In memory of T. A. Stephenson

Rhodium(I)–Iron(0) Carbonyl Complexes containing One Bridging $Ph_2PCH_2PPh_2$ Ligand, Including the Formation of a Tetranuclear Cluster from a Heterobimetallic Precursor: Crystal Structures of $[(OC)_4Fe(\mu\text{-}Ph_2PCH_2PPh_2)RhCl(CO)]$ and $[Fe_2Rh_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(CO)_8]$ †

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Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) with $[Rh_2Cl_2(CO)_4]$ in benzene gave $[(OC)_4Fe(\mu\text{-}dppm)RhCl(CO)]$ (**1**) in 90% yield. The structure of (**1**) has been established by a single-crystal *X*-ray diffraction study; the crystals are monoclinic, space group $P2_1/n$, with a = 1 246.5(2), b = 1 849.0(3), c = 1 612.3(2) pm, β = 110.34(1)°, and Z = 4; final R factor 0.0481 for 4 053 observed reflections. The structure shows that there is a metal–metal bond [Fe–Rh 269.9(4) pm], formulated as a donor ⟶ acceptor bond, *viz.* Fe ⟶ Rh. None of the carbonyl ligands shows any bridging interactions. Treatment of (**1**) with lithium acetate in dichloromethane–methanol converted the binuclear complex into the tetranuclear cluster $[Fe_2Rh_2(\mu\text{-}dppm)_2(CO)_8]$ (**3**) in 69% yield, also characterised by an *X*-ray diffraction study. Crystals of (**3**) are monoclinic, space group $P2_1/n$, with a = 2 074.6(5), b = 1 385.1(3), c = 2 271.6(5) pm, β = 117.48(2)°, and Z = 4; final R factor 0.0578 for 6 212 observed reflections. The structure is that of an unsupported Fe_2Rh_2 butterfly, the Rh–Rh distance of 405.4 pm indicating no interaction between the wing-tip atoms. Similar complexes are described for $Ph_2P(C{=}CH_2)PPh_2$.

In a recent publication[1] we reported the use of the monodentate phosphine iron complex $[Fe(CO)_4(dppm\text{-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) in the systematic synthesis of heterobimetallic complexes with Mn^I or Mo^0, containing a single bridging dppm ligand.

In the present paper we report on an extension of this type of chemistry to the synthesis of heterobimetallic complexes of iron(0) with rhodium(I) and also on an unusual, high yield, synthesis of a tetranuclear cluster from a heterobimetallic precursor. Part of this work has been the subject of a preliminary communication.[2]

Results and Discussion

Treatment of the monodentate dppm complex $[Fe(CO)_4(dppm\text{-}P)]$ with 0.5 mol equiv. of $[Rh_2Cl_2(CO)_4]$ in benzene gave the iron–rhodium heterobimetallic complex $[(OC)_4Fe(\mu\text{-}dppm)RhCl(CO)]$ (**1**) in 90% isolated yield. The compound was characterised by elemental analysis and i.r. spectroscopy (Table 1) and by $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy (Table 2); reactions are outlined in the Scheme and preparative details are given in the Experimental section. In addition, the structure of complex (**1**) has been determined by *X*-ray crystallography (see below). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**1**) consisted of two resonances, a low-field doublet (at δ 62.6 p.p.m.) assigned to the phosphorus atom bonded to iron and a double doublet at higher field, assigned to the phosphorus atom bonded to rhodium. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of (**1**) showed a single resonance for the PCH_2P protons at *ca.* 20 °C. The i.r. spectrum of (**1**) showed the absence of a bridging carbonyl group, the lowest frequency band assigned to ν(CO) being at 1 925 cm^{-1}.

The vinylidenebis(diphenylphosphine) (vdpp) analogue $[(OC)_4Fe(\mu\text{-}vdpp)RhCl(CO)]$ (**2**) was similarly prepared and showed similar n.m.r. and i.r. parameters. In particular, the i.r. spectrum of (**2**) in the carbonyl region was almost identical to that of (**1**), strongly arguing for an analogous structure.

The bimetallic complexes (**1**) and (**2**) are crystalline solids that do not decompose appreciably after several weeks in air. They are readily soluble in chlorinated hydrocarbons, slightly soluble in benzene, but insoluble in alkanes.

