Dinuclear Pentafluorophenyl Compounds of Rhodium(III) with Anionic Bridging Ligands. Molecular Structures of $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]$ and $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]$ †

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Homodinuclear anionic rhodium(III) complexes of formula $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}X)_2]^{2-}$ (X = Br **2**, I **3**, SCN **4**, $MeCO_2$ **7**, CF_3CO_2 **8** or NO_3 **9**) or $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}C_2O_4)]^{2-}$ **10** have been prepared by treating the anionic derivative $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]^{2-}$ **1** with the appropriate alkali-metal or silver salt. Complex **4** has also been obtained from $[Rh(C_6F_5)_5]^{2-}$ and AgSCN, at 0 °C in CH_2Cl_2. The reaction between $[Rh(C_6F_5)_5]^{2-}$ and the solvated species $[Rh(C_6F_5)_3(Et_2O)_x]$ rendered $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]^{2-}$ **6** which reacts with CO_2 giving $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]^{2-}$ **11**. The tetranuclear $[\{Rh(C_6F_5)_3\}_4(\mu\text{-}CN)_4]^{4-}$ complex **5** has been prepared by the reaction of $[Rh(C_6F_5)_5]^{2-}$ with AgCN. The structures of **4** and **11** have been established by single-crystal X-ray diffraction studies: **4**, triclinic, space group $P\bar{1}$, a = 11.954(2), b = 13.053(2), c = 15.236(3) Å, α = 89.94(1), β = 100.33(1), γ = 104.89(2)°, Z = 1, $R = R'$ = 0.052 for 3692 observed reflections; **11**, monoclinic, space group $C2/c$, a = 28.306(4), b = 13.413(2), c = 45.245(7) Å, β = 101.42(1)°, Z = 8, R = 0.069 and R' = 0.070 for 6142 observed reflections. Both anionic complexes are dinuclear with two $Rh(C_6F_5)_3$ units linked through a centrosymmetric double thiocyanate bridge in **4** or a tridentate bridging CO_3^{2-} group in **11**, co-ordinated in an unusual μ-1:2κ^2O, 1$\kappa O'$, 2$\kappa O''$ fashion. In both complexes the five co-ordinated metal centres exhibit square-pyramidal arrangements of the ligands with a slight asymmetry in the bonding mode of the basal C_6F_5 groups which gives rise to short interatomic Rh ··· *o*-F distances.

In contrast with the extensive and interesting use of perhalogenoaryl groups (C_6X_5, X = F or Cl) in the organometallic chemistry of Pd, Pt[1] and Au,[2] the number of related complexes described for their neighbouring metals in the Periodic Table, Co, Rh or Ir, is rather small.[3] Working in this field, and using the pentachlorophenyl group, we have recently reported the preparation of anionic complexes of rhodium(I) and iridium(I). By treating these complexes with oxidizing agents, mononuclear paramagnetic, neutral or anionic compounds of rhodium(II) and iridium(II) are obtained.[4] When the pentafluorophenyl group is used, arylation of $[RhCl_3(tht)_3]$ (tht = tetrahydrothiophene) gives the homoleptic anionic $[Rh(C_6F_5)_5]^{2-}$ derivative;[5] this compound reacts with HCl to give the homodinuclear complex $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]^{2-}$ **1**, in which cleavage of the chloro bridges or treatment with silver perchlorate and subsequent addition of mono-[6] or bi-dentate[7] neutral ligands gives a variety of neutral and anionic five-co-ordinated, mono- or di-nuclear, rhodium(III) complexes.

As a continuation of our work we have studied the substitution of the chloro bridges, in complex **1**, by other anionic groups such as halogens or pseudo-halogens. Although the presence of this type of bridging ligand in Group 8–10 metal complexes is not new, such complexes with only σ-bonded R groups (no neutral ligands) are unusual.[8]

Additionally, we have also prepared a di-μ-hydroxo-dirhodium complex. The hydroxo compounds and their reactions have been of special interest because there are still relatively few stable and accessible hydroxo complexes of the platinum-group metals. Recently some hydroxo-bridged complexes of nickel,[9] palladium,[10] platinum[11] and rhodium[12] have been described; their importance is doubtless related to their interesting reactivity and potential relevance to catalysis.

We have also investigated the replacement of the chloro bridges of compound **1** by polydentate oxoanions; the oxoanions, simple or substituted, are well known to act as ligands and a great variety of bonding modes has been established.[13] However, in spite of the interest in bridging acetate, trifluoroacetate,[14,15] oxalate,[16] carbonate[17,18] and nitrate[19] transition-metal complexes, the chemistry of rhodium(III) with these anions acting as ligands is rather scarce.[20]

In this paper we describe the synthesis and reactivity of a series of dinuclear rhodium(III) complexes containing halide, pseudo-halide or oxygen-donor bridging ligands. They are particularly unusual since no neutral donor ligands are present.

Results and Discussion

Treatment of acetone solutions of the anionic dinuclear complex $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]$ **1** with alkali-metal salts (KBr, NaI or KSCN), according to equation (1),

$$[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]^{2-} + 2MX \longrightarrow [\{Rh(C_6F_5)_3\}_2(\mu\text{-}X)_2]^{2-} + 2MCl \quad (1)$$
$$X = Br\ \mathbf{2}, I\ \mathbf{3}\text{ or }SCN\ \mathbf{4}$$

results in substitution of the chloro bridging groups without cleavage of the bridges nor of any of the M–C bonds. The reactions are very slow and it is necessary to keep the solutions stirring, at refluxing temperature, for several hours. The crude products obtained have to be recrystallized to obtain pure compounds. Complexes **2** and **4** are also prepared, at room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

temperature, using the silver salts, AgBr or AgSCN instead of the alkali-metal salts, while for **3** the silver salt AgI does not react with **1**. Complex **4** can also be obtained, in better yield, by reaction of dichloromethane suspensions of the homoleptic anionic complex $[Rh(C_6F_5)_5]^{2-}$ with AgSCN (molar ratio 1 : 1); this reaction proceeds at 0 °C, in a nitrogen atmosphere, and it is complete in about 30 min. Careful addition of diethyl ether and storage at −20 °C renders orange crystals of **4**. The ^{19}F NMR ($CDCl_3$, 20 °C) spectrum of the mother-liquors shows resonances at δ 202.4 (d), 149.8 (t) and 161.4 (t) characteristic[21] of the presence of AgC_6F_5, so the rhodium centre is acting as an arylating agent in this reaction.

Compound **1** does not react with NaCN but it reacts with AgCN although the reaction product is a mixture of unidentified compounds. However the addition of AgCN to a dichloromethane solution of $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (ratio 1 : 1) yields the complex $[P(CH_2Ph)Ph_3]_n[\{Rh(C_6F_5)_3\}_n(\mu\text{-}CN)_n]$ **5**. The analytical results and the ^{19}F NMR spectrum indicate the presence of three C_6F_5 groups and one CN ligand per rhodium atom. The position of the ν(C≡N) absorption in the IR spectrum, at 2140 cm^{-1}, is similar to those for cyano-bridged anionic complexes.[22] The equivalent conductivities of nitromethane solutions of **5** with concentrations ranging from 10^{-3} to 10^{-5} equivalent l^{-1} were determined and $\Lambda_0 - \Lambda_e$ was plotted as a function of c; a slope of 2532 was found, suggesting a 4 : 1 electrolyte.[23] These data, together with the known ability of the CN group to form linear bridges and tetrameric compounds,[22,24,25] are consistent with the tetranuclear structure shown.

