>1312.5±1</td>
</tr>
<tr>
<td>$^3J_{\text{PF}}$</td>
<td>15.4±1</td>
<td>15.2±1</td>
</tr>
<tr>
<td>$^2J_{\text{PP}}$</td>
<td>43.0±1</td>
<td>27.5±1</td>
</tr>
<tr>
<td>$^4J_{\text{FF}}$</td>
<td>4.4±0.2</td>
<td>4.6±0.2</td>
</tr>
<tr>
<td>$^2J_{\text{RhF}}$</td>
<td>31.6±0.2</td>
<td>31.6±0.2</td>
</tr>
<tr>
<td>$\delta$</td>
<td>+20.4±0.1</td>
<td>+19.2±0.1</td>
</tr>
</tbody>
</table>

$^a$ All coupling constants given in Hertz, chemical shifts as p.p.m. upfield of CFCl$_3$ in toluene.

With triphenylphosphite, $[\text{P(OPh)}_3]$

Reaction of $[\text{RhCl(PP}_3)_2]_2$ (3a) with an excess of $\text{P(OPh)}_3$ results in the complete displacement of coordinated phosphorus trifluoride, affording $\text{RhCl}[\text{P(OPh)}_3]_3$. Similarly $\text{P(OPh)}_3$ will displace all of the coordinated carbon monoxide in $[\text{RhCl(CO)}_2]_2$ (1a) and olefin in $[\text{RhCl(cod)}]_2$, producing the same species.

With 1,2-bis(diphenylphosphino)ethane, (diphos)

Complete displacement of coordinated phosphorus trifluoride may be accomplished by addition of diphos to a solution of $[\text{RhCl(PP}_3)_2]_2$ (3a). The product, $[\text{Rh(diphos)}_2]\text{Cl}$, is identical to that obtained from the reaction of diphos with $[\text{RhCl(CO)}_2]_2$, in which all of the coordinated carbon monoxide is displaced.

With tris(dimethylamino)phosphine, $[\text{P(NMe}_2)_3]$

The reaction of $\text{P(NMe}_2)_3$ with $[\text{RhCl(PP}_3)_2]_2$ (3a) either in
n-pentane or in the absence of a solvent, immediately affords a thermally unstable yellow solid with the evolution of a gas. The proton N.M.R. of a freshly prepared sample exhibits a triplet centered at $\delta_{\text{TMS}} = 2.90$ p.p.m. ($\text{C}_6\text{H}_6$) with a splitting of 9.3 Hz. Similar spectra have been noted in trans-disubstituted metal carbonyl complexes of this ligand. When the phosphine ligands are mutually trans, the methyl resonance appears as a virtual triplet arising from a system, AA'XX', where $J_{\text{AA'}}$ is large with respect to $|J_{\text{AX}} - J_{\text{AX'}}|$. This phenomenon has been discussed by Harris and others.

The IR spectrum of this substance shows three $v$(P-F) bands, characteristic of a single coordinated phosphorus trifluoride moiety (vide Table 5). It is reasonable, therefore, to formulate this complex as trans-RhCl[$\text{P(NMe}_2\text{)}_3$]$_2$PF$_3$ (10). The complex, however, is too unstable to be satisfactorily analysed.

On standing at room temperature, complex (10) darkens rapidly and eventually affords a dark-brown, air-sensitive oil. This substance appears to be a complex mixture resulting from a redistribution of groups within the ligands; it appears to contain coordinated Me$_2$NPF$_2$ and (Me$_2$N)$_2$PF. The proton N.M.R. spectrum of this oil is very complex and varies from sample to sample. However, in all spectra, separations of the order of 3-4 Hz are very common. These may be attributed to coupling between fluorine and hydrogen, i.e. to $J_{\text{FPNCH}}$ which is found to be of this magnitude in other systems (vide Chapter 3).

The IR spectrum of this oil is much more complex than that of complex (10). Absorptions expected for the coordinated PF(NMe$_2$)$_2$ are observed at 680 cm$^{-1}$ (s,br), $[v$(N$_2$PF$)]$, and at 780 cm$^{-1}$ (s,br), $[v$(P-F$)]$; for the coordinated PF$_2$NMe$_2$ at 820 cm$^{-1}$ (s,br) and
at 780 cm\(^{-1}\) (s, br) \(\nu(P-F)\). None of these absorptions are present in a freshly prepared sample of (10).

The elemental analysis of this mixture approached that expected for a dimeric species of the formula, \([\text{RhCl}(PF_3)P(NMe_2)_3]_2\).

The mass spectrum exhibits a series of parent peaks attributable to the ions \([\text{Rh}_2\text{Cl}_2P_4F_{x}NMe_{12-x}]^+\) \((x = 4, 5, 6, 7, 8)\) and fragmentation to their various daughter ions by loss of either fluorine atoms or dimethylamino-radicals.

Thus, from the above evidence the sample appears to contain species of the formula, \([\text{RhCl}(PF(NMe)_{12})_2]_2\), \(\text{Rh}_2\text{Cl}_2(\text{PF}_2\text{NMe})_2[\text{PF}(\text{NMe})_{12}]_3\), \([\text{RhCl}(\text{PF}_2\text{NMe})_2\text{PF}(\text{NMe})_2]_2\), \(\text{Rh}_2\text{Cl}_2(\text{PF}_2\text{NMe})_3[\text{PF}(\text{NMe})_3]\) and \([\text{RhCl}(\text{PF}_2\text{NMe})_2]_2\). These species result from the net loss of two to four \(P(NMe_3)\) ligands from two molecules of complex (10), and the subsequent combination of the products by formation of chloride bridges.

There are several reports of redistribution reactions of coordinated fluorophosphines, but in contrast to the above, these usually result in the loss of free phosphorus trifluoride.\(^{100, 126, 127}\)

The reaction of \(P(NMe_3)\) with \([\text{RhCl}(\text{CO})_2]_2\) affords the expected product, \(\text{trans-}\text{RhCl}[P(NMe_3)_3]_2\text{CO}\). This is a very air- and thermally-stable substance with no tendency to lose \(P(NMe_3)\). The IR spectrum exhibits a single strong \(\nu(C=O)\) band \((1951 \text{ cm}^{-1}; \text{Nujol})\). The proton N.M.R. spectrum exhibits a triplet centered at \(\delta_{\text{TMS}} = 2.27\) p.p.m. \((\text{CHCl}_3)\) with a splitting of 10.0 Hz. This complex resembles its phosphorus trifluoride analogue (10), in showing a deceptively simple proton N.M.R. spectrum.

With triphenylphosphine

The reaction of \([\text{RhCl}(PF_3)_2]_2\) (3a) with triphenylphosphine
in 1:2 molar ratio in dichloromethane results in only partial displacement of coordinated phosphorus trifluoride to produce an air-sensitive, binuclear species, [RhCl(PF$_3$)$_2$(PPh$_3$)$_2$]$_2$ (11). The stoichiometry of this compound was established by elemental analysis. The complex is analogous to that from [RhCl(CO)$_2$]$_2$ (1a). The carbonyl complex was originally formulated and characterised as trans-RhCl(CO)$_2$PPh$_3$. However, subsequent work has shown it to be the dimeric, mixed carbonyl-phosphine complex [RhCl(CO)(PPh$_3$)$_2$]$_2$.

The complex [RhCl(PF$_3$)(PPh$_3$)$_2$]$_2$ reacts with additional triphenylphosphine to produce trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a), and with one equivalent of triphenylarsine affording the mixed, arsine-phosphine complex, RhCl(AsPh$_3$)(PPh$_3$)$_2$PF$_3$ (12).

**Preparation of trans-halo(phosphorus trifluoride)bis(triphenylphosphine)-rhodium(I), and analogous complexes**

An excess of triphenylphosphine reacts with [RhCl(PF$_3$)$_2$]$_2$ (3a), to afford high yields the pale yellow complex, trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a), probably through the intermediacy of (11). This reaction has been reported previously and is analogous to the facile preparation of trans-RhCl(PPh$_3$)$_2$CO (2a), from triphenylphosphine and [RhCl(CO)$_2$]$_2$ (1a). The compound is soluble in benzene, chlorinated hydrocarbons, slightly soluble in diethyl ether and insoluble in aliphatic hydrocarbons. Although it is air-stable in the solid state, solutions are fairly sensitive to oxidation.

High yields of complex (5a) may also be obtained from the reaction of phosphorus trifluoride with RhCl(PPh$_3$)$_3$ in solution. This reaction is similar to that of RhCl(PPh$_3$)$_3$ with carbon monoxide.

Deep yellow crystals of the analogous bromo-complex, trans-RhBr(PF$_3$)(PPh$_3$)$_2$ (5b), can be prepared from RhBr(PPh$_3$)$_3$ and
phosphorus trifluoride, or from the reaction of triphenylphosphine with \([\text{RhBr}(\text{PF}_3)_2]_2\) (3b). The bromo-complex (3b) slowly decomposes at room temperature but is sufficiently stable to be characterised by elemental analysis.

In contrast, the reaction of the iodo-complex, \([\text{RhI}(\text{PF}_3)_2]_2\) (3c), with triphenylphosphine in n-pentane quickly gives a dark brown precipitate, which on work up affords a substance containing no coordinated phosphorus trifluoride (from IR spectrum). Despite an earlier report of its existence\(^{132}\) the analogous iodo-complex (3c) is probably too thermally unstable to be isolated. The instability of (3b) and its iodo-analogue contrasts with the corresponding carbonyl complexes which are both isolable and stable.\(^{131,133}\)

The arsine complex, trans-\(\text{RhCl(AsPh}_3\text{)}_2\text{PF}_3\) (13), may be obtained from the reaction of triphenylarsine with \([\text{RhCl}(\text{PF}_3)_2]_2\) (3a) and resembles its triphenylphosphine analogue (5a) in most of its chemical and physical properties.

Properties and Reactions of trans-chloro(phosphorus trifluoride)bis-(triphenylphosphine)rhodium(I) (5a) and its analogues

(a) Infra-red Spectra

The IR spectra of the complexes in the \(v(P-F)\) region are reported in Table 5. In gaseous phosphorus trifluoride there are two absorptions due to the modes of vibration which essentially involve the stretching of phosphorus-fluorine bonds - a mode of \(A_1\) symmetry at 891 cm\(^{-1}\) and an \(E\) mode at 860 cm\(^{-1}\) (c.f. lit.\(^{60}\) \(A_1\) at 892 cm\(^{-1}\), \(E\) at 860 cm\(^{-1}\)). Two observations may be made about the corresponding vibrations in coordinated phosphorus trifluoride. Firstly, a lowering of the symmetry of phosphorus trifluoride on coordination removes the degeneracy of the \(E\) mode so that a total of three bands which involve
TABLE 5

IR Spectra of Rh(I) and Rh(III) Complexes in the $\nu$(P-F) Region

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$(P-F)$^a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-RhCl(PPh$_3$)$_2$PF$_3$</td>
<td>862(s), 852(s), 837(s).</td>
</tr>
<tr>
<td>trans-RhBr(PPh$_3$)$_2$PF$_3$</td>
<td>860(s,br), 847(s), 833(s).</td>
</tr>
<tr>
<td>trans-RhCl(AsPh$_3$)$_2$PF$_3$</td>
<td>858(s), 850(s,sh), 835(s).</td>
</tr>
<tr>
<td>trans-RhCl[P(NMe$_2$)$_3$]$_2$PF$_3$</td>
<td>869(s), 858(s), 844(m,sh).</td>
</tr>
<tr>
<td>RhCl(AsPh$_3$)(PPh$_3$)PF$_3$</td>
<td>864(vs), 853(s), 839(s).</td>
</tr>
<tr>
<td>RhHCl$_2$(PPh$_3$)$_2$PF$_3$</td>
<td>887(vs), 863(s), 839(s).</td>
</tr>
<tr>
<td>RhHBrCl(PPh$_3$)$_2$PF$_3$</td>
<td>886(vs,br) 865(m,br).</td>
</tr>
<tr>
<td>RhCl$_3$(PPh$_3$)$_2$PF$_3$</td>
<td>918(m), 906(m), 892(s).</td>
</tr>
<tr>
<td>RhCl$_3$(AsPh$_3$)$_2$PF$_3$</td>
<td>917(m,br), 909(m,sh), 891(s).</td>
</tr>
<tr>
<td>RhCl(SO$_2$)(PPh$_3$)$_2$PF$_3$</td>
<td>896(m), 879(vs,br), 840(m).</td>
</tr>
<tr>
<td>RhCl(SO$_2$)(AsPh$_3$)$_2$PF$_3$</td>
<td>885(m,sh), 870(vs,br), 840(m,sh).</td>
</tr>
<tr>
<td>PF$_3$</td>
<td>891(vs), 860(vs,br).</td>
</tr>
</tbody>
</table>

$^a$ All samples as Nujol mulls.

$^b$ Gas (10 cm path length, 10 mm pressure). Values are for centres of Q branches.
$\nu(P-F)$ modes are observed. Secondly, there is an overall lowering of the vibrational frequencies on coordination to rhodium(I). This may be understood in terms of an increased occupancy of the phosphorus-fluorine antibonding orbitals, occurring upon the back donation of electrons from the rhodium to the phosphorus in the formation of a rhodium-phosphorus $\pi$-bond. Similar reasoning accounts for the observed lowering of the $\nu(C-O)$ on coordination [for example from 2155 cm$^{-1}$ in free carbon monoxide to 1960 cm$^{-1}$ in $\text{trans-RhCl(PPh}_3)_2\text{CO}$, (2a)]. Vibrational spectra in the region below 400 cm$^{-1}$ are discussed in Chapter 5.

**Fluorine Nuclear Magnetic Resonance Spectra**

The $^{19}\text{F N.M.R.}$ spectra of these complexes consist of widely spaced doublets (mainly coupling to directly bonded phosphorus, $-^{1\text{J}}_{\text{PF}}$) with each line further split into a doublet (coupling to rhodium $-^{2\text{J}}_{\text{RhF}}$). In the case of the triphenylphosphine complexes there is also broadening of the resulting four lines attributable to coupling to the triphenylphosphine phosphorus atoms ($^{3\text{J}}_{\text{PF}}$). The $^{19}\text{F N.M.R.}$ parameters are given in Table 6.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$ (p.p.m. upfield)</th>
<th>$^{1}\text{J}_{\text{PF}}$ (Hz)</th>
<th>$^{2}\text{J}_{\text{RhF}}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{RhCl(PPh}_3)_2\text{PF}_3$ $^b$</td>
<td>+16.0</td>
<td>1270</td>
<td>33</td>
</tr>
<tr>
<td>$\text{RhCl(AsPh}_3)_2\text{PF}_3$ $^b$</td>
<td>+15.2</td>
<td>1271</td>
<td>33</td>
</tr>
<tr>
<td>$\text{RhBr(PPh}_3)_2\text{PF}_3$ $^c$</td>
<td>+17.7</td>
<td>1298</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ In p.p.m. upfield of CFCI$_3$.

$^b$ Measured in CHCl$_3$ at 32°.

$^c$ Measured in C$_6$H$_6$ at 32°.
The N.M.R. of coordinated phosphorus trifluoride shows a characteristic downfield shift compared with that of the free ligand (which is 33.7 p.p.m. upfield of CFC13). $^{1}J_{PF}$ in the coordinated phosphorus trifluoride is about 150 Hz lower than that observed for the free ligand (which is solvent dependent: $^{1}J_{PF}$ is 1418 Hz in chloroform). This decrease in $^{1}J_{PF}$ on coordination is invariably noted in other metal-phosphorus trifluoride complexes. The magnitude of $^{2}J_{RhF}$ is also similar to that observed in other rhodium-phosphorus trifluoride systems.

The $^{19}F$ N.M.R. of trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a) provides excellent evidence for facile intermolecular ligand exchange in these systems. The unresolved fine structure attributable to coupling of the phosphorus atoms of the coordinated triphenylphosphines to the fluorine atoms ($^{3}J_{PF}$) disappears on the addition of small amounts of free triphenylphosphine. This loss of coupling is illustrated in Figure 2 and is ascribable to a rapid exchange of free and coordinated triphenylphosphine. If phosphorus trifluoride is passed into a solution of complex (5a) the spectrum collapses into a doublet, with only a slight change in the chemical shift or $^{1}J_{PF}$. This indicates a loss of rhodium-fluorine coupling ($^{2}J_{RhF}$) as coordinated and free phosphorus trifluoride undergo rapid exchange. Similarly, rapid intermolecular exchange between free and coordinated triphenylphosphine or phosphorus trifluoride can be observed in complexes (5b) and (13). This fast exchange appears to be characteristic of sixteen-electron, rhodium(I) species.

The rapid exchange of ligands possibly proceeds through a five-coordinate intermediate analogous to complex (9), described earlier. Moreover, it has been shown that the carbonyl complex, [RhCl(CO)$_2$]$_2$ (1a), rapidly exchanges free and coordinated carbon monoxide or chloride ion.
Figure 2

Intermolecular Ligand Exchange in trans-RhCl(PPh₃)₂PF₃
and the complex Rh(acac)(C₂H₄)₂ undergoes rapid exchange with free ethylene. In both cases bimolecular exchange processes are suggested. These phenomena contrast with the slow exchange found in the eighteen-electron systems, RhCl₃(PPh₃)₂CO, and Rh(π-C₅H₅)(PF₃)₂ (7). A five-coordinate iridium complex, IrCl(CO)₂(PPh₃)₂, which is similar to the intermediate suggested above, can be isolated, although it readily loses carbon monoxide to give trans-IrCl(CO)(PPh₃)₂. These square-planar rhodium(I) complexes are examples of kinetically labile but thermodynamically stable coordination complexes.

**Dipole Moments of trans-RhCl(PPh₃)₂L (L = CO, PF₃)**

The dipole moment of trans-RhCl(PPh₃)₂PF₃ (5a) and trans-RhCl(PPh₃)₂CO (2a) together with those of some related molecules are given in Table 7. The value for the phosphorus trifluoride complex (5a) agrees well with that reported by Kruck. An earlier report by Vallarino of 3.150 for the dipole moment of (2) appears to be an overestimate.

**TABLE 7**

Dipole Moments of Phosphorus Trifluoride and Carbon Monoxide Complexes (in Debyes)

<table>
<thead>
<tr>
<th>Complex</th>
<th>L = PF₃</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃B-L</td>
<td>1.64 ± 0.2</td>
<td>1.79 ± 0.1</td>
</tr>
<tr>
<td>cis-PtCl₂L₂</td>
<td>4.4 ± 0.5</td>
<td>4.65 ± 0.5</td>
</tr>
<tr>
<td>trans-RhCl(PPh₃)₂L</td>
<td>2.29d</td>
<td>2.67d</td>
</tr>
<tr>
<td>trans-RhCl(PPh₃)₂L</td>
<td>2.2e</td>
<td>3.15f</td>
</tr>
<tr>
<td>L</td>
<td>1.03 ± 0.01g</td>
<td>0.13h</td>
</tr>
</tbody>
</table>

a ref 25, b ref 139, c ref 5, d this work, e ref 112, f ref 120, g ref 140, h ref 141, i ref 142.
The relatively low dipole moment observed for the latter two complexes confirm a trans- stereochemistry in solution. cis-Diphosphine complexes invariably have a much higher dipole moment. For example, cis-PtCl₂(PPr₃)₂ has a dipole moment of 11.5D, whereas its trans-isomer has a zero moment.

As with other compounds in Table 7, the similarity of dipole moments of the two rhodium complexes, reflects the resemblance of coordinated carbon monoxide and phosphorus trifluoride (in terms of total charge distribution). However, the dipole moments of the free ligands themselves are quite different. On complexation to borane, phosphorus trifluoride undergoes a greater redistribution of charge than carbon monoxide does. The reason that the M-PF₃ group moment is comparable with the M-CO moment arises from the large M⁻-P⁺ bond moment, which more than cancels the contributions from the P⁺-F⁻ moments. This has been shown to be the case in BH₃PF₃,¹⁴,¹⁷ and is probably true in the transition metal complexes.

Molecular Weight of Rhodium(I) Complexes in Solution

Solutions of trans-RhCl(PPh₃)₂PF₃ (5a) in benzene under nitrogen, give molecular weight values (by osmometry) lower than that expected for an undissociated species (see Table 8). The apparent degree of dissociation increases with increasing dilution and is not markedly depressed by the addition of an excess of free triphenylphosphine. This contrasts with the complete absence of dissociation in the carbonyl complex (2a)¹²⁰ and the negligible dissociation observed for trans-RhCl(AsPh₃)₂PF₃ (13).

The molecular weight of trans-RhCl(PPh₃)₂PF₃ (5a) has been reported previously. Kruck¹¹² maintains that a value for an undissociated species is obtained by osmometry in benzene, but gives no other
<table>
<thead>
<tr>
<th>Concentration of complex (x10⁻³)M</th>
<th>Concentration of PPh₃ (x10⁻³)M</th>
<th>Observed M.W.</th>
<th>Calculated M.W.</th>
<th>Degree of Dissociation (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = P</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>26.6</td>
<td>0</td>
<td>657</td>
<td>751&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.14</td>
</tr>
<tr>
<td>10.6</td>
<td>0</td>
<td>570</td>
<td>751</td>
<td>0.31</td>
</tr>
<tr>
<td>4.25</td>
<td>0</td>
<td>439</td>
<td>751</td>
<td>0.70</td>
</tr>
<tr>
<td>5.31</td>
<td>5.66</td>
<td>398</td>
<td>498&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.51</td>
</tr>
<tr>
<td>5.31</td>
<td>22.6</td>
<td>327</td>
<td>354&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.45</td>
</tr>
<tr>
<td>5.31</td>
<td>39.6</td>
<td>304</td>
<td>318&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.44</td>
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<tr>
<td>17.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>560</td>
<td>751</td>
<td>0.34</td>
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<td>6.11</td>
<td>39.9</td>
<td>370</td>
<td>378&lt;sup&gt;c&lt;/sup&gt;</td>
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<tr>
<td>M = As</td>
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<td></td>
</tr>
<tr>
<td>39.2</td>
<td>-</td>
<td>789</td>
<td>839</td>
<td></td>
</tr>
<tr>
<td>16.3</td>
<td>-</td>
<td>833</td>
<td>839</td>
<td></td>
</tr>
<tr>
<td>8.71</td>
<td>-</td>
<td>769</td>
<td>839</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by vapour phase osmometry (VPO) in benzene at 25° in a stream of nitrogen.

<sup>b</sup> From ref 132, by VPO in chloroform at 25° in air.

<sup>c</sup> Molecular weight predicted assuming no dissociation occurs (i.e. x=0).

<sup>d</sup> Molecular weight predicted assuming 63% dissociation (i.e. x=0.63). This value is the approximate degree of dissociation of a 5.31x10⁻³M solution in the absence of PPh₃.
experimental details. However, Longstaff\textsuperscript{132}, determined the molecular weight of these complexes in chloroform solution in air. The values obtained are essentially the same as that found in the present work, which was performed in a system flushed with nitrogen. Since solutions of $\text{trans-RhCl(PPh}_3)\text{PF}_3 (5a)$ are air-sensitive, the above observation strongly suggests that the species whose molecular weight is being determined is not $(5a)$ but instead a dissociated, oxidation product, and that $(5a)$ is too oxygen-sensitive in solution to be handled in the normal manner. This is not the same conclusion drawn from $^{19}$F N.M.R. results. Solutions prepared in the same manner as for molecular weight determinations show coupling of the fluorine atoms of the phosphorus trifluoride to the phosphorus atoms of the triphenylphosphines ($^3J_{PF}$) indicating there is no marked dissociation of either of those two coordinated ligands. The spectrum also shows no other species present in solution in any appreciable concentration.

A similar contradiction between molecular weight determinations and N.M.R. evidence exists concerning the apparent dissociation of $\text{RhCl(PPh}_3)_3$. Again osmometric molecular weight determinations indicate that $\text{RhCl(PPh}_3)_3$ is dissociated in benzene and in chloroform.\textsuperscript{131,144a} However, from N.M.R. data\textsuperscript{144a} it can be concluded that if any dissociation is occurring it is small.

The problem has been partially clarified by Shriver\textsuperscript{145} and very recently by Wilkinson,\textsuperscript{146} who demonstrated that $\text{RhCl(PPh}_3)_3$ is not appreciably dissociated in benzene only if oxygen is rigorously excluded. When merely a trace of oxygen is introduced there is a marked drop in the molecular weight (determined cryoscopically). The nature of the reaction of $(5a)$ or $\text{RhCl(PPh}_3)_3$ with oxygen is not clear. As $\text{RhCl(AsPh}_3)_3$ also appears to dissociate in solution,\textsuperscript{147} it is anomalous that $\text{trans-RhCl(AsPh}_3)_2\text{PF}_3 (13)$ should exhibit a normal molecular weight.
No explanation can be given for these phenomena.

Oxidative Addition Reactions of trans-chloro(phosphorus trifluoride)bis-(triphenylphosphine)rhodium(1) (5a) and its Arsine Analogue (13)

The oxidative addition reactions of d^8 transition metal complexes have been the subject of intensive research by many groups. As the carbonyl complex, trans-RhCl(PPh_3)_3CO (2a) is frequently the substrate in such studies a brief comparison with the analogous phosphorus trifluoride complexes, (5a) and (13), appeared to be of interest. However, it is found in most cases that the adducts of the latter complexes are even less stable than the already quite unstable rhodium(III) carbonyl adducts.

Passage of hydrogen gas over trans-RhCl(PPh_3)_2PF_3 under a variety of conditions produces no detectable species containing rhodium-hydrogen bonds, (from IR spectra). The absence of a stable dihydride is also noted for the carbonyl complex, whereas RhCl(PPh_3)_3 forms a stable dihydride with the concurrent loss of a triphenylphosphine ligand.

Reaction of hydrogen chloride with complex (5a) affords a yellow adduct, presumably RhHCl_2(PPh_3)_2PF_3, which has a strong ν(Rh-H) at 2098 cm^{-1} (Nujol), compared with its carbonyl analogue with ν(Rh-H) at 2122 cm^{-1}. However, as is the case with the analogous carbonyl complex, RhHCl_2(PPh_3)_2PF_3 readily loses hydrogen chloride so the adduct cannot be isolated in a pure state. Hydrogen bromide adducts of (5a) and (2a) can be prepared in an analogous manner. In both the phosphorus trifluoride and carbonyl systems the hydrogen bromide adducts appear to be more thermally stable than the corresponding hydrogen chloride adducts, but they still cannot be isolated.
Gaseous sulphur dioxide reacts with solutions of trans-RhCl(PPh₃)₂PF₃ (5a) from which yellow-green crystals of an adduct, RhCl(SO₂)(PPh₃)₂PF₃ may be isolated. On standing, the solid readily loses sulphur dioxide, and so satisfactory elemental analyses cannot be obtained. Bands in the IR spectrum characteristic of coordinated sulphur dioxide are observed at 1222 cm⁻¹(s), 1194 cm⁻¹(m) and 1064 cm⁻¹(vs) (Nujol). The sulphur dioxide adduct of the carbonyl, trans-RhCl(PPh₃)₂CO (2a), has absorptions at 1214 cm⁻¹, 1188 cm⁻¹, and 1057 cm⁻¹. A sulphur dioxide adduct of the triphenylarsine complex trans-RhCl(AsPh₃)₂PF₃ (13) may be prepared similarly. This exhibits bands due to coordinated sulphur dioxide at 1218 cm⁻¹(s), 1185(m) and 1057(vs) (Nujol) which disappear slowly on standing.

Chlorine reacts with trans-RhCl(PPh₃)₂PF₃ (5a) to afford an orange solid with ν(P-F) characteristic of rhodium(III) (vide infra). This compound, presumably RhCl₃(PPh₃)₂PF₃, may also be prepared from the reaction of carbon tetrachloride with (5a). A similar reaction is known to occur with trans-RhCl(PEt₃)₂CO and carbon tetrachloride. A triphenylarsine analogue may be prepared in small yields from trans-RhCl(AsPh₃)₂PF₃ and chlorine but the major product is a substance not containing coordinated phosphorus trifluoride.