Crystal Structure of $[(OC)_4Fe(\mu\text{-}dppm)RhCl(CO)]$ (**1**).—Complex (**1**) was crystallised from chlorobenzene–methylcyclohexane (1:3). The structure is shown in Figure 1 and selected intramolecular distances and angles are in Table 3. The Fe and Rh moieties are linked by a single dppm bridge to give a five-membered FeP_2CRh ring. There are no bridging or semi-bridging carbonyl ligands but the Fe–Rh distance [269.9(4) pm] indicates a metal–metal bond and is similar to lengths reported in other Fe–Rh bimetallics, *viz.* $[(OC)_2Rh(\mu\text{-}C_7H_7)Fe(CO)_3]$ (C_7H_7 = cycloheptatrienyl), 276.4 pm;[3] $[Rh(\eta\text{-}C_5H_5)\{\eta\text{-}C_4H_4\text{-}Fe(CO)_3\}]$, 255.7 pm;[4] and $[(OC)_2Rh\{\mu\text{-}CH(PPh_2)_3\}Fe(CO)_3]^+$, 277.6 pm.[5]

In order to satisfy 18e and 16e configurations at the iron(0) and rhodium(I) centres respectively in $[(OC)_4Fe(\mu\text{-}dppm)RhCl(CO)]$ the metal–metal bond is formulated as a donor ⟶ acceptor bond, *viz.* Fe ⟶ Rh, *i.e.* the Fe atom can be viewed as occupying the fourth co-ordination site of Rh by electron pair donation from a filled orbital on Fe to an empty co-ordination site.

Reactions.—In view of the presence of a donor–acceptor bond in (**1**), and in the light of previous results on the breaking of the donor–acceptor bonds in the bimetallics $[(OC)_4Fe(\mu\text{-}$

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† μ-Bis(diphenylphosphino)methane-1,2,2,2,2-pentacarbonyl-1-chlororhodiumiron (*Fe–Rh*) and 1,2; 3,4-di-μ-bis(diphenylphosphino)methane-1,2,2,2,3,3,3,4-octacarbonyl-1,4-dirhodium-2,3-di-iron(4 *Fe–Rh*)(1 *Fe–Fe*) respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Infrared[a] and microanalytical[b] data

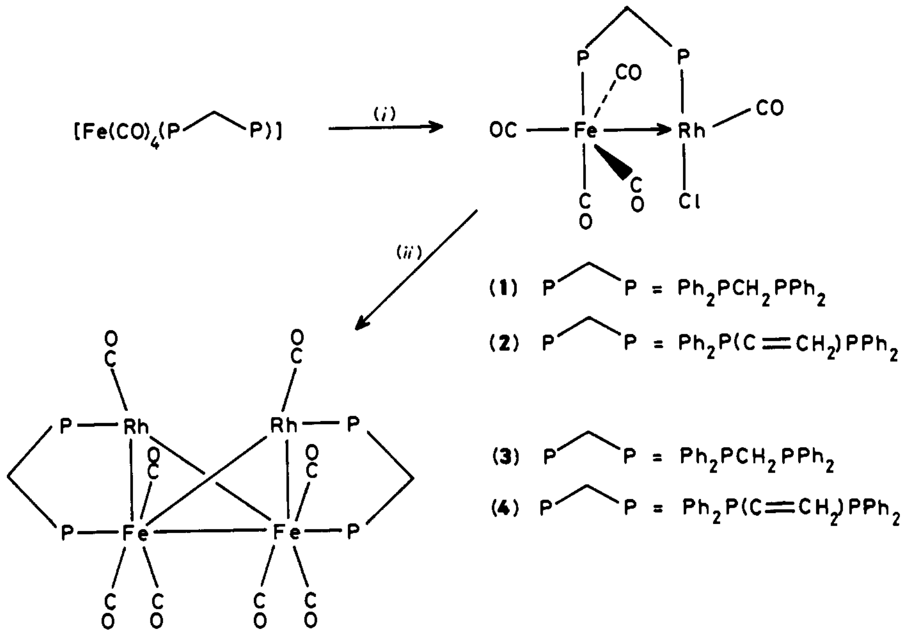
		Analysis (%)		
Complex	ν(CO)/cm^{-1}	C	H	Cl
(1)	2 065s, 2 018s, 1 992s, 1 955m, 1 925s	50.2 (50.1)	3.1 (3.1)	5.0 (4.95)
(2)	2 065s, 2 015s, 1 992s, 1 955m, 1 927s	51.05 (51.0)	2.85 (3.0)	5.3 (4.85)
(3)	1 960s, 1 940m, 1 920m, 1 860m	52.55 (53.15)	3.45 (3.40)	
(4)	1 960s, 1 940m, 1 920m, 1 880m			

[a] Measured in CH_2Cl_2 solution (s = strong, m = medium). [b] Calculated values in parentheses.