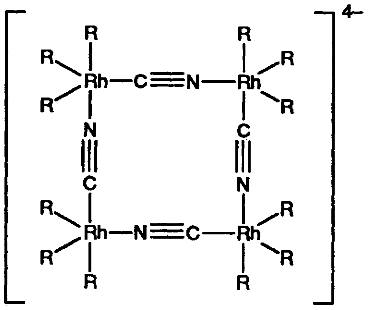
Considering that the pentafluorophenyl group is known to act as bridging ligand,[26] we designed a reaction pathway to enforce this co-ordination mode. A diethyl ether solution of $[Rh(C_6F_5)_3(Et_2O)_x]$ was evaporated to dryness and the residue dissolved in dichloromethane. This solution was slowly added to a dichloromethane suspension of the anion $[Rh(C_6F_5)_5]^{2-}$. In a few minutes the solid was completely dissolved. However, from this solution it was not possible to isolate the expected $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}C_6F_5)_2]$ compound; instead, an oily residue was obtained which can be crystallized by stirring in hexane. The final product is identified as $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]$ **6** (yield 90%). Complex **6** is also prepared, but in poorer yield, when an acetone solution of **1** is added to an aqueous solution of KOH (Rh : OH 1 : 1).

Other dinuclear rhodium(III) complexes containing oxygen-donor bridging ligands of formula $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}X)_2]$ (X = $MeCO_2^-$ **7**, $CF_3CO_2^-$ **8** or NO_3^- **9**) and $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}X')]$ (X′ = $C_2O_4^{2-}$ **10**) have been prepared by reaction of **1** with the appropriate silver salts AgX or Ag_2X'. If this reaction is carried out with Ag_2CO_3 compound **6** is obtained in a very low yield (< 20%); a similar result is found upon reaction of **1** with Na_2CO_3. Nevertheless the analogous μ-CO_3 compound, $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]$ **11**, is formed by bubbling CO_2 through a dichloromethane solution of **6** [equation (2)].

$$[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]^{2-} + CO_2 \longrightarrow [\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]^{2-} + H_2O \quad (2)$$

The silver salts of these oxoanions also react with the $[Rh(C_6F_5)_5]^{2-}$ anion but due to the great solubility of complexes **7**–**11** it was not possible to separate them from the AgC_6F_5 formed in the reaction.

The analytical results (C, H and N) and conductivities for the new complexes are listed in Table 1. Where complexes were obtained by different processes all the isolated samples gave satisfactory analyses. The syntheses to which the analytical data belong are marked by an asterisk (see Experimental section). The conductivities of the complexes, in acetone solutions, are those expected for 2 : 1 electrolytes (4 : 1 for complex **5**).[23,27] All the complexes are stable in the solid state and in solution. The ^{19}F NMR parameters are summarized in Table 2.



5 R = C_6F_5

Spectroscopic Data.—All the complexes show absorptions due to the pentafluorophenyl groups[28] at 1490s, 1050s and 950s cm^{-1}; the bands around 800 cm^{-1}, assignable to the X-sensitive mode of C_6F_5, cannot be unambiguously assigned since the cation $[P(CH_2Ph)Ph_3]^+$ also absorbs in this region. The absorptions due to the Rh(μ-X)Rh moiety (X = Br or I), for **2** and **3**, were not detected because they should lie below the lowest limit (200 cm^{-1}) of our spectrophotometer. The C≡N stretching mode, in **4**, at 2150 cm^{-1} is consistent with the presence of SCN bridges.[29]

The IR data, together with the analyses and the conductivities, provide evidence of dinuclear structures for the complexes (**6**–**11**) containing bridging oxygen-donor ligands. Complex **6** presents bands at 3670m (OH stretch) and 480s cm^{-1} (Rh–O stretch).[30] Its ^1H NMR spectrum displays a resonance at δ 5.22 (s, 2 H, OH) which is in agreement with that reported for the related rhodium(III) species[31] $[\{Rh(C_5Me_5)\}_2(\mu\text{-}OH)_3]^+$. The occurrence of a single ν(CO) band, in the 1500–1700 cm^{-1} region, at 1525vs and 1675vs cm^{-1} for **7** and **8** respectively, suggests that the acetate and trifluoroacetate groups are co-ordinated in a similar manner, and the values of the bands are consistent with those found for these groups acting as bridging ligands.[15] Further evidence for the co-ordination of the acetate groups comes from the ^1H NMR spectrum of complex **7**, which shows a resonance for the CH_3 groups at δ 1.76.

The nitrate group has been recognized as a versatile ligand and several modes of co-ordination have been proposed; the number and the positions of the N–O stretching frequencies have been used to distinguish them.[19] For complex **9** the unique absorption clearly assignable to the nitrate group occurs at 1360 cm^{-1}, since the usual bands located at *ca.* 1500 and *ca.* 1000 cm^{-1} would be obscured by the strong absorptions of the C_6F_5 groups. However, in agreement with the conductivity measurements, the analytical results and the structures determined for the related complexes **4** and **11** (see below), the nitrate groups are probably bridging.

The structure proposed for the oxalate complex, **10**, contains this anion acting as a bridging tetradentate ligand. The IR spectrum displays the characteristic bands of oxalate as a bridging ligand:[16] ν_{asym}(O–C–O) at 1620vs and ν_{sym}(O–C–O) at 1360 cm^{-1}; δ(O–C–O) expected in the region of 800 cm^{-1} cannot be assigned due to the accompanying presence of several absorptions of the cation and the pentafluorophenyl groups.

For complex **11** there are several alternative co-ordination modes of the carbonate ligand.[13] The observation of the O_2CO bands at 1535s and 1315s cm^{-1} and the signal of the ^{13}C NMR spectrum at δ 170 are consistent with a μ-$\eta^2:\eta^2$ co-ordination.[20a] In order to determine the molecular structure a single-crystal analysis was undertaken.

The ^{19}F NMR spectra of all the complexes (Table 2) show averaged signals at around room temperature; they consist of a broad signal for the *o*-fluorine atoms of the pentafluorophenyl

Table 1 Analytical results and conductivities for the new complexes

Complex[a]	Analysis (%)[b]			Λ_M[c]/Ω^{-1} cm^2 mol^{-1}	Colour
	C	H	N		
2 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Br)_2]$	49.30	1.90		193	Yellow
	(49.80)	(2.15)			
3 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}I)_2]$	47.20	2.10		200	Brown
	(47.65)	(2.05)			
4 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]$	52.75	2.05	1.45	182	Orange
	(52.05)	(2.20)	(1.40)		
5 $Q_4[\{Rh(C_6F_5)_3\}_4(\mu\text{-}CN)_4]$	53.40	2.55	1.35	320[d]	White
	(53.75)	(2.25)	(1.40)		
6 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]$	52.90	2.35		193	Orange
	(53.00)	(2.40)			
7 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}O_2CMe)_2]$	52.85	2.90		181	Pale yellow
	(53.15)	(2.50)			
8 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}O_2CCF_3)_2]$	50.75	2.50		173	Pale yellow
	(50.50)	(2.05)			
9 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}NO_3)_2]$	50.10	2.55	1.60	199	Pale yellow
	(50.65)	(2.15)	(1.35)		
10 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}C_2O_4)]$	52.40	2.30		194	Yellow
	(52.75)	(2.20)			
11 $Q_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]$	52.15	2.40		196	Yellow
	(52.90)	(2.25)			

[a] $Q^+ = [P(CH_2Ph)Ph_3]^+$. [b] Calculated values in parentheses. [c] In acetone. [d] In nitromethane.