Nitric oxide and trans-RhCl(PPh₃)₂PF₃ (5a) react in methanol solutions, from which a green amorphous solid may be isolated. The IR spectrum indicates the absence of coordinated phosphorus trifluoride, but the presence of coordinated nitrosyl, [bands at 1665(s) and 1629(vs)], and coordinated nitrite, [bands at 1441(m), 1312(s) and 818(m)]. This complex has an identical IR spectrum to the product obtained from the reaction of nitric oxide with the carbonyl complex trans-RhCl(PPh₃)₂CO, which has been reported to be an isomeric mixture of compounds, formulated as RhCl(NO)(NO₂)(PPh₃)₂. 151,152
The IR spectra of the rhodium(III) adducts containing phosphorus trifluoride exhibit a shift in the $\nu$(P-F) to higher frequencies than those observed in the rhodium(I) substrates (see Table 5). The magnitude of the increase is variable but exceeds 50 cm$^{-1}$ in some cases. This observation can be explained in the following manner. The increased formal positive charge on the metal in the rhodium(III) adducts enhances the $\sigma$-donating ability of the phosphorus trifluoride. The resultant greater delocalisation of the "lone pair" from the phosphorus to the rhodium decreases the phosphorus-fluorine antibonding component. This effect is supplemented by a smaller $\pi$-back-donation of electrons from the rhodium in the higher oxidation state to the LUMO of phosphorus trifluoride, which also has a phosphorus-fluorine antibonding component. The result is a larger phosphorus-fluorine bond order and hence stretching frequency in rhodium(III), compared with rhodium(I).

A similar dependence of $\nu$(C=O) on the oxidation state of the metal has been observed in rhodium-carbonyl complexes.\textsuperscript{153,154}

The instability of phosphorus trifluoride complexes of rhodium in its higher oxidation states may also be ascribed to a reduction in the $\pi$-bonding between the metal and the ligand. In fact the adducts described above represent the first phosphorus trifluoride complexes of a metal in as high an oxidation state. The previous highest oxidation state reported was platinum(II), in \textit{cis-PtCl$_2$(PF$_3$)$_2$}.\textsuperscript{5} It is also found that the phosphorus trifluoride adducts described above appear to be less stable to thermal decomposition than their carbonyl analogues. This may be contrasted to the increased ability of phosphorus trifluoride over carbon monoxide to stabilize very low oxidation states [for example, rhodium (-I),\textsuperscript{57} rhodium(0),\textsuperscript{57} palladium(0),\textsuperscript{155} iron(-II)\textsuperscript{66}]. This observation suggests that phosphorus trifluoride is a better $\pi$-acceptor (and a poorer $\sigma$-donor) than carbon monoxide, and so will stabilize very low oxidation states more effect-
ively by a greater removal of electronic charge from the metal atom. Conversely, the metal-ligand bond is destabilised in higher oxidation states containing phosphorus trifluoride with respect to the analogous carbonyl complexes.
3. Experimental Section

General

Unless stated otherwise all reactions in Chapters 2 and 3 were carried out in an atmosphere of dry nitrogen. Solvents were of Analytical Reagent grade, and before use were dried over Linde 4A molecular sieves, but not further purified.

Phosphorus trifluoride was either obtained commercially or prepared by the method of Hoffman. The following complexes were synthesised by literature methods: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{[RhCl(CO)]}_2$, $\text{[RhX(cod)]}_2$, $\text{[RhCl(C_2H_4)]}_2$, $\text{[RhCl(PPh_3)]}_3$, $\text{trans-RhCl(PPh_3)_2CO}$, $\text{[RhCl(C_8H_14)]}_2$, $\text{RhCl}[P(\text{OPh})_3]_3$, and $\text{[Rh(diphos)]}_2\text{Cl}$. All other substances were obtained commercially.

Preparation of $\mu,\mu'$-dihalotetrakis(phosphorus trifluoride)dirhodium(I) (3)

**From $\mu,\mu'$-dihalotetracarbonyldirhodium(I) (1)**

Phosphorus trifluoride was bubbled into a solution of $\text{[RhCl(CO)]}_2 \cdot 2$ (2.00g) in n-pentane (40 ml) at room temperature. The course of the reaction was monitored from changes in the IR spectrum in the $\nu(C=O)$ region. When all the $\nu(C=O)$ bands had disappeared (after about twenty-five minutes) the excess of phosphorus trifluoride was driven off in a stream of nitrogen. On cooling the solution to -78°, deep red crystals of $\text{[RhCl(PF}_3)_2 \cdot 2$ (3a) separated. These were collected and recrystallised from n-pentane at -78° to give 3.04g (94%) of product.

Similar products were obtained in the above manner from reaction of $\text{[RhBr(CO)]}_2 \cdot 2$ (1b) and $\text{[RhI(CO)]}_2 \cdot 2$ (1c) with phosphorus trifluoride. The yield of $\text{[RhBr(PF}_3)_2 \cdot 2$ (3b) was 83% and that of $\text{[RhI(PF}_3)_2 \cdot 2$ (3c) was 65%.
From µ,µ'-dichlorobis(1,5-cyclooctadiene)dirhodium(I)

Phosphorus trifluoride was bubbled into a stirred suspension of \([\text{RhCl(cod)}]_2\) (2.13 g) in n-pentane (40 ml). After fifteen minutes, when all of the starting material had dissolved, the solution was filtered and cooled to -78°, affording a dark red substance still containing coordinated cod (from IR). The yellow supernatant liquid was decanted, the solid redissolved in n-pentane (30 ml) and phosphorus trifluoride passed through the solution for a further ten minutes. On cooling the solution to -78°, decanting the supernatant liquid and then drying the red crystals in a stream of nitrogen, 1.98 g (73%) of \([\text{RhCl(PF}_3]_2\) (3a) was obtained.

By similar procedures \([\text{RhBr(PF}_3]_2\) was prepared from \([\text{RhBr(cod)}]_2\) in 60% yield, and \([\text{RhI(PF}_3]_2\) was prepared from \([\text{RhI(cod)}]_2\) in 44% yield.

From µ,µ'-dichlorotetrakis(ethylene)dirhodium(I)

Phosphorus trifluoride was bubbled through a suspension of \([\text{RhCl(C}_2\text{H}_4]_2\) (1.2 g) in n-pentane (20 ml) for fifteen minutes. The resulting yellow solution was filtered and cooled to -78°, whereupon dark red crystals slowly separated. The supernatant liquid was decanted and the crystals dried in a stream of nitrogen to give 1.78 g (92%) of the product \([\text{RhCl(PF}_3]_2\) (3a).

Samples prepared by the above procedures had identical spectroscopic, physical and chemical properties to samples prepared by published methods. 57

Reactions of µ,µ'-dihalotetrakis(phosphorus trifluoride)dirhodium(I) (3)

With carbon monoxide

Carbon monoxide was passed through a solution of \([\text{RhCl(PF}_3]_2\) (0.1 g) in n-pentane (10 ml) for twenty minutes. The IR spectrum of
the resultant solution showed the complete absence of any absorptions in the 800-900 cm\(^{-1}\) \(v(P-F)\) region, but absorptions in the \(v(C=O)\) region identical to that of an authentic sample of \([\text{RhCl}(CO)_2]_2\) (1a).

When carbon monoxide was passed over a finely powdered solid sample of \([\text{RhCl}(PF_3)_2]_2\), a dark, red oil was produced. On further passage of gas, this quickly resolidified and the resultant orange solid showed the presence of both coordinated carbon monoxide and phosphorus trifluoride. This substance was again powdered and carbon monoxide passed over for a further two hours. The product then had an IR spectrum identical to an authentic sample of \([\text{RhCl}(CO)_2]_2\) (1a), showing the complete absence of coordinated phosphorus trifluoride absorptions.

With \(\mu,\mu'-\text{dichlorotetracarbonylirhodium(I)}\) (1a)

A solution of \([\text{RhCl}(PF_3)_2]_2\) (0.16g) in \(n\)-pentane (10 ml) was slowly added to an equimolar quantity of \([\text{RhCl}(CO)_2]_2\) (0.10g) in \(n\)-pentane (15 ml). On cooling the mixture to -78\(^\circ\), orange-red crystals slowly separated. The supernatant liquid was decanted and the solid material recrystallised from \(n\)-pentane (10 ml) to yield 0.20g of product (melting point, 35\(^\circ\)-36\(^\circ\)). This substance was very moisture-sensitive and fairly air-sensitive. The IR spectrum showed absorptions at 2103 cm\(^{-1}\) (s), 2064(vs,br), 2039(s) and 2023 cm\(^{-1}\) (w), and \(v(P-F)\) absorptions in the region 800-900 cm\(^{-1}\). The mass spectrum showed peaks at m/e at 628, 568, 508 and 448 attributable to the presence of ions of the formula \(\text{[Rh}_2\text{Cl}_2(CO)_x(PF_3)_{4-x}]^+\) (\(x = 0,1,2,3\)).

\(n\)-Heptane solutions containing various relative concentrations of complex (1a) and (3a) were prepared. The IR spectra in the \(v(C-O)\) region of these solutions are given in Figure 3.

With \(\mu,\mu'-\text{dichlorotetrakis(ethylene)dirhodium(I)}\)

A solution of \([\text{RhCl}(PF_3)_2]_2\) (0.16g) in \(n\)-pentane (10 ml)
Figure 3

IR Spectra in Carbonyl Region of Mixtures of $[\text{RhCl(CO)}_2]_2$
and $[\text{RhCl(PF}_3)_2]_2$ (in n-Heptane)
was added to a stirred slurry of an equimolar quantity of $[\text{RhCl(C}_2\text{H}_4)]_2$ (0.10g) in $\text{n}$-pentane (10 ml). Most of the solid ethylene complex quickly dissolved and the solution was filtered and cooled to -78°. Orange crystals slowly separated over several days. The supernatant liquid was decanted and the crystals dried at -20° for two hours at 0.005 mm Hg. The product was very moisture-sensitive and slowly decomposed above 0°, but melted (with decomposition) at 55° when rapidly heated. The elemental analysis of a freshly prepared sample approached that for $[\text{RhCl(C}_2\text{H}_4)(\text{PF}_3)]_2$.

Found (%):  C 10.63;  H 2.10;  P 10.66;  Cl 14.42.

$\text{C}_4\text{H}_8\text{Cl}_2\text{F}_2\text{P}_x\text{Rh}_2$ requires:  C 9.44;  H 1.58;  P 12.17;  Cl 13.93.

Better analyses could not be obtained owing to the instability of this substance. The mass spectrum showed peaks at m/e = 628, 568, 508 and 448 attributable to the species $[\text{Rh}_2\text{Cl}_2(\text{PF}_3)_x(\text{C}_2\text{H}_4)_{4-x}]^+$ ($x = 1, 2, 3, 4$) as well as major peaks at m/e = 480, $[\text{Rh}_2\text{Cl}_2(\text{PF}_3)_2\text{C}_2\text{H}_4]^+,$ at 462 $[\text{Rh}_2\text{Cl}_2(\text{PF}_3)_2]^+$, at 374 $[\text{Rh}_2\text{Cl}_2(\text{PF}_3)]^+$ and at 286 $[\text{Rh}_2\text{Cl}_2]^+$. The IR spectrum showed the following absorptions: 1518(w), 1222(m), 1155(w), 985(s), 946(s), 890(vs,br), 740(m), 727(w,sh), 544(vs), 538(m), 488(w), 420(m), and 390(m) (Nujol)(cm$^{-1}$).

With phosphorus trifluoride

An excess of phosphorus trifluoride was condensed onto $[\text{RhCl(\text{PF}_3)}_2]_2$ (0.2678g) at -120° in a gas manometer. When the reaction was allowed to warm to -100° the unreacted phosphorus trifluoride boiled off, leaving a mixture of a pale yellow solid and crystals of the dark red, unreacted starting material (3a). This procedure was repeated until no $[\text{RhCl(\text{PF}_3)}_2]_2$ remained. The resultant solid was allowed to warm up from -78° to +17°, during which time phosphorus trifluoride (from IR) was liberated (41.4 ml corrected to STP) leaving the dark red $[\text{RhCl(\text{PF}_3)}_2]_2$ (from IR), which was recovered in 86% yield (0.2314g). The gas represented 2.09 moles of phosphorus trifluoride liberated per gram atom of rhodium.
Similarly the red-brown \([\text{RhBr}(\text{PF}_3)_2]_2\) (3b) afforded a bright yellow product upon reaction with phosphorus trifluoride at \(-120^\circ\), and the reaction of brownish-black \([\text{Rhl}(\text{PF}_3)_2]_2\) (3c) with phosphorus trifluoride yielded a dark orange solid.

**With tetrabutylammonium bromide**

Tetrabutylammonium bromide (0.22 g) and lithium bromide (1.0 g) were added to a solution of \([\text{RhCl}(\text{PF}_3)_2]_2\) (0.17 g) in diethyl ether (40 ml). The slurry was stirred at 0° for one hour then evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane (3x5 ml), the combined extracts centrifuged and \(n\)-pentane (100 ml) slowly added to the centrifugate. The resulting lemon-coloured crystals were separated by filtration, washed in \(n\)-pentane (2x50 ml) and dried in vacuo to afford 0.31 g (81%) of \(\text{Bu}_4^+\text{N}^+\text{cis-RhBr}_2(\text{PF}_3)_2^-\) (6b), melting at 107°.

*Found: C 28.23; H 5.31; N 2.17; P 9.06.*

\(\text{C}_{16}\text{H}_{36}\text{Br}_2\text{F}_6\text{NP}_2\text{Rh}\) requires: C 28.21; H 5.33; N 2.06; P 9.09.

**With triphenylphosphite**

The addition of an excess of triphenylphosphite (1.0 g) to \([\text{RhCl}(\text{PF}_3)_2]_2\) (3a) (0.31 g) in \(iso\)-pentane (20 ml) immediately afforded a yellow oil, which was washed with \(iso\)-pentane (2x30 ml). The oil was then dissolved in dichloromethane (5 ml) and \(iso\)-pentane (50 ml) slowly added. On standing at \(-5^\circ\) pale yellow crystals slowly separated from the mixture. An IR spectrum of the crystals showed the absence of coordinated phosphorus trifluoride and the spectrum was identical to that of an authentic sample of \(\text{RhCl}[\text{P(OPh)}_3]_3\).^{156f}

**With 1,2-bis(diphenylphosphino)ethane**

Diphos (0.40 g) was added to a solution of \([\text{RhCl}(\text{PF}_3)_2]_2\) (3a) (0.16 g) in benzene (20 ml). The resulting yellow precipitate was collected by filtration, washed with benzene (2x20 ml) then \(n\)-pentane.
(20 ml) and dried in vacuo. The IR spectrum was identical to that of an authentic sample of [Rh(diphos)$_2$]Cl$_{122}$ and showed no bands characteristic of coordinated phosphorus trifluoride.

With tris(dimethylamino)phosphine

Tris(dimethylamino)phosphine (0.32g) was added to [RhCl(PF$_3$)$_2$]$_2$ (3a) (0.16g) in the absence of a solvent. A yellow solid was formed with a vigorous evolution of gas. When the reaction had ceased, all unreacted phosphine was removed under high vacuum at 0°. The yellow substance was thermally unstable at room temperature, slowly forming a brown oil. The yellow product was too unstable for an elemental analysis, however, the oil formed after heating for one day at 100° approached [RhCl(PF$_3$)P(NMe$_2$)$_3$]$_2$ in elemental composition.

Found (%):  C 17.91; H 5.46; N 10.30; Cl 8.36; P 16.60.

[RhCl(PF$_3$)$_2$(NMe$_3$)$_2$]: C$_{12}$H$_{36}$Cl$_6$F$_6$P$_4$Rh$_2$ requires:
C 18.48; H 4.66; N 10.78; Cl 9.10; P 15.90.

RhCl(PF$_3$)$_2$[P(NMe$_2$)$_3$]: C$_6$H$_{18}$ClF$_6$N$_3$P$_3$Rh requires:
C 26.08; H 6.56; N 15.19; Cl 6.25; P 16.81.

RhCl(PF$_3$)$_2$P(NMe$_2$)$_2$: C$_6$H$_{18}$ClF$_6$N$_3$P$_3$Rh requires:
C 15.09; H 3.80; N 8.80; Cl 7.42; P 19.46.

With triphenylphosphine

A solution of triphenylphosphine (0.10g) in dichloromethane (4 ml) was slowly added to [RhCl(PF$_3$)$_2$]$_2$ (0.16g) in dichloromethane (3 ml). iso-Pentane (50 ml) was added and the mixture cooled to -5°, whereupon yellow crystals slowly separated. The supernatant liquid was decanted, the product washed with iso-pentane (2x5 ml) and dried in vacuo to give 0.09g (36%) of [RhCl(PF$_3$)(PPh$_3$)$_2$] (11), melting at 180-3° with decomposition. The product was characterised by elemental analysis.
Chemical reactions of [RhCl(\text{PF}_3)(\text{PPh}_3)]_2 (11)

With triphenylphosphine

An excess of triphenylphosphine (0.3 g) was added to a solution of [RhCl(\text{PF}_3)(\text{PPh}_3)]_2 (11) (0.1 g) in dichloromethane (10 ml). Addition of iso-pentane (100 ml) and cooling to -5° afforded pale yellow crystals of trans-RhCl(\text{PPh}_3)_2\text{PF}_3 (5a) which had a melting point and IR spectrum identical to that of an authentic sample of (5a).

With triphenylarsine

One molar equivalent of triphenylarsine (0.29 g) in dichloromethane (5 ml) was slowly added to a solution of [RhCl(\text{PF}_3)(\text{PPh}_3)]_2 (11) (0.48 g) in dichloromethane (7 ml). The resulting orange solution was filtered and iso-pentane (80 ml) added. On cooling to -5° yellow crystals of the product slowly separated. These were collected, washed with iso-pentane (3 x 20 ml) and dried in vacuo to give 0.34 g (44%) of RhCl(\text{AsPh}_3)_2(\text{PPh}_3)\text{PF}_3. The complex decomposed without melting at 130-3°.

Found (%) C 54.67; H 4.07; P 7.94; Cl 4.45.
C_{36}H_{30}AsClF_3P_2Rh requires: C 54.44; H 3.80; P 7.79; Cl 4.46.

Preparation of trans-chloro(phosphorus trifluoride)bis(triphenylphosphine)rhodium(I) (5a)

From chlorotris(triphenylphosphine)rhodium(I).

Phosphorus trifluoride was passed through a solution of RhCl(\text{PPh}_3)_3 (0.54 g) for about thirty minutes, to afford a yellow orange solution. n-Heptane, (10 ml) was added and the mixture evaporated under reduced pressure to a small volume (ca 5 ml), whereupon yellow crystals separated. The superantant liquid was decanted, the crystals
washed with \( n \)-pentane (3x10 ml) and the product dried in vacuo to give 0.28g (64%) of trans-RhCl(PPh\(_3\))\(_2\)PF\(_3\) (5a).

From \( \mu,\mu' \)-dichlorotetrakis(phosphorus trifluoride)dirhodium(I) (3a)

A solution of triphenylphosphine (0.35g) in \( n \)-pentane (20 ml) was added to a stirred solution of \([RhCl(PF_3)_2]_2\) (0.16g) in \( n \)-pentane (15 ml). Immediately a yellow precipitate was formed. The solid material was separated by filtration, washed with \( n \)-pentane (3x20 ml) and recrystallised from a mixture of dichloromethane (20 ml) and \( n \)-heptane (10 ml). The yield of trans-RhCl(PPh\(_3\))\(_2\)PF\(_3\) (5a) was 0.49g (71%). The substance decomposed without melting at 144-8°.

Found (%): C 57.75; H 4.78; P 11.97; Cl 4.88.

\( C_{36}H_{30}ClF_3P_3Rh \) requires: C 57.58; H 4.03; P 12.37; Cl 4.72.

trans-Bromo(phosphorus trifluoride)bis(triphenylphosphine)rhodium(I)

From bromotris(triphenylphosphine)rhodium(I)

Phosphorus trifluoride was bubbled into a solution of RhBr(PPh\(_3\))\(_3\) (0.19g) in dichloromethane (7 ml) cooled to -78° until the solution turned light brown. The mixture was allowed to warm to room temperature, quickly filtered and \( n \)-heptane (10 ml) added to the filtrate. On cooling to -78°, bright yellow crystals slowly formed. These were separated by decanting the cooled superantant liquid. After washing with \( n \)-pentane (3x10 ml) and drying in vacuo at 0°, 0.06g (26%) of trans-RhBr(PPh\(_3\))\(_2\)PF\(_3\) (5b) was obtained.

From \( \mu,\mu' \)-dibromotetrakis(phosphorus trifluoride)dirhodium(I) (3b)

A solution of triphenylphosphine (0.43g) in \( n \)-pentane (20 ml) was added to \([RhBr(PF_3)_2]_2\) (3b) (0.27g) in \( n \)-pentane (20 ml), affording a golden yellow precipitate. The solid was separated by centrifugation, washed with \( n \)-pentane (3x20 ml) and recrystallised from a mixture of...
dichloromethane and n-heptane at -78° to give deep yellow crystals. These were washed with n-pentane (2x20 ml) and dried in vacuo at 0°, affording 0.59g (59%) of trans-RhBr(PPh₃)₂PF₃ (5b). This complex slowly decomposed at room temperature.

Found (%):  
C 54.53; H 4.06; P 11.99; Br 9.86.

C₃₆H₅₀BrF₃₃Rh requires: C 54.36; H 3.80; P 11.68; Br 10.05.

Attempted Preparation of trans-iodo(phosphorus trifluoride)bis(triphenylphosphine)rhodium(I) (5c)

From µ,µ'-diiodotetrakis(phosphorus trifluoride)dirhodium(I) (3c)

A solution of [RhI(PF₃)₂]₂ (3c) (0.21g) in n-pentane (20 ml) was added to a stirred solution of triphenylphosphine (0.53g) in n-pentane (30 ml) at 0°. A black-brown precipitate immediately formed and was isolated by centrifugation, washed with cooled n-pentane and dried at 0° in vacuo. An IR spectrum of this product indicated the absence of coordinated phosphorus trifluoride.

From trans-chloro(phosphorus trifluoride)bis(triphenylphosphine)-rhodium(I) (5a)

The reaction of trans-RhCl(PPh₃)₂PF₃ (5a) (0.20g) and sodium iodide (0.73g) in acetone (30 ml) at 0° for one hour, afforded a deep brown solution. Addition of cooled (0°) n-pentane (150 ml) gave a brown precipitate, which was separated by centrifugation. Extraction of this precipitate with cooled (0°) dichloromethane (4x5 ml) and addition of n-pentane (150 ml) produced a substance containing no coordinated phosphorus trifluoride (from IR spectrum).

Oxidative Additive Reactions

With hydrogen

Hydrogen gas was bubbled through a solution of trans-RhCl(PPh₃)₂PF₃ (5a) (0.3g) in benzene (10 ml) for four hours.
The IR spectrum of the resulting solution showed no $\nu$(Rh-H), and the starting material was recovered unchanged (from IR and m.p.). Similarly, passage of hydrogen over the solid or through dichloromethane solutions of \textit{trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a)} produced no detectable hydride containing species.

**With Hydrogen Halides**

An excess of hydrogen chloride was condensed onto solid \textit{trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a)} at -78° to give a yellow solution and a yellow precipitate. This mixture was allowed to warm up slowly to room temperature, affording a pale yellow solid. The IR spectrum of this solid showed it to contain a hydride [$\nu$(Rh-H) = 2098 cm$^{-1}$ (s)]. The material readily lost hydrogen chloride on standing to produce the starting material (IR spectrum).

The reaction of \textit{trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a)} with hydrogen bromide was performed similarly to afford an orange solid [$\nu$(Rh-H) = 2092 cm$^{-1}$ (m)]. The reaction of the carbonyl analogue (2a) with hydrogen halides under these conditions also gave hydride complexes [hydrogen chloride adduct; $\nu$(Rh-H) = 2110 cm$^{-1}$, $\nu$(C=O) = 2045 cm$^{-1}$, hydrogen bromide adduct; $\nu$(Rh-H) = 2101 cm$^{-1}$, $\nu$(C=O) = 2040 cm$^{-1}$, (Nujol)].

**With Sulphur Dioxide**

Sulphur dioxide was bubbled through a solution of \textit{trans-RhCl(PPh$_3$)$_2$PF$_3$ (5a)} (0.3g) in benzene (5 ml) for ten minutes. n-Heptane (100 ml) was added and the solution further saturated with sulphur dioxide. On cooling to 0° yellow-green crystals separated. These were washed with n-pentane (2x30 ml) saturated with sulphur dioxide. The adduct readily lost sulphur dioxide reverting to the starting material (from IR spectrum). Elemental analysis did not give reproducible results.
Found (%): C 56.06, 55.21; H 4.25, 4.31; P 10.73, 10.97; Cl 4.10, 6.29, 8.36.

\[
\begin{align*}
C_{36}H_{30}ClF_3P_RhS & \text{ requires:} \\
C & 53.0; \quad H 3.8; \quad P 11.5; \quad Cl 4.4.
\end{align*}
\]

A triphenylarsine complex was prepared similarly from (13) but in smaller yield (ca 5%).

**With Chlorine**

Chlorine gas was bubbled through a solution of \(\text{trans-RhCl(PPh}_3\text{)}_2\text{PF}_3\) (5a) (0.29g) in benzene (20 ml) for twenty minutes. Addition of \(n\)-heptane (30 ml) and evaporation under reduced pressure afforded a yellow powder, which was washed with \(n\)-pentane (2x20 ml) and dried in vacuo. The complex did not give satisfactory analyses and slowly decomposed at room temperature.

Found (%): C 50.01, 47.19; H 4.4, 3.90; P 10.25, 10.47; Cl 16.41, 13.92.

\[
\begin{align*}
C_{36}H_{30}Cl_F_P_Rh & \text{ requires:} \\
C & 52.6; \quad H 3.7; \quad P 11.3; \quad Cl 12.9.
\end{align*}
\]

A similar arsine complex may be prepared from \(\text{trans-RhCl(AsPh}_3\text{)}_2\text{PF}_3\) (13) by the above method.

**With Carbon Tetrachloride**

A mixture of carbon tetrachloride (5 ml) and \(\text{trans-RhCl(PPh}_3\text{)}_2\text{PF}_3\) (5a) (0.3g) was allowed to stand for twelve hours at room temperature, affording an amorphous red precipitate and a yellow solution. The mixture was filtered and the filtrate evaporated to dryness, yielding a yellow solid which exhibited an IR spectrum identical with that obtained from the product of the reaction of chlorine with \(\text{trans-RhCl(PPh}_3\text{)}_2\text{PF}_3\) (5a).

**With Nitric Oxide**

Nitric oxide was passed through a stirred solution of \(\text{trans-RhCl(PPh}_3\text{)}_2\text{PF}_3\) (5a) (0.3g) in methanol (15 ml). The mixture
quickly turned green, and after decantation the resulting solid was recrystallised from a mixture of dichloromethane (20 ml) and n-heptane (20 ml) by evaporation under reduced pressure. The product was an amorphous green powder, decomposing without melting at 148°-154°, and whose IR spectrum indicated the absence of coordinated phosphorus trifluoride. The sample was identical to that prepared from the carbonyl analogue (2) by the above method and reported in the literature to be RhCl(NO)(NO₂)(PPh₃)₂.¹⁵¹,¹⁵²

Reactions of µ,µ'-dichlorotetracarbonyldirhodium(I) (1a)

With phosphorus trifluoride in the solid state

Phosphorus trifluoride was passed over a solid sample of [RhCl(CO)₂]₂ (1a) (0.38g) for one hour. The orange crystals quickly turned into a brown oil, and after several minutes more gave a deep red solid. The crude product was purified by vacuum sublimation (25°, 10⁻³ mm) and then recrystallised from n-pentane (30 ml) by cooling to -78°, to give 0.32g of red crystals. The IR spectrum shows the presence of both coordinated carbon monoxide (at 2064 cm⁻¹) and phosphorus trifluoride.

Elemental analysis corresponds to no definite composition.

Found (%): C 0.74, 0.91; H nil; P 18.87, 19.31; Cl 11.56, 11.31

RhCl(CO)(PF₃)₆: CCl₁F₆O₂₆Rh₂ requires:
C 3.50; H 0.00; P 18.09; Cl 10.35.

[RhCl(CO)(PF₃)]₂: C₂Cl₁₂F₆O₂₂P₃Rh₂ requires:
C 4.72; H 0.00; P 12.18; Cl 13.94.

Rh₂Cl₂(CO)(PF₃)₃: CCl₁₂F₉O₃₉Rh₂ requires:
C 2.11; H 0.00; P 16.34; Cl 6.23.

With tris(dimethylamino)phosphine

Tris(dimethylamino)phosphine (0.81g) was slowly added to a solution of [RhCl(CO)₂]₂ (1a) (0.81g) in n-pentane (20 ml). A
vigorously evolution of gas occurred with the formation of a yellow precipitate. When the reaction had ceased, the supernatant liquid was discarded and the solid washed with \( n \)-pentane (3x20 ml), and then dissolved in dichloromethane (7 ml). \( n \)-Pentane (40 ml) was added to the filtered solution and the mixture cooled to -5°. The yellow prisms which slowly separated were collected, washed with \( n \)-pentane (2x10 ml) and dried in vacuo, affording 0.41g (84%) of trans-RhCl\([P(NMe_2)_3]\)_2CO melting at 161-2°.