Table 2. ^{31}P-{^{1}H}[a] and ^{1}H[b] n.m.r. data

	^{31}P-{^{1}H}				^{1}H	
Complex	$\delta(P_{Fe})$	$\delta(P_{Rh})$	^1J(RhP)	$^2J(P_{Fe}P_{Rh})$	$\delta(CH_2)$	^2J(PH)
(1)	62.6	44.6	149	73	3.48	11
(2)	66.3	50.2	149	130	6.14	31, 28
					5.87	18, 16
(3)	59.6	15.8	176	49	4.25	10
(4)	72.1	33.8	178	98	5.96	31, 29
					5.67	18, 17

[a] Spectra (40.5 MHz) measured at +20 °C in CD_2Cl_2; chemical shifts (δ) in p.p.m. ($\pm$0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz ($\pm$3). [b] Spectra (100 MHz) measured in CD_2Cl_2 at +20 °C; chemical shifts (δ) in p.p.m. ($\pm$0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz ($\pm$0.1).



Scheme. (*i*) $[Rh_2Cl_2(CO)_4]$, (*ii*) LiO_2CMe, LiMe, or $NaBH_4$

dppm)MnBr(CO)$_3$] and [(OC)$_4$Fe(μ-dppm)Mo(CO)$_4$] with carbon monoxide,[1] we attempted the same reaction for (**1**). However, prolonged (2 h) treatment of (**1**) with carbon monoxide (*ca.* 10^5 Pa) at *ca.* 20 °C caused no reaction (i.r. evidence). Presumably the complex [(OC)$_4$Fe(μ-dppm)RhCl(CO)$_2$] is unstable.

We attempted to reduce complex (**1**) with sodium tetrahydroborate in dichloromethane–ethanol and obtained a dark green complex formulated as the cluster [Fe$_2$Rh$_2$(μ-dppm)$_2$(CO)$_8$] (**3**), in 44% isolated yield. This transformation could be better effected with methyl-lithium or lithium acetate (see Experimental section for details) in 66% and 69% yields respectively. Complex (**3**) was characterised by elemental analysis and i.r. spectroscopy (Table 1) and ^{31}P-{^{1}H} and ^{1}H n.m.r. spectroscopy (Table 2). In addition, the structure of complex (**3**) has been determined by *X*-ray crystallography. The ^{31}P-{^{1}H} n.m.r. spectrum of this cluster was very similar to that of (**1**) indicating that the Fe(μ-dppm)Rh backbone had remained intact. The i.r. spectrum suggested the absence of bridging carbonyl ligands, the lowest frequency ν(CO) band being at 1 860 cm^{-1}. The vdpp analogue [Fe$_2$Rh$_2$(μ-vdpp)$_2$(CO)$_8$] (**4**) was similarly prepared and showed similar n.m.r. and i.r. parameters (see Tables 1 and 2 and Experimental section).

The mechanism by which (**3**) is formed from (**1**) is not clear. We attempted the reverse reaction, *viz.* treatment of a

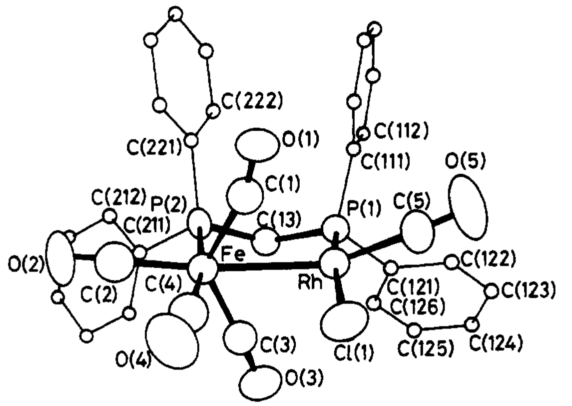


Figure 1. Molecular structure of [(OC)$_4$Fe(μ-dppm)RhCl(CO)] (**1**), showing the principal atomic numbering

