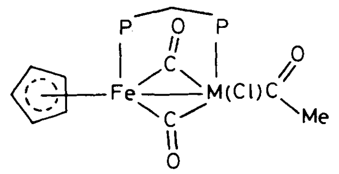
Iron–Rhodium and Iron–Iridium Complexes containing One Bridging $Ph_2PCH_2PPh_2$ (dppm) Ligand: Crystal Structure Determination of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})RhMe_{0.4}Cl_{1.6}]$†

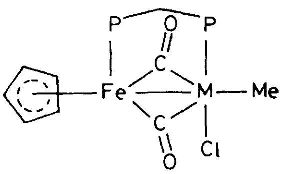
Bernard L. Shaw,* Martin J. Smith, Geoffrey N. Stretton, and Mark Thornton-Pett
School of Chemistry, The University, Leeds LS2 9JT

Treatment of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(\text{dppm-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) with $[Rh_2(CO)_4Cl_2]$ or $[Ir(CO)_2Cl(p\text{-}NH_2C_6H_4Me)]$ gave $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})M(COMe)Cl]$ (M = Rh or Ir), which decarbonylate slowly in solution to give $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})M(Me)Cl]$ (M = Rh or Ir). In the latter reduction, when M = Rh, the dichlororhodium complex $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})RhCl_2]$ coprecipitated with $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})Rh(Me)Cl]$ such that an *X*-ray crystal structure determination showed mixed Me/Cl occupancy, with the formula being approximately $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})RhMe_{0.4}Cl_{1.6}]$. Treatment of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})Rh(COMe)Cl]$ with $HBF_4\cdot Et_2O$ gave $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})Rh(\mu\text{-}Cl)_2Rh(\mu\text{-}CO)_2(\mu\text{-dppm})Fe(\eta^5\text{-}C_5H_5)][BF_4]_2$.

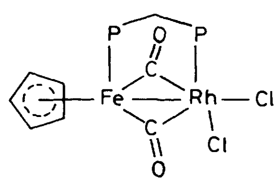
There have been relatively few reports of syntheses of heterobimetallic complexes in which the two different metals are bridged by one $Ph_2PCH_2PPh_2$ (dppm) ligand.[1–8] We have recently reported the preparation and some organic reactions of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(\text{dppm-}P)]$.[9] We reasoned that this monodentate dppm complex would be suitable for the generation of new kinds of heterobimetallic complexes, and report the results for rhodium and iridium.



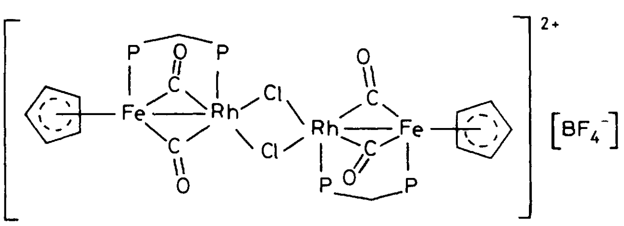
(**1a**) M = Rh
(**1b**) M = Ir



(**2a**) M = Rh
(**2b**) M = Ir



(**3**)



(**4**)

Results and Discussion

Treatment of a benzene solution of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(\text{dppm-}P)]$ with $[Rh_2(CO)_4Cl_2]$ or $[Ir(CO)_2Cl(p\text{-}NH_2C_6H_4Me)]$ gave red or orange crystalline complexes, respectively. We formulate these new complexes as $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})M(COMe)Cl]$ [M = Rh (**1a**) or Ir (**1b**)] on the basis of (*i*) elemental analysis (Table 1); (*ii*) the i.r. spectra, which both show two ν(CO) bands [1 848, 1 789 cm^{-1} (**1a**); 1 811, 1 762 cm^{-1} (**1b**)] assigned to bridging carbonyls and one band [1 659 cm^{-1} (**1a**) and 1 627 cm^{-1} (**1b**)] due to an acyl carbonyl; (*iii*) the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra, which consist of AMX [(**1a**)] and AX [(**1b**)] patterns; (*iv*) the ^1H n.m.r. spectra, both of which contain a Me resonance [δ 1.96 (**1a**), 1.72 p.p.m. (**1b**); Table 2]; and (*v*) the similarity between the spectroscopic data of complexes (**1a**) and (**1b**) and those of complexes (**2a**) and (**3**) (see later), a mixture of which has been characterised by *X*-ray crystal analysis (Tables 3 and 4). In both the i.r. spectra of (**1a**) and (**1b**) the two higher frequency carbonyl bands are at least 75 cm^{-1} lower than any of the carbonyl bands for $[(OC)_4Fe(\mu\text{-dppm})Rh(CO)Cl]$ for which an *X*-ray crystal structure showed that all the carbonyl ligands were terminal.[10] Thus the non-acyl carbonyl ligands are likely to be in either bridging or semi-bridging positions between the Fe and Rh atoms.