Found: C 31.30; H 7.36; N 16.82; P 12.34; Cl 7.47. 

C_{13}H_{36}ClN_6O_P_Rh requires: C 31.69; H 7.36; N 17.06; P 12.57; Cl 7.19.

It has been shown that electronegative fluorine atoms with dialkylamino-groups should enhance the \( 
\text{d} \)-donor capabilities of the ligand. This is supported by the observation that there is a sharp increase in basic strength (towards \( \text{Me}_2 \)) on proceeding from phosphorus trifluoride, through the Lewis phosphazenes, to \( \text{PMe}_2 \text{Me}_2 \).
Aminofluorophosphine Complexes of Rhodium(I)

Introduction

Although carbon monoxide and phosphorus trifluoride form complexes with most transition metals, the coordination chemistry of substituted fluorophosphine complexes is reasonably well established for nickel(0), molybdenum(0) and platinum(0) or (II) only. The coordination chemistry of substituted fluorophosphine complexes is reasonably well established for nickel(0), molybdenum(0) and platinum(0) or (II) only. It has been shown from IR studies that dialkylaminofluorophosphines [e.g. PF(NMe₂)₂] exhibit the poorest π-accepting ability of all fluorophosphines. The decrease in π-accepting ability on substituting a dialkylamino-group for a fluorine atom arises from the competition for the 5d orbitals of the phosphorus, between the nitrogen "lone pair" and filled metal d orbitals.

Evidence for P(3d)-N(2p) π-bonding is provided by the observed planar configuration about the nitrogen atom, the planarity being retained on complexation. This interaction causes a general lack of basic character on the part of the nitrogen. Only in Me₂NPF₂·BF₃, is there evidence for the participation of the nitrogen lone pair in complex formation. In all other complexes reported bonding is through the phosphorus lone-pair.

It would be expected that successively replacing highly electronegative fluorine atoms with dialkylamino-groups should enhance the σ-donor capabilities of the ligand. This is supported by the observation that there is a sharp increase in base strength (towards BH₃) on proceeding from phosphorus trifluoride, through the aminofluorophosphines, to P(NMe₂)₃.
14

Et₂NF₂P

Cl

Cl

Me₂NF₂P

PF₂NMe₂

PF₂NMe₂

Rh

Rh

15

Cl

Me₂NF₂P

PF₂NMe₂

PF₂NMe₂

CO

16

Cl

PF₂NMe₂

Me₂NF₂P

PF₂NMe₂

Rh

Me₂NF₂P

17 a, X = Cl

b, X = I

17

Et₂NF₂P

X

PF₂NMe₂

PF₂NMe₂

Rh

Rh

Et₂NF₂P

X

PF₂NEt₂

PF₂NEt₂

18 a, X = Cl

b, X = I

18

Et₂NF₂P

PF₂NEt₂

PF₂NEt₂

Rh

Me₂NF₂P

Cl

PF₂NMe₂

PF₂NMe₂

19
\[ \text{Rh} \begin{array}{c} \text{Cl} \\ \text{PF(NMe}_2\text{)}_2 \\ \text{(Me}_2\text{N)}_2\text{FP} \end{array} \begin{array}{c} \text{PF(NMe}_2\text{)}_2 \\ \text{Cl} \end{array} \]

20

\[ \text{Rh} \begin{array}{c} \text{PF}_2\text{NEt}_2 \\ \text{C} \\ \text{O} \end{array} \begin{array}{c} \text{H}_3\text{C} \\ \text{HC} \end{array} \]

21a, \( X = \text{PF}_2\text{NEt}_2 \)

b, \( X = \text{PF(NMe}_2\text{)}_2 \)

c, \( X = \text{P(NMe}_2\text{)}_3 \)

\[ \text{Rh} \begin{array}{c} \text{Et}_2\text{NF}_2\text{P} \\ \text{Cl} \end{array} \begin{array}{c} \text{PF}_2\text{NEt}_2 \\ \text{Ph}_3\text{P} \end{array} \]

22

\[ \text{Rh} \begin{array}{c} \text{Cl} \\ \text{PF}_2\text{NEt}_2 \\ \text{OC} \end{array} \begin{array}{c} \text{Cl} \\ \text{PF}_2\text{NEt}_2 \\ \text{ET}_2\text{NF}_2\text{P} \end{array} \]

25

\[ \text{Rh} \begin{array}{c} \text{Cl} \\ \text{PF}_2\text{NEt}_2 \\ \text{Ph}_3\text{M} \end{array} \begin{array}{c} \text{PF}_2\text{NEt}_2 \\ \text{Cl} \end{array} \]

24a, \( M = \text{P} \)

b, \( M = \text{As} \)
The present work represents an effort to compare the coordinating abilities of phosphorus trifluoride and the aminofluorophosphines to rhodium(I). While this research was in progress Nixon and co-workers briefly reported the preparation of complexes of rhodium(I) with PF₄NMe₂. They noted that this ligand completely displaces coordinated ethylene from [RhCl(C₂H₄)₂]₂ affording [RhCl(PF₄NMe₂)₂]₂ (14). The mixed carbonyl-phosphine complex, trans-RhCl(CO)(PF₄NMe₂)₂ (15), is reported to be formed in the reaction of PF₄NMe₂ with the dimeric carbonyl complex, [RhCl(CO)]₂ (1a). Complex (15) reacts with additional PF₄NMe₂, losing carbon monoxide to give RhCl(PF₄NMe₂)₃ (16). Complexes similar to the above, but containing other fluorophosphines are mentioned in a recent review by Nixon. 8
The Interconversion of Aminofluorophosphine Complexes of Rhodium(I)
Results and Discussion

The reactions discussed in this Chapter are shown in Figure 4.

Preparation and Properties of Halogeno(fluorophosphine)complexes of Rhodium(I).

The ethylene complex, [RhCl(C₂H₄)]₂, suspended in n-pentane readily reacts with PF₂Et₂ at room temperature, with the complete liberation of coordinated ethylene. On cooling the reaction mixture, waxy yellow crystals of the complex, [RhCl(PF₂NEt₂)]₂ (17a), are formed. This substance is moderately air stable, slightly volatile in vacuo and soluble in all common solvents. It can also be prepared by displacement of coordinated olefin from the cyclooctene complex, [RhCl(C₈H₁₄)]₂, or of carbon monoxide from [RhCl(CO)]₂. Heating the five-coordinate, RhCl(PF₂NEt₂)₄ (vide infra), in vacuo, also affords (17a).

The corresponding iodo-complex, [RhI(PF₂NEt₂)]₂ (17b), is obtained from the reaction of PF₂NEt₂ with the diolefin complex, [RhI(cod)]₂. Complex (17b) is a deep yellow, crystalline material with similar chemical and physical properties to its chloro-analogue (17a). Reaction of PF₂NMe₂ with the dimeric carbonyl, [RhCl(CO)]₂, affords pale yellow, fibrous crystals of [RhCl(PF₂NMe₂)]₂ (14).

The mass spectra of the dimers, (14), (17a) and (17b) show parent molecular ions of the type, [Rh₂X₂L₄]⁺ (X = Cl, I, L = PF₂NEt₂; X = Cl, L = PF₂NMe₂). The fragmentation patterns of these ions are complex, but the predominant features are daughter ions arising mainly from the loss of dialkylamino-radicals and fluorine atoms; peaks corresponding to the loss of complete fluorophosphine ligands, are not observed. This pattern contrasts with the fragmentation of the corresponding phosphorus trifluoride dimers (3), which show consecutive
TABLE 9
Proton N.M.R. Spectra of Fluorophosphine Rhodium(I) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta(-\text{CH}_2)^a$</th>
<th>$\delta(-\text{CH}_3)^b$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PF}_2\text{NET}_2$</td>
<td>3.11</td>
<td>1.10</td>
<td>$^4J_{\text{HF}} = 3.4$</td>
</tr>
<tr>
<td>$[\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2$</td>
<td>3.02</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>$\text{RhCl}(\text{PF}_2\text{NET}_2)_4$</td>
<td>3.19</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>$[\text{RhCl}(\text{CO})\text{PF}_2\text{NET}_2]_2$</td>
<td>3.09</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>$\text{Rhacac}(\text{PF}_2\text{NET}_2)_2$</td>
<td>3.35</td>
<td>0.96</td>
<td>acet: $-\text{CH}_3$, 1.87; $-\text{H}$, 5.36</td>
</tr>
<tr>
<td>$\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{PF}_2\text{NET}_2)_2$</td>
<td>3.26</td>
<td>0.93</td>
<td>$-\text{C}_5\text{H}_5$, 5.26</td>
</tr>
<tr>
<td>trans-$\text{RhCl}(\text{PPh}_3)_2(\text{PF}_2\text{NET}_2)_2$</td>
<td>3.03</td>
<td>0.64</td>
<td>Ph, 7.06 - 7.92</td>
</tr>
<tr>
<td>cis-$\text{RhCl}(\text{PPh}_3)(\text{PF}_2\text{NET}_2)_2$</td>
<td>3.27</td>
<td>1.02</td>
<td>Ph, 6.92 - 7.98</td>
</tr>
<tr>
<td>cis-$\text{RhCl}(\text{AsPh}_3)(\text{PF}_2\text{NET}_2)_2$</td>
<td>3.35</td>
<td>0.97</td>
<td>Ph, 7.03 - 7.74</td>
</tr>
<tr>
<td>$\text{PF}_2\text{NMe}_2$</td>
<td>-</td>
<td>2.35</td>
<td>$^3J_{\text{HP}} = 9.4$; $^4J_{\text{HF}} = 3.9$</td>
</tr>
<tr>
<td>$[\text{RhCl}(\text{PF}_2\text{NMe}_2)_2]_2$</td>
<td>-</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>$\text{PF}(\text{NMe}_2)_2$</td>
<td>-</td>
<td>2.58</td>
<td>$^3J_{\text{HP}} = 9.2$; $^4J_{\text{HF}} = 3.1$</td>
</tr>
<tr>
<td>$\text{RhCl}[\text{PF}(\text{NMe}_2)_2]_3$</td>
<td>-</td>
<td>2.8$d$</td>
<td></td>
</tr>
<tr>
<td>$\text{Rhacac}[\text{PF}(\text{NMe}_2)_2]_2$</td>
<td>-</td>
<td>2.8$d$</td>
<td>acet: $-\text{CH}_3$, 1.86; $-\text{H}$, 5.39</td>
</tr>
<tr>
<td>$\text{P}(\text{NMe}_2)_3$</td>
<td>-</td>
<td>2.48</td>
<td>$^3J_{\text{HP}} = 9.5$</td>
</tr>
<tr>
<td>$\text{Rhacac}[\text{P}(\text{NMe}_2)_3]_2$</td>
<td>-</td>
<td>2.56</td>
<td>$^3J_{\text{HP}} = 7.9$</td>
</tr>
<tr>
<td>$\text{RhCl}(\text{CO})[\text{P}(\text{NMe}_2)_3]_2$</td>
<td>-</td>
<td>2.27</td>
<td>acet: $-\text{CH}_3$, 1.83; $-\text{H}$, 5.33</td>
</tr>
<tr>
<td>$\text{RhCl}(\text{PF}_3)[\text{P}(\text{NMe}_2)_3]_2$</td>
<td>-</td>
<td>2.90</td>
<td></td>
</tr>
</tbody>
</table>

*a All spectra run in C$_6$D$_6$ unless stated otherwise. Chemical shifts are in p.p.m. downfield of TMS; coupling constants are in Hz.

*b Every methyl resonance of $\text{PF}_2\text{NET}_2$ is split into a triplet by coupling to the methylene protons ($^3J_{\text{HH}} = 7.0 - 7.5$ Hz).

*c Measured in CDC$_3$.

d Complex Multiplet.
loss of complete phosphorus trifluoride units as major pathways. 57,157d

The proton N.M.R. spectra of the above diethylamino-complexes (17) [and all other rhodium(I) complexes of PF₂NEt₂] exhibit broad resonances for the methylene protons. The width (often as large as 50 Hz at half peak height) is due to coupling of the methylene protons not only to the methyl protons but also to the 3¹P, ¹⁹F and ¹⁰³Rh nuclei (all 100%; I = ½). The resulting complex multiplet is further broadened by quadrupolar coupling to the nitrogen nucleus. The methyl resonances are split into triplets by coupling to the methylene protons (³Jₜₜ = 7.0 - 7.5 Hz). The proton N.M.R. spectra of the complexes discussed in this Chapter are given in Table 9, from which it can be seen that coordination does not greatly affect the chemical shifts of the protons in PF₂NEt₂.

The ¹⁹F N.M.R. spectra of these complexes each consists of two strong lines separated by about 1100 Hz, arising predominantly from phosphorus-fluorine coupling (both ¹JₚF and ³JₚF). 89,91 Each line is further split into a doublet by coupling of the fluorine to the rhodium atoms (²Jₐₙ₉F) and other fine structure is apparent but not resolved. The ¹⁹F N.M.R. parameters of the complexes discussed in this Chapter are shown in Table 10.

Addition of a small amount (<5 mole %) of the free fluorophosphine radically alters the ¹⁹F N.M.R. spectra of the dimeric complexes (14) and (17), as is shown for [RhCl(PF₂NEt₂)₂]₂ (17a) in Figure 5a. The spectrum collapses into a widely spaced doublet, implying coupling to the directly bonded phosphorus (¹JₚF) but loss of coupling of the fluorine atoms to the rhodium (²Jₐₙ₉F) and to other nuclei (e.g. ⁴J₉F). This loss of coupling arises from a rapid intermolecular exchange between free and coordinated PF₂NR₂ (R = Me,Et).
Figure 5

Intermolecular Ligand Exchange in Aminofluorophosphine Complexes of Rhodium
### TABLE 10

Fluorine N.M.R. Spectra of Fluorophosphine-Rhodium(I) Complexes.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ</th>
<th>$\nu J_{PF}$</th>
<th>$J_{RhF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF$_2$NET$_2$</td>
<td>63.9</td>
<td>1206</td>
<td>-</td>
</tr>
<tr>
<td>[RhCl(PF$_2$NET$_2$)$_2$]$_2$</td>
<td>38.1</td>
<td>1100</td>
<td>27</td>
</tr>
<tr>
<td>[RhI(PF$_2$NET$_2$)$_2$]$_2$</td>
<td>38.7</td>
<td>1106</td>
<td>32</td>
</tr>
<tr>
<td>Rhacac(PF$_2$NET$_2$)$_2$</td>
<td>43.7</td>
<td>1128</td>
<td>28</td>
</tr>
<tr>
<td>Rh(π-C$_5$H$_5$)(PF$_2$NET$_2$)$_2$</td>
<td>25.2</td>
<td>1128</td>
<td>24</td>
</tr>
<tr>
<td>trans-RhCl(PPh$_3$)$_2$(PF$_2$NET$_2$)$_2$</td>
<td>33.4</td>
<td>1086</td>
<td>-</td>
</tr>
<tr>
<td>cis-RhCl(PPh$_3$)(PF$_2$NET$_2$)$_2$</td>
<td>34.9</td>
<td>1106</td>
<td>-</td>
</tr>
<tr>
<td>cis-RhCl(AsPh$_3$)(PF$_2$NET$_2$)$_2$</td>
<td>32.9</td>
<td>1103</td>
<td>-</td>
</tr>
<tr>
<td>cis-RhCl(AsPh$_3$)(PF$_2$NET$_2$)$_2$</td>
<td>45.2</td>
<td>1159</td>
<td>-</td>
</tr>
<tr>
<td>PF$_2$NMe$_2$</td>
<td>64.5</td>
<td>1184</td>
<td>-</td>
</tr>
<tr>
<td>[RhCl(PF$_2$NMe$_2$)$_2$]$_2$</td>
<td>40.4</td>
<td>1106</td>
<td>27</td>
</tr>
</tbody>
</table>

---

*a All spectra measured in benzene. Chemical shifts in p.p.m. upfield of CFCl$_3$; separations given in Hz.

*b Separation of doublet due to phosphorus-fluorine couplings (both $^1J_{PF}$ and $^3J_{PF}$).
In Chapter 2 it was shown that free and coordinated phosphorus trifluoride undergo a similar exchange in $[\text{RhCl}(\text{PF}_3)_2]_2$ ($3a$).

The reaction of a large excess of PF$_2$NEt$_2$ with $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$ ($17a$) or its iodo-analogue ($17b$) in n-pentane results in a marked deepening in colour of the solution. On cooling to -78° clusters of crystals are slowly deposited. From elemental analysis the products may be formulated as the five-coordinate complexes, RhX(PF$_2$NEt$_2$)$_4$ ($X = \text{Cl, I}$) ($18$).

The complex, RhCl(PF$_2$NEt$_2$)$_4$ ($18a$), is a deep yellow solid melting just above room temperature (28-29°) apparently with decomposition to the dimer, $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$ ($17a$), and free PF$_2$NEt$_2$. Slowly on prolonged evacuation at room temperature or rapidly at elevated temperatures, RhCl(PF$_2$NEt$_2$)$_4$ affords the dimer $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$.

The complex, RhI(PF$_2$NEt$_2$)$_4$ ($18b$), is an orange-brown, crystalline material which has a higher melting point (58°) and is more stable than its chloro-analogue ($18a$). Again complex ($18b$) decomposes on melting or on evacuation to the corresponding dimer, $[\text{RhI}(\text{PF}_2\text{NEt}_2)_2]_2$ ($17b$). The mass spectra of complexes ($18$) are identical to those of the dimers ($17$), with no evidence for any mononuclear parent ions.

An analogous methyl complex, RhCl(PF$_2$NMe$_2$)$_4$ ($19$), is readily prepared from the dimeric $[\text{RhCl}(\text{PF}_2\text{NMe}_2)_2]_2$ ($14$) and an excess of PF$_2$NMe$_2$. It is less soluble in n-pentane and more thermally stable than its ethyl-analogue ($18a$). However, on heating in an open capillary tube ($19$) slowly decomposes at about 45-50° (the boiling point of PF$_2$NMe$_2$ is 50.3°$^\text{o}$)

The complex, RhCl(PF$_2$NMe$_2$)$_4$ ($19$), also loses free PF$_2$NMe$_2$ on evacuation at room temperature. In contrast to the ethyl analogues
an intermediate decomposition product may be readily isolated. This complex analyses as the four-coordinate, $\text{RhCl(PF}_2\text{NEt}_2)_3$ (16), which has been reported by Nixon. It is stable in vacuo at room temperature, but on heating affords $[\text{RhCl(PF}_2\text{NMe}_2)_2]_2$ (14). Complex (16) is not merely a mixture of $[\text{RhCl(PF}_2\text{NMe}_2)_2]_2$ (14) and $\text{RhCl(PF}_2\text{NMe}_2)_4$ (19), as its melting point (135-139°) is considerably higher than that of either the dimer (14), (111.5°), or the five-coordinate complex (19), (79°).

With the exceptions of the iridium complex, $\text{IrCl(CO)}_3$, and of trans-RhCl($\text{PF}_3)_2$CO (15) no other complexes analogous to (16) have been reported with carbon monoxide or phosphorus trifluoride.

Complexes corresponding to the four-coordinate (16) are not readily prepared from the reaction of PF$_2$NEt$_2$ with $[\text{RhX(PF}_2\text{NEt}_2)_2]_2$ (17). The addition of two equivalents of PF$_2$NEt$_2$ to one equivalent of (17a) in n-pentane affords only a mixture of (18a) and unreacted (17a) on cooling to -78°. Similarly evacuation of samples of the five-coordinate complexes (18) produce only the dimers (17) with no isolable four-coordinate intermediates. The reason for this is not clear, but in the reaction in solution, it may be related to the solubilities of the various species present. It should be noted, however, that diethylamino-complexes corresponding to RhCl($\text{PF}_2\text{NMe}_2)_3$ (16) have been reported by Nixon.

It is concluded that three different species are in equilibrium in the reaction between dimers, (14) or (17), and the corresponding free ligand, PF$_2$NR$_2$ (R = Me,Et). The equilibrium

$$[\text{RhXL}_2]_2 \rightleftharpoons \text{RhXL}_3 \rightleftharpoons \text{RhXL}_4$$

lies to the right for the less soluble complexes of PF$_2$NMe$_2$ and at
lower temperatures. In Chapter 2 it was shown that similar equilibria exist between five-coordinate phosphorus trifluoride complexes (9) and the dimeric \([\text{RhX(PF}_3\text{)}_{2}]_{2}\) \((X = \text{Cl, Br, I})\) \((3)\), and other systems analogous to the above were discussed there. Complexes of the type \((16), (18)\) and \((19)\) are probably the intermediates in the intermolecular exchange of free and coordinated phosphine observed in the \(^{19}\text{F}\) N.M.R. spectra of the dimers, \([\text{RhX(PF}_2\text{NR}_2\text{)}_{2}]_{2}\).

The ligands, \(\text{PF}_2\text{NR}_2\), resemble the phosphites \(^{120,121}\) in that the number of ligands which can coordinate to the metal varies under different experimental conditions. However, unlike some phosphite \(^{121}\) and phosphine \(^{121,157}\) complexes of rhodium(I), the fluorophosphines show no tendency to form cationic species of the type \([\text{RhL}_4]^+\) or \([\text{RhL}_5]^+\). Reaction of \(\text{RhI(PF}_2\text{NEt}_2\text{)}_{4}\) \((18b)\) with sodium tetraphenylborate in polar solvents gives no isolable ionic species. Similarly a conductimetric titration of \([\text{RhI(PF}_2\text{NEt}_2\text{)}_{2}]_{2}\) \((17b)\) with up to a tenfold excess of \(\text{PF}_2\text{NEt}_2\) in nitrobenzene shows no increase in conductance due to ionic species. Instead the molar conductance remains that of a non-electrolyte solution. \(^{158}\)

The inability of these complexes to form cationic species can be explained in terms of the relative \(\pi\)-bonding abilities of phosphite and fluorophosphine ligands. The fluorophosphines are probably stronger \(\pi\)-acceptors than the phosphites and, therefore, will exert a stronger electron withdrawing effect on the rhodium atom. This in turn will make the negative halide ion a poorer leaving group and the rhodium atom less able to support a formal positive charge.

A complex analogous to \(\text{RhCl(PF}_2\text{NMe}_2\text{)}_{3}\) \((16)\) is prepared by displacement of coordinated cyclooctene from \([\text{RhCl(C}_8\text{H}_{14}\text{)}_{2}]_{n}\) with the fluorophosphine, \(\text{PF(NMe}_2\text{)}_{2}\). This complex, \(\text{RhCl[PF(NMe}_2\text{)}_{2}]_{3}\) \((20)\), is a
waxy yellow solid, which is exceedingly air sensitive and soluble in all common solvents.

The mass spectrum of (20) shows a parent molecular ion and fragmentation in the usual manner (i.e. by loss of fluorine atoms and dimethylamino-radicals). The mass spectrum also indicates the presence of ions of weak intensity attributable to a dimeric species \{RhCl[PF(NMe₂)₂]₂\}_2. Attempts to prepare this species by reacting two equivalents of PF(NMe₂)₂ with one equivalent of \([RhCl(C₈H₁₄)₂]_n\) lead only to the mononuclear complex (20).

Preparation and Properties of other Fluorophosphine Complexes of Rhodium(I)

2,4-Pentanedionato Complexes

The chloride bridges of \([RhCl(PF₂NEt₂)₂]_2\) (17a) are readily cleaved and replaced when reacted with Tlacac in tetrahydrofuran. The mononuclear complex formed, Rh(acac)(PF₂NEt₂)₂ (21a), may be more conveniently prepared by displacing carbon monoxide from Rhacac(CO)₂ by PF₂NEt₂ in n-pentane. Complex (21a) is a diamagnetic, air-sensitive, volatile oil, very soluble in organic solvents and melting below room temperature (14.5°).

In the solid state (21a) is pale yellow, both by reflected and transmitted light; it is not noticeably dichroic and gives almost colourless solutions in organic solvents. The complex Rhacac(CO)₂ is also yellow in solution, but in contrast to (21a) forms dichroic crystals in the solid which are deep red by transmitted light and green by reflected light.\(^\text{159}\) It has been shown that the solid carbonyl complex consists of chains of monomeric units held together by metal-metal bonding (Rh-Rh distance 3.27 Å).\(^\text{160}\) The corresponding phosphorus trifluoride complex (8) resembles (21a) in not being dichroic. The
reason for the difference between Rhacac(CO)₂ and complexes (8) and (21a) is uncertain, but has been ascribed to intermolecular repulsion between the fluorophosphine groups. The fluorophosphines are more bulky than carbon monoxide but more importantly contain negatively polarised fluorine atoms which repel each other (see Chapter 1 for an account of the charge distribution in these ligands).

The mass spectrum of complex (21a) shows a parent molecular ion. The fragmentation of this species is complex, but ions arising from loss of fluorine atoms and diethylamino-radicals, as well as loss of PF₂NEt₂ groups, are observed.

The proton ¹⁹F N.M.R. spectrum of (21a) is given in Table 9. The relative intensities of the various resonances are those expected for Rhacac(PF₂NEt₂)₂.

The ¹⁹F N.M.R. spectrum of (21a) is given in Table 10 and Figure 5b. It consists of a widely spaced doublet due to phosphorus-fluorine coupling (both ¹JPF and ³JPF). Each line is split into another doublet by coupling to rhodium (²JRHF), and there is additional fine structure which is only partially resolved. On addition of a small amount (ca 10 mole %) of free PF₂NEt₂, the spectrum immediately collapses into a sharp doublet (Figure 5b). As was the case with the dimer, [RhCl(PF₂NEt₂)₂]₂ (17a) and the phosphorus trifluoride complexes discussed in Chapter 2, the loss in coupling indicates that Rhacac(PF₂NEt₂)₂ undergoes a rapid intermolecular exchange of free and coordinated PF₂NEt₂, probably through a five-coordinate intermediate.

Complexes analogous to (21a) but containing the ligands PF(NMe₂)₂ and P(NMe₂)₃ can be made by displacing coordinated cyclooctene or carbon monoxide from the corresponding 2,4-pentanedionato complexes, Rhacac(C₈H₁₄)₂ and Rhacac(CO)₂.
Rhacac[PF(NMe$_2$)$_2$]$_2$ (21b) is a yellow, waxy solid which is exceedingly air-sensitive and soluble in all common organic solvents. The mass spectrum of this compound shows a parent molecular ion and fragmentation by loss of dimethylamino-radicals and fluorine atoms. The proton N.M.R. is given in Table 9, and the IR spectrum in Table 12.

The complex Rhacac[P(NMe$_2$)$_3$]$_2$ (21c) is a yellow, fairly air-stable, and volatile solid, also soluble in all common organic solvents. The mass spectrum again shows a parent ion and fragmentation by loss of dimethylamino-radicals.

π-Cyclopentadienyl Complex

The reaction of Tl(ο-C$_5$H$_5$) with the dimer [RhCl(PF$_2$NEt$_2$)$_2$]$_2$ (17a) affords a mononuclear complex in which the chloride bridges have been both cleaved and replaced. The product, Rh(π-C$_5$H$_5$)(PF$_2$NEt$_2$)$_2$ (22), is a diamagnetic, slightly air sensitive, orange oil. It is similar to the phosphorus trifluoride complex, Rh(π-C$_5$H$_5$)(PF$_3$)$_2$ (2), made by an analogous method, and to Co(π-C$_5$H$_5$)(PF$_3$)$_2$ made from Co(n-C$_5$H$_5$)$_2$ and phosphorus trifluoride (170°, 350 atm).

The mass spectrum of (22) exhibits a parent molecular ion. This fragments by loss of diethylamino-radicals, fluorine atoms and complete fluorophosphine ligands to [Rh(π-C$_5$H$_5$)]$^+$, and then to small fragments.

The proton N.M.R. spectra of complex (22) is given in Table 9. Unlike the multiplet structure for the cyclopentadienyl resonance found in the phosphorus trifluoride complex, Rh(π-C$_5$H$_5$)(PF$_3$)$_2$, the resonance of (22) is only a slightly broadened singlet (half height width is 3.2 Hz). The cobalt-phosphorus trifluoride complex is similar to (22) in that no coupling of phosphorus and fluorine atoms to the cyclopentadienyl protons is observed.
The fluorine N.M.R. of \( \text{Rh}(\pi-C_5\text{H}_5)(\text{PF}_2\text{NEt}_2)_2 \) is given in Table 10. It is similar in general appearance to other complexes of \( \text{PF}_2\text{NEt}_2 \) with rhodium(I), in consisting of a widely spaced doublet \( J_{\text{PF}} \) and \( 3 J_{\text{PF}} \) further split into much smaller doublets \( J_{\text{RhF}} \). As is found in the analogous phosphorus trifluoride complex, the fluorine resonance of \( \text{(22)} \) is shifted further downfield than the resonances of the square-planar, sixteen-electron rhodium(I) complexes are. This is a reflection of the different stereochemistry and different electronic configuration of the cyclopentadienyl complexes.

