

Migration of a hydride ligand to a difluorocarbene ligand bound to rhodium. The synthesis and crystal structure of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

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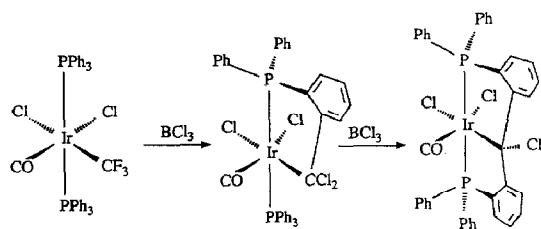
Abstract

$\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ has been made by treating $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with $\text{Hg}(\text{CF}_3)_2$, and found to display reactivity consistent with a 16 e^- , d^8 complex, in that it undergoes addition of a number of small molecules, including O_2 , X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and MeI . Treatment of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ with aqueous acids results in hydrolysis of the trifluoromethyl group to a carbonyl ligand. Confirmation that this reaction proceeds via a difluorocarbene intermediate came from the reaction with dry HCl , which gave $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$. A study of this reaction, by multinuclear NMR spectroscopy and ^2H -labelling experiments led to the proposal of a mechanism for the formation of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ that involves hydride migration to a cationic difluorocarbene ligand bound to rhodium. Another difluoromethyl complex $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ is formed when $\text{RhHCl}_2(\text{PPh}_3)_3$ is treated with $\text{Hg}(\text{CF}_3)_2$. The crystal structure of this complex has been determined, and displays square pyramidal geometry with the CF_2H ligand occupying the apical position.

Introduction

The study of rhodium(I) and iridium(I) complexes has provided a cornerstone for understanding of oxidative addition and reductive elimination reactions. Rhodium(I) complexes are involved in an ever-increasing array of organic transformations, many employing rhodium catalytically. This work is a study of trifluoromethyl and difluoromethyl derivatives of rhodium(I) and rhodium(III).

The unique reactivity demonstrated by coordinated fluorocarbons appears to be influenced by the electron density present at the metal centre. The difluorocarbene-ruthenium(II) complex, $\text{RuCl}_2(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$, for instance, is highly electrophilic, and is rapidly hydrolysed in the presence of water, whereas the ruthenium(0)



Scheme 1

complex, $\text{Ru}(\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$, reacts with water only under vigorous conditions [1,2].

The abstraction of the α -fluorines from σ -bonded transition metal fluorocarbon complexes by acids is a well known reaction [3–11]. The stability of the proposed difluorocarbene intermediates is directly linked to the electron density at the metal centre. The more electron deficient metal centres such as ruthenium(II), of which the fluorocarbon complex $\text{RuBr}(\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ is an example, form extremely electrophilic carbene centres when treated with Lewis acids. These electrophilic carbene centres rapidly undergo intramolecular reactions, often leading to metallacyclic complexes [9]. This type of behaviour is also seen for the iridium(III) complex $\text{IrCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$; when this d^6 trifluoromethyliridium complex is treated with BCl_3 , the products isolated are those derived from electrophilic addition of the carbene carbon to one of the phenyl rings of the PPh_3 groups [11] (Scheme 1).

It would be expected that similar reactions carried out on an trifluoromethyl-iridium(I) or -rhodium(I) complex would result in a less electrophilic, and therefore more stable, perhaps isolable, intermediate dihalocarbene complex.

Results and discussion

Syntheses of trifluoromethyl-rhodium and -iridium complexes have previously taken advantage of the ease with which a wide range of d^8 compounds undergo oxidative addition. The addition of such species as trifluoromethyl iodide, and fluoroacyl halides and anhydrides to d^8 rhodium and iridium complexes has, in most cases, resulted in d^6 trifluoromethyl complexes [11–13]. However, use of these rhodium(III) and iridium(III) complexes as substrates for reduction to d^8 complexes has not proved successful [11].

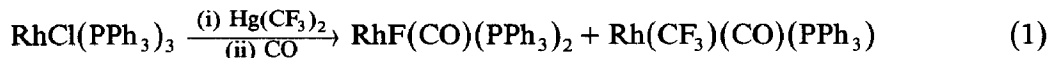
Synthesis of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$

The group 12 trifluoromethyl and difluorocarbene transfer reagents $\text{Hg}(\text{CF}_3)_2$ and $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ are known to react with a number of group 8 and group 10 metal complexes, resulting in trifluoromethyl complexes. In a number of cases $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ reacts with coordinatively unsaturated d^8 complexes to yield difluorocarbene complexes [2]. It was, therefore, expected that some of the reactions would be observed with triphenylphosphinerhodium(I) complexes. The reaction of $\text{RhCl}(\text{PPh}_3)_3$ with either $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ or $\text{Hg}(\text{CF}_3)_2$ gave $\text{RhF}(\text{CO})(\text{PPh}_3)_2$.

This carbonyl containing product was presumably generated by hydrolysis of a fluorocarbon ligand bonded to the rhodium. The use of rigorously anhydrous conditions enabled the detection of the fluorocarbon complex by IR spectroscopy.

Anhydrous work-up did not give a tractable product, but the presence of $\nu(\text{CF})$ stretches at $1100\text{--}850\text{ cm}^{-1}$ indicated the possible presence of a σ -trifluoromethyl ligand.

The treatment of the reaction mixture with CO caused a rapid change in the colour of the solution, from red to yellow. The products mixture isolated from this procedure was shown by ^{31}P NMR spectroscopy to be a mixture of $\text{RhF}(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (eq. 1):



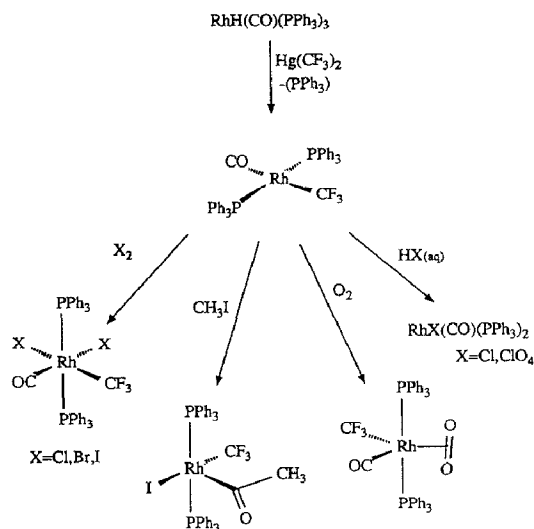
No method could be found to separate the $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ since it had similar solubility properties to $\text{RhF}(\text{CO})(\text{PPh}_3)_2$ and was not stable towards chromatography. The reaction must proceed through a coordinatively unsaturated rhodium(I) intermediate which contains a σ -bonded trifluoromethyl ligand. If the three-coordinate intermediate could be sufficiently stabilised, it might be possible to isolate cleanly either the $\text{Rh}(\text{CF}_3)\text{L}_2$ complex or $\text{Rh}(\text{CF}_3)\text{L}_2\text{L}'$ where L = a tertiary phosphine and L' = a neutral ligand. Three-coordinate rhodium(I) complexes have been isolated for L = tricyclohexylphosphine [14]. The isolation of species such as $\text{RhX}(\text{Pcy}_3)_2$ (X = F, Cl, Br) is only possible with the bulky tricyclohexylphosphine ligands.