The ^{103}Rh in complex (**1a**) was coupled to both ^{31}P atoms in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. A $^1J(RhP_B)$ value of 212 Hz is unusually large[11] and a $^2J(RhP_A)$ value of 7 Hz is unusual because in other Fe–Rh heterobimetallics containing a phosphine ligand, $^2J(RhP_A)$ was too small to be measured.[10,12] The observation of this coupling (7 Hz) suggests the presence of a metal–metal bond. With $\eta^5\text{-}C_5H_5$, P_A from dppm, two bridging/semi-bridging carbonyl groups and Rh bonded to Fe, the acyl group must bound to Rh. Thus during the reaction the acyl group has been transferred from Fe to Rh. It was noted that complex (**1b**) showed a marked tendency to decarbonylate in solution. This was promoted by light and when light was excluded, hardly occurred at all. Solutions of (**1a**) or (**1b**), in dichloromethane, chloroform, acetone, or benzene, underwent decomposition after a few days even in the dark. The complexes $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})M(Me)Cl]$ [M = Rh (**2a**) or Ir (**2b**)] precipitated from acetone and benzene solutions of complex (**1a**) or (**1b**) respectively, with coprecipitation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-dppm})RhCl_2]$ (**3**) occurring with (**2a**). Complexes (**2a**) and (**2b**) were characterised by i.r. spectroscopy, the spectra showing two bands at similar frequencies to those attributed to bridging carbonyls in (**1a**) and (**1b**), but no acyl

---

† μ-[Bis(diphenylphosphino)methane]-di-μ-carbonyl-1-chloro-2-(η^5-cyclopentadienyl)-1-methylrhodiumiron (*Fe–Rh*) (Cl/Me = 1.6/0.4).

Supplementary data available: see Instruction for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical and i.r. data for the iron–rhodium and iron–iridium complexes

Complex	Yield (%)	Analysis (%)[a] C	H	Cl	I.r. [ν(CO)/cm^{-1}][b]
(1a)·C_6H_6	83	58.4 (58.5)	4.45 (4.4)	4.8 (4.3)	1 848m, 1 789vs, 1 659s
(1b)	62	49.2 (49.1)	3.65 (3.65)	4.1 (4.25)	1 811m, 1 762vs, 1 627s
(2a)					1 852,[c] 1 788vs
(2b)·0.33 CH_2Cl_2	57	47.7 (48.1)	3.55 (3.7)		1 796m, 1 757vs
(3)					1 853m, 1 814vs
(4)	69	48.9 (48.85)	3.8 (3.45)	4.45 (4.5)	[d]1 871m, 1 837vs, 1 055vs, br
(2a)–**(3)**–Me_2CO (0.4:0.6:1.0)		53.9 (54.05)	4.35 (4.4)	7.6 (7.35)	

[a] Required values given in parentheses. [b] In dichloromethane unless otherwise stated. [c] Since complex **(2a)** was not isolated pure, this band is tentatively assigned. [d] As a Nujol mull.