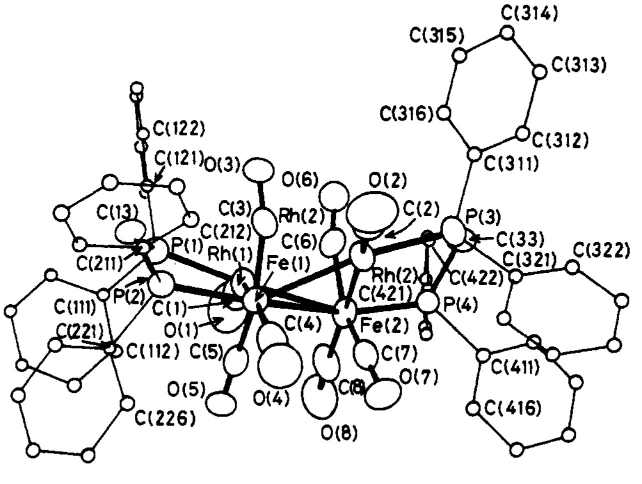


Figure 2. Molecular structure of [Fe$_2$Rh$_2$(μ-dppm)$_2$(CO)$_8$] (**3**), showing the principal atomic numbering

dichloromethane solution of (**3**) with one equivalent of chlorine in carbon tetrachloride: this caused an immediate colour change to yellow-brown. The ^{31}P-{^{1}H} n.m.r. spectrum indicated the formation of (**1**), as well as other minor uncharacterised products: carbon monoxide presumably arising from decomposition reactions. Efforts to effect a quantitative conversion were unsuccessful since treatment of (**3**) with an excess of carbon monoxide rapidly gave [Fe(CO)$_4$(dppm-*P*)] as a cleavage product [^{31}P-{^{1}H} n.m.r. evidence].

Haines *et al.*[6,7] have reported related halogenation/dehalogenation reactions for trirhodium phosphido clusters, *viz.* the interconversion of [Rh$_3$(μ-PPh$_2$)$_3$(μ-Cl)$_2$(μ-CO)(CO)$_3$] and [Rh$_3$(μ-PPh$_2$)$_3$(CO)$_5$].[6,7] However, in these systems the basic metal framework remained unaltered.

Crystal Structure of [Fe$_2$Rh$_2$(μ-dppm)$_2$(CO)$_8$] (**3**).—Complex (**3**) was crystallised from dichloromethane–light petroleum (b.p. 60—80 °C). The structure is shown in Figure 2 and selected intramolecular distances and angles are in Table 4. The structure is that of an unsupported tetrametal, Fe$_2$Rh$_2$, butterfly with a dihedral angle of 133°. The Rh–Rh distance of 405.4 pm indicates the absence of any interaction between these wing-tip atoms. The Fe–Rh bond lengths [264.8(4)—255.1(4) pm] are in a range normally associated with Fe–Rh single bonds;[3–5] the dppm bridged distances being slightly shorter than those unbridged. The Fe–Fe distance of 275.7(4) pm is similar to that found in previously reported complexes containing Fe–Fe bonds, *e.g.* [Fe$_2$Pt(CO)$_9$(PPh$_3$)], 278.0 pm;[8] [Fe$_2$Pt(CO)$_8$(cod)] (cod = cyclo-octa-1,5-diene), 270.4(4) pm;[9] and [Fe$_2$(CO)$_8$]$^{2-}$, 278.7(2) pm.[10] The cluster contains 58 valence electrons, which is comparable to related complexes, such as [Co$_2$Pt$_2$(μ-CO)$_3$(CO)$_5$(PPh$_3$)$_2$],[11] having two metals which prefer to exist as 16-electron species.