The reaction of $\text{RhCl}(\text{Pcy}_3)_2$ with either $\text{Hg}(\text{CF}_3)_2$ or $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ gave only $\text{RhF}(\text{CO})(\text{Pcy}_3)_2$. As with the triphenylphosphine compound, the three-coordinate trifluoromethyl species formed must be extremely moisture sensitive. Under no conditions examined could any fluorocarbon containing complex be isolated or detected. Even addition of carbon monoxide (which stabilises the triphenylphosphine complex) was of no avail.

After treatment of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with $\text{Hg}(\text{CF}_3)_2$ and $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ only starting material was recovered. However, when the chloride was replaced by an iodide ligand more promising results were obtained. The reaction of $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ with $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$ gave an inseparable mixture of $\text{RhI}(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. The yield of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ could not be improved even by use of prolonged reaction times and large excesses of $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$. As no suitable route to $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ could be found by transition metal halide exchange with group 12 trifluoromethyl reagents, other possible synthetic paths were explored.

Trifluoromethyl-cobalt(I) [15,16] and -iridium(I) [17] complexes can be readily prepared by treatment of trifluoroacetic anhydride with $\text{Co}(\text{CO})_4^-$ and $\text{Ir}(\text{CO})_3(\text{PPh}_3)_2^-$, respectively. The reaction of fluoroanhydrides $(\text{CF}_3\text{CO})_2\text{O}$ and $(\text{CF}_3\text{CF}_2\text{CO})_2\text{O}$ with the rhodium anion $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]^-$ has been shown to give fluoroacyl complexes [18]. These complexes were assigned a trigonal bipyramidal geometry, with the *trans* axial carbonyl ligands and the two triphenylphosphine ligands in the equatorial plane with the acyl group [18]. These acyl complexes were not successfully decarbonylated even under extreme conditions [18].

The preparation of these complexes was repeated to allow reinvestigation of the possible decarbonylation of the acyl group. The product isolated from the reaction of $[\text{Rh}(\text{CO})_3(\text{PPh}_3)]^-$ with $(\text{CF}_3\text{CO})_2\text{O}$ was a bright yellow crystalline solid, with properties identical to those previously described for $\text{Rh}(\text{C}[\text{O}]\text{CF}_3)(\text{CO})_2(\text{PPh}_3)_2$ [18]. The unreactivity of this complex was inconsistent with the assigned structure.



Scheme 2

There are very few examples of stable rhodium(I) complexes with two *trans* carbonyl ligands. Reassessment of the spectral and microanalytical data led to the conclusion that the complex was in fact the four coordinate trifluoroacetate complex $\text{Rh(O}_2\text{CCF}_3\text{)(CO)(PPh}_3)_2$, and thus that the previously assigned structure [18] was incorrect.

We thought that another possible route to $\text{Rh(CF}_3\text{)(CO)(PPh}_3)_2$ could be one involving replacement of a metal hydride by the trifluoromethyl ligand. A number of aryl- and alkyl-metal complexes have been synthesised by the reaction of diaryl(alkyl)mercury with transition metal hydride complexes [19]. When $\text{MHCl(CO)(PPh}_3)_3$ is heated with HgR_2 ($\text{M} = \text{Ru, Os}$; $\text{R} = \text{Ph, } o\text{-tolyl, } p\text{-tolyl and } \beta\text{-styryl}$) mercury is deposited and $\text{M(R)Cl(CO)(PPh}_3)_2$ is isolated. This type of reaction had not been observed for bis(trifluoromethyl)mercury. When $\text{RhH(CO)(PPh}_3)_3$ was heated with $\text{Hg(CF}_3)_2$ in benzene mercury was precipitated and $\text{Rh(CF}_3\text{)(CO)(PPh}_3)_2$ was isolated cleanly and in good yield (Scheme 2).

In the reaction of ruthenium and osmium hydride complexes with HgR_2 ($\text{R} = \text{Ph, } o\text{-tolyl, } p\text{-tolyl and } \beta\text{-styryl}$) the metal-bonded hydride is lost, along with one of the aryl groups, as an arene molecule [20]. Although the reaction of $\text{RhH(CO)(PPh}_3)_3$ with $\text{Hg(CF}_3)_2$ resulted in precipitation of elemental mercury, it was not possible to detect the fragment which contained the hydride (presumably CF_3H).

The d^8 complex $\text{Rh(CF}_3\text{)(CO)(PPh}_3)_2$ is a bright yellow crystalline solid. It is indefinitely stable under nitrogen, but slowly darkens in the presence of oxygen. This reaction with oxygen is presumably to form the $\eta^2\text{-O}_2$ adduct $\text{Rh(O}_2\text{)(CF}_3\text{)(CO)(PPh}_3)_2$. This oxygen complex was extremely unstable in solution and could not be isolated pure. The IR spectrum of a solid sample of $\text{Rh(CF}_3\text{)(CO)(PPh}_3)_2$ stored under oxygen for some days showed changes corresponding to the formation of $\text{Rh(O}_2\text{)(CF}_3\text{)(CO)(PPh}_3)_2$. The carbonyl stretch in the IR spectrum shifted from 1986 cm^{-1} in the parent compound to 1997 cm^{-1} , while another band appeared at 840 cm^{-1} and was attributed to the $\nu(\text{O}_2)$ (Scheme 2).

Other simple molecules such as CO , C_2H_4 , and H_2 all appeared to give reversible reactions with $\text{Rh(CF}_3\text{)(CO)(PPh}_3)_2$. The colour of the solutions of $\text{Rh(CF}_3\text{)(CO)-}$

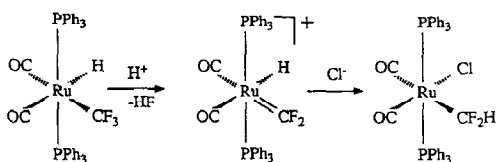
(PPh₃)₂ lightened appreciably on addition of hydrogen, ethylene, or carbon monoxide, but upon removal of the solvent the complexes reverted to starting material. Halogens oxidatively added to Rh(CF₃)(CO)(PPh₃)₂ to give rhodium(III) complexes of the general type RhX₂(CF₃)(CO)(PPh₃)₂ (X = Cl, Br, I). These complexes all had the geometry with *trans* triphenylphosphines and *cis* halides (Scheme 2).

The addition of methyl iodide to Rh(CF₃)(CO)(PPh₃)₂ did not give the expected *d*⁶ rhodium complex, RhI(CH₃)(CF₃)(CO)(PPh₃)₃. Although this was probably the initial product, the complex isolated was an acyl complex, Rh(CF₃)(C-[O]CH₃)(PPh₃)₂. The NMR evidence indicated that this was also the formulation of the compound in solution. The geometry depicted is based upon the relative *trans* effects of the iodide, trifluoromethyl, and acyl ligands. The large *trans* effect of the acyl ligand would place it in the apical position of square pyramidal geometry (Scheme 2).