Table 2 Fluorine-19 NMR data for the anionic dinuclear complexes

Compound	T/°C	δ(*o*-F)	δ(*m*-F)	δ(*p*-F)
2	20[a]	−120 (12 F, m, br)	−166.7 (12 F, m)	−164.5 (6 F, m)
	−80[b]	−111.1 (4 F, m, br), −121.2 (8 F, m, br)	(−162.0 to −167.1, 18 F)[c]	
3	20[b]	−116.4 (12 F, m, br)	−167.0 (12 F, m)	−165.1 (6 F, m)
	−80[b]	−103.1 (2 F, fd), −103.5 (2 F, fd),	(−162.6 to −167.4, 18 F)[c]	
		−120.8 (2 F, fd), −122.4 (2 F, fd),		
		−124.5 (2 F, m), −124.9 (2 F, m)		
4	20[a]	−121.9 (12 F, m, br)	−166.0 (12 F, m)	−163.9 (6 F, m)
	−80[b]	−111.2 (2 F, m), −114.5 (2 F, m),	(−161.4 to −166.4, 18 F)[c]	
		−123.9 (2 F, m), −124.4 (4 F, m), −127.4 (2 F, m)		
5	20[b]	−104.5 (16 F, m, br), −107.3 (8 F, m, br)	−166.6 (24 F, m)	−165.1 (12 F, m)
	−80[b]	−102.3 (4 F, m, br), −105.5 (16 F, m, br), −107.5 (4 F, m, br)	(−159.5 to −168.3, 36 F)[c]	
6	20[a]	−124.7 (12 F, m, br)	−167.2 (12 F, m)	−166.2 (6 F, m)
	−50[b]	−120.4 (4 F, fd), −128.0 (8 F, m)	(−164.6 to −167.5, 18 F)[c]	
7	20[a]	−127.3 (12 F, m)	−166.0 (12 F, ft)	−163.5 (6 F, ft)
	−50[b]	−124.0 (12 F, m)	−165.8 (12 F, ft)	−163.4 (6 F, ft)
8	20[a,d]	−127.3 (12 F, fd)	−165.4 (12 F, ft)	−162.5 (6 F, ft)
	−80[b,e]	−121.3 (12 F, m)	−165.8 (12 F, ft)	−163.5 (6 F, ft)
9	20[b]	−108.2 (12 F, m, br)	−167.8 (18 F, br)[c]	
	−50[b]	−108.0 (4 F, m, br), −118.2 (4 F, m, br)	(−160.1 to −170.3, 18 F, m)[c]	
		−124.8 (4 F, m, br)		
10	20[a]	−126.9 (12 F, m)	−165.8 (12 F, m)	−163.0 (6 F, ft)
	−80[b]	−121.3 (12 F, m, br)	−166.5 (12 F, m)	−164.0 (6 F, m)
11	20[a]	−124.5 (12 F, m, br)	−167.0 (12 F, m)	−165.1 (6 F, m)
	−50[b]	−112.2 (2 F, m), −119.1 (2 F, m)	(−163.1 to −167.2, 18 F)[c]	
		−122.6 (2 F, m), −123.7 (2 F, m)		
		−125.6 (2 F, m), −128.3 (2 F, m)		

[a] Solvent: $CDCl_3$. [b] Solvent: $(CD_3)_2CO$; br = broad, m = multiplet, fd = false doublet, ft = false triplet. [c] Complex signal including *m*- and *p*-F. [d] δ −78.83 (6 F, s, CF_3). [e] δ −76.7 (6 F, s, CF_3).

groups and two unresolved multiplets for the *m*- and *p*-fluorine atoms. This behaviour is similar to that found for related five-co-ordinated complexes[6,7] containing the unit $Rh(C_6F_5)_3$. At about −80 °C the *o*-F appear as six separate signals, each integrating for two *o*-F, for complexes **3**, **4** and **11**, only three signals (four *o*-F : four *o*-F : four *o*-F) for **9** while for the rest of the complexes the *o*-F multiplets are still unresolved.

Crystal Structures of $[P(CH_2Ph)Ph_3][\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]\cdot 2Et_2O$ **4** *and* $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]\cdot CH_2Cl_2$ **11**.—The structures consist of binuclear $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]^{2-}$ or $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]^{2-}$ anions, $[P(CH_2Ph)Ph_3]^+$ cations and diethyl ether or dichloromethane molecules of crystallization. Bond distances and angles are collected in Tables 3 (**4**) and 4 (**11**). Figs. 1 and 2 display the molecular structures.

In the anionic complexes two $Rh(C_6F_5)_3$ moieties are linked through a centrosymmetric double thiocyanate bridge in **4** or a symmetric CO_3^{2-} bridge in **11**. The bridging eight-membered ring, in **4**, is roughly planar, showing a maximum deviation from the ideal least-squares plane of 0.130(8) Å for atom C(1). In **11** the mean plane defined by the carbonate group and both rhodium atoms are also planar, with a maximum deviation of 0.063(8) Å [O(2)]. The ligands form square-pyramidal arrangements, involving three carbon atoms from the C_6F_5 ligands, and S and N atoms of the thiocyanate groups (**4**) or two

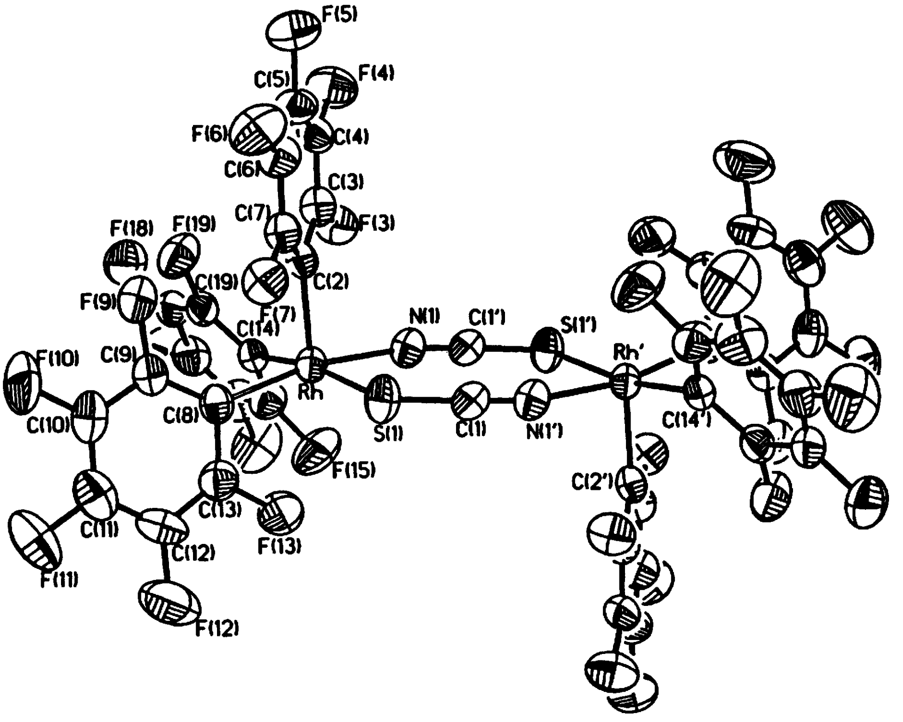


Fig. 1 Molecular diagram of the anion $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]^{2-}$