The addition of up to one mole equivalent of the free ligand to complex \( \text{(22)} \) has no effect on the \( ^{19}\text{F} \) N.M.R. spectrum. A similar lack of intermolecular ligand exchange has been noted for \( \text{Rh}(\pi-C_5\text{H}_5)(\text{PF}_3)_2 \) and for \( \text{Rh}(\pi-C_5\text{H}_5)(\text{C}_2\text{H}_4)_2 \). This difference in behaviour as compared with square-planar rhodium(I) complexes partly arises from the fact that the cyclopentadienyl complexes have an eighteen-electron, inert-gas configuration. This results in no empty bonding orbital (or coordination site) being readily available for an entering ligand. However the carbonyl complex, \( \text{Rh}(\pi-C_5\text{H}_5)(\text{CO})_2 \), undergoes a bimolecular displacement reaction with phosphines and phosphites, and \( \text{Co}(\pi-C_5\text{H}_5)(\text{CO})_2 \) rapidly exchanges free and coordinated carbon monoxide. The electronic configuration of the metal atom, therefore, is not the sole factor in determining the rates of exchange and the reactivity of this type of complex.

**Phosphine and Arsine Complexes**

One equivalent of \( \text{PF}_2\text{NEt}_2 \) slowly reacts with \( \text{RhCl}(\text{PPh}_3)_3 \) in dichloromethane to give a yellow solution, from which the complex, \( \text{trans-RhCl}(\text{PPh}_3)_2(\text{PF}_2\text{NEt}_2) \) (23), can be isolated. It is a yellow, diamagnetic, involatile material, dissolving in all organic solvents except alcohols and aliphatic hydrocarbons, to form air-sensitive
solutions. The configuration is assumed to be trans by analogy with the phosphorus trifluoride and carbonyl complexes, (5) and (2).

There is a rapid reaction between RhCl(PPh₃)₃ and an excess of PF₂NEt₂ in dichloromethane. From the reaction mixture a lemon-yellow, involatile, diamagnetic complex, cis-RhCl(PPh₃)(PF₂NEt₂)₂ (24a), may be isolated. trans-RhCl(PPh₃)(PF₂NEt₂) also reacts with an excess of PF₂NEt₂, to afford (24a). However, the best method for the preparation of cis-RhCl(PPh₃)(PF₂NEt₂)₂ is by the reaction of triphenylphosphine with [RhCl(PF₂NEt₂)₂]₂ (17a).

The complex, cis-RhCl(PPh₃)(PF₂NEt₂)₂, is soluble in all common organic solvents except aliphatic hydrocarbons. Elemental analysis and an integration of the proton N.M.R. spectrum establishes the stoichiometry. This is confirmed by molecular weight values (vapour phase osmometry) expected for an undissociated species.

The ¹⁹F N.M.R. spectrum of complex (24a) shows two broadly spaced doublets of equal intensity (Table 10). The spectrum is indicative of two chemically non-equivalent fluorophosphine ligands, and so suggests a cis-configuration for the complex.

There is some evidence for a cis-dicarbonyl analogue of complex (24a). On bubbling carbon monoxide through a solution of [RhCl(PPh₃)(CO)]₂ in benzene, a species with two ν(CO) bands is produced. It has been suggested that this species is cis-RhCl(PPh₃)(CO)₂, but the solution readily loses carbon monoxide, regenerating the starting material.

Crystal Structure of cis-RhCl(PPh₃)(PF₂NEt₂)₂ (24a)

An X-ray analysis, kindly carried out by Dr P.O. Whimp, shows that complex (24a) does have a square-planar, cis-stereochemistry. The results of the analysis are in Figure 6 and Table 11.
The Ethyl Group C121–C122 is disordered.

Molecular Structure of

\[ \text{cis-RhCl}(\text{PPh}_3)(\text{PF}_2\text{NEt}_2)_2 \]
present stage of refinement, \( R = 7.4\% \), e.s.d's of the bond lengths in Figure 6 are Rh-Cl, 0.002; Rh-P, 0.003; P-F, 0.007; P-N, 0.009; P-C, 0.01; N-C, 0.016; C-C, 0.02 Å.

### TABLE 11

**Bond Angles in cis-RhCl(PPh\(_3\))(PF\(_2\)NEt\(_2\))\(_2\) (24a)**

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Value (°)</th>
<th>e.s.d. (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_1)-Rh-P(_2)</td>
<td>91.7(1)</td>
<td>P(_1)-N(<em>1)-C(</em>{111})</td>
</tr>
<tr>
<td>Cl-Rh-P(_3)</td>
<td>86.6(1)</td>
<td>P(_1)-N(<em>1)-C(</em>{121})</td>
</tr>
<tr>
<td>Cl-Rh-P(_1)</td>
<td>86.3(1)</td>
<td>C(_{111})-N(<em>1)-C(</em>{121})</td>
</tr>
<tr>
<td>P(_2)-Rh-P(_3)</td>
<td>95.6(1)</td>
<td>P(_2)-N(<em>2)-C(</em>{211})</td>
</tr>
<tr>
<td>F(_{11})-P(<em>1)-F(</em>{12})</td>
<td>93.8(4)</td>
<td>P(_2)-N(<em>2)-C(</em>{221})</td>
</tr>
<tr>
<td>F(_{21})-P(<em>2)-F(</em>{22})</td>
<td>93.8(4)</td>
<td>C(_{211})-N(<em>2)-C(</em>{221})</td>
</tr>
<tr>
<td>F(_{11})-P(_1)-N(_1)</td>
<td>103.1(4)</td>
<td>F(_{21})-P(_2)-N(_2)</td>
</tr>
<tr>
<td>F(_{12})-P(_1)-N(_1)</td>
<td>102.7(4)</td>
<td>F(_{22})-P(_2)-N(_2)</td>
</tr>
</tbody>
</table>

- Numerical subscripts refer to atoms labelled as in Figure 6.
- Values given in degrees; numbers in parentheses are e.s.d's of the final figure.

From Table 11 it can be seen that the complex is square-planar. This is in contrast to \( \text{RhCl(PPh}_3\) \(_3\) \), which is markedly distorted towards a tetrahedral stereochemistry.\(^{165}\)

The rhodium-phosphorus bond lengths reflect the relative bonding abilities of the four ligands to the metal. Rh-P(2), \([2.136(3)\text{Å}, \text{PF}_2\text{NEt}_2 \text{trans to chloride}]\), is 0.08 Å, shorter than Rh-P(1), \([2.215(3)\text{Å}, \text{PF}_2\text{NEt}_2 \text{trans to triphenylphosphine}]\). As triphenylphosphine is a better \( \pi \)-acceptor than the chloride ion,\(^ {166}\) it competes more effectively with PF\(_2\)NEt\(_2\) for electrons than chloride ion does. This difference results in weaker bonding from the rhodium to the PF\(_2\)NEt\(_2\)
trans to the triphenylphosphine, and is reflected in a longer rhodium-phosphorus bond length in Rh-P(1) than in Rh-P(2) (trans to chloride). The magnitude of the difference is similar to that observed for metal-phosphorus bond distances in \( \text{mer-MCl}_3(\text{PPhMe}_2)_3 \)\(^{167} \) and in RhCl(\( \text{PPh}_3 \))\(^{165} \).

The distance Rh-P(3) [2.352(3)Å] is significantly longer than Rh-P(1) or Rh-P(2). This can be understood in terms of the smaller \( \pi \)-bonding ability of triphenylphosphine compared with the fluorophosphines.

The phosphorus-fluorine bond distances, P(1)-F(111) [1.546(7)Å] and P(2)-F(22) [1.550(7)Å] are considerably shorter than those found in the related free ligand PF\(_2\)NMe\(_2\) [1.610(4)Å by X-ray diffraction\(^\text{34} \) or 1.589(3)Å by electron diffraction\(^{168} \)]. This contraction of the phosphorus-fluorine bond by about 0.03Å is observed with other fluorophosphines on coordination.\(^{5,29,30,31} \) It arises from the delocalisation of the "lone-pair" of the phosphorus, this having a significant phosphorus-fluorine antibonding component.\(^{36} \) (see Chapter 1).

Surprisingly, the other pair of phosphorus-fluorine bonds, P(1)-F(12), [1.583(7)Å] and P(2)-F(21) [1.593(7)Å], are not markedly altered in length on coordination. The long bond lengths may be due to weak C-H...F interactions [C(212)-F(21), 3.31Å (intermolecular); C(112)-F(12), 3.41Å (intramolecular); C(222)-F(21), 3.24Å (intramolecular)].\(^{169} \) This is supported by the fact that the only ethyl group not involved in close approach to the fluorine atoms, F(12) and F(21), is disordered; the other groups are strictly as depicted in Figure 6.

As is found in other aminofluorophosphines\(^{34,157a} \) and the complex \( \text{H}_8\text{B}_4\text{PF}_2\text{NMe}_2 \),\(^{35} \) there is a planar arrangement of groups about the nitrogen atoms. This reflects the use of the nitrogen lone-pair in \( \pi \)-bond formation with the phosphorus.
The final feature to be noted in this structure is that there appears to be some axial rhodium-hydrogen interaction. The phenyl ring \( [C(301-306)] \) is almost co-planar with the rhodium atom and the rhodium-hydrogen \( [H(302)] \) distance is about 2.8Å (assuming C-H bond length is 1.1Å). 169

Other Reactions with Phosphorus and Arsenic Containing Ligands

Treatment of the dimer, \([\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2\) (17a), with an excess of triphenylarsine, yields the complex \(\text{cis-RhCl}(\text{AsPh}_3)(\text{PF}_2\text{NET}_2)_2\) (24b). This complex is similar to (24a) in its chemical and spectroscopic properties.

Treatment of complex \(\text{cis-RhCl}(\text{PPh}_3)(\text{PF}_2\text{NET}_2)_2\) (24a) with an excess of triphenylphosphine does not lead to the replacement of a \(\text{PF}_2\text{NET}_2\) ligand to form \(\text{trans-RhCl}(\text{PPh}_3)(\text{PF}_2\text{NET}_2)_2\) (23); instead complex (24a) can be recovered unchanged.

In contrast to \([\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2\) (17a), the corresponding dimers, \([\text{RhCl}(\text{PPh}_3)_2]_2\) and \([\text{RhCl}(\text{CO})_2]_2\), react with an excess of triphenylphosphine giving exclusively the complexes \(\text{trans-RhCl}(\text{PPh}_3)_2\text{L}\) (L = \(\text{PF}_3\), CO), through the intermediate formation of mixed dimers of the type \([\text{RhCl}(\text{PPh}_3)\text{L}]_2\).

The reaction of either \([\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2\) (17a) or \(\text{RhCl}(\text{PF}_2\text{NET}_2)_4\) (18a) with diphos, in benzene, results in the complete displacement of \(\text{PF}_2\text{NET}_2\), with the formation of the ionic complex, \([\text{Rh(diphos)}]_2\text{Cl}\). A similar reaction of \([\text{RhCl}(\text{PF}_3)_2]_2\) with diphos was noted in Chapter 2.

Mixed Complexes with \(\text{PF}_2\text{NET}_2\) and Carbon Monoxide

Reaction of equimolar proportions of \([\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2\) (17a) and \([\text{RhCl}(\text{CO})_2]_2\) (1a) results in a redistribution of coordinated ligands to give the mixed dimer, \([\text{RhCl}(\text{CO})(\text{PF}_2\text{NET}_2)]_2\); the most symmetrical
isomer is shown as (25). The crystalline complex is yellow, diamagnetic and soluble in all common organic solvents.

The IR spectrum of (25) shows strong absorptions in the \(\nu(C=O)\) region at 2029 and 2041 cm\(^{-1}\) (Nujol). The proton N.M.R. spectrum is given in Table 9. A parent molecular ion, \([\text{Rh}_2\text{Cl}_2(\text{PF}_2\text{NEt}_2)_2(\text{CO})_2]^+\), is seen in the mass spectrum, together with less intense peaks attributable to \([\text{Rh}_2\text{Cl}_2(\text{PF}_2\text{NEt}_2)_x(\text{CO})_{4-x}]^+(x = 4,3,1)\). No ions attributable to mononuclear rhodium(I) complexes were apparent.

The reaction of \([\text{RhCl}(\text{CO})_2\text{J}_2\) with four equivalents of \(\text{PF}_2\text{NEt}_2\) in \(n\)-pentane does not result in the cleavage of the chlorine bridges to give mononuclear species. Instead, essentially complete replacement of carbon monoxide occurs, affording the dimer, \([\text{RhCl}(\text{PF}_2\text{NEt}_2)\text{J}_2\) \(17a\).

Carbon monoxide rapidly reacts with \([\text{RhCl}(\text{PF}_2\text{NEt}_2)\text{J}_2\) both in the solid and in \(n\)-heptane to give a carbonyl containing material. The material very readily loses carbon monoxide and cannot be easily characterised.

Nixon \(^7\) has prepared a species, trans-RhCl(\(\text{PF}_2\text{NEt}_2\))\text{J}CO from the reaction of \(\text{PF}_2\text{NEt}_2\) with \([\text{RhCl}(\text{CO})_2\text{J}_2\), but this could not be confirmed in the present study.

**Spectroscopic Properties of Substituted Fluorophosphine Complexes of Rhodium(I)**

**Fluorine N.M.R. Spectra**

On coordination to rhodium(I) the chemical shifts of the fluorine resonances move downfield, as can be seen from Table 10. This is a characteristic of all coordinated substituted fluorophosphines. The separation between the pairs of doublets (mainly due to \(^1J_{PF}\)) decreases on coordination. This is also a feature of nearly all
fluorophosphine ligands on coordination. It suggests that in these complexes of the aminofluorophosphines, coordination is by the phosphorus lone-pair and not by the nitrogen.

**Infra-red Spectra**

Table 12 shows the IR spectra of the aminofluorophosphine ligands and their complexes in the region involving phosphorus-fluorine vibrations. Assignments of the vibrational modes are those suggested by Fleming and others for the methyl ligands. The ethyl ligand, PF₂NEt₂, is assigned similarly as there are apparently no skeletal vibrations involving the ethyl moiety in this region.

The salient features of the vibrational spectra of these complexes are that the vibrations due essentially to ν(P-F) move to a higher frequency on coordination. In contrast, the symmetric ν(N-P-F₂), ν(N₂-P-F) and δ(P-F) are shifted only slightly to higher frequencies on complexation.

The increase in frequency of ν(P-F) on coordination to rhodium(I) contrasts with the decrease in frequency when phosphorus trifluoride is complexed to rhodium(I). The coordination of aminofluorophosphines to molybdenum(O) and nickel(O) results in only small changes in frequency, whereas complexation to cobalt(II) gives a sharp increase over the free ligand value.

The shifts in frequencies in fluorophosphines (and in carbon monoxide) were partially discussed in Chapter 1. From the results presented above and in Chapter 2 it may be concluded that:

In cases where σ-donation to the metal is predominant there is an increase in stretching frequencies [i.e., in ν(P-F) and ν(C-O)] in the ligand on coordination. This is obviously the case with the
borane adducts of phosphorus trifluoride, carbon monoxide and PF$_2$NR$_2$, where $\pi$-bonding is very small (Table 2). This is also the case in higher oxidation state complexes where the positive charge on the metal increases $\sigma$-bonding but decreases $\pi$-bonding, as found in the phosphorus trifluoride complexes of rhodium(III) compared with rhodium(I) (Table 5). The PF$_2$NR$_2$ are better $\sigma$-donors and poorer $\pi$-acceptors than either PF$_3$ or CO and this is reflected in the increase in $\nu$(P-F) on complexation to rhodium(I). Similarly, an increase could be expected for cobalt(II)-PF$_2$NR$_2$ complexes. In nickel(0) or molybdenum(0) complexes, the effect of the strong $\pi$-bonding, which tends to decrease the $\nu$(P-F), cancels the $\sigma$-bonding effect, resulting in little or no change in $\nu$(P-F).

In summary, the factors which tend to increase the positive charge on the metal or tend to increase the $\sigma$-donating ability on the fluorophosphine, will increase the $\nu$(P-F). In contrast, factors which tend to increase the negative charge on the metal or tend to increase the $\pi$-accepting ability of the fluorophosphine, will decrease $\nu$(P-F). These results are entirely consistent with the bonding in fluorophosphine complexes described in Chapter 1.
### TABLE 12

**Infra-Red Spectra of Fluorophosphines and their Rhodium(I) Complexes Involving Phosphorus-Fluorine Vibrations.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(P-F)</th>
<th>$\nu$(N-P-F$_2$)</th>
<th>$\delta$(P-F$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF$_2$NEt$_2$</td>
<td>819(vs),768(vs)</td>
<td>682(m)</td>
<td>520(m),485(m)</td>
</tr>
<tr>
<td>PF$_2$NEt$_2$</td>
<td>796(vs,br),741(s)</td>
<td>687(m)</td>
<td>517(m),486(m)</td>
</tr>
<tr>
<td>[RhCl(PF$_2$NEt$_2$)$_2$]</td>
<td>852(m),818(vs,br),</td>
<td>701(m),</td>
<td>537(m),</td>
</tr>
<tr>
<td></td>
<td>794(s)</td>
<td>694(s)</td>
<td>521(s,br)</td>
</tr>
<tr>
<td>RhCl(PF$_2$NEt$_2$)$_4$</td>
<td>850(s,sh),820(vs,br)</td>
<td>685(vs)</td>
<td>519(vs),497(s,sh)</td>
</tr>
<tr>
<td>[RhCl(CO)(PF$_2$NEt$_2$)$_2$]</td>
<td>341(s),822(vs,br),</td>
<td>701(m),</td>
<td>546(w),</td>
</tr>
<tr>
<td></td>
<td>795(m)</td>
<td>693(vs)</td>
<td>533(m)</td>
</tr>
<tr>
<td>Rhacac(PF$_2$NEt$_2$)$_2$</td>
<td>850(s),820(vs),</td>
<td>704(s),</td>
<td>550(m,sh),</td>
</tr>
<tr>
<td></td>
<td>805(s,sh),794(s)</td>
<td>693(vs)</td>
<td>532(s)</td>
</tr>
<tr>
<td>Rh($\pi$-C$_5$H$_5$)(PF$_2$NEt$_2$)$_2$</td>
<td>832(s,sh),824(s),</td>
<td>700(m),</td>
<td>531(s,br),</td>
</tr>
<tr>
<td></td>
<td>796(vs,br),775(s)</td>
<td>689(s)</td>
<td>485(w,sh)</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_2$(PF$_2$NEt$_2$)</td>
<td>820(s),776(m)</td>
<td>-d</td>
<td>-d</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_2$(PF$_2$NEt$_2$)</td>
<td>837(s),827(s),</td>
<td>-d</td>
<td>-d</td>
</tr>
<tr>
<td></td>
<td>810(vs),786(m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PF$_2$NMe$_2$</td>
<td>814(s),770(s)</td>
<td>704(m)</td>
<td>501(m)</td>
</tr>
<tr>
<td>[RhCl(PF$_2$NMe$_2$)$_2$]</td>
<td>856(m),825(s),</td>
<td>716(s)</td>
<td>529(m),</td>
</tr>
<tr>
<td></td>
<td>807(s),783(m)</td>
<td></td>
<td>514(s)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$\nu$(N$_2$-P-F)</th>
<th>$\delta$(P-F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF(NMe$_2$)$_2$</td>
<td>742(s)</td>
<td>674(s)</td>
</tr>
<tr>
<td>PF(NMe$_2$)$_2$</td>
<td>728(s)</td>
<td>673(s)</td>
</tr>
<tr>
<td>RhCl[PF(NMe$_2$)$_2$]$_3$</td>
<td>775(m),768(m,sh)</td>
<td>679(m)</td>
</tr>
<tr>
<td>Rhacac[PF(NMe$_2$)$_2$]$_2$</td>
<td>780(m), -d</td>
<td>681(s)</td>
</tr>
</tbody>
</table>

---

*All spectra measured as Nujol mulls unless otherwise stated.*

*b* Gas phase (10 mm Hg, 10 cm path length).

*c* Liquid film.

*d* Partly or completely obscured by other ligand vibrations.
Experimental Section

Preparation of $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$ (17a)

The ligand, $\text{PF}_2\text{NEt}_2$ (0.25g, 1.8 mmole) was added to a stirred suspension of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (0.17g, 0.44 mmole) in n-pentane (8 ml), immediately affording a yellow solution with a vigorous effervescence of gas. After filtering, the solution was cooled to -78°. The resulting waxy yellow crystals were separated from the supernatant liquid by decanting and then dried in vacuo to yield 0.30g (0.36 mmole, 81%) of $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$ (17a) melting at 103-4°.

Using similar procedures the complex $[\text{RhCl}(\text{PF}_2\text{NEt}_2)_2]_2$ was prepared from $[\text{RhCl} (\text{CO})_2]_2$ instead of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (in 89% yield). The cyclooctene complex, $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_n$ was also employed. However, in the latter case the liberated free cyclooctene was removed from the crude product by evacuation (0.005 mmHg, 2 hours, RT). A pure product was obtained by recrystallisation from n-pentane (yield -73%), melting at 102-4°.

Found (%): C 22.67; H 5.20; N 6.30; P 14.86; Cl 8.61. 
C$_{16}$H$_{14}$Cl$_2$F$_2$N$_2$P$_2$Rh$_2$ requires: C 22.85; H 4.79; N 6.66; P 14.73; Cl 8.42. Molecular weight (mass spectrum) - 840 - 844 (calc. 841).

Preparation of $[\text{RhI}(\text{PF}_2\text{NEt}_2)_2]_2$ (17b)

A solution of $\text{PF}_2\text{NEt}_2$ (0.28g, 2.0 mmole) in iso-pentane (20 ml) was added to a stirred solution of $[\text{RhI}(\text{cod})]_2$ (0.34g, 0.5 mole) in iso-pentane (20 ml). Most of the solid quickly dissolved and the solution was filtered. On cooling the filtrate to -78°, a yellow solid precipitated and was isolated by decanting the supernatant liquid. The crude product was recrystallised firstly from n-pentane (30 ml) by cooling to -78° and then from iso-pentane (50 ml) at -5° to afford yellow needles. These were isolated by decanting the supernatant liquid and dried in vacuo (0.005 mm Hg, 2 hours, 26°) to afford 0.32g
(0.31 mmole, 63%) of [RhI(PF₂NEt₂)₂] (17b), melting at 87°.

Found (%): C 20.23; H 4.35; N 5.65; P 13.04.

C₁₆H₄₀F₈I₂N₄P₄Rh₂ requires: C 19.85; H 4.17; N 5.47; P 12.80.

Molecular weight (mass spectrum) - 1023 (calc. 1024).

Preparation of [RhCl(PF₂NMe₂)₂]₂-(14)

A solution of PF₂NMe₂ (0.23g, 2.0 mmole) in n-pentane (20 ml) was added to a solution of [RhCl(CO)]₂ (0.19g, 0.5 mmole) in n-pentane (25 ml), resulting in a vigorous evolution of gas and a pale yellow solution. On filtering and cooling to -78°, the solution afforded a pale yellow precipitate, which was collected by decanting the cooled supernatant liquid, and dried in vacuo (0.005 mm Hg, 1 hour, RT), to remove any unreacted ligand. The solid was dissolved in benzene (5 ml), the solution filtered and iso-pentane (50 ml) added to the filtrate. On cooling to -5°, fibrous yellow crystals were obtained. These were washed with iso-pentane (2 x 20 ml) and dried in vacuo (0.001 mm Hg, 1 hour, RT) to afford 0.31g (0.43 mmole, 86%) of [RhCl(PF₂NMe₂)₂]₂, melting at 112°.

Found (%): C 13.12; H 3.10; N 7.89; P 16.53; Cl 9.57.

C₁₈H₂₄Cl₂F₄N₄P₂Rh₂ requires: C 13.18; H 3.32; N 7.68; P 17.00; Cl 9.72.

Molecular weight (mass spectrum) - 728 - 732 (calc. 729).

Preparation of RhCl(PF₂NEt₂)₄-(18a)

An excess of PF₂NEt₂ (0.70g, 5.0 mmole) was added to a solution of [RhCl(PF₂NEt₂)₂] (0.42g, 0.50 mmole) in iso-pentane (20 ml). On cooling to -78°, yellow crystals slowly formed. These were isolated by decanting the cooled supernatant liquid and the resultant crude product was recrystallised three times from iso-pentane (20 ml) and dried in vacuo (0.005 mm Hg, 2 hours, 0°) to afford orange-yellow crystals of RhCl(PF₂NEt₂)₄ (18a) (0.29g, 0.41 mmole, 41%), which decomposed on melting at 28-9°.
On standing in vacuo at room temperature, complex (18a) loses phosphine to afford the dimeric \([\text{RhCl(PF}_2\text{NEt}_2])_2\) (17a) (m.p. 102-3°).

**Preparation of RhI(PF\(_2\)NEt\(_2\))\(_4\) (18b)**

An excess of PF\(_2\)Et\(_2\) (0.87 g, 6.2 mmole) in n-pentane (10 ml) was added to a stirred suspension of [RhI(cod)]\(_2\) (0.34 g, 0.5 mmole) in n-pentane (20 ml). The solid quickly dissolved, affording a cloudy orange solution, which was filtered. The filtrate was evaporated to dryness in a stream of nitrogen and the unreacted ligand and free 1,5-cyclooctadiene removed from the red tarry residue in vacuo (0.001 mm Hg, 5 hours, RT). n-Pentane (10 ml) was added to the product, the solution filtered and the filtrate cooled to -78°, slowly affording dark, orange-brown clusters of crystals. The supernatant liquid was decanted and the product dried in vacuo to give 0.38 g (0.48 mmole, 48%) of RhI(PF\(_2\)NEt\(_2\))\(_4\) (18b), melting with decomposition at 58°.

Found (%): C 24.63; H 5.24; N 6.82; P 15.69; I 15.23.

**RhI(PF\(_2\)NEt\(_2\))\(_4\):** C\(_{16}\)H\(_{40}\)F\(_8\)I\(_4\)N\(_4\)P\(_4\) Rh requires:

- C 24.20; H 5.08; N 7.05; P 15.60; I 15.98.
- C 22.07; H 4.63; N 6.43; P 14.73; I 19.43.

**Attempted Preparation of RhX(PF\(_2\)NEt\(_2\))\(_3\) (X = Cl, I)**

Reaction of [RhI(PF\(_2\)NEt\(_2\))\(_2\)]\(_2\) (17b) (0.51 g, 0.50 mmole) in n-pentane with PF\(_2\)NEt\(_2\) (0.41 g, 1.0 mmole) in n-pentane (5 ml) produced a darkening in the colour of the solution. On cooling to -78° a mixture of yellow and dark orange crystals resulted. The supernatant
liquid was discarded, and the residue dissolved in iso-pentane (20 ml). On cooling to -5°, yellow crystals were deposited and collected by decantation. A melting point of 86-87° indicated these were crystals of \([\text{RhI}(\text{PF}_2\text{NET}_2)_2]_2\). The supernatant liquid was cooled to -78° and after one day a mixture of yellow and orange crystals had formed. The supernatant liquid was decanted and further cooled to -78° for four days, after which time a small yield of orange-brown crystals of \(\text{RhI}(\text{PF}_2\text{NET}_2)_4\) (m.p. 56°) had formed. The complex \([\text{RhCl}(\text{PF}_2\text{NET}_2)_2]_2\) behaved similarly on reaction with \(\text{PF}_2\text{NET}_2\).

Preparation of \(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_4\) (19)

An excess of \(\text{PF}_2\text{NMMe}_2\) (0.43g, 3.8 mmole) in \(\pi\)-pentane (10 ml) was added to a solution of \([\text{RhCl(CO)}_2]_2\) (0.10g, 0.26 mmole) in \(\pi\)-pentane (10 ml) to afford a yellow solid on cooling to -78°. The supernatant liquid was decanted and benzene (1 ml), followed by iso-pentane (20 ml) was added to the solid. On cooling to -5° yellow crystals formed slowly. The product was collected and dried in vacuo (0.005 mm Hg, 1 hour, 0°) to afford 0.22g (0.37 mmole, 72%) of \(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_4\) (19).

Found (%): C 16.11; H 4.05; N 9.22; P 21.13; Cl 6.11.

\(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_4\): \(\text{C}_8\text{H}_{24}\text{ClF}_8\text{N}_4\text{P}_4\text{Rh}\) requires:

C 16.26; H 4.10; N 9.48; P 20.98; Cl 6.00.