In contrast to the reactions described above, the action of acids on Rh(CF₃)(CO)(PPh₃)₂ resulted in modification of the trifluoromethyl ligand. Acids are known to react with the α -fluorines of σ -bonded transition metal fluorocarbon complexes to remove a fluorine substituent [1,3,21]. The reaction of Rh(CF₃)(CO)(PPh₃)₂ with aqueous acids such as HCl and HClO₄ involved conversion of the trifluoromethyl group into a carbonyl ligand, to give RhX(CO)(PPh₃)₂ (X = Cl, ClO₄) (Scheme 2). Reactions of this type are known to go via carbene intermediates [3–10]. Evidence for the presence of a difluorocarbene complex in these reactions was obtained from a study of the reaction of Rh(CF₃)(CO)(PPh₃)₂ with anhydrous HCl.

The reaction of Rh(CF₃)(CO)(PPh₃)₂ with dry HCl gas did not give an isolable carbene complex, but the major product from the reaction, *cis*-RhCl₂(CF₂H)(CO)(PPh₃)₂, must have been formed via a difluorocarbene intermediate. Difluoromethyl ligands are known to arise from the treatment with acids of complexes containing *cis* hydride and trifluoromethyl ligands, as demonstrated by the conversion of RuH(CF₃)(CO)₂(PPh₃)₂ into Ru(CF₂H)Cl(CO)₂(PPh₃)₂ [1] (Scheme 3). Therefore in the reaction of Rh(CF₃)(CO)(PPh₃)₂ with HCl there must be an intermediate complex that has a hydride and a difluorocarbene bound at adjacent coordination sites. Such an intermediate would be a cationic difluorocarbene complex such as [RhHCl(CF₂)(CO)(PPh₃)₂]⁺.

The mechanism of this reaction was investigated more fully by NMR spectroscopy and labelling studies. The reaction was quenched before completion, the solvent removed, and the mixture examined by NMR spectroscopy. This gave the ³¹P NMR spectrum shown in Fig. 1. All of the compounds in this mixture (shown in Scheme 4), except for RhHCl(CF₃)(PPh₃)₂, were identified by comparison of their spectral data with those of pure samples. The ¹H NMR spectrum of the same reaction mixture showed only signals corresponding to the aromatic protons of the



Scheme 3

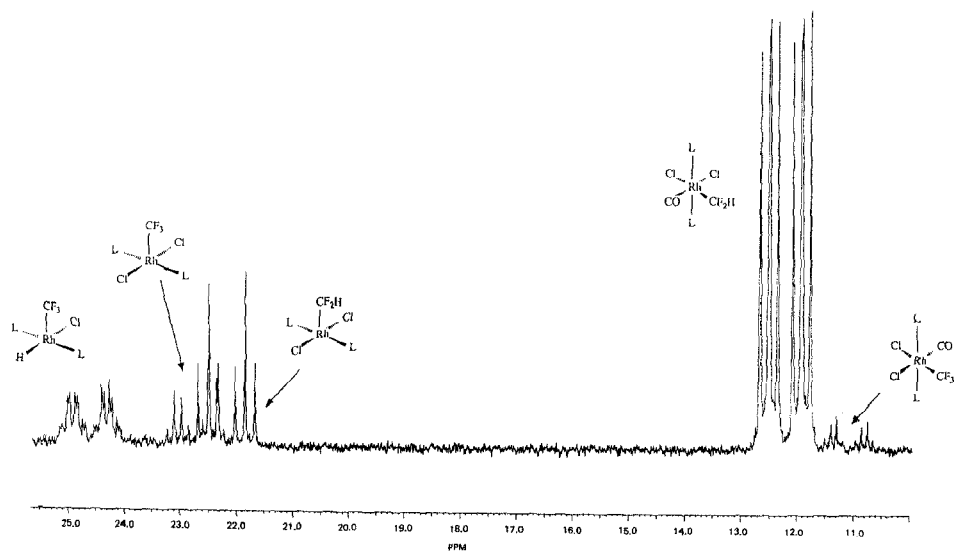
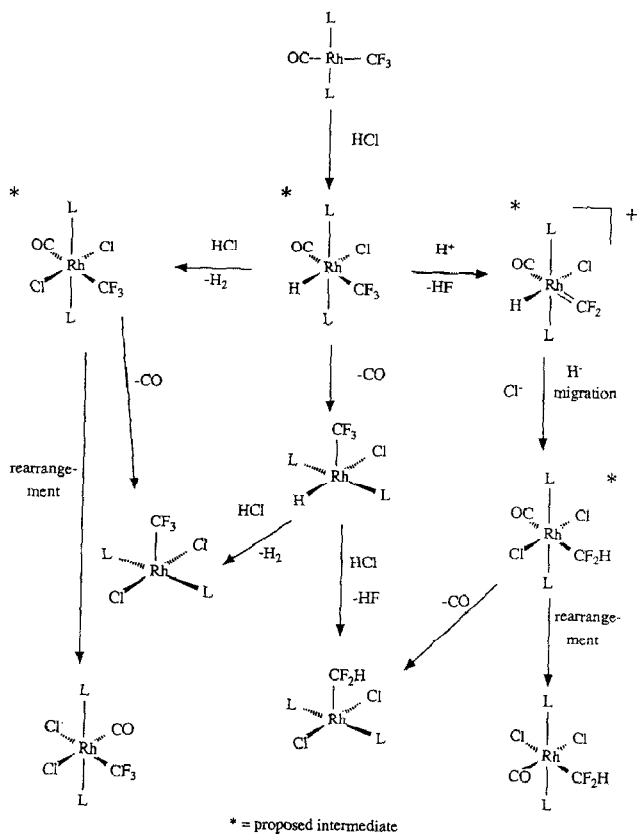


Fig. 1. ^{31}P NMR spectrum of the reaction of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ with HCl .



Scheme 4. Proposed mechanism for the reaction of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ with HCl .

triphenylphosphines, and a hydride signal at -12.8 ppm. The ^{31}P NMR signal corresponding to the hydride ^1H resonance (determined by incompletely decoupling the high field hydride), appeared at a chemical shift associated with coordinatively unsaturated rhodium complexes. This resonance also showed couplings assigned as $^1J(\text{RhP})$, $^2J(\text{HP})$ and $^3J(\text{FP})$. From this information the complex was judged to be the five-coordinate $\text{RhHCl}(\text{CF}_3)(\text{PPh}_3)_2$. When the reaction was carried out in an NMR tube a similar result was obtained, but it was possible to monitor the progress of reaction to some extent. For example, the concentration of the complex $\text{RhHCl}(\text{CF}_3)(\text{PPh}_3)_2$ diminished as the reaction proceeded. No other intermediates were observed, as they were probably only short-lived species and so, not present in large enough quantities to be detected.