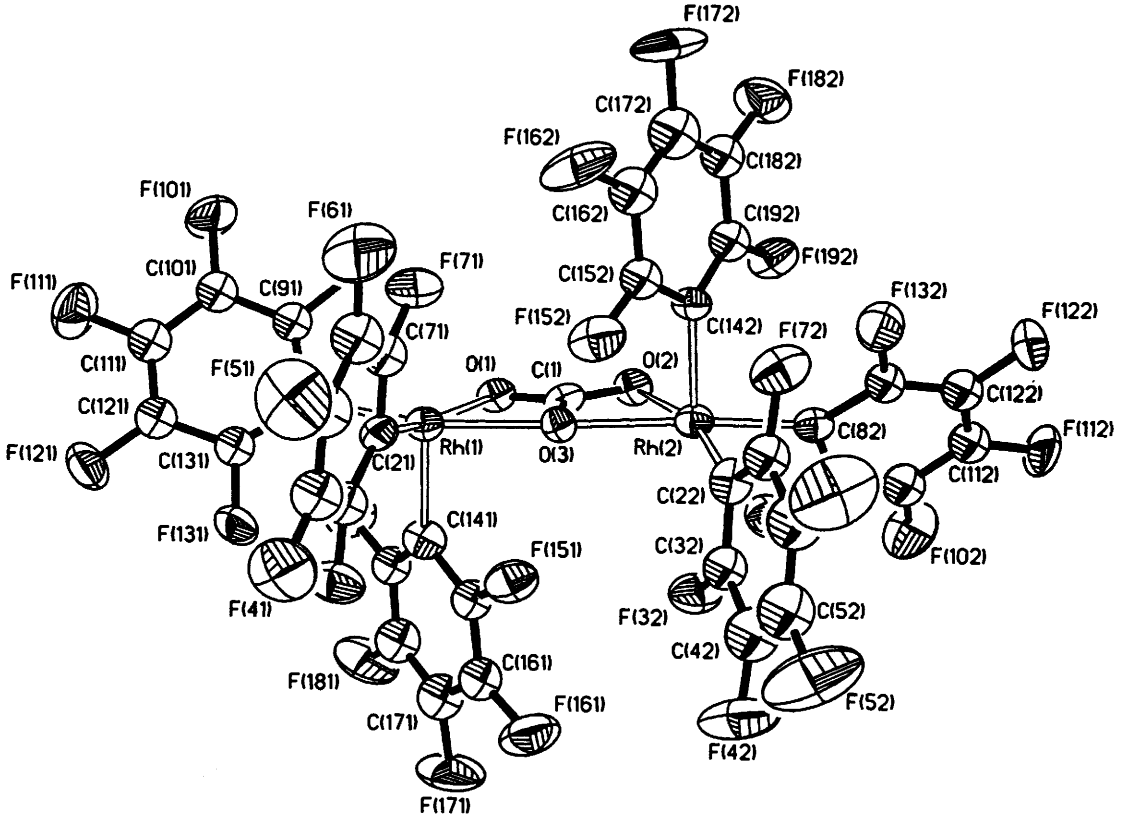


Fig. 2 Molecular diagram of the anion $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]^{2-}$

oxygens of the carbonate (**11**). The square pyramids are rather flattened since the Rh atom lies 0.179(1) (**4**) or 0.183(1) Å (**11**) above the basal plane. The whole anions resemble the related $[Rh(C_6F_5)_5]^{2-}$ parent complex[5] where two of these units are connected through double bridges, after elimination of two basal C_6F_5 groups.

As in related five-co-ordinated rhodium(III) complexes with a similar pyramidal distribution of ligands, *i.e.* $[Rh(C_6F_5)_3L_2]$[6] (L = PEt_3 or $AsPh_3$) or $[Rh(C_6F_5)_5]^{2-}$,[5] the apical Rh–C bond distance in complex **4**, 1.987(7) Å, is significantly shorter than the corresponding distances for the basal ligands, 2.032(8) and 2.036(9) Å. In the case of **11**, although difficulties were encountered owing to the low accuracy of the data, a similar trend can be envisaged for the Rh–C bond distances.

Table 3 Selected bond lengths (Å) and angles (°) for the complex $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]\cdot 2Et_2O$ **4***

Rh–S(1)	2.468(2)	S(1)–C(1)	1.641(9)
Rh–N(1)	2.075(7)	C(1)–N(1′)	1.164(11)
Rh–C(2)	1.987(7)	Rh ··· F(13)	2.788(5)
Rh–C(8)	2.032(8)	Rh ··· F(15)	2.989(6)
Rh–C(14)	2.036(9)		
S(1)–Rh–N(1)	89.2(2)	N(1)–Rh–C(8)	168.4(3)
S(1)–Rh–C(2)	94.1(2)	N(1)–Rh–C(14)	93.7(3)
S(1)–Rh–C(8)	88.2(3)	C(2)–Rh–C(8)	99.0(3)
S(1)–Rh–C(14)	170.9(2)	C(2)–Rh–C(14)	94.4(3)
N(1)–Rh–C(2)	92.5(3)	C(8)–Rh–C(14)	87.3(3)
Rh–C(2)–C(3)	123.0(6)	Rh–C(8)–C(9)	136.4(7)
Rh–C(2)–C(7)	123.1(6)	Rh–C(8)–C(13)	110.4(6)
C(3)–C(2)–C(7)	113.7(7)	C(9)–C(8)–C(13)	113.3(8)
Rh–S(1)–C(1)	104.0(3)	Rh–C(14)–C(15)	116.6(6)
S(1)–C(1)–N(1′)	177.6(8)	Rh–C(14)–C(19)	130.5(6)
Rh–N(1)–C(1′)	165.3(7)	C(15)–C(14)–C(19)	112.9(8)

* Primed atoms are related to unprimed ones by the symmetry operation $-x, -y, 1 - z$.