\(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_3\): \(\text{C}_6\text{H}_{16}\text{ClF}_6\text{N}_3\text{P}_2\text{Rh}\) requires:

C 15.09; H 3.80; N 8.80; P 19.46; Cl 7.43.

Complex (19) melted at 79° in a sealed capillary under nitrogen without decomposition. However, when heated in an open tube (19) decomposed to \([\text{RhCl}(\text{PF}_2\text{NMMe}_2)_2]_2\) (mp. 112-113°).

Preparation of \(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_3\) (16)

A sample of \(\text{RhCl}(\text{PF}_2\text{NMMe}_2)_4\) (19) (0.31g, 0.52 mmole) was evacuated (0.005 mm Hg) at room temperature (27-30°) for twenty-seven
hours. After this time the yellow powder, \( \text{RhCl(PF}_2\text{NMe}_2)_3 \) (0.26 g, 0.54 mmole, 104%), remained.

**Found (%):**
- C 15.33; H 3.80; N 8.56; P 19.72; Cl 7.04.
- \( \text{C}_6\text{H}_{18}\text{ClF}_6\text{N}_3\text{P}_3\text{Rh} \) requires: C 15.09; H 3.80; N 8.80; P 19.46; Cl 7.43.

\( \text{RhCl(PF}_2\text{NMe}_2)_3 \), melted at 135-139° in a sealed capillary under nitrogen, but decomposed at about 45-50° to \( [\text{RhCl(PF}_2\text{NMe}_2)_2]_2 \) (m.p. 112°) in an open tube.

**Preparation of \( \text{RhCl}[\text{PF(NMe}_2)]_2_3 \) (20)**

A solution of \( \text{PF(NMe}_2)_2 \) (0.27 g, 2.4 mmole) in \( \text{n-pentane} \) (10 ml) was added to a stirred solution of \( [\text{RhCl(C}_8\text{H}_{14})_2]_n \) (0.12 g, 0.34 mmole) in \( \text{n-pentane} \) (10 ml). The solid quickly dissolved and the resulting yellow solution was filtered (under nitrogen). The filtrate was evaporated in a stream of nitrogen and any unreacted ligand removed in vacuo (0.001 mm Hg, 30 minutes, ca 25°). The oily residue was recrystallised from \( \text{n-pentane} \) (15 ml) by cooling to -78° to afford waxy yellow crystals, which were collected and dried in vacuo, yielding 0.16 g (0.29 mmole, 43%) of the exceedingly air-sensitive \( \text{RhCl}[\text{PF(NMe}_2)]_2_3 \) (20), melting at 92-94°.

**Found (%):**
- C 26.08; H 6.94; N 14.84; P 16.75; Cl 6.84.
- \( \text{C}_{12}\text{H}_{36}\text{ClF}_6\text{N}_3\text{P}_{13}\text{Rh} \) requires: C 26.01; H 6.57; N 15.20; P 16.81; Cl 6.42.

**Attempted Preparation of \( \text{[RhCl(PF(NMe}_2)]_2_2 \) (21)**

The ligand, \( \text{PF(NMe}_2)_2 \) (0.12 g, 1.1 mmole), was added to \( [\text{RhCl(C}_8\text{H}_{14})_2]_n \) (0.19 g, 0.53 mmole) in \( \text{n-pentane} \) (10 ml). The resultant yellow solution was worked up as in the previous preparation to afford waxy, yellow crystals. These had the same melting point (92-4°) and an elemental analysis expected for \( \text{RhCl}[\text{PF(NMe}_2)_2]_3 \) (20).

**Found (%):**
- C 25.84; H 6.81; N 14.69; P 16.91; Cl 6.70.

**Attempted Preparation of the Cationic Species \( \text{[Rh(PF}_2\text{NET}_2]_4}^+ \)**

**Conductimetric Titration of \( \text{[RhI(PF}_2\text{NET}_2)_2]_2 \) with \( \text{PF}_2\text{NET}_2 \)**

A solution of \( \text{PF}_2\text{NET}_2 \) (2.56 x 10^{-3} M) was titrated against
an aliquot (25 ml) of $[\text{RhI(PF}_2\text{NEt}_2]_2 \ (4.45 \times 10^{-4} \text{M})$ in nitrobenzene.

The conductivity of the solution rose only slightly over the value for pure nitrobenzene, even after 11.3 equivalents of PF$_2$NEt$_2$ had been added. The equivalent conductivity of the solution at a ratio $[\text{RhI(PF}_2\text{NEt}_2]_2 : \text{PF}_2\text{NEt}_2 = 1:4$ was $1.06 \text{ n}^{-1} \text{ cm}^{-1}$. This compares with an average value of $33 \text{ n}^{-1} \text{ cm}^{-1}$ found for 1:1 electrolytes in nitrobenzene.

Addition of Sodium Tetraphenylborate to RhI(PF$_2$NEt$_2$)$_2$-

A large excess of sodium tetraphenylborate (0.7 g) was added to a solution of RhI(PF$_2$NEt$_2$)$_4$ (0.16 g, 0.20 mmole) in methanol (10 ml). No precipitate was formed, even on cooling to 0°. Similar results were obtained in dichloromethane or acetone.

Preparation of Rhacac(PF$_2$NEt$_2$)$_2$-(21a)

From Rhacac(CO)$_2$-

A solution of Rhacac(CO)$_2$ (0.13 g, 0.50 mmole) in n-pentane (10 ml) was treated with PF$_2$NEt$_2$ (0.14 g, 1.0 mmole). When the vigorous effervescence of gas had ceased, the pale yellow solution was filtered and the filtrate cooled to -78°. After several days the supernatant liquid was decanted, and the resultant pale yellow crystals dried in vacuo (0.005 mm Hg, 2 hours, 0°) to give 0.20 g (0.41 mmole, 82%) of Rhacac(PF$_2$NEt$_2$)$_2$ (21a), melting at 14.5°.

The complex (21a) was also prepared from Rhacac(C$_8$H$_{14}$)$_2$ instead of Rhacac(CO)$_2$, by a similar method to the above (yield 47%).

From $[\text{RhCl(PF}_2\text{NEt}_2]_2 \ (0.34 g, 0.40 \text{ mmole})$ in tetrahydrofuran (25 ml) was stirred for one hour at room temperature with an excess of 2,4-pentanedionatothallium(1) (1.0 g, 3.3 mmole). The mixture was evaporated to dryness under reduced pressure (100 mm Hg)
and the residue extracted with n-pentane (3 x 10 ml). The combined extracts were evaporated to a small volume (ca 10 ml) in a stream of nitrogen. On cooling the solution to -78° pale yellow crystals of the product separated over several days. These were collected and dried in vacuo (0.01 mm Hg, 4 hours, 0°) to afford 0.26 g (0.54 mmole, 69%) of Rhacac(PF$_2$NEt$_2$)$_2$ (21a), melting at 14-15°.

Found (%): C 32.43; H 5.67; N 5.66; P 12.61.

Molecular weight (mass spectrum) - 484 (calc. 484).

**Preparation of Rhacac[PF(NMe$_2$)$_2$)$_2$ (21b)**

A solution of PF(NMe$_2$)$_2$ (0.14 g, 1.24 mmole) in n-pentane (3 ml) was added to Rhacac(C$_8$H$_{14}$)$_2$ (0.16 g, 0.50 mmole) in n-pentane (5 ml). The mixture was left for one hour, filtered under nitrogen and the filtrate reduced to a small volume (ca 3 ml) in a stream of nitrogen. The resultant solution was cooled to -78° to afford waxy yellow crystals, which were collected by decanting the supernatant liquid and drying in vacuo (0.05 mm Hg, 30 minutes, ca 26°). The yield of the exceedingly air-sensitive Rhacac[PF(NMe$_2$)$_2$]$_2$ was 0.11 g (0.23 mmole, 46%), melting at 86-7°.

Found (%): C 32.14; H 6.97; N 11.58; P 12.96.

C$_{13}$H$_{27}$F$_2$N$_2$O$_2$P$_2$Rh requires: C 32.25; H 5.67; N 5.75; P 12.79.

**Preparation of Rhacac[P(NMe$_2$)$_3$]$_2$ (21c)**

A solution of P(NMe$_2$)$_3$ (0.21 g, 1.29 mmole) in n-pentane (5 ml) was slowly added to Rhacac(CO)$_2$ (0.13 g, 0.50 mmole) in n-pentane (5 ml), resulting in a vigorous effervescence of gas. Diethyl ether (20 ml) was added to the solution, which was then cooled to -5°. Yellow crystals slowly separated and were collected by decanting the supernatant liquid. The crude product was recrystallised from diethyl ether (25 ml) and dried in vacuo (0.001 mm Hg, 4 hours, 0°) to afford
0.17g (0.32 mmole, 64%) of the lemon-yellow crystalline, Rhacac[P(NMe₂)₃]₂ (2lc), melting at 83-5°.

Found (%): C 38.33; H 8.09; N 16.14; P 11.28.

C₁₇H₁₄₅N₁O₁₆P₁₂Rh requires: C 38.64; H 8.20; N 15.90; P 11.72.

Molecular weight (mass spectrum) - 478 (calc. 478).

Preparation of Rh(π-C₅H₅)(PF₂NEt₂)₂ (22)

A solution of [RhCl(PF₂NEt₂)₂]₂ (0.41g, 0.49 mmole) in diethyl ether (20 ml) was stirred with an excess of cyclopentadienyl-thallium(I) (0.9g, 3.3 mmole) for one hour at 0°. The solvent was removed in a stream of nitrogen and the residue extracted with n-pentane (3 x 15 ml) to afford a deep yellow solution. This was concentrated in a stream of nitrogen to a small volume (ca 5 ml), which was then cooled to -78°. After about one week impure crystals of the product were obtained. These were collected and purified by sublimation (0.001 mm Hg, 90°) onto a -196° probe to yield 0.29g (0.64 mmole, 65%) of a golden orange oil, Rh(π-C₅H₅)(PF₂NEt₂)₂ which forms a glass on cooling to below -10°.

Found (%): C 34.93; H 5.86; N 6.41; P 13.38.

C₁₃H₂₅F₁₄N₂₁₂P₁₂Rh requires: C 34.68; H 5.60; N 6.22; P 13.76.

Molecular weight (mass spectrum) - 450 (calc. 450).

Preparation of trans-RhCl(PPh₃)₂PF₂NEt₂ (23)

A mixture of RhCl(PPh₃)₃ (0.38g, 0.41 mmole) and PF₂NEt₂ (0.05g, 0.36 mmole) in dichloromethane was left to stand for two hours, the solution slowly going yellow. n-Heptane (8 ml) was added and the mixture evaporated under reduced pressure to a small volume (ca 10 ml), affording a yellow powder. The solid was collected by filtration, washed with n-pentane (3 x 20 ml) and dried in vacuo to yield 0.21g (0.17 mmole, 41%) of trans-RhCl(PPh₃)₂PF₂NEt₂ (23), melting at 132-133° with decomposition.
Preparation of cis-RhCl(PPh₃)(PF₂NEt₂)₂ (24a)

From RhCl(PPh₃)₃

The reaction of an excess of PF₂NEt₂ (0.30g, 2.21 mmole) with RhCl(PPh₃)₃ (0.44g, 0.48 mmole) in dichloromethane (5 ml) immediately afforded a yellow solution. iso-Pentane (50 ml) was added and the solution cooled to -5°. After several days pale yellow prisms had formed and these were isolated by decanting the supernatant liquid. The product was washed with iso-pentane (2 x 20 ml) and dried in vacuo to afford 0.24g (0.35 mmole, 74%) of cis-RhCl(PPh₃)(PF₂NEt₂)₂ (24a), melting at 122-124° with decomposition.

From [RhCl(PF₂NEt₂)₂]₂ (17a)

Triphenylphosphine (0.16g, 0.61 mmole) dissolved in dichloromethane (3 ml), was added to a solution of [RhCl(PF₂NEt₂)₂]₂ (0.23g, 0.27 mmole) in n-pentane (25 ml). The mixture was filtered and left to stand overnight at -5° to afford pale yellow prisms. These were collected by decanting the supernatant liquid, washed with n-pentane (3 x 5 ml), and dried in vacuo to yield 0.31g (0.46 mmole, 85%) of cis-RhCl(PPh₃)(PF₂NEt₂)₂, melting at 123-125° with decomposition.

Preparation of cis-RhCl(AsPh₃)(PF₂NEt₂)₂ (24b)

An excess of triphenylarsine (0.51g, 1.7 mmole) in dichloromethane (3 ml) was added to [RhCl(PF₂NEt₂)₂]₂ (0.24g, 0.29 mmole) in n-heptane (60 ml). The reaction mixture was left for a week.
at -5° affording olive-yellow prisms. These were isolated by decanting the supernatant liquid, washed with n-pentane (2 x 10 ml) and dried in vacuo to afford 0.16g, (0.23 mmole, 39%) of cis-RhCl(AsPh₃)(PF₂NEt₂)₂, (24b) melting at 98°.

Found (%): C 42.56; H 4.96; N 3.83; P 8.22; Cl 5.22.
C₂₆H₃₅AsClF₅N₂P₂Rh requires: C 42.97; H 4.85; N 3.85; P 8.52; Cl 4.88.

Attempted Preparation of trans-RhCl(PPh₃)₂PF₂NEt₂ from cis-RhCl(PPh₃)(PF₂NEt₂)₂

A mixture of an excess of triphenylphosphine (1.0g, 3.8 mmole) and cis-RhCl(PPh₃)(PF₂NEt₂)₂ (0.20g, 0.31 mmole) in dichloromethane (15 ml) was left to stand two weeks at room temperature. After this time the mixture was filtered and iso-pentane (100 ml) was added to the filtrate. On cooling to -5° pale yellow crystals separated. These had identical IR and proton N.M.R. spectra to the starting material, cis-RhCl(PPh₃)(PF₂NEt₂)₂.

Reactions with 1,2-Bis(diphenylphosphino)ethane

An excess of diphos (1.0g, 2.5 mmole) in benzene (5 ml) was added to a solution of [RhCl(PF₂NEt₂)₂]₂ in benzene (5 ml) to immediately afford a yellow precipitate. The solid was collected by filtration, washed with benzene (3 x 10 ml) and then n-pentane (2 x 5 ml) to give 0.39g (0.42 mmole, 83%) of the complex, [Rh(diphos)₂]Cl, identical (IR spectrum and melting point) to that prepared by the method of Sacco.¹²² Under the above conditions, RhCl(PF₂NEt₂)₄ also gave [Rh(diphos)₂]Cl.

Preparation of [RhCl(CO)(PF₂NEt₂)₂]₂ (25)

A mixture of [RhCl(PF₂NEt₂)₂]₂ (0.21g, 0.25 mmole) and [RhCl(CO)₂]₂ (0.10g, 0.25 mmole) in n-pentane (10 ml) was cooled to -78° to afford yellow crystals. The supernatant liquid was discarded and the solid recrystallised from n-pentane (10 ml) to yield 0.24g
(0.39 mmole, 78%) of $[\text{RhCl}(\text{CO})(\text{PF}_2\text{NET})_2]_2$, melting at 49-50°.

**Found (%):**  
C 20.13; H 3.57; N 4.90; P 9.97; Cl 11.34.

**C$_{10}$H$_{20}$Cl$_2$F$_4$N$_2$O$_2$P$_2$Rh$_2$ requires:** C 19.53; H 3.27; N 4.55; P 10.07; Cl 11.53.

**Molecular weight (mass spectrum) - 614 - 618** (calc. 615).

**Attempted Preparation of trans-RhCl(CO)(PF$_2$NET)$_2$**

When PF$_2$NET$_2$ (0.28g, 2.0 mmole) was slowly added to $[\text{RhCl(CO)}_2]_2$ (0.19g, 0.50 mmole) in the absence of a solvent, a vigorous evolution of gas occurred, resulting in a yellow-brown oil. The oil was dissolved in n-pentane (15 ml), the solution filtered and the filtrate cooled to -5° to afford yellow crystals. The supernatant liquid was decanted, and the crystals dried in vacuo (0.001 mm Hg, 3 hours, 0°) to give a product melting at 96° with decomposition. The IR spectrum showed a weak band at $\nu$(C=O) = 2028 cm$^{-1}$. The mass spectrum was identical to that of a sample of $[\text{RhCl(PF}_2\text{NET})_2]_2$ (m.p. 103-104° with decomposition).

**Found (%):**  
C 23.00; H 5.17; N 6.45; P 14.17; Cl 8.77.

However, RhCl(CO)(PF$_2$NET)$_2$: C$_9$H$_{10}$Cl$_4$F$_4$ON$_2$P$_2$Rh requires:

C 24.09; H 4.49; N 6.24; P 13.81; Cl 7.90.

The supernatant liquid also showed only a weak $\nu$(C=O) at 2028 cm$^{-1}$.

If carbon monoxide is passed over solid $[\text{RhCl(PF}_2\text{NET})_2]_2$ it quickly reacts giving a semi-solid, dark yellow product. The IR spectrum of this substance shows the presence of carbonyl bands $\nu$(C=O) = 2084 (w,sh), 2030(vs,br), 1970(w,sh) cm$^{-1}$ (liquid film). On standing, or more quickly on evacuation the oil resolidifies, the $\nu$(C=O) bands disappear and $[\text{RhCl(PF}_2\text{NET})_2]_2$ is obtained (from m.p.).

If carbon monoxide is passed into a solution of $[\text{RhCl(PF}_2\text{NET})_2]_2$ in n-heptane, the solution quickly goes pale yellow and the IR spectrum
shows bands at $\nu(\text{C}=\text{O}) = 2112(\text{w}), 2095(\text{w}), 2040(\text{vs}), 2004(\text{m,sh})$ $1983(\text{m})\text{cm}^{-1}$.

On passing nitrogen through the solution the band $2112\text{ cm}^{-1}$ disappears within a minute and the others decrease in intensity. The bands at $2095\text{ cm}^{-1}$ and $1983\text{ cm}^{-1}$ disappear after 30 minutes and the band at $2040\text{ cm}^{-1}$ after several hours. The complexes formed were too unstable for characterisation.
CHAPTER 4

Preparation and Properties of Acetylenic Complexes of Rhodium(0)

Introduction

The transition metal catalysed polymerisation of acetylenes has stimulated a general expansion of interest in the unusual properties of these ligands. Acetylenes can act as polydentate ligands by coordinating to several metal centres simultaneously [for example, to four cobalt atoms in Co$_4$(CO)$_{10}$$(EtC≡CEt)$$_{176}$ (26; R = Et) or to three iron atoms in Fe$_3$(CO)$_9$(PhC≡CPh)$_{177}$ (27)]. They also possess the ability to insert into metal-carbon bonds; in the cyclopentadienone complex, Fe(CO)$_3$(C$_5$H$_4$O)$_{178}$ (28), two acetylene molecules have formally been inserted into a metal-carbon monoxide linkage, and in Co$_2$(CO)$_4$(HC$_2$Bu$^t$)$_2$(HC$_2$H)$_{179}$ (29) two molecules of HC$_2$Bu$^t$ have been inserted into a metal-acetylene linkage. The various modes of bonding that are open to acetylenes inevitably lead to a very diverse range of complexes with metal carbonyls.

Treatment of Co$_2$(CO)$_8$ with most acetylenes at room temperature results in the displacement of the bridging carbonyl groups and the formation of complexes of the type, Co$_2$(CO)$_6$(RC≡CR) (30). X-ray studies, have shown that the acetylenic unit is normal to and above the metal-metal bond, as shown in (30). It may be regarded as forming either two π-bonds, one to each cobalt atom, or that the acetylenic carbon atoms are essentially sp$^3$ hybridised and form σ-bonds, with each metal atom. The complex, Co$_2$(CO)$_6$(RC≡CR) (30), can react with more acetylene at higher temperatures to give complexes of the type, Co$_2$(CO)$_4$(RC≡CR)$_3$ (29), which have a bis-allyl "flyover" structure. These species are probably the intermediates in the Co$_2$(CO)$_8$ catalysed cyclotrimerisation of acetylenes,
as they can be decomposed to give substituted benzenes.

As $\text{Rh}_2(\text{CO})_8$ exists only under high pressures of carbon monoxide, little is known about the reaction of rhodium(0) carbonyls with acetylenes. The only derivative of $\text{Rh}_2(\text{CO})_8$ reported, is $\text{Rh}_2(\text{CO})_3(\text{PhC}≡\text{CPh})_2\text{PPh}_3$ (31), prepared by the reaction of $\text{Rh}_4(\text{CO})_{12}$ with diphenylacetylene and triphenylphosphine. The proposed structure is one in which the acetylenes are not linked together in a butadiene unit, but are merely coordinated, one to each rhodium atom. Rhodium carbonyl analogues of $\text{Co}_4(\text{CO})_{10}(\text{RC}≡\text{CR})$ (29) are also known.

The reaction of $\text{Rh}_2(\text{PF}_3)_8$ with acetylenes was of interest, therefore, as the rhodium carbonyl analogues of the cobalt complexes (29) and (30), are not readily accessible. In addition, the effect of ligands other than carbon monoxide on the properties of acetylene complexes has not been studied in detail.
Results and Discussion

1. Preparation and Properties of Monoacetylene Complexes

Diphenylacetylene and Rh$_2$(PF$_3$)$_8$ (4) react in refluxing n-hexane to afford a dark-red solution, from which the complex, Rh$_2$(PF$_3$)$_6$(PhC=CPH), may be isolated with difficulty by cooling the reaction mixture to -78°. A small amount of insoluble polymeric material is formed in the same reaction. The complex, Rh$_2$(PF$_3$)$_6$(PhC=CMe), may be prepared similarly from 1-phenylpropyne. Other acetylenes (e.g. PhC=CH, BuC=CH, MeC=CMe) also react with Rh$_2$(PF$_3$)$_8$ in refluxing n-hexane, with the formation of large amounts of polymeric material. If any acetylene complex is formed in the reaction it is too soluble in n-hexane at -78° to permit isolation.

However, if Rh$_2$(PF$_3$)$_8$ is heated (in a vacuum system) with an excess of the free acetylene in the absence of any solvent, complexes of the type, Rh$_2$(PF$_3$)$_6$(RC=CR'), are readily formed. They may be isolated by fractional sublimation if the acetylene is sufficiently volatile or less efficiently by recrystallisation from n- or iso-pentane at -78°.

These complexes are analogous to the cobalt carbonyl species, Co$_2$(CO)$_6$(RC=CR') (50), mentioned above. In all cases they are very volatile, diamagnetic substances, red to yellow in colour and very soluble in all common organic solvents. The acetylenes which form complexes of the type, Rh$_2$(PF$_3$)$_6$(RC=CR), are given in Table 13.

The mass spectra of the complexes, Rh$_2$(PF$_3$)$_6$(RC=CR'), are similar to those found for other phosphorus trifluoride complexes; there is consecutive loss of molecules of phosphorus trifluoride and loss of fluorine atoms. All complexes show metastable ions for the fragmentation,

\[ \text{[Rh}_2\text{(PF}_3\text{)}_{x}^+(\text{RC}=\text{CR}') + \text{PF}_3 \] (x = 1 to 6)
and often metastable transitions for,

\[
[\text{Rh}_2(\text{PF}_3)_y(\text{PF}_2)(\text{RC}=\text{CR}')]^+ \to [\text{Rh}_2(\text{PF}_3)_{y-1}(\text{PF}_2)(\text{RC}=\text{CR}')]^+ + \text{PF}_3
\]

(\(y = 1 \text{ to } 5\)).

As \(y\) decreases, ions of the type \([\text{Rh}_2(\text{PF}_3)_y(\text{PF}_2)(\text{RC}=\text{CR}')]^+\) become more predominant.

**TABLE 13**

Rhodium Complexes formed by Acetylenes

<table>
<thead>
<tr>
<th>(\text{Rh}_2(\text{PF}_3)_6(\text{RC}=\text{CR}'))</th>
<th>(\text{Rh}_2(\text{PF}_3)_5(\text{RC}=\text{CR}')_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PhC} = \text{CPh})</td>
<td>(\text{HC} = \text{CCO}_2\text{Me})</td>
</tr>
<tr>
<td>(\text{PhC} = \text{CMe})</td>
<td>(\text{MeO}_2\text{CC} = \text{CCO}_2\text{Me})</td>
</tr>
<tr>
<td>(\text{PhC} = \text{CCO}_2\text{Me})</td>
<td></td>
</tr>
<tr>
<td>(\text{PhC} = \text{CH})</td>
<td></td>
</tr>
<tr>
<td>(\text{MeC} = \text{CMe})</td>
<td></td>
</tr>
<tr>
<td>(\text{MeC} = \text{CCO}_2\text{Me})</td>
<td></td>
</tr>
<tr>
<td>(\text{Bu}^n\text{C} = \text{CH})</td>
<td></td>
</tr>
<tr>
<td>(\text{Bu}^t\text{C} = \text{CH})</td>
<td></td>
</tr>
<tr>
<td>(\text{CF}_3\text{C} = \text{CCF}_3)</td>
<td></td>
</tr>
<tr>
<td>(\text{HC} = \text{CH})</td>
<td></td>
</tr>
</tbody>
</table>

No mononuclear phosphorus trifluoride containing species are observed in any of the mass spectra. Fragmentation of \([\text{Rh}_2(\text{RC}=\text{CR}')]^+\) proceeds by a variety of pathways, depending upon the nature of the acetylene. Rhodium containing ions of the type \([\text{Rh}_2\text{C}_2\text{R}]^+\), \([\text{Rh}_2\text{CR}]^+\), \([\text{Rh}_2\text{R}]^+\), \([\text{RhC}_2\text{R}]^+\), and \([\text{RhR}]^+\) are common among the fragments derived from \([\text{Rh}_2(\text{RC}=\text{CR}')]^+\). The fragmentation pattern described above is found with all the monoacetylene complexes of the type, \(\text{Rh}_2(\text{PF}_3)_6(\text{RC}=\text{CR}'),\) in Table 13, and is summarised in Figure 7. It strongly suggests that all of the monoacetylene complexes have the same basic structure.
Figure 7

Mass Spectral Fragmentation Pattern of $\text{Rh}_2(\text{PF}_3)_6(\text{RC} \equiv \text{CR}^{'})$
### Table 14

**Proton N.M.R. Spectra of Acetylenes and Their Rhodium(O) Complexes**

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>Resonance</th>
<th>Acetylene&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rh&lt;sub&gt;2&lt;/sub&gt;(PF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;(RC≡CR')</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC≡CH</td>
<td>≡C-H</td>
<td>1.80(s)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.88(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.3 Hz</td>
</tr>
<tr>
<td>PhC≡CH</td>
<td>≡C-H</td>
<td>3.09(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.39(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.2 Hz</td>
</tr>
<tr>
<td>Bu&lt;sup&gt;n&lt;/sup&gt;C≡CH</td>
<td>≡C-H</td>
<td>1.99(s)</td>
<td>5.55(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.5 Hz</td>
</tr>
<tr>
<td></td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>2.21(m)</td>
<td>2.75(br,m)</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>1.50(m)</td>
<td>1.35(m)</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.94(m)</td>
<td>0.83(m)</td>
</tr>
<tr>
<td>Bu&lt;sup&gt;t&lt;/sup&gt;C≡CH</td>
<td>≡C-H</td>
<td>2.10(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.77(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.2 Hz</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.22(s)</td>
<td>1.19(s)</td>
</tr>
<tr>
<td>PhC≡CMe</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.74(s)</td>
<td>2.75(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.5 Hz</td>
</tr>
<tr>
<td>MeC≡CMe</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.70(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.83(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.0 Hz</td>
</tr>
<tr>
<td>MeC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.42(s)</td>
<td>2.73(hpt),&lt;sup&gt;d&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.5 Hz</td>
</tr>
<tr>
<td></td>
<td>-CO&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.41(s)</td>
<td>3.72(s)</td>
</tr>
<tr>
<td>PhC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>-CO&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.39(s)</td>
<td>3.57(s)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>HC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>≡C-H</td>
<td>2.56(s)</td>
<td>7.76(d), separation 3.3 Hz and 8.13(m)</td>
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<tr>
<td></td>
<td>-COCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.41(s)</td>
<td>3.30(s)</td>
</tr>
<tr>
<td>MeO&lt;sub&gt;2&lt;/sub&gt;C≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>-CO&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.56(s)</td>
<td>3.50(s)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Chemical shift in p.p.m. downfield from TMS. Measured in CD<sub>6</sub> unless otherwise stated. s = singlet, d = doublet, hpt = heptet, m = multiplet.


<sup>c</sup> Measured in CDCl<sub>3</sub>.  
<sup>d</sup> In CF<sub>3</sub>CICF<sub>3</sub>.  
<sup>e</sup> In CF<sub>2</sub>CICF<sub>3</sub>.  