Table 3. Selected distances between interatomic vectors (pm) and angles (°) for [(OC)$_4$Fe(μ-dppm)RhCl(CO)] (**1**)

Fe–Rh	269.9(4)		
Cl(1)–Rh	238.6(4)	P(1)–Rh	224.8(3)
C(1)–Rh	237.0(8)	C(3)–Rh	257.8(9)
C(5)–Rh	183.3(9)	P(2)–Fe	226.3(4)
C(1)–Fe	184.7(9)	C(2)–Fe	177.4(9)
C(3)–Fe	178.9(9)	C(4)–Fe	181.8(9)
C(13)–P(1)	183.2(5)	C(13)–P(2)	182.9(7)
C(1)–O(1)	114.1(8)	C(4)–O(4)	112.0(8)
C(2)–O(2)	114.2(9)	C(5)–O(5)	114.0(9)
C(3)–O(3)	117.1(8)		
P(1)–Rh–Fe	94.75(4)	Cl(1)–Rh–Fe	91.72(5)
Cl(1)–Rh–P(1)	169.8(1)	C(5)–Rh–Fe	158.5(2)
C(5)–Rh–P(1)	90.6(3)	C(5)–Rh–Cl(1)	86.2(3)
P(2)–Fe–Rh	93.02(5)	C(1)–Fe–Rh	59.4(3)
C(1)–Fe–P(2)	93.4(3)	C(2)–Fe–Rh	172.6(2)
C(2)–Fe–P(2)	85.2(3)	C(2)–Fe–C(1)	113.6(4)
C(3)–Fe–Rh	66.6(3)	C(3)–Fe–P(2)	89.8(3)
C(3)–Fe–C(1)	126.0(4)	C(3)–Fe–C(2)	120.5(4)
C(4)–Fe–Rh	97.0(3)	C(4)–Fe–P(2)	170.0(2)
C(4)–Fe–C(1)	92.1(4)	C(4)–Fe–C(2)	84.9(4)
C(4)–Fe–C(3)	93.6(4)	C(13)–P(1)–Rh	112.4(3)
C(13)–P(2)–Fe	111.1(3)	P(2)–C(13)–P(1)	110.8(4)
Fe–C(1)–O(1)	163.9(5)	Fe–C(3)–O(3)	175.3(6)
Fe–C(2)–O(2)	176.4(6)	Fe–C(4)–O(4)	172.4(6)

Table 4. Selected distances between interatomic vectors (pm) and angles (°) for [Fe$_2$Rh$_2$(μ-dppm)$_2$(CO)$_8$] (**3**)

Fe(1)–Fe(2)	275.7(4)	Fe(1)–Rh(2)	263.4(4)
Fe(1)–Rh(1)	255.1(4)	Fe(2)–Rh(1)	264.8(4)
Fe(2)–Rh(2)	258.1(4)	C(1)–Rh(1)	185.4(11)
P(1)–Rh(1)	222.9(4)	C(2)–Rh(2)	185.4(10)
P(3)–Rh(2)	223.8(4)	C(3)–Fe(1)	178.9(9)
P(2)–Fe(1)	220.3(4)	C(5)–Fe(1)	181.2(8)
C(4)–Fe(1)	176.3(11)	C(6)–Fe(2)	180.3(11)
P(4)–Fe(2)	220.9(4)	C(8)–Fe(2)	177.9(9)
C(7)–Fe(2)	181.3(12)	C(13)–P(2)	184.6(10)
C(13)–P(1)	184.9(9)	C(33)–P(4)	184.0(7)
C(33)–P(3)	183.5(10)		
Rh(1) ··· Rh(2)	405.4(1)		
Fe(2)–Rh(1)–Fe(1)	64.01(4)	P(1)–Rh(1)–Fe(1)	95.8(2)
P(1)–Rh(1)–Fe(2)	158.8(1)	Fe(2)–Rh(2)–Fe(1)	63.82(4)
P(3)–Rh(2)–Fe(1)	158.1(1)	P(3)–Rh(2)–Fe(2)	94.30(5)
Rh(2)–Fe(1)–Rh(1)	102.84(3)	Fe(2)–Fe(1)–Rh(1)	59.70(4)
Fe(2)–Fe(1)–Rh(2)	57.15(4)	P(2)–Fe(1)–Rh(1)	96.3(2)
P(2)–Fe(1)–Rh(2)	138.69(6)	P(2)–Fe(1)–Fe(2)	155.9(1)
Rh(2)–Fe(2)–Rh(1)	101.65(3)	Fe(1)–Fe(2)–Rh(1)	56.29(4)
Fe(1)–Fe(2)–Rh(2)	59.03(4)	P(4)–Fe(2)–Rh(1)	137.6(1)
P(4)–Fe(2)–Rh(2)	97.27(6)	P(4)–Fe(2)–Fe(1)	156.3(1)