Table 4 Selected bond lengths (Å) and angles (°) for the complex $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]\cdot CH_2Cl_2$ **11**

Rh(1)–O(1)	2.171(9)	Rh(2)–O(2)	2.188(9)
Rh(1)–O(3)	2.154(9)	Rh(2)–O(3)	2.151(9)
Rh(1)–C(21)	1.973(13)	Rh(2)–C(22)	2.001(13)
Rh(1)–C(81)	1.981(13)	Rh(2)–C(82)	1.985(13)
Rh(1)–C(141)	1.974(12)	Rh(2)–C(142)	1.959(11)
C(1)–O(1)	1.303(16)	C(1)–O(2)	1.256(18)
C(1)–O(3)	1.315(15)		
O(1)–Rh(1)–O(3)	61.5(3)	O(2)–Rh(2)–O(3)	61.5(3)
O(1)–Rh(1)–C(21)	163.2(4)	O(2)–Rh(2)–C(22)	164.8(4)
O(1)–Rh(1)–C(81)	106.3(4)	O(2)–Rh(2)–C(82)	103.9(4)
O(1)–Rh(1)–C(141)	89.9(5)	O(2)–Rh(2)–C(142)	90.9(4)
O(3)–Rh(1)–C(21)	104.9(4)	O(3)–Rh(2)–C(22)	107.2(4)
O(3)–Rh(1)–C(81)	165.4(4)	O(3)–Rh(2)–C(82)	163.5(4)
O(3)–Rh(1)–C(141)	91.1(5)	O(3)–Rh(2)–C(142)	90.5(4)
C(21)–Rh(1)–C(81)	85.5(5)	C(22)–Rh(2)–C(82)	85.5(5)
C(21)–Rh(1)–C(141)	100.8(5)	C(22)–Rh(2)–C(142)	99.8(5)
C(81)–Rh(1)–C(141)	97.2(5)	C(82)–Rh(2)–C(142)	97.9(5)
O(1)–C(1)–O(2)	125(1)	Rh(1)–O(3)–Rh(2)	177.7(4)
O(1)–C(1)–O(3)	115(1)	Rh(1)–O(3)–C(1)	91.7(7)
O(2)–C(1)–O(3)	119(1)	Rh(2)–O(3)–C(1)	89.5(7)

Interestingly, the apical Rh–C distances compare well with the values reported for $[Rh(C_6F_5)_5]^{2-}$, 1.973(10), or $[Rh(C_6F_5)_3(AsPh_3)_2]$, 1.954(15) Å;[5,6] however the basal Rh–C bond lengths observed in both complexes represent the shortest values described for rhodium(III) complexes containing *trans* or pseudo-*trans* ligands, to the C_6F_5 groups [range 2.070(5)–2.135(11) Å].[5,6,32]

All the carbon atoms of the pentafluorophenyl rings are planar with the F atoms slightly out of the mean planes [deviations up to 0.053(6) for F(17) in **4**, and 0.080(9) Å for F(161) in **11**]. However, all the C_6 rings exhibit severe distortions of the C–C–C angles, especially at the carbons directly bonded to the metals, which show mean values of 113.3(8) (**4**) and 114(1)° (**11**). Similar distortions have been reported in related C_6F_5 transition-metal complexes with different phenyl ligands.[33] Also noteworthy is the different geometrical co-ordination of the apical and basal perfluoroaryl ligands. Whereas the apical ligand is linked to the metal in a symmetric way, in terms of the angle between the M–C direction and the binary axis defined through C_{ipso} and C_{para}, 2.9(3) (**4**) and 4.7(6), 5.3(6)° (**11**), on the other hand the basal C_6F_5 groups show significantly higher values for these angles of 7.5(4) and 13.5(4)° for complex **4** and from 8.0(6) to 14.7(5)° for **11**. An analogous behaviour has been found in $[Rh(C_6F_5)_5]^{2-}$ or in $[Rh(C_6F_5)_3L_2]$ [interlinear angle 7.2(4)–17.7(6)].[5,6] This asymmetric co-ordination results in short interatomic distances between each metal and two *o*-fluorine atoms [Rh with F(13) and F(15), 2.788(5) and 2.990(6) (**4**); Rh(1) with F(71) and F(91), 2.763(8) and 2.957(7), and Rh(2) with F(32) and F(92), 2.757(7) and 2.915(8) Å (**11**)]. To determine precisely whether steric or electronic effects are responsible for the behaviour of C_6F_5 five-co-ordinated rhodium(III) complexes would require further structural and/or theoretical studies.

The Rh–S bond distance observed in complex **4**, 2.468(2) Å, is significantly longer than analogous distances reported in mono- or di-nuclear rhodium(III) complexes containing terminal thiocyanate ligands {*i.e.* 2.393(6) in $[\{Rh(C_5Me_5)(\mu\text{-}CH_2)(SCN)\}_2]$[34] or 2.401 and 2.388 Å in $[Rh(C_5Me_5)(SCN)_2(C_{10}H_{11}NO_2)]$[35]} or in related dinuclear complexes of Pd^{II} or Pt^{II} with a symmetric (μ-SCN)(μ-NCS) bridge {*i.e.* 2.387(5) Å in $[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]^{2-}$}.[36] Probably, this relative lengthening of the Rh–S bond may be due to the high *trans* influence of the perfluoroaryl ligands. As far as we know, no thiocyanate derivative of Rh or Ir which has been structurally characterized shows nitrogen co-ordination. However, the Rh–N bond distance determined, 2.075(7) Å, is identical to that reported in the related anionic $[Pd_2(C_6F_3H_2)_4(\mu\text{-}SCN)_2]^{2-}$ complex.[36] The internal dimensions of the SCN group, *i.e.* S–C 1.641(9) and C–N 1.163(11) Å, compare well with mean values in bridging thiocyanate complexes, 1.642(17) and 1.144(20) Å respectively.[37] The bond angle observed around the S atom, 104.0(3)°, clearly identifies an sp^3 hybridization for this atom.

In complex **11**, the planar carbonate anion is acting as a bridging as well as a chelating ligand to both rhodium(III) centres. One oxygen atom sits between the two rhodium atoms and each of the two others co-ordinates to one of the rhodiums. This bonding mode has been found in several dinuclear copper,[17d] nickel,[18a] and cobalt[18b,c] complexes and in one rhodium compound.[20a] The bond distances Rh(1)–O(3) and Rh(2)–O(3), 2.154(9) and 2.151(9) Å, are identical and considerably shorter than the Rh^{III}–O distance, 2.324(2) Å, in the related complex $[Rh_2H_2(O_2CO)(Ph_2C_2)(PPr^i_3)_3]$.[20a] The remaining Rh–O bond distances, Rh(1)–O(1) 2.171(9) Å and Rh(2)–O(2) 2.188(9) Å, are also similar. The C–O bond lengths in the carbonate [C(1)–O(1) 1.303(16), C(1)–O(2) 1.256(18), C(1)–O(3) 1.315(15) Å] are comparable with those observed for other carbonato complexes.[20a] The Rh(1)–O(3)–Rh(2) bridge is approximately linear with an angle of 177.7(4)°.