---

TABLE 14

**Proton N.M.R. Spectra of Acetylenes and Their Rhodium(O) Complexes**

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<thead>
<tr>
<th>Acetylene</th>
<th>Resonance</th>
<th>Acetylene&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rh&lt;sub&gt;2&lt;/sub&gt;(PF&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;(RC≡CR')</th>
</tr>
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<tbody>
<tr>
<td>HC≡CH</td>
<td>≡C-H</td>
<td>1.80(s)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.88(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.3 Hz</td>
</tr>
<tr>
<td>PhC≡CH</td>
<td>≡C-H</td>
<td>3.09(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.39(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.2 Hz</td>
</tr>
<tr>
<td>Bu&lt;sup&gt;n&lt;/sup&gt;C≡CH</td>
<td>≡C-H</td>
<td>1.99(s)</td>
<td>5.55(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.5 Hz</td>
</tr>
<tr>
<td></td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>2.21(m)</td>
<td>2.75(br,m)</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;-</td>
<td>1.50(m)</td>
<td>1.35(m)</td>
</tr>
<tr>
<td></td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.94(m)</td>
<td>0.83(m)</td>
</tr>
<tr>
<td>Bu&lt;sup&gt;t&lt;/sup&gt;C≡CH</td>
<td>≡C-H</td>
<td>2.10(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5.77(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 7.2 Hz</td>
</tr>
<tr>
<td></td>
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<td>1.22(s)</td>
<td>1.19(s)</td>
</tr>
<tr>
<td>PhC≡CMe</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.74(s)</td>
<td>2.75(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.5 Hz</td>
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<td>MeC≡CMe</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.70(s)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.83(hpt),&lt;sup&gt;c&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.0 Hz</td>
</tr>
<tr>
<td>MeC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>≡C-C≡CH&lt;sub&gt;-&lt;/sub&gt;</td>
<td>1.42(s)</td>
<td>2.73(hpt),&lt;sup&gt;d&lt;/sup&gt; J&lt;sub&gt;HP&lt;/sub&gt; = 6.5 Hz</td>
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<td>3.72(s)</td>
</tr>
<tr>
<td>PhC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>-CO&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.39(s)</td>
<td>3.57(s)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>HC≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>≡C-H</td>
<td>2.56(s)</td>
<td>7.76(d), separation 3.3 Hz and 8.13(m)</td>
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<td></td>
<td>-COCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.41(s)</td>
<td>3.30(s)</td>
</tr>
<tr>
<td>MeO&lt;sub&gt;2&lt;/sub&gt;C≡CCO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>-CO&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.56(s)</td>
<td>3.50(s)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Chemical shift in p.p.m. downfield from TMS. Measured in CD<sub>6</sub> unless otherwise stated. s = singlet, d = doublet, hpt = heptet, m = multiplet.


<sup>c</sup> Measured in CDCl<sub>3</sub>.  
<sup>d</sup> In CF<sub>3</sub>CICF<sub>3</sub>.  
<sup>e</sup> In CF<sub>2</sub>CICF<sub>3</sub>.
The proton N.M.R. spectra of Rh₂(PF₃)₆(RC=CR') and of the free acetylenes are given in Table 14. On coordination, protons of the type =C-H or =C-C-H are deshielded. Two of the factors affecting the chemical shifts of these protons are the (diamagnetic anisotropic) effect of the unsaturated linkage and the shielding effect of the metal orbitals. On coordination, the hybridisation of the acetylenic carbon atoms approaches sp². This change in hybridisation and consequent alteration in bond angles places the protons in a deshielding environment with respect to the acetylene bond. The =C-H chemical shift in the vinyl region is consistent with the coordinated acetylene having double bond character. As the shift on complexation is downfield, the shielding contribution made by the metal d orbitals is small.

An important feature of the =C-H and =C-C-H protons is that they are split into symmetrical septets (although in some spectra the outermost pair of lines is not discernible). This splitting is assigned to coupling of the protons to the ³¹P nuclei of the six phosphorus trifluoride groups. It strongly suggests that these groups are symmetrically distributed in the molecule, with respect to the acetylenic unit. The magnitude of these couplings varies markedly with stereochemistry in similar acetylene complexes.

The room temperature ¹⁹F N.M.R. spectrum of Rh₂(PF₃)₆(RC=CR') consists of a widely spaced doublet (mainly due to ¹JPF). The chemical shift and separation of this doublet is given for the various acetylenes in Table 15. The magnitude of the coupling does not vary greatly with the nature of the acetylene, and is comparable with that found for ¹JPF in free phosphorus trifluoride. Each half of the doublet is quite broad (up to 80 Hz at half peak height) probably owing to the complexity of the spin system. As there is only one doublet observed, the coordinated phosphorus trifluoride ligands are apparently in magnetically
### TABLE 15

F N.M.R. Spectra of Acetylene Complexes above Their Coalescence Temperatures

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>δ</th>
<th>&quot;J&quot;&lt;sub&gt;PF&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Solvent</th>
</tr>
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<tbody>
<tr>
<td>PhC≡CCO₂Me</td>
<td>+8.9</td>
<td>1428</td>
<td>C₆H₆</td>
</tr>
<tr>
<td>PhC≡CMe</td>
<td>+8.7</td>
<td>1410</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td>MeC≡CCO₂Me</td>
<td>+8.7</td>
<td>1404</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td>PhC≡CPh</td>
<td>+8.5</td>
<td>1415</td>
<td>Et₂O:C₆F₅Br:CFC₁₃ (3:3:1)</td>
</tr>
<tr>
<td>CF₅C≡CCF₃&lt;sup&gt;c&lt;/sup&gt;</td>
<td>+7.5</td>
<td>1417</td>
<td>CF₂Cl₂</td>
</tr>
<tr>
<td>BuⁿC≡CH</td>
<td>+6.6</td>
<td>1401</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td>BuᵗC≡CH</td>
<td>+3.5</td>
<td>1397</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td>Rh₂(PF₅)₆(RC≡CR')&lt;sub&gt;2&lt;/sub&gt;:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC≡CCO₂Me</td>
<td>+10.3&lt;sup&gt;d&lt;/sup&gt; (2)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1361</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td></td>
<td>+14.3 (3)</td>
<td>1412</td>
<td></td>
</tr>
<tr>
<td>MeO₂CC≡CCO₂Me</td>
<td>+13.4&lt;sup&gt;d&lt;/sup&gt; (2)</td>
<td>1349</td>
<td>CFC₁₃</td>
</tr>
<tr>
<td></td>
<td>+15.9 (3)</td>
<td>1416</td>
<td></td>
</tr>
</tbody>
</table>

---

a  Chemical shift in p.p.m. upfield from CFC₁₃.

b  Separation of doublet due to phosphorus-fluorine coupling (both $^1J_{PF}$ and $^3J_{PF}$) in Hz.

c  CF₃ resonance at +52.9 p.p.m.

d  Values of chemical shifts are only approximate as the resonances are partly obscured by the solvent resonance.

e  Relative intensity.
equivalent environments. As will be shown, the molecule is fluxional and only an "average environment" is observed in the $^{19}$F N.M.R. spectrum at room temperature.

The only structure consistent with all of the above data and giving every atom an inert gas configuration is that of a metal-metal bonded, binuclear species with a bridging acetylene ligand. This structure is similar to that of cobalt complexes of the type, $\text{Co}_2(\text{CO})_6(\text{RC}==\text{CR}')$, and has been confirmed by an X-ray study (vide infra).

Although structurally analogous there are some marked chemical differences between $\text{Rh}_2(\text{PF}_3)_6(\text{RC}==\text{CR}')$ and $\text{Co}_2(\text{CO})_6(\text{RC}==\text{CR}')$. The reaction of an excess of acetylene with $\text{Co}_2(\text{CO})_8$ at elevated temperatures affords $\text{Co}_2(\text{CO})_4(\text{RC}=\text{RCR})_3$. In contrast the reaction of $\text{Rh}_2(\text{PF}_3)_8$ with most acetylenes gave no isolable organometallic product, other than $\text{Rh}_2(\text{PF}_3)_6(\text{RC}==\text{CR}')$.

The rhodium complexes are active catalysts for the polymerisation of acetylenes. The polymers appear to be linear and have high molecular weights. With phenylacetylene ($\text{PhC}==\text{CH}$), a polymer with an average molecular weight between 2,000 and 10,000 is formed. This substance is a yellow-brown, amorphous solid, very soluble in benzene and chlorinated hydrocarbons but insoluble in aliphatic hydrocarbons. It is similar in properties to a "polyphenylacetylene" reported to be formed on refluxing phenylacetylene in chlorobenzene. Only in the polymerisation of acetylene itself was the formation of the cyclic trimer (i.e. benzene) noted; the major portion of the product appeared to be a high polymer. In contrast, polymerisation of acetylenes by complexes of the type, $\text{Co}_2(\text{CO})_6(\text{RC}==\text{CR}')$, affords predominantly the 1,2,4-trisubstituted benzene.
In the reaction with \( \text{Rh}_2(\text{PF}_3)_8 \), yields of the acetylenic complex vary greatly with the acetylene used and appear to be related to the amount of polymeric material formed. An excess of a disubstituted acetylene, such as \( \text{CF}_3\text{C} = \text{CCF}_3 \) or \( \text{MeC} = \text{CMe} \), reacts with \( \text{Rh}_2(\text{PF}_3)_8 \) quantitatively giving no isolable residue. Primary acetylenes (e.g. \( \text{PhC} = \text{CH} \), \( \text{Bu}^t\text{C} = \text{CH} \)) in excess, afford considerable quantities of polymeric material, and the complexes are not obtained in high yields.

The reaction of \( \text{Rh}_2(\text{PF}_3)_6(\text{PhC} = \text{CPh}) \) with triphenylphosphine or triphenylarsine affords burgundy coloured crystals of \( \text{Rh}_2(\text{PF}_3)_4(\text{MPh}_3)_2(\text{PhC} = \text{CPh}) \) (\( \text{M} = \text{P, As} \)). No complex containing only one triphenylphosphine could be prepared. This is in contrast to the cobalt system in which both \( \text{Co}_2(\text{CO})_4(\text{PPh}_3)_2(\text{PhC} = \text{CPh}) \) and \( \text{Co}_2(\text{CO})_6(\text{PPh}_3)(\text{PhC} = \text{CPh}) \) are known.

Crystal Structure of \( \text{Rh}_2(\text{PF}_3)_4(\text{PPh}_3)_2(\text{PhC} = \text{CPh}) \cdot \text{Et}_2\text{O} \)

The results of a preliminary X-ray analysis, kindly carried out by Dr P.O. Whimp, are shown in Figure 8, and the corresponding structure parameters at the present stage of refinement (\( R = 9.1\% \)) are given in Tables 16 and 17. The molecule has a distorted octahedral configuration about each rhodium atom, with the carbon-carbon bond of the acetylene normal to the metal-metal bond. Neglecting the orientation of the phenyl rings the molecule has approximately \( C_{2v} \) symmetry. The crystal contains one molecule of diethyl ether for each molecule of complex.

The rhodium-rhodium interatomic distance \( [2.741(2)\text{Å}] \) is comparable with that found in other polynuclear rhodium(0) complexes containing bridging groups. \(^{192,193}\) A shorter value of \( 2.46 \text{Å} \) for the cobalt-cobalt distance in \( \text{Co}_2(\text{CO})_6(\text{PhC} = \text{CPh}) \) reflects the smaller atomic radius of cobalt compared with that of rhodium.
Molecular Structure of $\text{Rh}_2(\text{PF}_3)_4(\text{PPh}_3)_2(\text{PhC}=\text{CPh})$. 
## TABLE 16

Interatomic Distances in Rh₂\(_{2}(PF₃)₄(PPh₃)₂(PhC=CPh)\cdot Et₂O

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond Length(Å)</th>
<th>Atoms</th>
<th>Bond Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(_1)-Rh(_2)</td>
<td>2.74(2)</td>
<td>C(_1)-C(_2)</td>
<td>1.34(2)</td>
</tr>
<tr>
<td>Rh(<em>1)-P(</em>{10})</td>
<td>2.39(4)</td>
<td>P(<em>{11})-F(</em>{111})</td>
<td>1.57(2)</td>
</tr>
<tr>
<td>Rh(<em>2)-P(</em>{20})</td>
<td>2.39(4)</td>
<td>P(<em>{11})-F(</em>{112})</td>
<td>1.57(2)</td>
</tr>
<tr>
<td>Rh(<em>1)-P(</em>{11})</td>
<td>2.22(5)</td>
<td>P(<em>{11})-F(</em>{113})</td>
<td>1.51(2)</td>
</tr>
<tr>
<td>Rh(<em>1)-P(</em>{12})</td>
<td>2.21(5)</td>
<td>P(<em>{12})-F(</em>{121})</td>
<td>1.56(2)</td>
</tr>
<tr>
<td>Rh(<em>2)-P(</em>{21})</td>
<td>2.21(5)</td>
<td>P(<em>{12})-F(</em>{122})</td>
<td>1.54(1)</td>
</tr>
<tr>
<td>Rh(<em>2)-P(</em>{22})</td>
<td>2.22(5)</td>
<td>P(<em>{12})-F(</em>{123})</td>
<td>1.56(1)</td>
</tr>
<tr>
<td>Rh(_1)-C(_1)</td>
<td>2.11(2)</td>
<td>P(<em>{21})-F(</em>{211})</td>
<td>1.52(1)</td>
</tr>
<tr>
<td>Rh(_1)-C(_2)</td>
<td>2.11(2)</td>
<td>P(<em>{21})-F(</em>{213})</td>
<td>1.56(1)</td>
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<tr>
<td>Rh(_2)-C(_1)</td>
<td>2.15(2)</td>
<td>P(<em>{22})-F(</em>{221})</td>
<td>1.52(1)</td>
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<tr>
<td>Rh(_2)-C(_2)</td>
<td>2.09(2)</td>
<td>P(<em>{22})-F(</em>{223})</td>
<td>1.53(1)</td>
</tr>
</tbody>
</table>

*Subscripts refer to atoms as shown in Figure 8.*

The carbon-carbon bond length [1.34(2)Å] in the coordinated acetylene is substantially longer than that found in free acetylenes [1.20Å]. This is consistent with the change in hybridisation of the acetylenic carbon atoms to approximately sp\(^2\). Similar bond lengths have been found in other acetylene complexes; e.g. Co\(_2(CO)_6(PhC=CPh)\) - 1.37Å,\(^{195}\) Co\(_4(CO)_{10}(Ph₂PC=CCF₃)₂\) - 1.38Å and 1.37Å,\(^{181}\) Co\(_5(CO)_{15}C₃H\) - 1.34(2)Å,\(^{196}\) Co\(_8(CO)₂₄C₆\) - 1.37(3)Å,\(^{197}\) and Pt(PPh₃)\(_2(PhC=CPh)\) - 1.32(4)Å.\(^{198}\) It is also similar to the carbon-carbon bond length found in the "trans-bent" excited state of acetylene (1.39Å).\(^{199}\)
<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle(deg.)</th>
<th>Atoms</th>
<th>Angle(deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Rh}_1-\text{C}_1-\text{Rh}_2$</td>
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<td>$\text{Rh}_1-\text{Rh}<em>2-\text{P}</em>{20}$</td>
<td>148.5(1)</td>
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<tr>
<td>$\text{Rh}_1-\text{C}_2-\text{Rh}_2$</td>
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<td>$\text{Rh}_1-\text{Rh}<em>2-\text{P}</em>{21}$</td>
<td>101.2(1)</td>
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<td>$\text{Rh}_1-\text{C}<em>1-\text{C}</em>{21}$</td>
<td>141(1)</td>
<td>$\text{Rh}_2-\text{Rh}<em>1-\text{P}</em>{10}$</td>
<td>149.0(1)</td>
</tr>
<tr>
<td>$\text{C}_2-\text{C}<em>1-\text{C}</em>{11}$</td>
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<td>$\text{Rh}_2-\text{Rh}<em>1-\text{P}</em>{11}$</td>
<td>108.2(1)</td>
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<tr>
<td>$\text{F}<em>{111}-\text{P}</em>{11}-\text{F}_{112}$</td>
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<td>$\text{P}_{11}-\text{Rh}<em>1-\text{P}</em>{12}$</td>
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<tr>
<td>$\text{F}<em>{112}-\text{P}</em>{11}-\text{F}_{113}$</td>
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<td></td>
<td></td>
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<tr>
<td>$\text{F}<em>{111}-\text{P}</em>{11}-\text{F}_{113}$</td>
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<td>$\text{P}_{12}-\text{Rh}<em>1-\text{P}</em>{10}$</td>
<td>95.4</td>
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<td>$\text{P}_{11}-\text{Rh}<em>1-\text{P}</em>{10}$</td>
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<td>$\text{F}<em>{122}-\text{P}</em>{12}-\text{F}_{123}$</td>
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<td>$\text{P}_{21}-\text{Rh}<em>1-\text{P}</em>{22}$</td>
<td>98.0</td>
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<td>$\text{F}<em>{121}-\text{P}</em>{12}-\text{F}_{123}$</td>
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<td>$\text{P}_{22}-\text{Rh}<em>2-\text{P}</em>{20}$</td>
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<td>$\text{P}_{21}-\text{Rh}<em>2-\text{P}</em>{20}$</td>
<td>96.6</td>
</tr>
<tr>
<td>$\text{F}<em>{212}-\text{P}</em>{21}-\text{F}_{213}$</td>
<td>93.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{F}<em>{211}-\text{P}</em>{21}-\text{F}_{213}$</td>
<td>96.3</td>
<td></td>
<td></td>
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<tr>
<td>$\text{F}<em>{221}-\text{P}</em>{22}-\text{F}_{222}$</td>
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<tr>
<td>$\text{F}<em>{222}-\text{P}</em>{22}-\text{F}_{223}$</td>
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<td></td>
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<tr>
<td>$\text{F}<em>{221}-\text{P}</em>{22}-\text{F}_{223}$</td>
<td>95.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Subscripts refer to atoms as shown in Figure 8.

b The e.s.d.'s have not been calculated for these angles.
The tendency towards sp\textsuperscript{2} hybridisation of the acetylenic carbon atoms is also evidenced by the bending (by 39°) of the phenyl rings of the diphenylacetylene away from the remainder of the molecule. A deviation from linearity of this magnitude is noted on other acetylenes on complexation,\textsuperscript{195,196,197,198} or on electronic excitation.\textsuperscript{199}

The structure in Figure 8 shows the triphenylphosphine moieties occupying coordination positions on the same side of the rhodium-rhodium bond as the diphenylacetylene. This may be seen more clearly from the Newman projection in Figure 9a (the molecule is viewed along the Rh-Rh bond). A similar stereochemistry is found in the phosphinoacetylene complex, Co\textsubscript{4}(CO)\textsubscript{10}(Ph\textsubscript{2}PC=CCF\textsubscript{3})\textsubscript{2}.\textsuperscript{181}

The distance between the rhodium atoms and the phosphorus atoms of the triphenylphosphines is significantly longer \([2.394(4) \text{ and } 2.388(4)\AA]\) than that between the rhodium atoms and the phosphorus trifluoride groups \([2.208(5) \text{ to } 2.224(5)\AA]\). This is indicative of the increased \(\pi\)-bonding ability of the fluorophosphines over that of triphenylphosphine, and was also noted in the crystal structure of cis-RhCl(PPh\textsubscript{3})(PF\textsubscript{2}NEt\textsubscript{2})\textsubscript{2}, in Chapter 3. A similar contraction has been observed in metal-carbon bond lengths in the metal-fluoroalkyls relative to the metal-alkyls.\textsuperscript{200}

The phosphorus-fluorine bond distance varies from 1.513\AA{} to 1.567\AA{} [average 1.543(6)\AA{}]. This represents a significant decrease over the free ligand value and is noted in all other complexes of the fluorophosphines (Table 1). It is due to a decrease in the phosphorus-fluorine antibonding component on coordination of the "lone-pair" orbital (see Chapter 1).

The fluorine-phosphorus-fluorine bond angles vary from 92.7° to 97.6° [average 95.2(4)°]. The average value represents a contraction
Newman Projections along Rh–Rh Bond
over the free ligand value \[97.8(2)^\circ\]. There is almost invariably an increase in this bond angle on coordination in other complexes (Table 1). The only other example of a decrease on coordination is in HCo(PF₃)₄. The e.s.d.'s are high at the present stage of refinement, and so no comment is made about this apparent anomaly [R = 11% for HCo(PF₃)₄, 9.1% for Rh₂(PF₃)₄(PPh₃)₂(PhC=CPhe₂O)].

Preparation and Properties of Bisacetylene Complexes

When an excess of MeO₂CC=CCO₂Me is condensed onto a solid sample of Rh₂(PF₃)₈ in a vacuum system and the mixture warmed slightly (ca 40°) a violent explosion invariably occurs. If the reaction is performed at a lower temperature (ca 20°) phosphorus trifluoride is evolved. On removal of the excess of acetylene by prolonged evacuation at room temperature a red solid remains. The only other acetylene which behaves similarly is HC=CCO₂Me; the carboxymethyl acetylenes, MeC=CCO₂Me and PhC=CCO₂Me, behave normally to give Rh₂(PF₃)₆(RC=CR₂)₂ (R = Me,Ph).

These red, diamagnetic complexes are soluble in all common organic solvents. In the absence of the free acetylene they are volatile and quite stable substances (decomposing only above 200°). However, they catalyse the polymerisation of the free acetylene with explosive violence.

The mass spectra of these two complexes show parent molecular ions attributable to the species, \([\text{Rh}_2(\text{PF}_3)_5(\text{RC}_2\text{CO}_2\text{Me})_2]^+ (R = \text{H,MeO}_2\text{C})\). As was also found in the monoacetylene complexes, Rh₂(PF₃)₆(RC=CR₂)₂, these complexes lose phosphorus trifluoride consecutively to give the ions, \([\text{Rh}_2(\text{RC}_2\text{CO}_2\text{Me})_2]^+\). Ions of the type, \([\text{Rh}_2(\text{PF}_3)_y\text{PF}_2(\text{RC}_2\text{CO}_2\text{Me})_2]^+\), arising from loss of fluorine atoms are also observed. The species, \([\text{Rh}_2(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})_2]^+\) fragments by loss of CO₂CH₂ units until \([\text{Rh}_2\text{C}_4\text{H}_4]^+\) is obtained. This in turn, loses a rhodium atom presumably giving the
rhodiacyclopentadiene ion, \([\text{RhC}_4\text{H}_4]^+\), and then only small fragments are formed. The species, \([\text{Rh}^2(\text{HC}_2\text{CO}_2\text{Me})_2]^-\), fragments similarly.

The \(^{19}\text{F}\) N.M.R. spectra of these complexes are very similar. Each consists of a pair of doublets (phosphorus-fluorine coupling) in the ratio of 2:3 (see Table 15). The phosphorus trifluoride groups are, therefore, in two different environments.

The only structure consistent with the above data and giving all atoms an inert gas configuration is shown in Figure 10. The complex contains a rhodiacyclopentadiene ring, to which the second rhodium atom is bound both by a metal-metal bond and by two \(\pi\)-olefinic bonds. As two different ring proton resonances are observed in the proton N.M.R. spectrum of \(\text{Rh}_2(\text{PF}_3)_5(\text{HC}_2\text{CO}_2\text{Me})_2\) (Table 14) the acetylene units are probably joined "head-to-tail" as shown in Figure 10.

Although crystals of both complexes may be grown, they disintegrate in the X-ray beam.

Iron complexes of the type \(\text{Fe}_2(\text{CO})_6(\text{RC}_2\text{R})_2\) (32) are well known and very stable systems which can be obtained from a variety of routes. The structures of the iron complexes, are very similar to those suggested for the rhodium bisacetylene complexes. A corresponding osmium complex is also known. Several rhodiacyclopentadiene-containing systems have been reported: \(\text{RhCl(C}_8\text{F}_8)\text{(SbPh}_3\text{)}_2\) from \(\text{CF}_3\text{C} = \text{CCF}_3\) and \(\text{RhCl(SbPh}_3\text{)}_3\), \(\text{RhCl(AsPh}_3\text{)}_2(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})_2\), and others. The complex, \(\text{Rh}_2(\text{CO})_3(\text{PPPh}_3)(\text{PhC}_2\text{Ph})_2\), reported by Iwashita and co-workers, to contain two separate acetylene moieties, may instead be structurally similar to the complexes reported in the present study.

These complexes are of considerable interest as similar structures have been proposed as intermediates in the cyclotrimerisation
Figure 10

\[ R = H \text{ or } CO_2Me, \quad R' = CO_2Me \]

Proposed Structure of \( Rh_2(PF_3)_5(\text{RC}_2\text{R'})_2 \)
of acetylenes. When a binuclear catalyst such as \( \text{Co}_2(\text{CO})_8 \) is used the first intermediate is probably stereochemically similar to \( \text{Rh}_2(\text{PF}_3)_6(\text{RC}_2\text{R}) \). The second intermediate contains a metallocyclopentadiene system, as found in \( \text{Rh}_2(\text{PF}_3)_5(\text{RC}_2\text{C}_2\text{Me})_2 \), and the final intermediate is probably of the bis-allyl "flyover" type, found in \( \text{Co}_2(\text{CO})_4(\text{RC}_2\text{R})_3 \). On degradation or replacement the appropriately substituted benzene is obtained.
Stereochemical Non-rigidity

Introduction

In recent years, compounds with non-rigid molecular skeletons have attracted wide interest. All molecules possess some degree of non-rigidity by virtue of their vibrational modes. If the amplitudes of vibration due to thermal motion are sufficiently large then the molecule may pass from one stereoisomer into another (the various isomeric configurations are often equivalent and hence of equal energy). The inversion of ammonia and of cyclohexane are two well known examples of this phenomenon.

Much of the current interest in stereochemical non-rigidity has centered on five-coordinate phosphorus compounds, such as the fluorophosphoranes or organophosphates. Of the several alternative mechanisms for "pentatopal" isomerisations, only two are consistent with the large amount of experimental data. These are the Berry pseudorotation (BPR) and the turnstile rotation (TR), and are illustrated for the molecule, $\text{PF}_4\text{NET}_2$, in Figure 11.

Although both BPR and TR processes yield the same final product, there are differences between them. In the BPR there is a pairwise exchange of axial and equatorial groups with one of the latter not participating in the rearrangement, but instead, acting as a "pivot". The symmetry of the transition state is $C_{4v}$. In contrast to BPR, TR is a rearrangement by an actual internal rotation of groups. TR corresponds to one axial and one equatorial group rotating as a pair, and the remaining three groups rotating in unison in the opposite direction. The rotation resembles that of a turnstile, with a transition state of $C_5$ symmetry. As the transition states for the two processes are geometrically different, BPR and TR will have different energies of activation. In constrained systems, such as the
Two Possible Mechanisms for Pentatopic Rearrangements in Et$_2$NPF$_5$

Figure 11

a. Berry Pseudorotation

Et$_2$N – P 
\[ \right\] 
[ ] 
\[ \left\] 
\[ +\] 
Et$_2$N – P

b. Turnstile Rotation

Et$_2$N – P 
\[ \right\] 
[ ] 
\[ +\] 
Et$_2$N – P

or

Et$_2$N – P 
\[ \right\] 
[ ] 
\[ +\] 
Et$_2$N – P
fluorophosphoranes, \((\text{CH}_2)_4\text{PF}_3\) or \((\text{CH}_2\text{O})_2\text{PF}_3\), which contain four- or five-membered rings, the TR mechanism appears to be favoured. This is mainly due to the ring strain in the transition state of the BPR mechanism. In acyclic pentacoordinate systems both mechanisms are possible.\(^{215,216}\)

Unlike BPR, which is restricted to trigonal bipyramidal systems, TR mechanisms may be readily extended to other polytopal forms. The trigonal or "Bailar" twist involved in the racemisation of tris-chelate complexes is an example of a TR mechanism in a hexatopal system. The internal rotation of the cyclopentadienyl rings in metalloccenes is a decatopal TR process.

Stereochemical non-rigidity was not established in five- and six-coordinated transition metal complexes until quite recently,\(^{213,217}\) and since then there have been several studies involving phosphorus trifluoride complexes. The apparent equivalence of coordinated phosphorus trifluoride groups at room temperature in \(M(\text{PF}_3)_5\) (\(M = \text{Fe,Ru}\))\(^67\) and \(M_2(\text{PF}_3)_8\) (\(M = \text{Rh,Ir}\))\(^57,105\) has been demonstrated by \(^{19}\)F N.M.R. spectroscopy. Clark and co-workers\(^{217}\) have examined the variable temperature \(^{19}\)F N.M.R. spectrum of \(\text{CF}_3\text{Co(PF}_3\text{)(CO)}_3\) and have shown the presence of two distinct isomers at low temperatures. At room temperature the rapid interconversion of the two isomers results in an averaging of the N.M.R. parameters, so that the spectrum produced can be accounted for on the basis of one isomer.