Table 2. ^{31}P-{^1H} and hydrogen-1 n.m.r. data

	^{31}P-{^1H} n.m.r.[a]					Hydrogen-1 n.m.r.[b]						
						η^5-C_5H_5		–CH_2–		Me		
Complex	δ(P_A)	$^2J(RhP_A)$	δ(P_B)	$^1J(RhP_B)$	$^2J(P_AP_B)$	δ(H)	J(PH)	δ(H)	J(PH)	δ(H)	J(PH)	J(RhH)
(1a)	75.7	7	36.5	212	76	4.71	1.5	2.49	10.2 1.0	1.96		
(1b)[c]	78.6		8.7		64	4.67	1.5	2.42	10.5	1.72		
(2a)	76.4	7	52.5	190	73	4.71	1.3	2.41	10.5	1.33	5.1	1.5
(2b)[c,d]	80.4		21.1		59	4.60	1.2	2.29	10.5	1.35	5.4	
(3)	77.1	7	46.6	127	71	4.90	1.2	2.28	10.3			
(4)[c,d]	70.6	5	52.2	129	59	4.67		2.66	11.3			

[a] Spectra (40.25 MHz) measured at *ca.* +21 °C. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of 85% H_3PO_4 and coupling constants (*J*) in Hz (±3). P_A is bonded to iron. Solvent $CDCl_3$ unless otherwise indicated. [b] Spectra (100 MHz) measured at *ca.* +21 °C. Chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$, and coupling constants (*J*) in Hz (±0.1). Solvent $CDCl_3$ unless otherwise indicated. [c] Solvent for ^{31}P-{^1H} n.m.r. spectrum 20% CD_2Cl_2. [d] Solvent for ^1H n.m.r. spectrum CD_2Cl_2.

Table 3. Selected bond lengths (pm) and angles (°)

Fe–Rh	263.3(4)		
P(1)–Rh	225.1(3)	P(2)–Fe	221.0(3)
Cl(1)–Rh	240.8(3)	C(1)–Fe	209.3(5)
Cl/Me–Rh	230.5(4)	C(2)–Fe	210.2(6)
C(6)–Rh	205.5(7)	C(3)–Fe	211.8(6)
C(7)–Rh	204.1(7)	C(4)–Fe	211.9(6)
		C(5)–Fe	210.4(6)
		C(6)–Fe	185.4(7)
		C(7)–Fe	185.6(7)
O(6)–C(6)	117.1(6)	O(7)–C(7)	117.9(6)
P(1)–Rh–Fe	93.9(1)	P(2)–Fe–Rh	97.1(1)
Cl(1)–Rh–Fe	93.4(1)	C(1)–Fe–Rh	144.3(1)
Cl/Me–Rh–Fe	177.9(1)	C(2)–Fe–Fh	111.8(2)
Cl(1)–Rh–P(1)	172.6(1)	C(3)–Fe–Rh	105.9(2)
Cl/Me–Rh–P(1)	84.8(2)	C(4)–Fe–Rh	130.6(1)
Cl/Me–Rh–Cl(1)	87.8(2)	C(5)–Fe–Rh	169.9(1)
C(6)–Rh–Fe	44.5(1)	C(6)–Fe–Rh	51.0(2)
C(7)–Rh–Fe	44.6(1)	C(7)–Fe–Rh	50.5(2)
		C(7)–Fe–C(6)	101.2(3)
Fe–C(6)–Rh	84.6(3)	Fe–C(7)–Rh	84.9(3)
O(6)–C(6)–Rh	124.7(5)	O(7)–C(7)–Rh	125.5(5)
O(6)–C(6)–Fe	150.0(4)	O(7)–C(7)–Fe	149.4(4)

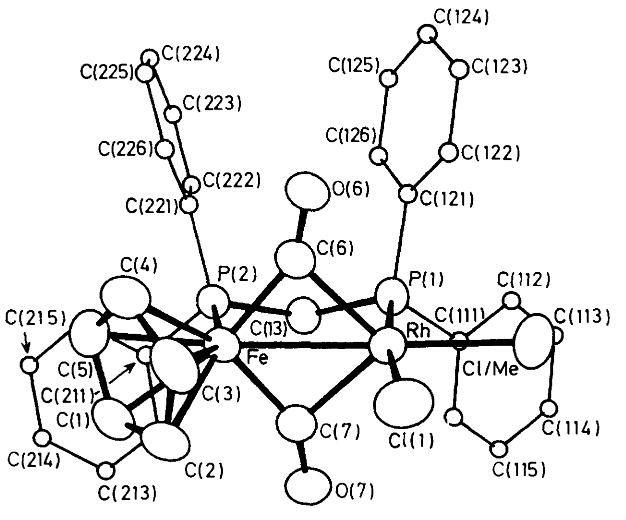


Figure. Molecular structure of [(η^5-C_5H_5)Fe(μ-CO)$_2$(μ-dppm)Rh-$Me_{0.4}Cl_{1.6}$], showing the atomic numbering scheme