The proposed mechanism which accounts for the formation of all of the products depicted in Fig. 1 (Scheme 4), begins with the oxidative addition of HCl to $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, to give $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. The geometry $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ is inferred from comparison with the isolated and fully characterised product from the addition of HCl to $\text{Ir}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ [17]. The intermediate $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ then reacts rapidly in one of three possible ways;

(i) α -Fluorine abstraction by H^+ would give the cationic difluorocarbene complex $[\text{RhHCl}(\text{CF}_2)(\text{CO})(\text{PPh}_3)_2]^+$. Subsequent hydride migration and chloride addition results in the difluoromethyl complex, *trans*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ (where *trans* refers to the chloride ligands). This geometry, with the carbonyl group *trans* to the fluorocarbon ligand, is not favoured in rhodium(III) complexes. This is most clearly seen in the five-coordinate complex *trans*- $\text{RhCl}_2(\text{CF}_2\text{CF}_2\text{H})(\text{PPh}_3)_2$, which will not take up a carbonyl in the vacant coordination site *trans* to the fluorocarbon ligand [22]. Therefore this unstable geometry is avoided, by either rapid rearrangement or loss of the carbonyl ligand, to give *cis*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ or *trans*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$, respectively.

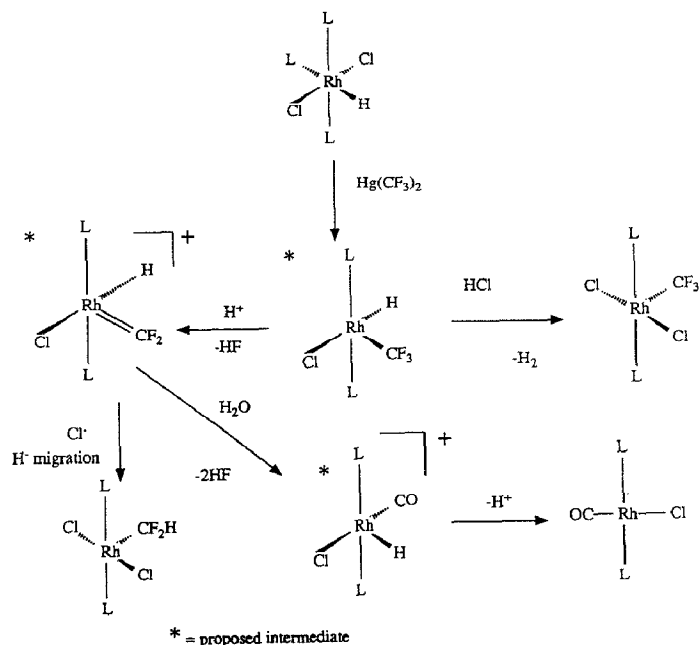
(ii) Dehydrogenation of the intermediate complex $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ with HCl would give H_2 and *trans*- $\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. Again, this is the least favoured position for the carbonyl ligand in rhodium(III) fluorocarbon complexes, and so this compound also rearranges, to give *cis*- $\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, or is decarbonylated to give *trans*- $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$.

(iii) The intermediate complex $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ also has the least favourable arrangement of carbonyl and fluorocarbon ligands. Loss of the carbonyl from this complex gives the observed hydride complex $\text{RhHCl}(\text{CF}_3)(\text{PPh}_3)_2$. As with $\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, the new five coordinate complex can react with HCl in two possible ways:

(a) The HCl may abstract an α -fluorine to give the cationic difluorocarbene complex $[\text{RhHCl}(\text{CF}_2)(\text{PPh}_3)_2]^+$. Hydride migration and addition of chloride then gives the five coordinate difluoromethyl product *trans*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$.

(b) HCl may also cleave hydride from $\text{RhHCl}(\text{CF}_3)(\text{PPh}_3)_2$, to generate H_2 and the five coordinate trifluoromethyl complex $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$.

The presence of a difluoromethyl ligand in the complexes $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and *cis*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ was inferred from the coupling pattern for the ^{31}P NMR signals. The proton of the CF_2H group could not be detected in the ^1H NMR spectrum, but was expected, in the light of the position of the corresponding signal from $\text{Mn}(\text{CF}_2\text{H})(\text{CO})_5$ (δ 7.23), [23] to be concealed by the triphenylphos-



Scheme 5

phine protons. This was confirmed, when the reaction was carried out with deuterium chloride instead of HCl. The ^{31}P NMR spectrum of the reaction mixture formed from ^2HCl and $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ indicated that the same products were present. The ^2H NMR spectrum of the reaction mixture had a broad signal attributed to the deuterium of the difluoromethyl ligand at 7.6 ppm. Furthermore as expected the deuteride resonance for $\text{Rh}^2\text{HCl}(\text{CF}_3)(\text{PPh}_3)_2$ appeared at higher field, viz. -12.8 ppm.

The complexes $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$ were also obtained from the reaction between $\text{Hg}(\text{CF}_3)_2$ and $\text{RhHCl}_2(\text{PPh}_3)_3$.

Synthesis of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$

The success with the rhodium(I) hydride complex $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ as a precursor to $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ prompted the investigation of other rhodium hydride compounds. The only other hydride complex which was found to react satisfactorily with $\text{Hg}(\text{CF}_3)_2$ was $\text{RhHCl}_2(\text{PPh}_3)_2$.

When $\text{RhHCl}_2(\text{PPh}_3)_2$ was heated in benzene with $\text{Hg}(\text{CF}_3)_2$, the solution rapidly became dark and mercury was precipitated. Filtration of the cooled solution and isolation of the rhodium phosphine complexes gave a mixture of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$, which were successfully separated by column chromatography. This reaction provided a good route to five-coordinate rhodium(III) fluorocarbon complexes.

The mechanism of formation of these products (Scheme 5) must initially involve the transfer of a trifluoromethyl group to the rhodium. The other possibility is transfer of a difluorocarbene fragment, as difluorocarbene complexes are known to be precursors to both difluoromethyl and trifluoromethyl ligands [2,11]. However, $\text{Hg}(\text{CF}_3)_2$ has never been observed to transfer a difluorocarbene ligand directly to a

transition metal centre, and so our proposed mechanism for this reaction (Scheme 5) concentrates on the modification of an introduced trifluoromethyl ligand. For the reaction to produce significant amounts of the difluoromethyl complex, $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ it must have as an intermediate a complex which contains a hydride ligand *cis* to the trifluoromethyl group. Replacement of both rhodium(I) bound chloride (as in $\text{RhCl}(\text{PPh}_3)_3$) and rhodium(I) bound hydride (as in $\text{RhH}(\text{CO})(\text{PPh}_3)_3$) by use of $\text{Hg}(\text{CF}_3)_2$ has been demonstrated previously. Treatment of the d^6 rhodium hydride complex $\text{RhHCl}_2(\text{CO})(\text{PPh}_3)_3$ with $\text{Hg}(\text{CF}_3)_2$ gave large amounts of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$. We thus suggest that the chloride is replaced in preference to the hydride ligand. The proposed mechanism which accounts for the formation of these products is shown in Scheme 5.

The d^6 difluoromethyl complex $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ was characterised by a single crystal X-ray diffraction study.