Experimental

All solvents were distilled and dried by standard methods.[38] The reactions were carried out under a nitrogen atmosphere by standard Schlenk techniques. Proton, ^{19}F and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 188.220 and 50.309 MHz respectively; chemical shifts are relative to $CFCl_3$ and $SiMe_4$ as external references. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. The starting materials $[Rh(C_6F_5)_3(Et_2O)_x]$, $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ and $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]$ were prepared according to the reported methods.[5,6]

Preparations.—$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}X)_2]$ (X = Br **2**, I **3** *or* SCN **4**). A typical preparation (complex **2**) was as follows. To a solution of complex **1** (100 mg, 0.05 mmol) in acetone (20 cm^3) was added KBr (11.99 mg, 0.10 mmol). After stirring at refluxing temperature for 24 h the mixture gave an orange solution and a white solid which was filtered off. The solution was evaporated to dryness and extracted with dichloromethane; addition of heptane gave a yellow solid (yield

Table 5 Crystal data and data collection and refinement for $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}L)]$ [μ-L = (μ-SCN)$_2$ **4** or μ-CO_3 **11**] *

	4	**11**
Formula	$C_{88}H_{44}F_{30}N_2P_2Rh_2S_2\cdot 2Et_2O$	$C_{87}H_{44}F_{30}O_3P_2Rh_2\cdot CH_2Cl_2$
M	2179.40	2059.95
Colour and habit	Orange, irregular block	Yellow, prismatic needle
Crystal size/mm	0.262 × 0.163 × 0.239	0.114 × 0.118 × 0.406
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*C*2/*c*
a/Å	11.954(2)	28.306(4)
b/Å	13.053(2)	13.413(2)
c/Å	15.236(3)	45.245(7)
α/°	89.94(1)	90.0
β/°	100.33(1)	101.42(1)
γ/°	104.89(2)	90.0
U/Å^3	2257.8(7)	16 838(4)
Z	1	8
D_c/g cm^{-3}	1.603	1.625
T/K	295	223
μ/cm^{-1}	5.48	5.99
F(000)	1092	8176
Data collected	7861 (±*h*, ±*k*, −*l*)	11 813 (±*h*, −*k*, +*l*)
Unique data	5903	10 962
Unique observed data	3692 [$F_o \geqslant 5\sigma(F_o)$]	6142 [$F_o \geqslant 4\sigma(F_o)$]
Parameters refined	486	908
R, *R*′	0.0516, 0.0516	0.0694, 0.0695
R, *R*′ (all data)	0.0926, 0.0744	0.1284, 0.1038
Goodness of fit	1.17	1.34

* $2\theta = 3\text{–}45°$; $R(F_o) = (\Sigma||F_o| - |F_c||)/\Sigma F_o$; $R'(F_o) = [\Sigma w(||F_o| - |F_c||)^2/\Sigma F_o^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o) + gF_o^2$; g = 0.0012 for complex **4** and 0.0019 for **11**.

Table 6 Final atomic coordinates (× 10^4; × 10^5 for Rh) for the non-hydrogen atoms for $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]\cdot 2Et_2O$ **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	645(6)	17 356(5)	38 304(5)	C(19)	−1 628(7)	3 128(6)	3 125(6)
S(1)	1 495(2)	649(2)	3 989(2)	C(20)	3 450(7)	232(6)	2 103(5)
N(1)	−844(6)	762(6)	4 690(5)	C(21)	4 442(8)	758(7)	2 706(6)
C(1)	1 123(7)	−159(7)	4 776(6)	C(22)	4 859(9)	1 857(8)	2 671(7)
P(1)	2 904(2)	−1 188(2)	2 110(2)	C(23)	4 296(8)	2 387(8)	2 056(7)
F(3)	−2 722(4)	797(4)	3 305(3)	C(24)	3 318(8)	1 881(7)	1 453(6)
F(4)	−4 040(4)	−407(4)	1 913(4)	C(25)	2 885(7)	782(7)	1 474(6)
F(5)	−3 085(5)	−978(4)	576(3)	C(26)	3 190(7)	−1 814(6)	1 159(5)
F(6)	−707(5)	−331(5)	677(3)	C(27)	3 627(7)	−1 220(7)	481(6)
F(7)	662(4)	845(4)	2 060(3)	C(28)	3 802(8)	−1 735(7)	−262(6)
F(9)	303(5)	2 734(4)	1 680(4)	C(29)	3 521(8)	−2 839(8)	−337(7)
F(10)	2 087(6)	4 192(5)	1 275(4)	C(30)	3 122(8)	−3 400(8)	352(6)
F(11)	3 965(5)	5 150(5)	2 546(5)	C(31)	2 948(7)	−2 925(7)	1 109(6)
F(12)	4 006(6)	4 572(5)	4 270(5)	C(32)	3 548(7)	−1 646(6)	3 134(6)
F(13)	2 189(5)	3 079(4)	4 694(3)	C(33)	3 215(8)	−1 431(7)	3 921(7)
F(15)	−158(5)	3 067(5)	5 352(3)	C(34)	3 717(9)	−1 742(8)	4 715(8)
F(16)	−1 388(6)	4 461(5)	5 562(4)	C(35)	4 603(12)	−2 227(10)	4 728(10)
F(17)	−2 832(6)	4 984(5)	4 149(4)	C(36)	4 976(12)	−2 458(10)	3 962(9)
F(18)	−2 970(5)	4 119(4)	2 514(4)	C(37)	4 436(9)	−2 143(8)	3 150(7)
F(19)	−1 788(5)	2 730(4)	2 274(3)	C(38)	1 317(7)	−1 480(6)	2 024(6)
C(2)	−954(7)	904(6)	2 757(5)	C(39)	687(7)	−2 655(6)	1 841(6)
C(3)	−2 163(8)	539(6)	2 667(6)	C(40)	684(8)	−3 359(7)	2 507(6)
C(4)	−2 854(7)	−74(6)	1 960(6)	C(41)	156(9)	−4 422(8)	2 311(7)
C(5)	−2 387(9)	−368(7)	1 281(6)	C(42)	−376(9)	−4 782(9)	1 451(7)
C(6)	−1 193(8)	−47(7)	1 341(6)	C(43)	−376(9)	−4 087(8)	774(8)
C(7)	−513(7)	565(6)	2 063(6)	C(44)	174(8)	−3 005(7)	970(7)
C(8)	1 181(7)	2 815(6)	3 215(6)	O(1)	6 836(23)	7 231(22)	1 963(15)
C(9)	1 202(8)	3 152(7)	2 368(6)	C(45)	8 084(18)	7 931(14)	3 317(11)
C(10)	2 106(9)	3 924(8)	2 136(7)	C(46)	7 779(24)	7 059(24)	2 583(20)
C(11)	3 062(9)	4 404(7)	2 769(8)	C(47)	6 122(19)	6 373(20)	1 435(14)
C(12)	3 079(8)	4 111(8)	3 629(8)	C(48)	6 471(24)	6 258(22)	546(14)
C(13)	2 158(8)	3 337(7)	3 824(6)	O(1A)	6 901(29)	7 107(32)	2 125(24)
C(14)	−905(7)	2 811(6)	3 818(6)	C(45A)	8 575(19)	8 109(15)	3 226(13)
C(15)	−867(8)	3 295(7)	4 609(6)	C(46A)	7 604(21)	7 210(20)	2 961(17)
C(16)	−1 479(9)	4 019(8)	4 738(7)	C(47A)	7 193(27)	6 559(36)	1 460(22)
C(17)	−2 186(9)	4 310(7)	4 048(7)	C(48A)	6 166(22)	5 812(19)	861(17)
C(18)	−2 267(8)	3 861(6)	3 225(7)				

40%) which was recrystallized from dichloromethane–hexane. For complexes **3** and **4** the following reaction conditions were used: **3**, complex **1** (100 mg, 0.05 mmol), NaI (15.3 mg, 0.10 mmol), acetone (20 cm^3), stirring at refluxing temperature for 36 h, brown solid, yield 56%; **4**, complex **1** (100 mg, 0.05 mmol), KSCN (9.79 mg, 0.10 mmol), acetone (20 cm^3),

Table 7 Final atomic coordinates (× 10^4; × 10^5 for Rh) for $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]\cdot CH_2Cl_2$ **11**