carbonyl band. The ^1H n.m.r. spectra showed resonances at δ 1.33 p.p.m. (doublet of doublets) [^2J(RhH) 1.5 Hz, ^3J(PH) 5.1 Hz] for **(2a)** and δ 1.35 p.p.m. (doublet) [^3J(PH) 5.4 Hz] for **(2b)**. Further evidence that Me was bound to Rh in **(2a)** was obtained from a selective decoupling experiment. Irradiation at a frequency corresponding to P_B caused complete collapse of the 5.1 Hz coupling of the methyl signal leaving a doublet resonance, ^2J(RhH) = 1.5 Hz. The presence of a dichloro-complex **(3)** was inferred from the i.r. and n.m.r. spectroscopic data which were very similar to those of **(2a)** (except for the absence of a methyl resonance in the ^1H n.m.r. pattern). The *X*-ray crystal structure determination (see below) on a mixed crystal showed it to contain **(2a)** and **(3)**. The molecular structure is shown in the Figure and selected bond lengths and angles in Table 3. Mixed MeCl occupancy of one site has been reported previously in the crystal structure of $[TiMe_{1.3}Cl_{0.7}(Me_2PCH_2CH_2PMe_2)]$.[13]

The Fe–Rh distance of 263.3(4) pm is typical of Fe–Rh distances in heterobimetallic complexes where a metal–metal bond has been proposed.[10,14–17] The distances from both metals to the carbonyl carbons and the M–C–O bond angles show that the two carbonyls are almost identically positioned with respect to Fe and Rh, and that these ligands both make a significant contribution to metal–metal bonding, and thus may be considered as bridging Fe and Rh.

A ^1H-$\{^{31}P\}$ n.m.r. spectrum of a solution of the crystals from which the crystal for *X*-ray analysis was selected showed a mixture of (**2a**), (**3**), and acetone in the mole ratio 0.4:0.6:1.0. Elemental analysis of other crystals from the same solution gave results consistent with such a mixture (Table 1).

The Rh–Me complex (**2a**) was found to be converted into the Rh–Cl complex (**3**). The relative proportion of (**3**) to (**2a**) was increased by: (*i*) a reaction time of 2 weeks instead of 3 d, suggesting conversion of (**2a**) to (**3**); (*ii*) by using chloroform as the solvent; and (*iii*) addition of the chloride salt Adogen 464* to $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(dppm\text{-}P)]$ and $[Rh_2(CO)_4Cl_2]$ in benzene. Formation of complex (**3**) requires a source of chloride ions. These were probably supplied by the solvent when chloroform or dichloromethane were used, or by the chloride salt Adogen 464 when it was added. In the situation where the solvent was acetone, the source of chloride was most likely provided by another decomposition pathway for complex (**2a**), which produced a benzene soluble Fe(dppm-*PP'*) species detected by ^{31}P-$\{^1H\}$ n.m.r. (singlet, δ 25.2 p.p.m.) and ^1H n.m.r. spectroscopy [doublet at δ 4.28 p.p.m., *J*(PH) = 1 Hz, doublet at δ 3.54 p.p.m., *J*(HH) = 15 Hz], but not characterised.

Treatment of a dichloromethane solution of complex (**1a**) with a 17:1 excess of $HBF_4\cdot Et_2O$, followed by addition of light petroleum (b.p. 40—60 °C), and storage of the resultant mixture at -20 °C, gave a dark red solid which was recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C). We tentatively formulate this complex as $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(\mu\text{-}Cl)_2Rh(\mu\text{-}CO)_2(\mu\text{-}dppm)Fe(\eta^5\text{-}C_5H_5)][BF_4]_2$ (**4**) on the basis of (*i*) elemental analysis (Table 1); (*ii*) the ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra, which were similar to but not identical with those of complex (**3**) (Table 2); (*iii*) a conductivity measurement in acetonitrile which was typical of a 2:1 electrolyte (see Experimental section); and (*iv*) the i.r. spectrum, which contained bands at 1 871 and 1 837 cm^{-1} assigned to bridging carbonyls, and a band at 1 055 cm^{-1} assigned to ν(B–F). The tetranuclear complex (**4**) was converted into the binuclear complex (**3**) upon standing in dichloromethane solution for 1 h.