Description of the structure of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

The X-ray crystallographic study of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ showed that the complex exists in the solid state as a distorted square pyramid (or distorted trigonal bipyramid). $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ crystallises in the monoclinic space group *Cc*. The refinement with all atoms anisotropic gave $R = 0.0368$ and $R_w = 0.0442$. The ORTEP representation of the structure is depicted in Fig. 2. Tables 1 and 2 list the relevant bond lengths and angles. It should be noted that the data for this structure were collected at room temperature and so the thermal motion of the fluorine atoms is high. Thus the parameters involving these atoms are unreliable, as can be readily seen by examination of the Cl–F distances. The geometry is that of a distorted square pyramid, with the chloride and phosphine ligands bent slightly away from

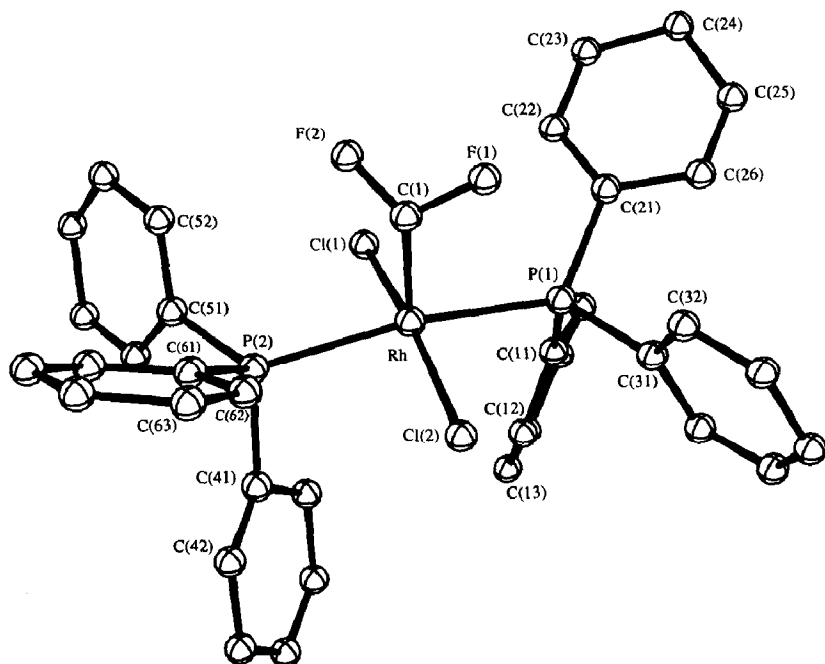


Fig. 2. ORTEP Representation of the molecular structure of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$.

Table 1

Selected bond distances (Å) for $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

C1–Rh	1.98(1)
P1–Rh	2.379(5)
P2–Rh	2.368(5)
Cl1–Rh	2.324(5)
Cl2–Rh	2.316(4)
C1–F1	1.28(3)
C1–F2	1.17(2)

the difluoromethyl group. The two phosphorus atoms and two chlorine atoms do not all lie in the same plane. The calculated best fit plane places the phosphines (P1–Rh–P2 168.7(1)°) (≈ 0.025 Å) above the plane. The chloride (Cl1–Rh–Cl2 166.0(2)°) ligands are displaced below the plane by the same amount ≈ 0.025 Å. This gives the geometry as a puckered square pyramid, with the rhodium 0.258 Å out of the P1–P2–Cl1–Cl2 plane.

The geometry is comparable to that of other rhodium(III) five-coordinate complexes with the metal carbon bond length falling within the range for carbon rhodium single bonds with vacant *trans* coordination sites [24–26].

Reactions of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

The trifluoromethyl complex $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$ is unstable and slowly decomposes in solution. In contrast, the difluoromethyl complex $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ is stable under normal conditions.

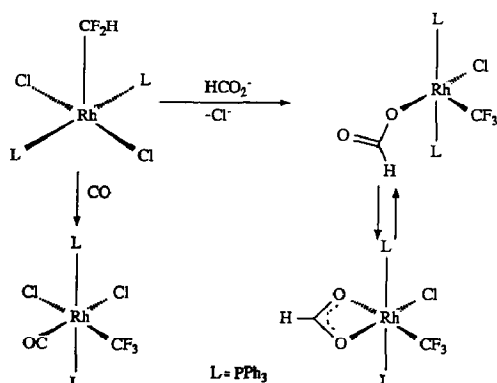
The five-coordinate complexes $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$ react with coordinating ligands such as carbon monoxide and formate. Both $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$ reacted with carbon monoxide, to give the six-coordinate fluorocarbon complexes *cis*- $\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ and *cis*- $\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, respectively. This reaction was slow, requiring high pressures of carbon monoxide overnight, to give the product (Scheme 6).

The low rate of the carbonylation of these coordinatively unsaturated compounds is a result of the requirement for rearrangement before the carbonyl ligand can

Table 2

Selected bond angles (°) for $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

P1–Rh–P2	168.7(1)
Cl1–Rh–Cl2	166.0(2)
Cl1–Rh–P1	88.8(1)
Cl1–Rh–P2	89.7(1)
Cl2–Rh–P1	89.3(1)
Cl2–Rh–P2	89.5(1)
C1–Rh–P1	97.1(8)
C1–Rh–P2	94.1(8)
C1–Rh–Cl1	96.1(5)
C1–Rh–Cl2	97.9(5)
F1–C1–Rh	114(2)
F2–C1–Rh	119(1)
F1–C1–F2	109(1)



Scheme 6

remain coordinated. The initial products from CO addition to these complexes would be *trans*- $RhCl_2(CF_2H)(CO)(PPh_3)_2$ and *trans*- $RhCl_2(CF_3)(CO)(PPh_3)_2$. However, as previously mentioned, the geometry in which a carbonyl ligand is situated *trans* to a fluorocarbon ligand on rhodium(III) complexes is not favoured. The only other known example of a five-coordinate d^6 rhodium fluorocarbon complex is $RhCl_2(CF_2CF_2H)(PPh_3)_2$. This tetrafluoroethyl complex, while apparently coordinating CO in the site *trans* to the fluorocarbon ligand, did not retain the carbonyl ligand when the carbon monoxide atmosphere was released [22]. Reactions of $RhCl_2(CF_2H)(PPh_3)_2$ and $RhCl_2(CF_3)(PPh_3)_2$ with other neutral ligands (CH_3CN , *p*-tolylisocyanide and triphenylphosphine) returned only starting materials or resulted in decomposition of the metal complex.

The five-coordinate $RhCl_2(CF_2H)(PPh_3)_2$ reacts rapidly with sodium formate to give $RhCl(O_2CH)(CF_2H)(PPh_3)_2$ (Scheme 6). This complex gives all the indications of having the formate η^2 -bonded in the solid state. The complex is only pale yellow, whereas $RhCl_2(CF_2H)(PPh_3)_2$, $RhCl_2(CF_2CF_2H)(PPh_3)_2$ and $RhCl_2(CF_3)(PPh_3)_2$ are all bright orange. The Nujol mull IR spectrum indicated the presence of an η^2 -formate ligand. However, the NMR data indicated that the complex was monohapto in solution.