Atom	x	y	z	Atom	x	y	z
Rh(1)	5 325(3)	70 944(8)	13 064(2)	F(162)	355(3)	9 749(7)	317(2)
Rh(2)	18 323(4)	80 525(8)	10 325(2)	F(172)	569(4)	8 983(7)	−196(2)
C(1)	1 271(5)	6 644(10)	1 088(3)	F(182)	1 353(3)	7 799(7)	−160(2)
O(1)	964(3)	5 972(6)	1 138(2)	F(192)	1 905(3)	7 377(6)	369(2)
O(2)	1 628(3)	6 483(6)	968(2)	P(1)	1 415(1)	4 184(3)	440(1)
O(3)	1 191(3)	7 552(6)	1 175(2)	C(201)	2 008(5)	4 711(10)	484(3)
C(21)	200(4)	8 349(9)	1 367(3)	C(211)	2 326(5)	4 761(11)	765(3)
C(31)	154(5)	8 913(10)	1 623(3)	C(221)	2 789(6)	5 142(13)	783(4)
C(41)	−81(6)	9 827(12)	1 599(4)	C(231)	2 928(6)	5 491(12)	532(3)
C(51)	−293(6)	10 197(12)	1 328(4)	C(241)	2 632(6)	5 490(12)	266(4)
C(61)	−259(6)	9 646(13)	1 075(4)	C(251)	2 150(6)	5 079(12)	224(4)
C(71)	−17(5)	8 762(11)	1 104(3)	C(261)	1 393(5)	3 062(11)	223(3)
F(31)	344(3)	8 595(6)	1 905(2)	C(271)	969(6)	2 778(12)	40(3)
F(41)	−109(3)	10 332(7)	1 857(2)	C(281)	953(7)	1 828(13)	−102(4)
F(51)	−528(4)	11 062(7)	1 311(2)	C(291)	1 345(7)	1 257(15)	−56(4)
F(61)	−485(3)	9 989(7)	799(2)	C(301)	1 760(7)	1 523(15)	117(4)
F(71)	10(3)	8 240(6)	848(2)	C(311)	1 803(6)	2 474(13)	262(4)
C(81)	−81(5)	6 435(9)	1 340(3)	C(321)	975(4)	5 044(9)	243(3)
C(91)	−332(5)	6 008(10)	1 076(3)	C(331)	922(5)	5 140(10)	−61(3)
C(101)	−781(5)	5 553(11)	1 044(3)	C(341)	598(5)	5 846(11)	−212(3)
C(111)	−1 006(5)	5 530(10)	1 284(3)	C(351)	329(5)	6 432(11)	−62(3)
C(121)	−777(5)	5 950(10)	1 550(3)	C(361)	389(5)	6 300(10)	246(3)
C(131)	−324(5)	6 392(10)	1 573(3)	C(371)	714(5)	5 633(10)	397(3)
F(91)	−135(3)	6 025(6)	825(2)	C(381)	1 310(4)	3 866(9)	814(3)
F(101)	−1 003(3)	5 183(7)	775(2)	C(391)	854(4)	3 320(9)	821(3)
F(111)	−1 449(3)	5 130(7)	1 256(2)	C(401)	785(5)	2 311(10)	736(3)
F(121)	−1 000(3)	5 943(7)	1 787(2)	C(411)	366(5)	1 852(11)	741(3)
F(131)	−136(3)	6 784(6)	1 842(2)	C(421)	0(5)	2 319(10)	841(3)
C(141)	880(5)	6 823(10)	1 721(3)	C(431)	58(5)	3 292(11)	943(3)
C(151)	1 208(5)	7 523(10)	1 877(3)	C(441)	479(4)	3 796(10)	929(3)
C(161)	1 493(5)	7 314(13)	2 153(3)	P(2)	1 521(2)	1 057(3)	2 573(1)
C(171)	1 451(6)	6 398(14)	2 290(3)	C(202)	1 241(5)	1 388(11)	2 192(3)
C(181)	1 147(6)	5 717(14)	2 146(3)	C(212)	1 296(5)	750(11)	1 960(3)
C(191)	874(5)	5 912(11)	1 863(3)	C(222)	1 089(6)	955(13)	1 663(3)
F(151)	1 247(3)	8 439(6)	1 750(2)	C(232)	858(6)	1 857(12)	1 603(4)
F(161)	1 810(3)	8 025(8)	2 279(2)	C(242)	790(7)	2 487(14)	1 822(4)
F(171)	1 739(3)	6 242(8)	2 555(2)	C(252)	980(6)	2 289(12)	2 131(4)
F(181)	1 120(4)	4 827(7)	2 275(2)	C(262)	1 386(5)	1 980(11)	2 828(3)
F(191)	582(3)	5 180(6)	1 731(2)	C(272)	1 612(7)	2 902(14)	2 859(4)
C(22)	1 977(5)	9 425(10)	1 199(3)	C(282)	1 469(7)	3 633(17)	3 043(4)
C(32)	2 185(5)	9 343(11)	1 500(3)	C(292)	1 119(7)	3 433(16)	3 193(5)
C(42)	2 350(6)	10 162(14)	1 686(4)	C(302)	848(8)	2 521(17)	3 152(5)
C(52)	2 312(7)	11 072(14)	1 559(5)	C(312)	1 016(7)	1 793(16)	2 978(4)
C(62)	2 102(6)	11 185(12)	1 269(4)	C(322)	1 301(5)	−121(11)	2 679(3)
C(72)	1 939(5)	10 369(11)	1 086(3)	C(332)	1 523(7)	−554(16)	2 952(4)
F(32)	2 248(3)	8 434(6)	1 626(2)	C(342)	1 335(8)	−1 497(17)	3 024(5)
F(42)	2 546(4)	10 009(8)	1 981(2)	C(352)	962(7)	−1 924(16)	2 836(4)
F(52)	2 457(5)	11 877(8)	1 735(3)	C(362)	718(7)	−1 493(15)	2 583(4)
F(62)	2 053(4)	12 121(7)	1 143(3)	C(372)	900(5)	−551(12)	2 495(3)
F(72)	1 746(3)	10 562(6)	793(2)	C(382)	2 163(5)	1 036(12)	2 573(3)
C(82)	2 481(4)	8 112(10)	929(3)	C(392)	2 469(5)	470(11)	2 832(3)
C(92)	2 817(5)	7 516(12)	1 085(3)	C(402)	2 604(5)	896(12)	3 113(3)
C(102)	3 277(6)	7 409(12)	1 046(4)	C(412)	2 895(6)	351(12)	3 346(3)
C(112)	3 429(5)	7 958(13)	833(3)	C(422)	3 059(6)	−562(13)	3 289(4)
C(122)	3 113(5)	8 598(12)	660(3)	C(432)	2 927(6)	−1 012(14)	3 013(4)
C(132)	2 653(5)	8 672(10)	712(3)	C(442)	2 630(6)	−490(12)	2 782(4)
F(92)	2 689(3)	6 930(7)	1 306(2)	C(1s)*	95(15)	4 693(14)	2 699(6)
F(102)	3 587(3)	6 759(8)	1 210(2)	Cl(1)*	0	3 612(9)	2 500
F(112)	3 884(3)	7 885(8)	785(2)	Cl(2)*	0	5 751(12)	2 500
F(122)	3 251(3)	9 149(7)	440(2)	C(2s)*	1 614(19)	7 759(28)	4 240(6)
F(132)	2 357(3)	9 343(6)	535(2)	Cl(3)*	1 364(6)	8 121(13)	3 886(4)
C(142)	1 453(5)	8 389(9)	634(3)	Cl(4)*	1 935(7)	6 704(14)	4 333(4)
C(152)	1 055(5)	8 988(10)	611(3)	C(3s)*	1 674(22)	7 459(74)	4 353(9)
C(162)	759(5)	9 183(11)	332(3)	Cl(5)*	1 259(11)	8 016(26)	4 070(8)
C(172)	857(6)	8 768(13)	81(3)	Cl(6)*	2 095(11)	7 049(27)	4 158(8)
C(182)	1 245(6)	8 187(11)	92(3)	C(4s)*	1 941(32)	6 764(46)	4 100(10)
C(192)	1 526(5)	7 992(10)	366(3)	Cl(7)*	1 725(13)	7 755(25)	3 872(7)
F(152)	929(3)	9 423(6)	849(2)	Cl(8)*	1 828(14)	6 843(28)	4 458(7)