Experimental

The general procedures and apparatus were the same as in other recent publications from this laboratory.[18] $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(dppm\text{-}P)]$ was prepared as described previously.[9]

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(COMe)Cl]$ (**1a**).—$[Rh_2(CO)_4Cl_2]$ (0.034 g, 0.088 mmol) was added to a solution of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(dppm\text{-}P)]$ (0.102 g, 0.177 mmol) in benzene (3.0 cm^3) under nitrogen, resulting in gas evolution. A benzene solvate of the required compound (**1a**) precipitated as dark red crystals. Yield: 0.121 g; Λ = 4.4 Ω^{-1} cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} solution in acetonitrile at 20 °C.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Ir(COMe)Cl]$ (**1b**).—$[Ir(CO)_2Cl(p\text{-}NH_2C_6H_4Me)]$ (0.070 g, 0.180 mmol) was added to a solution of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(dppm\text{-}P)]$ (0.104 g, 0.180 mmol) in benzene (2.0 cm^3) under nitrogen, resulting in gas evolution. The flask was immediately sealed to the light. After 0.5 h, the title compound (**1b**) precipitated as fine orange crystals. Yield: 0.093 g. A ^{31}P-$\{^1H\}$ n.m.r. spectrum of the product showed the presence of a small amount of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Ir(Me)Cl]$ as an impurity.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)RhMe_{0.4}Cl_{1.6}]$ (**2a**)–(**3**) (0.4:0.6).—A saturated solution of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(COMe)Cl]$ (**1a**) in acetone (2.0 cm^3) when put aside at 20 °C for 1 week deposited dark red crystals. Both microanalysis (Table 1) and the ^1H n.m.r. spectrum (Table 2) of the product showed it to be an acetone solvate of a mixture of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(Me)Cl]$ (**2a**) and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$ (**3**) in the ratio 0.4:0.6. A similar mixture of complexes (**2a**) and (**3**) was obtained when the solvent was dichloromethane. However, when dichloromethane was used as solvent for a longer period (several days) or chloroform was used as the solvent, the ratio of (**2a**):(**3**) changed to 0.3:0.7. A (**2a**):(**3**) ratio of 0.2:0.8 was obtained when the reaction between $[Fe(\eta^5\text{-}C_5H_5)(CO)(COMe)(dppm\text{-}P)]$ (0.0342 g, 0.0593 mmol) and $[Rh_2(CO)_4Cl_2]$ (0.0114 g, 0.0293 mmol) in benzene (2.0 cm^3) was carried out in the presence of Adogen 464 [trialkyl(C_8—C_{10})methylammonium chloride] (0.062 g, 0.14 mmol) for 1 d. During the first 3 h of this reaction a slow stream of nitrogen was passed over the reaction solution, the volume of which was maintained by addition of more benzene.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Ir(Me)Cl]$ (**2b**).—Slow evaporation of a warm solution of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Ir(COMe)Cl]$ (**1b**) (0.0284 g, 0.034 mmol) in benzene (5.0 cm^3) over 1 week deposited orange-brown crystals of the title compound. Yield: 0.0163 g.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(\mu\text{-}Cl)_2Rh(\mu\text{-}CO)_2(\mu\text{-}dppm)Fe(\eta^5\text{-}C_5H_5)][BF_4]_2$ (**4**).—$HBF_4\cdot Et_2O$ (approx. 0.3 cm^3, 2 mmol) was added to a cold (0 °C) solution of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(COMe)Cl]$ (**1a**) (0.115 g, 0.155 mmol) in dichloromethane (5.0 cm^3). After 15 min, light petroleum (b.p. 40—60 °C, 10 cm^3) was layered on to the solution. Upon storing the mixture for 3 weeks at -20 °C, a dark red solid precipitated. The supernatant liquid was decanted off, and the residue recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give (**4**) as a red-brown precipitate. Yield: 0.0874 g; Λ = 230 Ω^{-1} cm^2 mol^{-1} for a 5.18×10^{-4} mol dm^{-3} solution in acetonitrile at 20 °C. An i.r. spectroscopic examination of a solution of (**4**) in dichloromethane showed that it was converted into $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$ (**3**) after 1 h.