Carbon monoxide could not be added to $RhCl(O_2CH)(CF_2H)(PPh_3)_2$; even when high pressures were used for prolonged periods this complex did not retain carbon monoxide. Attempts to reduce $RhCl(O_2CH)(CF_2H)(PPh_3)_2$ by heating its solution in the presence of other coordinating ligands gave only unchanged starting material or complexes without fluorocarbon ligands.

The ^{31}P spectra of difluoromethyl complexes have provided a sensitive probe of the metal coordination geometry. Comparison of the ^{31}P spectrum of $RhCl_2(CF_2H)(PPh_3)_2$ (dt) with that of *cis*- $RhCl_2(CF_2H)(CO)(PPh_3)_2$ (ddd) highlights this feature. The difference between these complexes is only a subtle one and yet results in distinctly different coupling patterns. Both spectra are the result (assuming free rotation about the metal carbon bond) of coupling of two apparently chemically equivalent fluorines to two chemically equivalent phosphorus atoms. The different coupling patterns in the ^{31}P spectrum can be accounted for when the possible rotamers are considered (see Fig. 3). The five-coordinate complex $RhCl_2(CF_2H)(PPh_3)_2$ has two positions in a 360° rotation in which the fluorines are both

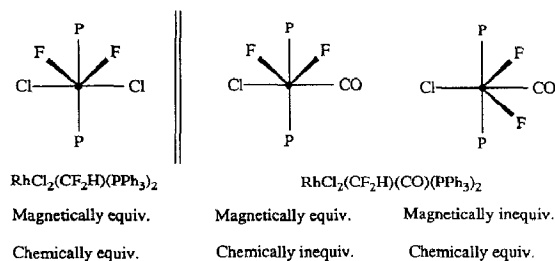


Fig. 3. View down carbon-rhodium bond in $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ and $\text{cis-RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$.

magnetically and chemically equivalent in relation to the phosphorus. In contrast the six-coordinate complex $\text{cis-RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ has no position in which the fluorines are both magnetically and chemically equivalent. This is a result of the relative coordination geometry around the difluoromethyl ligand, and is seen in any case in which the molecule, as viewed in Fig. 3, is unsymmetrical. For example the ^{31}P spectra of $\text{RhCl}(\text{O}_2\text{CH})(\text{CF}_2\text{H})(\text{PPh}_3)_2$, $\text{OsCl}_2(\text{CF}_2\text{H})(\text{NO})(\text{PPh}_3)_2$, $\text{cis-IrCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$ and $\text{RuCl}(\text{CF}_2\text{H})(\text{CO})_2(\text{PPh}_3)_2$ show the same type of pattern [27].

Conclusion

The σ -fluorocarbon chemistry of triphenylphosphinerhodium complexes is dominated by the reactivity of the α -fluorines. While there are a number of reactions which involve metal bonded difluorocarbene ligands, particularly the addition of HCl to $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$, no isolable difluorocarbene complexes of rhodium have been obtained. Even $\text{Cd}(\text{CF}_3)_2 \cdot \text{DME}$, which has proved to be a good source of the difluorocarbene ligand for d^8 irridium, ruthenium and osmium complexes, gave no isolable difluorocarbene derivatives. However, the bonding of the trifluoromethyl ligand to rhodium(I) has resulted in a clearer picture of the factors which influence the stability of σ -fluorocarbon complexes. One of the most important appears to be the electron density at the metal centre, with more electron rich metal fragments activating the α -fluorines in σ -fluorocarbon metal complexes.

Experimental

General

Standard Schlenk techniques were used for all manipulations involving oxygen or moisture sensitive compounds. Benzene, toluene, THF, diethyl ether, and hexane were distilled from sodium/benzophenone and dichloromethane and acetonitrile from calcium hydride.

When procedures involved materials that were not air sensitive, the solvents were purified by chromatography on alumina (Spence type H, 100–200 mesh) or filtered prior to use. In these cases, solvent removal under reduced pressure involved use of a rotary evaporator. In routine recrystallizations the sample was dissolved in a low boiling point solvent, and a higher boiling point solvent in which the compound was insoluble was added. Evaporation under reduced pressure resulted in gradual crystallization.

Table 3

IR data ^a for rhodium compounds

	$\nu(\text{CO})$ ^b	$\nu(\text{CF})$ ^b	Others ^c
$\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	1986	1083,974,967,954	
$\text{RhI}(\text{C}[\text{O}]\text{CH}_3)(\text{CF}_3)(\text{PPh}_3)_2$	1638m	1095,1044,1026	
$\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	2105	1096,1036	300w,305w
$\text{Rh}(\text{O}_2)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	1996	1094,1060	840m $\nu(\text{O}_2)$
$\text{RhBr}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	2100	1094,1066	
$\text{RhI}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	2098	1088,1026	
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$		1096,1015	295w
$\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$		1110,1094,1045,999	298w
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$	2103	1091,1088,964	298w,304w
$\text{RhCl}(\text{O}_2\text{CH})(\text{CF}_2\text{H})(\text{PPh}_3)_2$	1557	1010,982	804w,1307m(O_2CH)

^a Recorded as Nujol mulls on KBr or CsI and reported as cm^{-1} . ^b All bands are strong unless otherwise stated (w, weak; m, medium). ^c $\nu(\text{RhCl})$ unless otherwise stated.

Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) (Table 3) were recorded on a Perkin Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film. All spectra were recorded with Nujol mulls between KBr plates or as a dichloromethane solution in KBr cells. Far-infrared spectra ($400\text{--}200\text{ cm}^{-1}$) were recorded with concentrated Nujol mulls between CsI plates. ^1H NMR (Tab. 5) were recorded on a Bruker AM-400 spectrometer operating at 400 MHz and are quoted in ppm down field from TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR (Tab. 4) were recorded on a Bruker AM-400 at 162 MHz and are quoted relative to 85% phosphoric acid solution (external). ^2H NMR were recorded on a Bruker AM-400 instrument at 61.4 MHz and referenced to CDCl_3 (7.26 ppm). Melting points were determined on a Reichert microscope hot stage and are uncorrected. Elemental analyses for carbon, hydrogen, and fluorine were preformed by Professor A.D. Campbell and associates of the University of Otago, whose help is gratefully acknowledged. $\text{RhCl}(\text{PPh}_3)_3$ [22], $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ [29], $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [30], $\text{RhHCl}_2(\text{PPh}_3)_3$ [31] and $\text{RhCl}(\text{Pcy}_3)_2$ [14] were all prepared by standard procedures.