* Atom of disordered solvent.

stirring at refluxing temperature for 10 h, precipitation with diethyl ether and recrystallization from CH_2Cl_2–diethyl ether, orange solid, yield 60%.

$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Br)_2]$ **2*** *and* $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]$ **4**. The alternative preparation of complex **2** was as follows. To a solution of **1** (100 mg, 0.05 mmol) in CH_2Cl_2 (20 cm^3), under a nitrogen atmosphere and with exclusion of light, was added AgBr (18.9 mg, 0.10 mmol) and the suspension was stirred at room temperature for 24 h. The white solid (AgCl) was filtered off. The solution was evaporated to *ca.* 1 cm^3 and addition of heptane gave a yellow solid which was filtered off and washed with heptane (yield 60%). For complex **4** the following reaction conditions were used: **1** (100 mg, 0.05 mmol), CH_2Cl_2 (10 cm^3), AgSCN (16.7 mg, 0.10 mmol), stirring at room temperature for 8 h, precipitation with diethyl ether, yield 51%.

$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]$ **4*** *and* $[P(CH_2Ph)Ph_3]_4[\{Rh(C_6F_5)_3\}_4(\mu\text{-}CN)_4]$ **5**. To a yellow suspension of $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (100 mg, 0.06 mmol) in CH_2Cl_2 (15 cm^3), under a nitrogen atmosphere and with exclusion of light was added AgSCN (10 mg, 0.06 mmol) and the mixture was stirred for 1 h. Partial evaporation of the CH_2Cl_2 and addition of diethyl ether led to the precipitation of compound **4** as an orange solid (yield 72%) which was filtered off, washed with diethyl ether and vacuum dried. For compound **5** the following conditions were used: $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (100 mg, 0.06 mmol), AgCN (9.95 mg, 0.06 mmol), CH_2Cl_2 (20 cm^3), stirring at room temperature for 1 h, precipitation with propan-2-ol, recrystallization from CH_2Cl_2–hexane, yield 48%.

$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]$ **6**. A yellow diethyl ether solution of $[Rh(C_6F_5)_3(Et_2O)_x]$ (0.10 mmol) was evaporated to dryness and the residue treated with CH_2Cl_2 (10 cm^3); this solution was added to a dichloromethane (10 cm^3) suspension of $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ (165.6 mg, 0.10 mmol). The solid dissolved in about 10 min and the solution turned orange; after 30 min, the solvent was pumped off. The residual oil was washed with hexane (1 cm^3) and stirred with hexane to give orange crystalline **6**, yield 90%. Complex **6** was also prepared as follows. To an aqueous solution (5 cm^3) of KOH (5.6 mg, 0.10 mmol) an acetone solution (10 cm^3) of **1** (100 mg, 0.05 mmol) was added. After stirring for 15 min at room temperature the solution was concentrated to 5 cm^3. The solid obtained was filtered off, washed with water and recrystallized from CH_2Cl_2 ($MgSO_4$)–hexane, yield 50%.

$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}X)_2]$ ($X = MeCO_2$ **7** CF_3CO_2 **8** *or* NO_3 **9**) *and* $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}C_2O_4)]^{2-}$ **10**. A typical preparation for complex **7** was as follows. Solid AgO_2CMe (16.81 mg, 0.10 mmol) was added to a solution of **1** (100 mg, 0.05 mmol) in CH_2Cl_2 (15 cm^3), under a nitrogen atmosphere and with exclusion of light. The suspension was stirred at room temperature in the absence of light for 12 h. The AgCl was filtered off; the resulting solution was vacuum concentrated to *ca.* 1 cm^3 and addition of diethyl ether (10 cm^3) led to the precipitation of pale yellow solid **7** (94%). For complexes **8–10** the following reaction conditions were used: **8**, complex **1** (100 mg, 0.05 mmol), AgO_2CCF_3 (22.25 mg, 0.10 mmol), precipitation with pentane, yield 56%, pale yellow; **9**, **1** (100 mg. 0.05 mmol), $AgNO_3$ (17.11 mg, 0.10 mmol), precipitation with pentane, yield 55%, yellow; **10**, **1** (100 mg, 0.05 mmol), $Ag_2C_2O_4$ (15.30 mg, 0.05 mmol), stirring for 24 h, precipitation with diethyl ether, yield 83%, yellow.

$[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]$ **11**. Carbon dioxide was bubbled through a solution of compound **6** (97.5 mg, 0.05 mmol) in dichloromethane (15 cm^3) for 2 h while the volume of the solvent was reduced to *ca.* 1 cm^3; pentane (5 cm^3) was added and the suspension was stirred for 30 min maintaining the CO_2 atmosphere. The yellow solid was filtered off, washed with pentane, and vacuum dried, yield 61%.

Crystal Structure Determinations of $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}SCN)_2]\cdot 2Et_2O$ **4** *and* $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}CO_3)]\cdot CH_2Cl_2$ **11**.—Suitable crystals were obtained as transparent orange irregular blocks, **4**, or yellow prismatic needles, **11**, by slow diffusion of diethyl ether or hexane respectively into a concentrated solution of the complex in dichloromethane at −20 °C. Intensity data were collected on a four-circle Siemens AED diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å), in the ω–2θ scan mode. Details of the crystal data and data collection and refinement for both complexes are summarized in Table 5. Standard intensities measured every hour showed no evidence for crystal decay. The data were corrected for Lorentz and polarization effects, and a semiempirical (ψ scan) absorption correction was applied for **11**. Cell parameters were calculated by least-squares refinement of the 2θ values of 58 (**4**) and 64 (**11**) accurately measured reflections in the range 20–33° approximately.

Both structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms of the anions and the P atoms. Hydrogen atoms were included in idealized positions in the last cycles of refinement using a riding model (C–H 0.97 Å). Disordered solvent molecules of crystallization were present in each structure (diethyl ether in **4**, dichloromethane in **11**). These were included in the refinement with bond distances constrained, and disordered in two (**4**) or four (**11**) different positions. The SHELXTL-PLUS system of computer programs was used for all calculations.[39] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 40. Final atomic coordinates for the non-hydrogen atoms are given in Tables 6 and 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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