X-Ray Crystallography.—Crystals suitable for a single-crystal diffraction analysis were grown by the slow evaporation of a solution of a mixture of $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)RhCl_2]$ and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_2(\mu\text{-}dppm)Rh(Me)Cl]$ in acetone at ambient temperature. The red block-like crystals were found to be solvent dependent and so one of appropriate size (*ca.* 0.7 × 0.4 × 0.25 mm) was coated in epoxy resin prior to data collection.

Crystal data for (**2a**)–(**3**). $C_{35.4}H_{34.2}Cl_{1.6}FeO_3P_2Rh$, *M* = 786.12, triclinic, *a* = 1 109.7(3), *b* = 1 130.2(3), *c* = 1 404.4(3) pm, α = 108.53(2), β = 89.22(2), γ = 105.39(2)°, *U* = 1.723 nm^3, *Z* = 2, space group $P\bar{1}$, D_c = 1.51 g cm^{-3}, μ = 10.60 cm^{-1}, *F*(000) = 798.

Data collection. Scans running from 1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$.

---

* Trialkyl(C_8—C_{10})methylammonium chloride.

Table 4. Atomic co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*
Rh	−2 308.2(3)	−654.0(3)	2 378.4(3)
Fe	−16.1(5)	261.9(6)	2 585.8(4)
P(1)	−2 612(1)	1 327(1)	2 819(1)
P(2)	54(1)	2 345(1)	3 112(1)
Cl(1)	−2 251(1)	−2 882(1)	1 845(1)
Cl/Me	−4 317(2)	−1 411(2)	2 158(2)
C(111)	−3 745(3)	1 600(3)	3 675(2)
C(112)	−4 666(3)	2 041(3)	3 453(2)
C(113)	−5 488(3)	2 281(3)	4 154(2)
C(114)	−5 390(3)	2 080(3)	5 075(2)
C(115)	−4 469(3)	1 639(3)	5 297(2)
C(116)	−3 646(3)	1 399(3)	4 596(2)
C(121)	−2 888(3)	1 817(3)	1 741(2)
C(122)	−3 364(3)	852(3)	832(2)
C(123)	−3 534(3)	1 191(3)	−17(2)
C(124)	−3 229(3)	2 494(3)	43(2)
C(125)	−2 753(3)	3 458(3)	952(2)
C(126)	−2 583(3)	3 120(3)	1 801(2)
C(13)	−1 349(4)	2 582(4)	3 574(3)
C(211)	1 096(2)	3 295(3)	4 204(2)
C(212)	932(2)	2 991(3)	5 093(2)
C(213)	1 785(2)	3 593(3)	4 897(2)
C(214)	2 802(2)	4 499(3)	5 812(2)
C(215)	2 967(2)	4 803(3)	4 923(2)
C(216)	2 114(2)	4 201(3)	4 119(2)
C(221)	383(3)	3 286(3)	2 257(2)
C(222)	322(3)	4 567(3)	2 580(2)
C(223)	596(3)	5 312(3)	1 941(2)
C(224)	929(3)	4 774(3)	979(2)
C(225)	989(3)	3 493(3)	655(2)
C(226)	716(3)	2 748(3)	1 294(2)
C(1)	1 510(3)	304(3)	3 333(2)
C(2)	791(3)	−994(3)	2 958(2)
C(3)	642(3)	−1 349(3)	1 893(2)
C(4)	1 269(3)	−271(3)	1 610(2)
C(5)	1 806(3)	750(3)	2 500(2)
C(6)	−1 035(4)	−115(4)	1 476(3)
O(6)	−1 195(3)	−268(3)	620(2)
C(7)	−1 053(4)	−21(4)	3 541(4)
O(7)	−1 219(3)	−23(4)	4 370(2)

4 376 Unique data collected, 3 984 observed [$I > 2.0\sigma(I)$], $T = 290$ K.