Table 4

^{31}P NMR data for rhodium compounds (recorded at room temperature in CDCl_3 and quoted in ppm, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet)

	δ		$^1J(\text{RhP})$ (Hz)	$^3J(\text{FP})$ (Hz)
$\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	22.87	dq	100.8	19.7
$\text{RhI}(\text{C}[\text{O}]\text{CH}_3)(\text{CF}_3)(\text{PPh}_3)_2$	19.42	dq	120.8	21.3
$\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	11.02	dq	87.3	11.02
$\text{RhHCl}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	24.63	dq	100.4	20.2
$\text{RhBr}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	8.40	dq	88.1	17.1
$\text{RhI}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$	5.12	dq	89.3	16.8
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$	22.16	dt	102.2	25.2
$\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$	22.79	dq	101.2	20.4
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$	12.22	ddd	93.5	22.8, 27.1
$\text{RhCl}(\text{O}_2\text{CH})(\text{CF}_2\text{H})(\text{PPh}_3)_2$	22.79	ddd	111.2	27.7, 32.7

Table 5

^1H NMR data for rhodium compounds (recorded at room temperature in CDCl_3 and quoted as downfield shift from TMS)

	δ	$^2J(\text{RhH})$ (Hz)
$\text{RhI}(\text{C}[\text{O}]\text{CH}_3)(\text{CF}_3)(\text{PPh}_3)_2$	1.55 CH_3	12.0(dt)
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$	7.4 ^a CF_2H	^b
$\text{RhCl}_2(\text{CF}_2\text{H})(\text{CO})(\text{PPh}_3)_2$	7.4 ^a CF_2H	^b
$\text{RhCl}(\text{O}_2\text{CH})(\text{CF}_2\text{H})(\text{PPh}_3)_2$	6.18 O_2CH	^c
$\text{RhHCl}(\text{CF}_3)(\text{PPh}_3)_2$	-12.8 Rh-H	^c

^a From ^2H NMR recorded in CH_2Cl_2 at room temperature as downfield shift from $\text{TMS}-d_1$. ^b Broad due to quad. nuclei. ^c Complex multiple coupling not assigned.

Reactions

$\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. To a suspension of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (1 g, 1.09 mmol) in benzene (40 ml) was added $\text{Hg}(\text{CF}_3)_2$ (700 mg, 2.07 mmol). This mixture was heated under reflux for 30 min, during which mercury was deposited. The solution was allowed to cool to room temperature and filtered through Celite, and ethanol (50 ml) was added. The solvent volume reduced, to give yellow crystals of the product (600 mg, 77%). An analytical sample was recrystallized from dichloromethane/ethanol. m.p. 170–172°C. Anal. Found: C, 62.06; H, 4.37; F, 7.57. $\text{C}_{38}\text{H}_{30}\text{F}_3\text{OP}_2\text{Rh}$ calcd.: C, 62.00; H, 4.17; F, 7.87%.

$\text{RhCl}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. (a) Chlorine (0.3 mmol) in dichloromethane was added to a solution of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (200 mg, 0.28 mmol) in dichloromethane (10 ml). The solution was stirred for 3 min then ethanol (20 ml) was added and the solvent volume reduced to give crystals of the product (184 mg, 84%); m.p. 166–168°C. Anal. Found: C, 56.78; H, 4.61. $\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{F}_3\text{OP}_2\text{Rh}$ calcd.: C, 57.38; H, 3.87%.

(b) A solution of $\text{RhCl}_2(\text{CF}_3)(\text{PPh}_3)_2$ (100 mg, 0.13 mmol) in dichloromethane (10 ml) was stirred for 15 h at room temperature under carbon monoxide (400 kPa). Ethanol was added and the solvent volume reduced to give the product (98 mg, 95%).

$\text{RhBr}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. Bromine (0.3 mmol) was added to a solution of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (200 mg, 0.28 mmol) in dichloromethane (10 ml). The solution was stirred for 10 min then ethanol (20 ml) was added and the solvent volume reduced to give crystals of the product (164 mg, 68%); m.p. 160–164°C. Anal. Found: C, 51.40; H, 4.41; F, 5.75. $\text{C}_{38}\text{H}_{30}\text{Br}_2\text{F}_3\text{OP}_2\text{Rh}$ calcd.: C, 51.61; H, 3.42; F, 6.45%.

$\text{RhI}_2(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. To a solution of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (200 mg, 0.28 mmol) in dichloromethane (10 ml) was added iodine (0.3 mmol) in dichloromethane. The solution was stirred for 20 min then ethanol (20 ml) was added and the solvent volume reduced to give crystals of the product (138 mg, 51%); NMR data indicate the presence of $\frac{1}{2}\text{CH}_2\text{Cl}_2$ solvate. m.p. 154–155°C. Anal. Found: C, 45.62; H, 3.31; F, 5.31. $\text{C}_{38}\text{H}_{30}\text{I}_2\text{F}_3\text{OP}_2\text{Rh} \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ calcd.: C, 45.30; H, 3.70; F, 5.58%.

$\text{RhI}(\text{C}[\text{O}]\text{CH}_3)(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$. To a solution of $\text{Rh}(\text{CF}_3)(\text{CO})(\text{PPh}_3)_2$ (200 mg, 0.28 mmol) in benzene (10 ml) was added iodomethane (5 ml). The solution was

stirred for 2 h then all the solvent was removed in vacuo. The residue was taken up in dichloromethane (15 ml) and ethanol was added to give crystals of the product (170 mg, 70%); m.p. 158–160°C. Anal. Found: C, 54.66; H, 4.47; F, 6.07. $C_{39}H_{33}IF_3OP_2Rh$ calcd.: C, 54.05; H, 3.81; F, 6.58%.

$RhCl_2(CF_2H)(CO)(PPh_3)_2$. (a) Dry HCl gas was bubbled through a solution of $Rh(CF_3)(CO)(PPh_3)_2$ (300 mg, 0.42 mmol) in freshly distilled dichloromethane (20 ml), for ca. 5 s. The mixture was then allowed to stand for 1 min then all the solvent was removed in vacuo. The solid was taken up in dichloromethane and chromatographed on a silica gel column. The second band was collected (see text for description of other products) and recrystallized from ethanol (160 mg, 48%). m.p. 208–209°C. Anal. Found: C, 58.41; H, 4.36. $C_{38}H_{31}Cl_2F_2OP_2Rh$ calcd.: C, 58.70; H, 4.00%.

(b) A solution of $RhCl_2(CF_2H)(PPh_3)_2$ (100 mg, 0.13 mmol) in dichloromethane (10 ml) was stirred for 15 h at room temperature under carbon monoxide (400 kPa). Ethanol was added and the solvent volume reduced to give the product (98 mg, 95%).