Experimental

General methods were as previously described in recent papers from this laboratory.[12] The complexes [Fe(CO)$_4$(dppm-*P*)] and [Fe(CO)$_4$(vdpp-*P*)] were prepared by published methods.[1]

Preparations.—[(OC)$_4$Fe(μ-dppm)RhCl(CO)] (**1**) *from* [Fe(CO)$_4$(dppm-*P*)] *and* [Rh$_2$Cl$_2$(CO)$_4$]. Solid [Rh$_2$Cl$_2$(CO)$_4$]

Table 5. Fractional atomic co-ordinates (× 10^4) for (1)·C_6H_5Cl with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	3 237.0(4)	1 849.0(2)	1 426.5(3)	C(124)	1 098(4)	4 613(2)	1 632(3)
Fe(1)	4 156.6(7)	1 473.8(4)	200.0(5)	C(125)	1 397(4)	4 620(2)	875(3)
P(1)	1 743(1)	2 441(1)	468(1)	C(126)	1 583(4)	3 971(2)	505(3)
P(2)	2 647(1)	1 908(1)	−930(1)	C(13)	1 971(5)	2 663(3)	−566(3)
Cl(1)	4 370(1)	1 411(1)	2 598(1)	C(211)	3 046(3)	2 305(2)	−1 823(2)
C(1)	3 273(5)	825(4)	552(4)	C(212)	2 391(3)	2 184(2)	−2 709(2)
O(1)	2 835(4)	313(2)	669(3)	C(213)	2 721(3)	2 488(2)	−3 375(2)
C(2)	4 634(6)	1 134(4)	−641(5)	C(214)	3 706(3)	2 912(2)	−3 156(2)
O(2)	4 996(5)	909(4)	−1 149(4)	C(215)	4 361(3)	3 033(2)	−2 270(2)
C(3)	4 510(5)	2 374(4)	610(4)	C(216)	4 031(3)	2 729(2)	−1 603(2)
O(3)	4 794(4)	2 965(3)	846(3)	C(221)	1 498(3)	1 280(2)	−1 484(2)
C(4)	5 476(6)	1 092(4)	960(5)	C(222)	379(3)	1 522(2)	−1 900(2)
O(4)	6 312(4)	832(3)	1 348(4)	C(223)	−481(3)	1 033(2)	−2 342(2)
C(5)	2 460(6)	1 747(4)	2 199(5)	C(224)	−222(3)	301(2)	−2 367(2)
O(5)	2 007(6)	1 598(4)	2 679(4)	C(225)	897(3)	59(2)	−1 951(2)
C(111)	344(2)	2 008(2)	113(3)	C(226)	1 757(3)	548(2)	−1 509(2)
C(112)	−633(2)	2 399(2)	−366(3)	Cl(1s)	3 170(4)	6 212(3)	10 482(3)
C(113)	−1 696(2)	2 057(2)	−673(3)	C(1s)	3 028(8)	5 595(4)	9 758(5)
C(114)	−1 783(2)	1 323(2)	−503(3)	C(2s)	2 091(8)	5 585(4)	8 971(5)
C(115)	−807(2)	962(2)	−25(3)	C(3s)	1 956(8)	5 018(4)	8 373(5)
C(116)	256(2)	1 275(2)	283(3)	C(4s)	2 759(8)	4 460(4)	8 562(5)
C(121)	1 470(4)	3 314(2)	892(3)	C(5s)	3 696(8)	4 470(4)	9 349(5)
C(122)	1 171(4)	3 306(2)	1 649(3)	C(6s)	3 831(8)	5 037(4)	9 947(5)
C(123)	985(4)	3 956(2)	2 019(3)				