Clark has shown that the complexes, \((\text{butadiene})\text{Fe(CO)}_x(\text{PF}_3)_3-x\) \((x = 0,1,2)\), are fluxional molecules.\(^{217a}\) At room temperature the \(^{19}\)F N.M.R. spectra show a time-averaged equivalence which is not present in the low temperature limiting spectra. The suggested mechanism for the rapid intramolecular rearrangement is a turnstile rotation of the three phosphorus trifluoride groups about the iron-butadiene bond.
Very recently a different type of non-rigidity has been noted in the five-coordinate hydrides, $\text{HM(PF}_3\text{)}_4$ ($M = \text{Co,Rh,Ir}$) and $[\text{HM(PF}_3\text{)}_4]^-$ ($M = \text{Ru,Os}$). Both $^1\text{H}$ and $^{19}\text{F}$ N.M.R. studies indicate that the hydrogen atom tunnels the "tetrahedral" faces of the $\text{MP}_4$ substructure. A similar mechanism has been proposed for the non-rigidity of complexes of the type, $\text{H}_2\text{ML}_4$ ($M = \text{Fe,Ru; L = phosphine or phosphite}$).

Results and Discussion

At room temperature the $^{19}\text{F}$ N.M.R. spectra of the symmetrically substituted monoacetylene complexes of the type, $\text{Rh}_2(\text{PF}_3)_6(\text{RC} = \text{CR})$, exhibit only a single resonance (split into a doublet by phosphorus-fluorine coupling, Figure 12a). However, from a consideration of the (instantaneous) structure of the complexes (Figure 9b, $R = R'$) there are two magnetically inequivalent environments for the phosphorus trifluoride groups. Two different resonances in the ratio of 1:2 should be observed.

This disparity between observation and prediction may be interpreted in terms of a rapid intramolecular rearrangement of coordinated phosphorus trifluoride, or as a fast intermolecular exchange between coordinated phosphorus trifluoride and traces of free phosphorus trifluoride. Although the latter alternative has not yet been disproved, any exchange would have to proceed by a dissociative process; it has been shown in the related complex, $\text{Co}_2(\text{CO})_6(\text{PhC} = \text{CPh})$, that exchange between free and coordinated carbon monoxide has a half-time of 240 hours. This is very much slower than the N.M.R. time scale. In addition, the broadness of the peaks (due to interligand couplings) in the $^{19}\text{F}$ N.M.R. spectrum of $\text{Rh}_2(\text{PF}_3)_6(\text{PhC} = \text{CPh})$ is unaltered on saturating a benzene solution with phosphorus trifluoride.
Variable Temperature $^1\text{H}$ N.M.R. of $\text{Rh}_2(\text{PF}_3)_6\text{PhC}≡\text{CPh}$
Therefore, the possibility of rapid intermolecular exchange in these complexes is considered unlikely.

Another alternative is that the structure of \( \text{Rh}_2(\text{PF}_3)_6(\text{RC} = \text{CR}) \) in solution is not the same as that inferred from the crystal structure described earlier. This cannot be disproved but no alternative structure consistent with other physical data in solution can be proposed. It is concluded then, that the complex, \( \text{Rh}_2(\text{PF}_3)_6(\text{RC} = \text{CR}) \), is stereochemically non-rigid in solution.

On cooling a solution of \( \text{Rh}_2(\text{PF}_3)_6(\text{RC} = \text{CR}) \) the \( ^{19}\text{F N.M.R.} \) spectrum begins to broaden (Figure 12b) and eventually splits into a pair of doublets (Figure 12c). The phenomenon is reversible and the temperature at which each pair of peaks just coalesce \( (T_c) \) is very dependent upon the nature of the acetylenic substituents \( (R) \), as can be seen from Table 18.

That the low temperature limiting \( ^{19}\text{F N.M.R.} \) spectrum consists of two pairs of doublets of unequal intensity, is consistent with the instantaneous structure shown in Figure 9b. The fact that the spectrum collapses to a single doublet again on warming is good evidence for a rapid site exchange on the N.M.R. time scale at room temperature.

However, it must be noted that for the symmetrically disubstituted acetylenic complexes, the ratios observed [ca 2.8:1] are invariably higher than those predicted [2.0:1]. The only explanation for this is that the spin system is so complex, the resonances for the two types of coordinated phosphorus trifluoride are not resolved at any temperature. Approximately the same ratios are obtained on a variety of spectrometers at different frequencies. Simplification of the spectra by spin decoupling of the \( ^{31}\text{P} \) is not possible (if \( ^1J_{\text{PF}} \) is
TABLE 18

Low Temperature Limiting $^{19}$F N.M.R. Spectra of

$\text{Rh}_2(\text{PF}_3)_6(\text{RC} \equiv \text{CR}')$

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>$T_c$ (high)</th>
<th>$T_c$ (low)</th>
<th>$\delta$</th>
<th>$''J_{PF}''$</th>
<th>R.I.</th>
<th>Solvent</th>
</tr>
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<tbody>
<tr>
<td>$\text{HC} \equiv \text{CBu}_n$</td>
<td>-138°</td>
<td>-136°</td>
<td>A + 4.4</td>
<td>1400</td>
<td>$f$</td>
<td>$\text{CF}_3\text{Cl}:\text{CF}_2\text{Cl}_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B + 6.7</td>
<td>1415</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C + 7.1</td>
<td>1375</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{PhC} \equiv \text{CMe}$</td>
<td>-110°</td>
<td>-108°</td>
<td>A + 5.8</td>
<td>1388</td>
<td>1.1</td>
<td>$\text{CFCl}_3$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>B + 7.5</td>
<td>1403</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C +10.8</td>
<td>1359</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
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<td>-106°</td>
<td>A - 0.1</td>
<td>1378</td>
<td>$f$</td>
<td>$\text{CF}_2\text{Cl}_2$</td>
</tr>
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<td></td>
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<td></td>
<td>B + 3.5</td>
<td>1397</td>
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<tr>
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<td>C + 6.8</td>
<td>1392</td>
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<td>-107°</td>
<td>-104°</td>
<td>A + 7.2</td>
<td>1410</td>
<td>2.7</td>
<td>$\text{CFCl}_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B +11.2</td>
<td>1384</td>
<td>1.0</td>
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</tr>
<tr>
<td>$\text{PhC} \equiv \text{CPh}$</td>
<td>- 78°</td>
<td>- 74°</td>
<td>A + 6.6</td>
<td>1404</td>
<td>2.8</td>
<td>$\text{C}_6\text{F}_5\text{Br}:\text{CFCl}_3$</td>
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<td></td>
<td></td>
<td></td>
<td>B +11.1</td>
<td>1352</td>
<td>1.0</td>
<td>$\text{Et}_2\text{O} (3:1:3)$</td>
</tr>
<tr>
<td>$\text{CF}_3\text{C} \equiv \text{CCF}_3$</td>
<td>- 54°</td>
<td>- 54°</td>
<td>A + 6.4</td>
<td>1403</td>
<td>2.8</td>
<td>$\text{CFCl}_3:\text{CF}_2\text{Cl}_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B + 7.9</td>
<td>1360</td>
<td>1.0</td>
<td>(2:3)</td>
</tr>
</tbody>
</table>

---

a Coalescence temperatures for highfield and lowfield halves of spectrum.
b Chemical shift of each doublet in p.p.m. upfield from $\text{CFCl}_3$.
c Separation of each doublet due to phosphorus-fluorine coupling (in Hz).
d Relative intensity.
e Resonance at lowest field - A, B and C are the resonances at progressively higher fields.
f Spectrum not sufficiently well resolved to measure relative intensities.
Figure 13

Variable Temperature $^{19}$F N.M.R. of $\text{Rh}_2(\text{PF}_3)_6\text{PhC}≡\text{CMe}$
1400 Hz then the $^{31}$P resonance is spread over 5 KHz, which is too broad for decoupling with sufficient power.\textsuperscript{218a}

In the complexes containing unsymmetrically substituted acetylenes, $\text{Rh}_2(\text{PF}_3)_6(\text{RC} \equiv \text{CR'})$, the room temperature $^{19}$F N.M.R. spectrum consists of a single doublet. On cooling, the spectrum again broadens, but at still lower temperatures each half of the doublet is split into three, as can be seen in Figure 13. The $^{19}$F N.M.R. spectral parameters of the three doublets are given in Table 18. As with the symmetrically substituted acetylene complexes, the spectrum of $\text{Rh}_2(\text{PF}_3)_6(\text{RC} \equiv \text{CR'})$ reverts to a doublet on warming.

The presence of three different environments for the coordinated phosphorus trifluoride ligands in $\text{Rh}_2(\text{PF}_3)_6(\text{RC} \equiv \text{CR'})$ is, therefore, indicated by the low temperature limiting spectrum. This is entirely consistent with predictions (see Figure 9b; $\text{R} \neq \text{R'}$). In the cases where the three resonances are sufficiently well resolved, the relative ratios are close to the expected 1:1:1.

The differences between the symmetrically and unsymmetrically substituted acetylenic complexes confirm that the origin of the stereochemical non-rigidity lies in the intermolecular exchange between the three phosphorus trifluoride groups coordinated to each rhodium atom.

The coalescence temperatures ($T_c$), which are directly related to the activation energy for the rearrangement process,\textsuperscript{219} vary markedly with the nature of the substituent on the acetylene (Table 18). However, the nature of the variation cannot be readily correlated with the electronic properties of the substituent (e.g. Taft or Hammett constants), nor does it appear to be solely related to the steric requirements of the substituent. A systematic examination of a closely
Proposed Mechanism for Site Exchange in

$$\text{Rh}_2(PF_3)_2(RC=CR')$$
related series of acetylene complexes is needed (e.g. of a series a para-disubstituted diphenylacetylene complexes).

The dependence of the nature of the acetylene on the rate of site exchange implies that the rhodium-acetylene linkage is intimately concerned with the exchange of the phosphorus trifluoride groups. A mechanism (shown in Figure 14) consistent with this observation is a rotation of the coordinated acetylene about the rhodium-rhodium bond with the acetylene always remaining at right angles to the bond. This is similar to the proposed exchange noted in Fe(CO)$_x$(PF$_3$)$_{3-x}$(C$_6$H$_4$) by Clark, and is in effect the "turnstile rotation" mechanism described earlier, but involving a concerted rotation of both -Rh(PF$_3$)$_3$ moieties with respect to a stationary acetylene.

Experimental observations involving the non-rigidity in fluorophosphoranes and related molecules have been usually explained in terms of a Berry pseudorotation. However, recently it has been shown that the observations fit a turnstile rotation equally well. It is very difficult to picture a Berry pseudorotation occurring about each rhodium atom in Rh$_2$(PF$_3$)$_6$(RC=CR'). Moreover, such a mechanism is unrealistic in this case as the coordination sphere of each rhodium atom departs significantly from the idealised trigonal bipyramid on which the Berry pseudorotation mechanism is based.

The $^{19}$F N.M.R. spectra of the two complexes of the type Rh$_2$(PF$_3$)$_5$(RC$_2$R)$_2$ exhibit two pairs of doublets (ratio 2:3) at room temperature (Figure 15a). On cooling, however, the doublet of relative intensity = 3 broadens and eventually splits into two doublets of relative intensities = 2:1 (Figure 15b and 15c). The coalescence temperatures are very similar in the two complexes, Rh$_2$(PF$_3$)$_5$(HC$_2$CO$_2$Me)$_2$ [$T_c = -49^\circ$] and Rh$_2$(PF$_3$)$_5$(MeOCC$_2$CO$_2$Me)$_2$ [$T_c = -54^\circ$, both for the high-field halves of the spectra]. The lowfield halves of the spectra are
obscured by the CFC$_3$ resonances and so chemical shifts and separations have not been determined.

The observed $^{19}$F N.M.R. spectra support the structure proposed in Figure 10. There are two magnetically inequivalent sites for the phosphorus trifluoride groups in the Rh(PF$_3$)$_3$ moiety. However, the $^{19}$F N.M.R. results do not distinguish between the two possible orientations for the Rh(PF$_3$)$_3$ moiety. The unique phosphorus trifluoride may be on the same side of the RhC$_4$ plane as the other rhodium atom, or it may be on the opposite side. In the structurally similar iron system, Fe$_2$(CO)$_6$[C$_4$Me$_2$(OH)$_2$]$_2$ (32), the unique carbon monoxide is on the side of the FeC$_4$ ring opposite to that of the other iron atom. 179

The mechanism of the rearrangement in Rh$_2$(PF$_3$)$_5$(RC$_2R'$)$_2$ almost certainly involves a turnstile rotation of the phosphorus trifluoride groups about the rhodium atom in the ring.

The room temperature $^{19}$F N.M.R. spectrum of Rh$_2$(PF$_3$)$_8$ consists of a pair of broad peaks (Figure 16). This suggests that the molecule is fluxional as the coordinated phosphorus trifluoride groups are not magnetically equivalent if the coordination about each rhodium atom is trigonal bipyramidal. A similar spectrum has been observed with Ir$_2$(PF$_3$)$_8$. 57,215

On cooling the $^{19}$F N.M.R. spectrum of Rh$_2$(PF$_3$)$_8$ sharpens and three peaks are observed (in the ratio of 1:3.2:4.8) for the upfield half of the spectrum; the lowfield half is only partially resolved. It appears that the coalescence temperature is about room temperature, but as Rh$_2$(PF$_3$)$_8$ is thermally unstable in solution above +30° the high temperature limiting spectrum cannot be obtained.

The number and relative intensities of the highfield peaks at the low temperature limit are unusual. They are not those predicted for
Variable Temperature $^{19}$F N.M.R. Spectra of $\text{Rh}_2(\text{PF}_3)_3(\text{HC}_2\text{CO}_2\text{Me})_2$

(highfield halves only)
a trigonal bipyramidal stereochemistry (only two peaks in the ratio of 3:1 when the metal-metal bond is axial) nor those based on a square pyramid (all phosphorus trifluoride groups are equivalent with an axial metal-metal bond). The non-integral ratios, which are quite reproducible, may be a feature of the very large and complex spin system (34 nuclei with $I = 1/2$).
Variable Temperature $^{19}$F N.M.R. Spectra of $\text{Rh}_2(\text{PF}_3)_8$
Experimental Section

General

The starting material, \( \text{Rh}_2(\text{PF}_3)_8 \), was prepared by the method of Bennett and Patmore\(^{57} \) but in variable and often poor yields; (5% to 20% based on \( [\text{RhCl}(\text{PF}_3)_2]_2 \)). The two acetylenes \( \text{PhC} = \text{C} \text{CO}_2 \text{Me} \) and \( \text{MeC} = \text{C} \text{CO}_2 \text{Me} \) were synthesised from diazomethane and the corresponding acid. All other acetylenes were obtained commercially.

Preparation of \( \text{Rh}_2(\text{PF}_3)_6(\text{RC} = \text{CR}') \)

Diphenylacetylene \( (R = R' = \text{Ph}) \)

A solution of \( \text{Rh}_2(\text{PF}_3)_8 \) (0.20g) and diphenylacetylene (0.04g) in n-hexane (10 ml) was refluxed in an atmosphere of nitrogen for 15 minutes, during which time the mixture turned deep red. After cooling to room temperature, the solution was filtered and the filtrate cooled to -78\(^\circ\). Red plates slowly separated over several days. These were collected by decanting the cooled supernatant liquid and were recrystallised from iso-pentane (10 ml) to afford 0.11 (55%) of \( \text{Rh}_2(\text{PF}_3)_6(\text{PhC} = \text{CPh}) \) as carmine red crystals melting at 143-145\(^\circ\) (with partial sublimation in a sealed tube) and slowly decomposing at about 185\(^\circ\).

The mother liquors were evaporated to dryness, extracted with iso-pentane (5 ml). After filtering and cooling to -78\(^\circ\) a further 0.05g of impure product was obtained. This was purified by vacuum sublimation (0.005 mm hg, 120\(^\circ\)).

Found (%): C 18.22; H 1.22; P 20.28.

\( \text{C}_{14} \text{H}_{10} \text{F}_{18} \text{P}_{6} \text{Ph}_2 \) requires: C 18.44; H 1.11; P 20.38.

Molecular weight (mass spectrum) - 910 (calc. 910).

1-Phenylpropyne \( (R = \text{Ph}, R' = \text{Me}) \)

The complex was prepared as above but using 1-phenylpropyne (0.04g) instead of diphenylacetylene. Yield- 0.08g (43%) of an orange
powder, very soluble in all organic solvents and melting at 68°.

Found (%):  
C 12.96;  
H 1.13;  
P 21.79.

C₉₈F₁₈₀P₆Rh₂ requires:  
C 12.72;  
H 1.23;  
P 21.87.

Molecular weight (mass spectrum) - 849 (calc. 849).

2-Butyne (R = R' = Me)

An excess of 2-butyne (0.8 g) was partially vaporised in a high vacuum system. The gaseous acetylene (ca 500 mm pressure) was heated with solid Rh₂(PF₃)₈ (0.18 g), slowly increasing the temperature to 70°. During this time phosphorus trifluoride (IR spectrum) was evolved. When the reaction had ceased and no more gas was liberated, the excess of 2-butyne and the phosphorus trifluoride were removed from the reaction mixture and collected in a -196° trap. The solid was then sublimated at 0.005 mm Hg and room temperature into a -196° trap, leaving only a trace of buff coloured residue. The yield of orange sublimate was 0.15 g (97%), melting at 118°.

Found (%):  
C 6.36;  
H 0.87;  
P 23.44.

C₄₆F₁₈₀P₆Rh₂ requires:  
C 6.01;  
H 0.76;  
P 23.59.

Molecular weight (mass spectrum) - 787 (calc. 787).

Phenylacetylene (R = Ph, R' = H)

An excess of phenylacetylene was reacted with Rh₂(PF₃)₈ in a vacuum system in the manner described for the preparation of the 2-butyne complex, except that the acetylene was condensed onto the Rh₂(PF₃)₈ and the reaction temperature was 40°. A large amount of polymeric material was formed. A dark brown oil in 23% yield was obtained by vacuum sublimation at 80°.

Found (%):  
C 11.86;  
H 0.59;  
P 21.86.

C₈₆F₁₈₀P₆Rh₂ requires:  
C 11.50;  
H 0.72;  
P 22.24.

Molecular weight (mass spectrum) - 835 (calc. 835).
Acetylene (R = R' = H)

The complex Rh₂(PF₃)₆(HC≡CH) was prepared in a vacuum system (as above) with the reaction temperature about 60°. Yellow crystals, melting at 60-61° were obtained in 38% yield, together with a considerable quantity of polymeric material.

Found (%): C 3.47; H 0.47; P 24.26.

C₂H₂F₁₈P₆Rh₂ requires: C 3.16; H 0.27; P 24.46.

Molecular weight (mass spectrum) - 759 (calc. 759).

1-Hexyne (R = Bu, R' = H)

The complex was prepared as above, with a reaction temperature of about 45°. A brown oil was obtained in ca 40% yield by vacuum sublimation at 60°.

Molecular weight (mass spectrum) - 815 (calc. 815).

2,2-Dimethylbutyne (R = Bu, R' = H)

The reaction was performed as above, with the reaction temperature about 70°. An orange brown oily solid (m.p., ca 18°) was obtained in ca 60% yield by vacuum sublimation at 50°.

Molecular weight (mass spectrum) - 815 (calc. 815).

Perfluoro-2-butyne (R = R' = CF₃)

As above; reaction temperature was about 90°. Very volatile, yellow prisms of Rh₂(PF₃)₆(CF₃C≡CCF₃) were obtained in 100% yield by vacuum sublimation at room temperature.

Found (%): C 5.41; H nil; P 20.51.

C₄F₂₄P₆Rh₂ requires: C 5.36; H 0.00; P 20.75.

Methyl Tetrolate (R = Me, R' = CO₂Me)

As above; reaction temperature was about 80°. A volatile yellow oil was obtained and partially separated from the unreacted ligand by fractional sublimation (0.005 mm Hg) at room temperature.
The mixture was dissolved in iso-pentane, filtered and cooled to \(-78^\circ\), to afford yellow crystals of \(\text{Rh}_2(\text{PF}_3)_6(\text{MeC\equivC}CO_2\text{Me})\) in about 30% yield. Molecular weight (mass spectrum) - 831 (calc. 831).

**Methyl Phenylpropiolate \((R = \text{Ph}, R' = CO_2\text{Me})\)**

\(\text{Rh}_2(\text{PF}_3)_8\) (0.21g) and methyl phenylpropiolate (1.0g) were mixed in a test tube, which was then evacuated (0.005 mm Hg). On warming to 80° phosphorus trifluoride was evolved and a dark red oil produced. Extraction of this oil with iso-pentane (2 x 5 ml), then filtering and cooling to \(-78^\circ\) afforded orange crystals. A proton N.M.R. spectrum showed these crystals to be a mixture of \(\text{Rh}_2(\text{PF}_3)_6(\text{PhC\equivC}CO_2\text{Me})\) and the free ligand. Separation of the mixture by either fractional crystallisation or by fractional sublimation was unsuccessful. Molecular weight (mass spectrum) - 893 (calc. 893).

**Preparation of \(\text{Rh}_2(\text{PF}_3)_4(\text{PPh}_3)_2(\text{PhC\equivCPH})\)**

A sample of \(\text{Rh}_2(\text{PF}_3)_6(\text{PhC\equivCPH})\) (0.09) was dissolved in diethyl ether (5 ml) and triphenylphosphine (0.20g) was added to the solution, which was then filtered. After 30 minutes when the filtrate had turned dark red, it was cooled to \(-5^\circ\). Burgandy coloured crystals slowly separated over several days. These were collected and dried in vacuo to afford 0.06g (46%) of \(\text{Rh}_2(\text{PF}_3)_4(\text{PPh}_3)_2(\text{PhC\equivCPH})\cdot\text{Et}_2\text{O}\), melting at 164-165° with decomposition.

Found (%):  
C 48.80; H 3.78; P 13.28.

\(\text{C}_{50}^4\text{H}_{40}^2\text{F}_{12}^6\text{P}_{10}^2\text{Rh}_2\) requires:  
C 47.64; H 3.19; P 14.74.

\(\text{C}_{54}^4\text{H}_{50}^2\text{F}_{12}^6\text{OP}_{10}^2\text{Rh}_2\) requires:  
C 48.60; H 3.77; P 13.92.

**Preparation of \(\text{Rh}_2(\text{PF}_3)_4(\text{AsPh}_3)_2(\text{PhC\equivCPH})\)**

This was prepared in a similar manner to its triphenylphosphine analogue by using triphenylarsine, to afford deep red-purple crystals in 31% yield.
C_{50}H_{40}As_{2}F_{12}P_{4}Rh_{2} requires: C 44.21; H 2.97; P 9.12.
C_{54}H_{50}As_{2}F_{12}OP_{4}Rh_{2} requires: C 45.28; H 3.52; P 8.65.

**Preparation of Rh_{2}(PF_{3})_{5}(RC_{2}R')_{2}**

**Dimethyl Acetylenedicarboxylic Acid (R = R' = CO_{2}Me)**

**Warning:** Reaction of Rh_{2}(PF_{3})_{8} with MeO_{2}CC=CCO_{2}Me (and HC=CCO_{2}Me) at room temperature always leads to a violent explosion.

An excess of MeO_{2}CC=CCO_{2}Me (0.6 g) was condensed under a high vacuum onto a solid sample of Rh_{2}(PF_{3})_{8} (0.26 g) cooled to -196°. The reaction was cautiously allowed to warm to about +20°, whereupon a gas was evolved. The reaction was slightly exothermic (CARE!) and so the mixture was kept at about +20° by cooling until the evolution of gas had ceased. The mixture was then evacuated (at 0.005 mm Hg) for 12 hours at room temperature to remove all unreacted acetylene, leaving a red solid. This was extracted with iso-pentane (4 x 5 ml) and the combined extracts filtered. The filtrate was cooled to -5°, whereupon large red crystals of Rh_{2}(PF_{3})_{5}(MeO_{2}CC=CO_{2}Me)_{2} separated in 58% (0.15 g) yield. Melting point - 162°.

**Methyl Propiolate (R = H, R' = CO_{2}Me)**

The reaction was carried out as described above for MeO_{2}CC=CCO_{2}Me, except that the excess of HC=CCO_{2}Me was separated from the complex by a trap-to-trap sublimation and the solid complex recrystallised from iso-pentane at -78° to afford a 40% yield of Rh_{2}(PF_{3})_{5}(HC_{2}CO_{2}Me)_{2}.

Molecular weight (mass spectrum) - 817 (calc. 817).
Mass Spectra

Owing to the high volatility of the acetylene complexes, all mass spectra were recorded using a cooled probe between -10° and +15°.

N.M.R. Spectra

In variable temperature measurements the temperatures of the solutions were determined by a copper-constantan thermocouple.

The intensities of the low temperature limiting spectra of Rh₂(PF₃)₆(PhC≡CPh) were measured on a JEOLCO-60HL, a Varian HA100 and a Brucker Spectrospin (84.67 MHz). Only a slight variation in relative intensities was noted. All other low temperature spectra were measured on a JEOLCO-60HL.

Estimated errors in N.M.R. parameters are: chemical shift 0.3 p.p.m., separation of doublets 20 Hz and intensities > 10%.

Spectral parameters for the three doublets in the low temperature limiting spectra of Rh₂(PF₃)₈ (at -33°) are: [chemical shift in p.p.m. upfield from CFC₁₃, separation of doublet in Hz, relative intensity]  A, -7.8 ± 0.5 p.p.m., 900 ± 20 Hz, 1.  B, +0.7 ± 0.5 p.p.m., 1220 ± 30 Hz, 3.2.  C, +7.6 ± 0.5 p.p.m., 1410 ± 30 Hz, 4.8.
CHAPTER 5

Low Frequency Vibrational Spectra of Rhodium(I) Fluorophosphine Complexes

Introduction

The vibrational spectra of fluorophosphine complexes have rarely been measured below 400 cm\(^{-1}\). The region 100 cm\(^{-1}\) to 400 cm\(^{-1}\) is of particular interest in the present work as both metal-halogen and metal-phosphorus stretching vibrations occur in this region. As these vibrational modes are well characterised in other metal phosphine and in substituted metal carbonyl complexes, an examination of the spectra of the fluorophosphine complexes of rhodium(I) was undertaken.

Only for the following complexes have fairly complete vibrational assignments been made: \(\text{M(PF}_3\text{)}_4\) (\(\text{M} = \text{Ni, Pd, Pt}\)), \(\text{Ni(CO)}_4-x(\text{PF}_3)_x\) (\(x = 1\) to 3), \(\text{K[Co(PF}_3\text{)}_4]\) and \(\text{HCo(PF}_3\text{)}_4\), and \(\text{BH}_3\text{PF}_3\). All exhibit absorptions assigned to asymmetric fluorine-phosphorus-fluorine deformations \(\delta_a\) (F-P-F) within the region 310 cm\(^{-1}\) to 420 cm\(^{-1}\), and to metal-phosphorus stretching vibrations between 200 cm\(^{-1}\) and 250 cm\(^{-1}\). Partial far IR spectral data have been published for \(\text{M(PF}_3\text{)}_5\) (\(\text{M} = \text{Fe, Ru, Os}\)), \(\text{H}_2\text{M(PF}_3\text{)}_4\) (\(\text{M} = \text{Ru, Os}\)), \(\text{B}_4\text{H}_8\text{PF}_3\), \(\text{BH}_3\text{PF}_3\), and \(\text{ReCl(PF}_3\text{)}_5\). The limited data for these complexes support the above assignments for \(\delta_a\) (F-P-F) and \(\nu\) (M-P) regions. In the last compound, \(\nu\) (Re-Cl) was assigned to an absorption at 329 cm\(^{-1}\). This is 37 cm\(^{-1}\) higher than \(\nu\) (Re-Cl) in the corresponding carbonyl complex, \(\text{ReCl(CO)}_5\). This higher rhenium-chlorine bond order in \(\text{ReCl(PF}_3\text{)}_5\) was ascribed to increased chlorine to rhenium (Cl-Re) \(\pi\)-bonding. However, it was not proposed which orbitals are involved in such an interaction. It was implied that this greater \(\pi\)-overlap was induced by the stronger \(\pi\)-accepting ability of phosphorus trifluoride over that of carbon monoxide.
In most complexes, \(v(M-X)\) \((M = \text{transition metal}, X = \text{halogen})\), is quite dependent upon the coordination number and oxidation state of the metal, and upon the nature of the other ligands present. Moreover, the position of \(v(M-X)\) is often of use in making structural assignments, as the nature of the ligand \text{trans} to the halogen has a marked effect on the value of \(v(M-X)\). This "trans effect" has been noted for a number of systems and has been related, with moderate success, to the \(\sigma\)- and \(\pi\)-bonding abilities of the \text{trans}-ligand. From a low frequency vibrational study of the carbon monoxide and phosphorus trifluoride complexes of rhodium(I), a correlation between the bonding abilities of these two ligands should be obtained.