$RhCl_2(CF_2H)(PPh_3)_2$ and $RhCl_2(CF_3)(PPh_3)_2$. To a suspension of $RhHCl_2-(PPh_3)_3$ (400 mg, 0.43 mmol) in benzene (20 ml) was added $Hg(CF_3)_2$ (440 mg, 1.2

Table 6

Crystal data and details of the structure determination of $RhCl_2(CF_2H)(PPh_3)_2$

<i>Crystal data</i>	
Formula	$C_{37}H_{31}Cl_2F_2P_2Rh$
Molecular weight	749.42 g mol ⁻¹
Space group	Cc
Crystal system	monoclinic
<i>a</i>	18.391(2) Å
<i>b</i>	9.753(1) Å
<i>c</i>	21.664(3) Å
β	120.094(8)°
<i>V</i>	3362.0 Å ³
<i>Z</i>	4
<i>d</i> (calcd)	1.4806 g cm ⁻³
<i>F</i> (000)	1520
μ	7.9 cm ⁻¹
<i>Data collection and reduction</i>	
Diffractionmeter	Nonius Cad-4
Radiation	Mo-K α (λ 0.71069 Å)
Temperature	294–296 K
Scan technique	$2\theta/\omega$
2θ (min-max)	2–54°
Scan speed	2–30° min ⁻¹
No. unique reflections	3567
No. unique obsd. reflections	3229
σ criterion	3.0
<i>Structure determination and refinement</i>	
<i>R</i> and <i>R_w</i> ^a	0.0368, 0.0442
Weight	$1/(\sigma^2(F) + 0.003076F^2)$

^a $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

mmol). The solution was then heated under reflux for 1 h, during which time mercury was deposited. The solution was allowed to cool to room temperature and all the solvent removed in vacuo. The residue was taken up in dichloromethane filtered through Celite, and transferred to a silica column. Elution with dichloromethane gave a rapidly moving yellow band, the solid from which was recrystallized

Table 7

Atomic coordinates for non-hydrogen atoms in $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$

Atom	x	y	z
Rh	0.0000(0)	0.16828(4)	0.25000(0)
F1	0.0249(8)	0.4273(9)	0.2122(5)
F2	-0.0556(5)	0.4295(8)	0.2486(8)
P1	0.0085(2)	0.1440(4)	0.1445(2)
P2	-0.0083(2)	0.1447(4)	0.3551(2)
Cl1	0.1446(2)	0.1374(5)	0.3167(2)
Cl2	-0.1443(2)	0.1410(5)	0.1824(2)
C1	0.003(1)	0.371(1)	0.254(1)
C11	-0.0349(7)	-0.020(1)	0.1162(6)
C12	0.0008(9)	-0.127(1)	0.1655(8)
C13	-0.0267(9)	-0.255(1)	0.1571(8)
C14	-0.095(1)	-0.299(1)	0.0911(8)
C15	-0.133(1)	-0.197(1)	0.0358(8)
C16	-0.1016(9)	-0.047(1)	0.0422(8)
C21	-0.0527(6)	0.256(1)	0.0647(6)
C22	-0.1265(7)	0.299(1)	0.0504(7)
C23	-0.1767(8)	0.374(1)	-0.0117(7)
C24	-0.1499(9)	0.407(2)	-0.0623(7)
C25	-0.071(1)	0.344(1)	-0.0440(8)
C26	-0.0199(8)	0.284(1)	0.0197(8)
C31	0.1071(8)	0.138(1)	0.1549(6)
C32	0.1579(8)	0.252(1)	0.1753(8)
C33	0.2429(8)	0.250(1)	0.1842(7)
C34	0.2770(8)	0.133(2)	0.1741(8)
C35	0.2253(9)	0.030(2)	0.1552(9)
C36	0.1426(8)	0.012(1)	0.1425(7)
C41	0.0309(4)	-0.0350(7)	0.3842(4)
C42	0.1009(4)	-0.0602(8)	0.4480(4)
C43	0.1350(6)	-0.183(1)	0.4701(5)
C44	0.1048(6)	-0.280(1)	0.4233(6)
C45	0.0371(6)	-0.2679(8)	0.3549(5)
C46	-0.0018(6)	-0.1338(8)	0.3293(5)
C51	-0.1204(4)	0.1471(8)	0.3407(4)
C52	-0.1646(6)	0.2689(9)	0.3172(5)
C53	-0.2426(6)	0.280(1)	0.3045(5)
C54	-0.2775(5)	0.157(1)	0.3126(5)
C55	-0.2344(5)	0.019(1)	0.3394(5)
C56	-0.1532(5)	0.031(1)	0.3523(5)
C61	0.0498(4)	0.2492(7)	0.4301(4)
C62	0.1312(5)	0.3150(9)	0.4472(5)
C63	0.1763(5)	0.3900(9)	0.5092(5)
C64	0.1453(5)	0.405(1)	0.5537(4)
C65	0.0677(6)	0.363(1)	0.5397(5)
C66	0.0238(5)	0.272(1)	0.4801(5)

from ethanol to give $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (27%). A second slower band was then collected and the isolated solid recrystallized from ethanol to give orange crystals of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2 \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ (38%). m.p. 192–193°C. Anal. Found: C, 57.77; H, 4.49. $\text{C}_{37}\text{H}_{31}\text{Cl}_2\text{F}_2\text{P}_2\text{Rh}$ calcd.: C, 58.05; H, 4.12%.

Further elution with CH_2Cl_2 /acetone 10/1 gave the final band. Recrystallization from ethanol gave an orange powder $\text{RhCl}_2(\text{CF}_3)\text{L}_2$ (32 mg, 10%), m.p. 167–171°C. Anal. Found: C, 57.73; H, 4.47. $\text{C}_{37}\text{H}_{30}\text{Cl}_2\text{F}_3\text{P}_2\text{Rh}$ calcd.: C, 57.91; H, 3.94%.

$\text{RhCl}(\text{O}_2\text{CH})(\text{CF}_2\text{H})(\text{PPh}_3)_2$. To a solution of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ (100 mg, 0.14 mmol) in dichloromethane (10 ml) was added sodium formate (50 mg, 0.74 mmol) in ethanol (15 ml). The mixture was stirred for 4 h, ethanol (15 ml) was added, and the dichloromethane removed in vacuo. The product was recrystallized from dichloromethane/ethanol (95 mg, 94%). m.p. 140–142°C. Anal. Found: C, 59.82; H, 4.26; F, 4.84. $\text{C}_{38}\text{H}_{32}\text{ClF}_2\text{O}_2\text{P}_2\text{Rh}$ calcd.: C, 60.13; H, 4.25; F, 5.01%.

Crystal structure determination

Crystals suitable for data collection were mounted on glass fibres and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least squares fits to the observed setting angles of 25 reflections, monochromated Mo-K_α (λ 0.71069 Å) radiation being used. Crystal alignment and decomposition were monitored throughout data collection by measuring three standard reflections every 100 measurements, no non-statistical variation being observed. The data were corrected for Lorentz and polarisation effects and equivalent reflections averaged. Absorption corrections were applied by the empirical azimuthal method [28], with the maximum and minimum correction factors being 0.9991 and 0.8898 respectively. Computing was carried out by using the SDP suite of programmes on a PDP-11 for initial data processing, SHELX-76 on an IBM 4341 for structure solution and refinement.

Structure solution was by conventional Patterson and Fourier techniques and refinement was by full-matrix least-squares. The molecule has a pseudo-two-fold axis but satisfactory convergence could not be obtained in space group $\text{C2}/c$. All atoms were refined individually with anisotropic thermal parameters. A final electron density map showed no significant features and hydrogen positions could not be resolved. Hydrogen atoms have been omitted from the refinement. Details of crystal data and intensity data collection parameters are summarised in Table 6 and final atomic coordinates are in Table 7. Tables of thermal parameters and observed and calculated structure factors may be obtained from the authors.

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