Structure refinement. Weighting factor $g = 0.0002$, number of parameters = 322, $R = 0.0377$, $R' = 0.0416$.

All crystallographic measurements were made on a Nicolet *P3/F* diffractometer operating in the $\omega/2\theta$ scan mode using graphite-monochromatised Mo-K_α radiation ($\lambda = 71.069$ pm) following a standard procedure described in detail elsewhere.[19] The data set was corrected for absorption empirically once the structure had been solved.[20] The structure was solved *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[21] During the course of refinement it was noted that one of the atoms initially thought to be a chlorine atom displayed a rather large isotropic thermal parameter (>95 pm^2) and also ripples appeared around the atom in the Fourier difference map, both factors suggesting some kind of site disorder. N.m.r. studies of some redissolved crystals confirmed them to be a 60–40 mixture of [$(\eta^5$-$C_5H_5)$Fe(μ-CO)$_2$(μ-dppm)RhCl$_2$] and [$(\eta^5$-$C_5H_5)$Fe(μ-CO)$_2$(μ-dppm)Rh(Me)Cl] indicating disorder of the Me and Cl moieties on the second 'chloride' position in the crystal structure, a type of disorder that has been noted previously.[13] The position was therefore refined as a mixed-atom site (60% Cl, 40% C) which resulted in an isotropic thermal parameter comparable to that of Cl(1). All non-hydrogen atoms were then assigned anisotropic thermal parameters except those on an acetone molecule which were assigned to an overall isotropic thermal parameter. All phenyl rings were included in the refinement as rigid bodies with idealised hexagonal symmetry (C–C = 139.5 pm). All the hydrogen atoms were included in calculated positions (C–H = 108 pm). The weighting scheme $w = [\sigma^2(F_o) + g(F_o)]^{-1}$ was used at the end of the refinement in order to obtain acceptable agreement analyses. Final non-hydrogen atomic co-ordinates are given in Table 4.

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

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey plc for the generous loan of rhodium salts.

References

1 M. E. Wright, T. M. Mezza, G. O. Nelson, N. R. Armstrong, V. W. Day, and M. R. Thompson, *Organometallics*, 1983, **2**, 1171.
2 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 13.
3 F. Sato, M. Sato, and T. Uemura, *J. Organomet. Chem.*, 1973, **56**, C27.
4 K. Mead, I. Moore, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2083.
5 B. Delavaux, B. Chaudret, F. Dahan, and R. Poilblanc, *Organometallics*, 1985, **4**, 935.
6 J. C. Jeffrey, A. G. Orpen, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1986, 173.
7 C. de Meric de Bellefon, P. Braunstein, L. Lanfranchi, and A. Tiripicchio, *Organometallics*, 1984, **3**, 1772.
8 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 2751.
9 B. L. Shaw, M. J. Smith, and G. N. Stretton, *J. Chem. Soc., Dalton Trans.*, 1988, 725.
10 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 13.
11 P. S. Pregosin and R. W. Kunz, '^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes,' Part 16 in 'NMR Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, 1979, pp. 38—41, 110—114.
12 M. J. Breen, M. R. Duttera, G. L. Geoffroy, G. C. Novotnak, D. A. Roberts, P. M. Shulman, and G. R. Steinmetz, *Organometallics*, 1982, **1**, 1008.
13 G. S. Girolami, G. Wilkinson, A. M. R. Galas, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 1339.
14 M. J. Bennett, J. L. Pratt, K. A. Simpson, L. K. K. Li Shing Man, and J. Takats, *J. Am. Chem. Soc.*, 1976, **98**, 4810.
15 M. King, E. M. Holt, P. Radnia, and J. S. McKennis, *Organometallics*, 1982, **1**, 1718.
16 R. G. Ball, F. Edelan, G. Y. Kiel, J. Takats, and R. Drews, *Organometallics*, 1986, **5**, 829.
17 A. A. Bahsoun, J. A. Osborn, P. H. Bird, D. Nucciarone, and A. V. Peters, *J. Chem. Soc., Chem. Commun.*, 1984, 72.
18 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.
19 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
20 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
21 G. M. Sheldrick, SHELX 76, Program System for *X*-Ray Structure Determinations, University of Cambridge, 1976.

Received 18*th September* 1987; *Paper* 7/1674