The final problem to be examined in this study is the structure of \([\text{Rh}X(L)_2]_2\) \((L = \text{CO}, \text{PF}_3; X = \text{Cl}, \text{Br}, \text{I})\) in solution. X-ray studies have shown that \([\text{RhCl(cod)}]_2\) is planar in the solid state, whereas \([\text{RhCl(CO)}]_2\) and \([\text{RhCl(C}_2\text{H}_4)]_2\) are both bent about the bridging chlorine atoms in the solid. Far IR results are consistent with bent structures for the carbonyl and ethylene dimers, and with planar structures for the cod and nbd complexes in the solid state. That \([\text{RhX(CO)}]_2\) \((X = \text{Cl}, \text{Br})\) have appreciable dipole moments suggests that the bent structure for the carbonyl is retained in solution. However, no spectral studies have been carried out to show this is so. It is of interest, therefore, to examine the vibrational spectra of \([\text{RhX(CO)}]_2\) in solution and to determine whether the phosphorus trifluoride analogues, \([\text{RhX(PF}_3)]_2\), have similar structures.
Results and Discussion

\(\mu,\mu'-\text{Dihalotetracarbonyldirhodium(I)}\) (1)

Table 19 shows the far IR spectra (in n-heptane) and Raman spectra (solid and in benzene) of \([\text{RhX(CO)}_2]_2\) (\(X = \text{Cl, Br, I}\)) (1). The number of coincidences in absorptions between the IR and Raman spectra immediately suggests that these molecules have no centre of symmetry.

In a centrosymmetric molecule no Raman active vibration is IR active, and no IR active vibration is Raman active. This immediately excludes a planar structure (\(D_{2h}\) symmetry) for \([\text{RhX(CO)}_2]_2\) in solution.

By an examination of the changes in the spectra on changing the halogen atoms, an unambiguous assignment of bridging \(v(\text{Rh-X})\) modes can be made. In each case only two absorptions are found, both in the IR and Raman spectra. Three IR active and four Raman active modes are predicted of \([\text{RhX(CO)}_2]_2\) with \(C_{2v}\) symmetry. However, in the IR spectrum of solid \([\text{RhCl(CO)}_2]_2\), Adams has found three \(v(\text{Rh-Cl})\) modes, two of which are only partially resolved.

The \(v(\text{Rh-X})\) vibrations lie in the regions observed for the bridging \(v(\text{M-X})\) modes in other metal complexes. They are not substantially lower than the terminal \(v(\text{Rh-X})\) frequencies found in rhodium(I) complexes, [for example, in \([\text{Bu}_4^\text{N}]_{\text{cis-RhCl}_2(\text{CO})}_2\), \(v(\text{Rh-Cl}) = 320 \text{ and } 290 \text{ cm}^{-1}\) (Nujol)]. In most metal complexes the bridging \(v(\text{M-X})\) absorption is usually found at lower frequencies than the terminal \(v(\text{M-X})\) absorption. It has been observed that there is very little difference between terminal and bridging rhodium-chlorine bond lengths in rhodium(I) complexes, whereas the bridging metal-chlorine bond lengths are usually significantly longer in most other metal complexes. For example, the rhodium-chlorine bond length in \([\text{RhCl(CO)}_2]_2\) (2.23 to 2.38\(\text{Å}\)) is not significantly shorter than that in \([\text{Bu}_4^\text{N}]_{\text{cis-RhCl}_2(\text{CO})}_2\) (2.345(6)\(\text{Å}\)) or in
### TABLE 19

**Far Infra-Red and Raman Spectra of \([\text{RhX(CO)}_2]_2\) (1)**

<table>
<thead>
<tr>
<th></th>
<th>Infra-Red (solution)</th>
<th>Raman (solution)</th>
<th>Raman (solid)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X = \text{Cl})</td>
<td>480(m)</td>
<td>482(s,p)</td>
<td>482(m)</td>
<td>474(w,sh)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>440(m,dp)</td>
<td>444(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>310(s)</td>
<td>307(m,p)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>290(vs)</td>
<td>302(w,sh)</td>
<td>304(w,br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150(w)</td>
<td>165(w,br)</td>
<td></td>
<td>128(m)</td>
</tr>
<tr>
<td>(X = \text{Br})</td>
<td>475(m)</td>
<td>481(s,p)</td>
<td>486(m)</td>
<td>472(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>431(m,dp)</td>
<td>443(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220(m)</td>
<td>221(m,p)</td>
<td>223(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>209(s)</td>
<td>206(w)</td>
<td>204(w)</td>
<td></td>
</tr>
<tr>
<td>(X = \text{I})</td>
<td>181(m,sh)</td>
<td>n.m.</td>
<td>n.m.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>173(s)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Absorptions between 500 and 600 cm\(^{-1}\) in the infra-red spectrum of \([\text{RhX(CO)}_2]_2\) are absent in the spectra of \([\text{RhX(CO)}_2]_2\) and \([\text{RhX(CO)}_2]_2\) and not in \([\text{RhX(CO)}_2]_2\). Although the latter usually occurs above 500 cm\(^{-1}\) in solution samples, the absorptions of \([\text{RhX(CO)}_2]_2\) are determined in the presence of halogen. It can be seen that the presence of halogen has little effect on \(\nu(\text{Rh-C})\).
Absorptions at 150 cm$^{-1}$ in the IR spectrum and at 128 cm$^{-1}$ and 165 cm$^{-1}$ in the Raman spectrum of $[\text{RhCl(CO)}_2)_2$ are absent in the spectra of both the bromo- and iodo-dimers. These absorptions are tentatively assigned to rhodium-chlorine bridge bending vibrations, i.e. to $\delta(\text{Rh}_2\text{Cl}_2)$. Adams has assigned an absorption at 122 cm$^{-1}$ in solid $[\text{RhCl(CO)}_2)_2$ and at 137 cm$^{-1}$ in $[\text{RhCl(C}_2\text{H}_4)_2)_2$ to $\delta(\text{Rh}_2\text{Cl}_2)$.

Absorptions between 430 cm$^{-1}$ and 500 cm$^{-1}$ are assigned to $\nu(\text{Rh-C})$ and not to $\delta(\text{Rh-C-O})$ as the latter usually occur above 500 cm$^{-1}$ in rhodium complexes. There are absorptions between 500 cm$^{-1}$ and 600 cm$^{-1}$ in $[\text{RhX(CO)}_2)_2$ but their positions have not been determined in the present study. It can be seen that changing the halogen has little effect on $\nu(\text{Rh-C})$.

**Phosphorus Trifluoride**

There are two bands in phosphorus trifluoride primarily due to fluorine-phosphorus-fluorine deformation modes - at 486 cm$^{-1}$ and at 364 cm$^{-1}$ (gas; centres of Q branches). These values are in good agreement with those obtained by other workers. The absorption at lower frequency is assigned to the doubly degenerate asymmetric deformation, $\delta_a(\text{F-P-F})$.

$\mu,\mu'$-dihalotetakis(phosphorus trifluoride)dirhodium(I) (3)

The vibrational spectra of $[\text{RhX(PF}_3)_2)_2$ (X = Cl, Br, I) are shown in Table 20. There are some coincidences between the IR and Raman spectra. It is not at all certain whether these are due to the same vibrational mode being both IR and Raman active, or to the accidental degeneracy of different modes. The number of coincidences is much less than that found in the carbonyl dimers (1), and the possibility that the $[\text{RhX(PF}_3)_2)_2$ molecules are planar in solution can not be excluded from the available evidence.
TABLE 20

Far Infra-Red and Raman Spectra of $[\text{RhX(PF}_3)_2]_2^-$ (3)

<table>
<thead>
<tr>
<th>Infra-Red</th>
<th>Raman</th>
<th>Raman</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(solution)</td>
<td>(solution)</td>
<td>(solid)</td>
<td></td>
</tr>
<tr>
<td>X = Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n.m.</td>
<td>387 (vs)</td>
<td>421 (m, p)</td>
<td>$\delta_a (F-P-F)$</td>
</tr>
<tr>
<td></td>
<td>336 (vs)</td>
<td>341 (w, dp)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>315 (s)</td>
<td>343 (w)</td>
<td>$\nu (\text{Rh-CI})$</td>
</tr>
<tr>
<td></td>
<td>284 (w)</td>
<td>285 (m, p)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>267 (m)</td>
<td>287 (w)</td>
<td>$\delta (\text{Rh}_2\text{Cl}_2) - \nu (\text{Rh-P})$</td>
</tr>
<tr>
<td></td>
<td>257 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>245 (w)</td>
<td>248 (m, br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>225 (s)</td>
<td>215 (m, dp)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>148 (w)</td>
<td>163 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>125 (w)</td>
<td></td>
</tr>
<tr>
<td>X = Br</td>
<td>384 (vs)</td>
<td></td>
<td>$\delta_a (F-P-F)$</td>
</tr>
<tr>
<td></td>
<td>324 (s)</td>
<td>329 (w, dp)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>298 (m)</td>
<td>328 (w)</td>
<td>$\nu (\text{Rh-P}) - \nu (\text{Rh-Br})$</td>
</tr>
<tr>
<td></td>
<td>278 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>245 (w)</td>
<td>246 (m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>226 (s)</td>
<td>222 (w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>218 (m, sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>201 (m)</td>
<td>201 (m, p)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>185 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X = I</td>
<td>381 (vs, br)</td>
<td></td>
<td>$\delta_a (F-P-F)$</td>
</tr>
<tr>
<td></td>
<td>317 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>297 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>274 (w)</td>
<td>n.m.</td>
<td>n.m.</td>
</tr>
<tr>
<td></td>
<td>240 (m, sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>226 (s)</td>
<td></td>
<td>$\nu (\text{Rh-P})$</td>
</tr>
<tr>
<td></td>
<td>216 (m, sh)</td>
<td></td>
<td>$\nu (\text{Rh-I})$</td>
</tr>
<tr>
<td></td>
<td>167 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>158 (w)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The three strong absorptions in the IR spectra of \([\text{RhX(PF}_3)_2]\), between 300 cm\(^{-1}\) and 400 cm\(^{-1}\) are predominantly phosphorus trifluoride asymmetric deformations, \(\delta_a^{(\text{F-P-F})}\). The deformations derived from the symmetric \(\delta^{(\text{F-P-F})}\) in free phosphorus trifluoride are in the region 450 cm\(^{-1}\) to 550 cm\(^{-1}\) but have not been measured here. The corresponding \(\delta^{(\text{F-P-F})}\) vibrations in \(\text{M(PF}_3)_4\) (\(\text{M} = \text{Ni}, \text{Pd}, \text{Pt}\)), \(\text{HCo(PF}_3)_4^{2-}\), and in \(\text{Ni(CO)}_4\text{X(PF}_3)_x\) (\(x = 0\) to 3) occur in the same regions.

The absorptions between 300 cm\(^{-1}\) and 400 cm\(^{-1}\) are not due solely to \(\delta_a^{(\text{F-P-F})}\) as they are halogen sensitive. The frequencies corresponding to \(\delta_a^{(\text{F-P-F})}\) change considerably more on proceeding from chlorine to bromine than they do from bromine to iodine. This is ascribed to a coupling of the lowest frequency \(\delta_a^{(\text{F-P-F})}\) to the \(\nu^{(\text{Rh-Cl})}\), the two vibrations having similar energies. Neither the absorption assigned as \(\nu^{(\text{Rh-Cl})}\) nor as the lowest \(\delta_a^{(\text{F-P-F})}\) is a "pure" vibrational mode. In comparison, coupling between \(\delta_a^{(\text{F-P-F})}\) and \(\nu^{(\text{Rh-Br})}\) or \(\nu^{(\text{Rh-I})}\) is expected to be small.

The absorptions most sensitive to the nature of the halogen are assigned as being predominantly bridging \(\nu^{(\text{Rh-X})}\) vibrations. In the IR spectra there are only two \(\nu^{(\text{Rh-X})}\) observed. In the Raman spectra one polarised band, due to the totally symmetric \(\nu^{(\text{Rh-X})}\) is found. This would be IR active in \(C_{2v}\) but IR inactive in \(D_{2h}\) symmetry. In the Raman spectrum of \([\text{RhCl(PF}_3)_2]\) this band is at 285 cm\(^{-1}\) (m,p), and there is a weak band at 284 cm\(^{-1}\) in the IR spectrum. However, corresponding absorptions occur in the IR spectra of the bromo- [at 278 cm\(^{-1}\)(w)] and iodo- [at 274 cm\(^{-1}\)(w)] complexes, so that this absorption does not appear to be due to the totally symmetric \(\nu^{(\text{Rh-Cl})}\) in the IR spectra of \([\text{RhCl(PF}_3)_2]\). In contrast, in the IR spectrum of \([\text{RhBr(PF}_3)_2]\) there is a halogen sensitive absorption at 201 cm\(^{-1}\)(m), which is coincident
with the totally symmetric $\nu$(Rh-Br) in the Raman spectrum.

One result suggests a bent structure, the other a planar structure for $[\text{RhX(PF}_3\text{)}_2]_2$. The differences in relative positions in the $\nu$(Rh-X) modes in the IR and Raman spectra may be ascribed to the mixing of $\nu$(Rh-Cl) with $\delta_a$(F-P-F). For this reason no conclusions may be drawn with confidence about the structure of $[\text{RhX(PF}_3\text{)}_2]_2$ in solution or in the solid from the above data.

The frequencies of the $\nu$(Rh-X) absorptions in the IR spectra of $[\text{RhX(PF}_3\text{)}_2]_2$ ($X = \text{Cl, Br, I}$) are about 10% lower than those of the corresponding bands in $[\text{RhX(CO)}_2]_2$. This may reflect different structures in solution, that is, different angles of intersection of the planes defined by RhXL$_2$ ($L = \text{CO, PF}_3$) in $[\text{RhXL}_2]_2$. If the origin of this difference is electronic, then it appears that there is a weaker rhodium-halogen bond in the phosphorus trifluoride complexes than in the corresponding carbonyls.

The weak bands observed between 274 cm$^{-1}$ and 284 cm$^{-1}$ (and possibly the ones at 245 cm$^{-1}$) in the IR spectra of $[\text{RhX(PF}_3\text{)}_2]_2$ are tentatively assigned to phosphorus trifluoride rocking modes. Weak bands at 287 cm$^{-1}$ and 281 cm$^{-1}$ were observed in Ni(PF$_3$)$_4$ and Pt(PF$_3$)$_4$ respectively, and these have been assigned to this type of vibration.

The $\nu$(Rh-P) vibrations in $[\text{RhX(PF}_3\text{)}_2]_2$ occur in the region 215 cm$^{-1}$ to 230 cm$^{-1}$. This is within the region found for this mode in other phosphorus trifluoride complexes. Three IR active $\nu$(Rh-P) modes are predicted for $C_{2v}$ symmetry, but only two in $D_{2h}$. One or two (depending upon the nature of X) are observed; however, the third may be the absorption found at about 245 cm$^{-1}$. 


Tetrabutylanamonium cis-Dihalobis(phosphorus trifluoride)rhodate(I) (6)

The IR spectra of these complexes are given in Table 21.

**TABLE 21**

Far Infra-Red Spectra of $[\text{Bu}_4^N][\text{RhX}_2(PF_3)_2]$ (6). a

<table>
<thead>
<tr>
<th>$X = \text{Cl}$</th>
<th>$X = \text{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>385 (s)</td>
<td>383 (vs)</td>
</tr>
<tr>
<td>346 (s)</td>
<td>329 (m)</td>
</tr>
<tr>
<td>313 (s)</td>
<td>301 (s)</td>
</tr>
<tr>
<td>275 (m)</td>
<td></td>
</tr>
<tr>
<td>257 (m)</td>
<td></td>
</tr>
<tr>
<td>243 (w, br)</td>
<td>247 (w, br)</td>
</tr>
<tr>
<td>233 (w)</td>
<td>233 (w, br)</td>
</tr>
<tr>
<td>219 (w)</td>
<td>215 (w)</td>
</tr>
<tr>
<td>201 (w, br)</td>
<td>201 (w, br)</td>
</tr>
<tr>
<td>182 (m)</td>
<td></td>
</tr>
</tbody>
</table>

a Measured as Nujol Mulls.

These spectra confirm some of the conclusions drawn above. The $\delta_a$ (F-P-F) vibrations are halogen sensitive. The values of $\nu$(Rh-X) for these complexes are close to those in $[\text{RhX}(PF_3)_2]^2_2$, again showing the small difference in frequency between bridging and terminal $\nu$(Rh-X). The terminal $\nu$(Rh-X) vibrations in these complexes are about 15% lower in frequency than the corresponding modes in the carbonyl complexes. 118,236 That the $\nu$(Rh-Br) modes [where the effects of coupling to $\delta_a$ (F-P-F) are minimal] are lower in the phosphorus trifluoride complex than in the carbonyl, is almost certainly electronic in origin. This suggests that the similar effect observed in the dimers does not arise from structural differences between $[\text{RhX(CO)}_2]^2_2$ and $[\text{RhX}(PF_3)_2]^2_2$ in solution, but is also electronic. It appears, therefore, that the rhodium-halogen bond order in the phosphorus
trifluoride complexes is less than that in the corresponding carbonyl complexes. This conclusion is opposite to that made by Kruck (who has probably based his conclusions on incorrect assignments). 6,225

The presence of two \( \nu(\text{Rh-X}) \) and two \( \nu(\text{Rh-P}) \) vibrations confirms the \textit{cis}-stereochemistry (\( C_{2v} \) symmetry) of ligands in \([\text{RhX}_2(\text{PF}_3)_2]^-\) (\( X = \text{Cl,Br} \)).

\textit{trans}-chlorocarbonylbis(triphenylphosphine)rhodium(I) and its analogues

The vibrational spectra of \textit{trans}-RhX(MPh\(_3\))\(_2\)CO (\( X = \text{Cl, M = P, As}; X = \text{Br, M = P} \)) are given in Table 23. The unambiguous assignment of most modes is made impossible by the complex spectra shown by the ligands, triphenylphosphine and triphenylarsine (Table 22).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
 & \textbf{Infra-Red (Nujol Mull)} & \textbf{Raman (solid)} \\
\hline
\text{PPh}_3 & 471(vs) & 431(w) \\
 & 425(s) & \\
 & 420(s,sh) & \\
 & 394(m) & 407(w) \\
 & 244(w) & 272(w) \\
 & & 254(s) \\
 & & 195(w) \\
 & & 186(w) \\
\hline
\text{AsPh}_3 & 464(vs) & \\
 & 350(w,br) & \\
 & 312(s) & 315(m) \\
 & & 239(s) \\
 & & 199(s) \\
\hline
\end{tabular}
\caption{Far Infra-Red and Raman Spectra of Triphenylphosphine and -Arsine}
\end{table}

The absorption at 308 cm\(^{-1}\) in the IR spectrum (315 cm\(^{-1}\) in the Raman spectrum) of \textit{trans}-RhCl(PPh\(_3\))\(_2\)CO is not present in the bromide and so
### TABLE 23

**Far Infra-Red and Raman Spectra of trans-RhCl(PPh\_3\_2CO and Analogues**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Infra-Red (benzene solution)</th>
<th>Raman (solid)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-RhCl(PPh_3_2CO</td>
<td>n.m.</td>
<td>443(w)</td>
<td>v(Rh-Cl)</td>
</tr>
<tr>
<td></td>
<td>397(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>266(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308(m)</td>
<td>315(w,br)</td>
<td>v(Rh-Cl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>278(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>255(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>235(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>224(w)</td>
<td>225(w,br)</td>
<td>v(Rh-Br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>155(m)</td>
<td></td>
</tr>
<tr>
<td>trans-RhCl(AsPh_3_2CO</td>
<td>n.m.</td>
<td>471(m)</td>
<td>v(Rh-Cl) + AsPh_3</td>
</tr>
<tr>
<td></td>
<td>331(vs,br)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>312(s,sh)</td>
<td>315(w,br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>249(m,sh)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>238(w)</td>
<td>241(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>205(m,br)</td>
<td>202(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180(w)</td>
<td>188(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>161(m)</td>
<td></td>
</tr>
<tr>
<td>trans-RhBr(PPh_3_2CO</td>
<td>n.m.</td>
<td>284(w)</td>
<td>v(Rh-Br)?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>257(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>237(w,br)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>203(w)</td>
<td>198(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>159(m)</td>
<td></td>
</tr>
</tbody>
</table>

*The vibrational spectra of [RhBr(PPh\_3\_2CO] are consistent with a C\_2v symmetry but not a S\_6 symmetry in solution, but cannot be unambiguously assigned.*
is assigned as $\nu$(Rh-Cl). The corresponding $\nu$(Rh-Br) in \text{trans-RhBr(PPh}_3\text{)}_2\text{CO} is at either 203 cm$^{-1}$ or 198 cm$^{-1}$ (Raman). In \text{trans-RhCl(AsPh}_3\text{)}_2\text{CO} the very strong triphenylarsine band at 331 cm$^{-1}$ in the IR spectrum is Raman inactive. This allows a tentative assignment of $\nu$(Rh-Cl) at 312 cm$^{-1}$ in both the IR and Raman spectra of \text{trans-RhCl(AsPh}_3\text{)}_2\text{CO}, the vibration being coincident with a weak triphenylarsine mode.

\text{trans-chloro(phosphorus trifluoride)bis(triphenylphosphine)rhodium(I) and its Analogues}

The vibrational spectra of \text{trans-RhX(MPh}_3\text{)}_2\text{PF}_3 (X = \text{Cl}, M = \text{P,As}; X = \text{Br}, M = \text{P}) are given in Table 24. The degeneracy of the $\delta_a$ (F-P-F) in free phosphorus trifluoride is removed on coordination in $C_{2v}$ local symmetry. The resulting two vibrations are observed in these complexes at 314 cm$^{-1}$ to 340 cm$^{-1}$ and at 388 cm$^{-1}$ to 398 cm$^{-1}$. The absorption at lower frequency is quite halogen sensitive, and hence, not a "pure" $\delta_a$ (F-P-F). The lower $\delta_a$ (F-P-F) mode is obscured by triphenylarsine vibrations in \text{trans-RhCl(AsPh}_3\text{)}_2\text{PF}_3.

Absorptions due to $\nu$(Rh-X) are in the same region as found for [RhX(PF$_3$)$_2$]$_2$ and for [Bu$_4^+$N][RhX$_2$(PF$_3$)$_2$]. No other modes can be assigned with certainty.

The conclusions drawn from this study may be summarised as follows:

* The vibrational spectra of [RhX(CO)$_2$]$_2$ are consistent with a $C_{2v}$ symmetry but not a $D_{2h}$ symmetry in solution.
* The structure of [RhX(PF$_3$)$_2$]$_2$ in solution cannot be unambiguously assigned.
* The IR spectra of [Bu$_4^+$N][RhX$_2$(PF$_3$)$_2$] are consistent with a \textit{cis} stereochemistry.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Infra-Red (benzene solution)</th>
<th>Raman (solid)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>trans-RhCl(PPh₃)₂PF₃</strong></td>
<td>398(s)</td>
<td></td>
<td>δₐ(F-P-F)</td>
</tr>
<tr>
<td></td>
<td>340(vs)</td>
<td>270(m,br)</td>
<td>v(Rh-Cl)</td>
</tr>
<tr>
<td></td>
<td>268(m)</td>
<td>250(m,br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>255(m)</td>
<td>231(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>218(w)</td>
<td>201(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>161(m)</td>
<td></td>
</tr>
<tr>
<td><strong>trans-RhCl(AsPh₃)₂PF₃</strong></td>
<td>394(s)</td>
<td>δₐ(F-P-F)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>327(vs,sh)</td>
<td>AsPh₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>316(vs)</td>
<td>AsPh₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td>275(m)</td>
<td>272(w,br)</td>
<td>v(Rh-Cl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>251(m,br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>239(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>203(m,br)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>172(m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>140(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>trans-RhBr(PPh₃)₂PF₃</strong></td>
<td>388(s)</td>
<td>δₐ(F-P-F)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>314(m)</td>
<td>318(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>277(w)</td>
<td>270(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>255(w)</td>
<td>254(m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>231(w,br)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220(w)</td>
<td>203(w)</td>
<td>v(Rh-Br)</td>
</tr>
<tr>
<td></td>
<td>198(w)</td>
<td>193(w)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>159(w)</td>
<td></td>
</tr>
</tbody>
</table>
* There is coupling between $\nu$(Rh-Cl) and $\delta_a$(F-P-F), so that the observed absorptions do not represent pure modes of vibrations.

* The rhodium-halogen bond orders in the phosphorus trifluoride complexes are lower than those of the corresponding carboxyls.

All Raman spectra were recorded with a 500 mW, krypton 6471 Å laser line as the source. All spectra were recorded of samples in capillary tubes. Solutions were in hexane under nitrogen in a sealed capillary tube.

Most of the complexes described in this Chapter are both airsensitive and somewhat photosensitive (to the laser beam). In addition, the rhodium complexes (in) and (d) are unstable in solution. The Raman effect was particularly weak for the krypton 6471 Å line. Despite the greater power in an 800 mW argon 4880 Å line, no Raman effect was observed with this source. Instead the coupling strongly absorbed the radiation, resulting either in the evaporation of the solvent or decomposition. Other groups have not been able to observe any Raman effect for $\text{[RhCl}(\text{CO})_2]_2$. 238,239

All complexes were prepared by the methods given in Chapter 2.
Experimental Section

Far IR solution measurements were carried out on saturated n-heptane or benzene solutions under nitrogen. Solution cells were of 2.0mm path length with polythene windows. Solids were run as Nujol mulls on polythene. The IR spectrum of gaseous phosphorus trifluoride (at 30 mm Hg) was measured in a 10 cm path length gas cell with polythene windows.

All Raman spectra were recorded with a 300 mW, krypton 6471\textsuperscript{R}, laser line as the source. All spectra were recorded of samples in capillary tubes. Solutions were in benzene under nitrogen in a sealed capillary tube.

Most of the complexes described in this Chapter are both air-sensitive and somewhat photosensitive (in the laser beam). In addition the iodo-complexes (lc) and (3c) are unstable in solution. The Raman effect was particularly weak for the krypton 6471\textsuperscript{R} line. Despite the greater power in an 800 mW, argon 4880\textsuperscript{R} line, no Raman effect was observed with this source. Instead the samples strongly absorbed the radiation, resulting either in the evaporation of the solvent or decomposition. Other groups have not been able to observe any Raman effect for [RhCl(CO)\textsubscript{2}]\textsubscript{2}\textsuperscript{238,239}.

All complexes were prepared by the methods given in Chapter 2.
1. Melting Point Determinations

All samples were sealed in capillary tubes under nitrogen unless stated otherwise. Melting points were recorded on a Gallenkamp hot stage melting point apparatus and are uncorrected.

2. Molecular Weight Determinations

These were measured at 25° in Analytical Reagent grade benzene, using a vapour pressure osmometer (Model 301A, Mechrolab, California). Benzil was used as the calibrant. In all determinations a stream of benzene-saturated nitrogen (7-10 ml/min) was passed into the chamber, using the Mechrolab inert gas attachment.

3. Infra-Red Spectra

In the region 4000-400 cm\(^{-1}\) these were recorded on a Perkin-Elmer 457 or a 225 Infra-red Grating Spectrophotometer. In the region 400-30 cm\(^{-1}\) a Hitachi FIS-3 with a 700 mW Hg source was employed.

4. Raman Spectra

A Spex Ramalog 1401, 3/4 meter Czerny-Turner Double Monochromator-Spectrophotometer was used. Carson Model 101 Argon and Model 103 Krypton ion lasers were employed as light sources.

5. Nuclear Magnetic Resonance Spectra

Proton N.M.R. spectra were recorded on a Varian Associates HA100, a JEOLCO C-60HL or a JEOLCO MINIMAR. The spectra were measured using TMS as internal standard (60 MHz) or internal lock signal (100 MHz).

Fluorine N.M.R. spectra were recorded at 56.45 MHz on a JEOLCO C-60HL with CFC\(_3\) as an internal standard, unless otherwise stated.

6. Mass Spectra

These were recorded on a A.E.I. MS.902 mass spectrometer.
REFERENCES


218a. R.N. Johnson, Personal communication.