Table 6. Fractional atomic co-ordinates (× 10^4) for (3)·$0.5CH_2Cl_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	7 532.5(3)	435.7(3)	5 641.0(2)	C(321)	5 490(3)	−2 360(3)	2 816(2)
Rh(2)	6 407.8(3)	−338.8(3)	3 707.3(2)	C(322)	4 959(3)	−3 078(3)	2 604(2)
Fe(1)	7 627.5(4)	485(1)	4 561.0(4)	C(323)	4 971(3)	−3 818(3)	2 193(2)
Fe(2)	7 048(1)	−1 108(1)	4 872.4(4)	C(324)	5 514(3)	−3 839(3)	1 993(2)
P(1)	7 880(1)	1 959(1)	5 931(1)	C(325)	6 045(3)	−3 121(3)	2 205(2)
P(2)	8 162(1)	1 905(1)	4 732(1)	C(326)	6 033(3)	−2 381(3)	2 617(2)
P(3)	5 472(1)	−1 370(1)	3 329(1)	C(33)	5 368(3)	−1 926(5)	4 013(3)
P(4)	6 255(1)	−2 278(1)	4 693(1)	C(411)	6 376(3)	−3 505(3)	4 454(3)
C(111)	8 779(2)	2 149(3)	6 617(2)	C(412)	5 813(3)	−4 172(3)	4 278(3)
C(112)	9 268(2)	1 380(3)	6 839(2)	C(413)	5 893(3)	−5 106(3)	4 090(3)
C(113)	9 976(2)	1 526(3)	7 338(2)	C(414)	6 535(3)	−5 372(3)	4 078(3)
C(114)	10 194(2)	2 441(3)	7 616(2)	C(415)	7 098(3)	−4 705(3)	4 254(3)
C(115)	9 705(2)	3 210(3)	7 394(2)	C(416)	7 019(3)	−3 772(3)	4 442(3)
C(116)	8 998(2)	3 064(3)	6 894(2)	C(421)	6 059(2)	−2 557(3)	5 383(2)
C(121)	7 279(2)	2 649(3)	6 166(2)	C(422)	5 478(2)	−2 148(3)	5 445(2)
C(122)	6 777(2)	3 315(3)	5 738(2)	C(423)	5 370(2)	−2 373(3)	5 992(2)
C(123)	6 321(2)	3 807(3)	5 933(2)	C(424)	5 843(2)	−3 006(3)	6 476(2)
C(124)	6 367(2)	3 633(3)	6 556(2)	C(425)	6 423(2)	−3 414(3)	6 415(2)
C(125)	6 869(2)	2 967(3)	6 984(2)	C(426)	6 531(2)	−3 190(3)	5 868(2)
C(126)	7 325(2)	2 475(3)	6 789(2)	C(1)	7 689(4)	139(6)	6 493(4)
C(13)	7 884(3)	2 667(4)	5 243(3)	O(1)	7 900(5)	−58(6)	7 037(3)
C(211)	7 935(2)	2 681(3)	4 009(2)	C(2)	6 151(4)	168(5)	2 873(4)
C(212)	7 350(2)	2 450(3)	3 399(2)	O(2)	6 055(4)	437(5)	2 372(3)
C(213)	7 172(2)	3 049(3)	2 851(2)	C(3)	6 789(4)	1 115(5)	4 313(3)
C(214)	7 580(2)	3 879(3)	2 915(2)	O(3)	6 328(3)	1 681(4)	4 220(3)
C(215)	8 165(2)	4 110(3)	3 525(2)	C(4)	7 866(4)	193(5)	3 931(3)
C(216)	8 343(2)	3 512(3)	4 072(2)	O(4)	8 059(3)	49(5)	3 532(3)
C(221)	9 155(2)	1 960(3)	5 154(2)	C(5)	8 374(4)	−23(5)	5 293(3)
C(222)	9 545(2)	2 604(3)	5 669(2)	O(5)	8 936(3)	−334(3)	5 678(2)
C(223)	10 303(2)	2 610(3)	5 969(2)	C(6)	6 402(4)	−338(5)	4 970(4)
C(224)	10 670(2)	1 972(3)	5 753(2)	O(6)	5 906(3)	31(4)	4 971(3)
C(225)	10 280(2)	1 328(3)	5 238(2)	C(7)	7 334(4)	−1 513(5)	4 271(4)
C(226)	9 522(2)	1 322(3)	4 939(2)	O(7)	7 573(3)	−1 909(4)	3 960(3)
C(311)	4 574(2)	−826(3)	2 877(2)	C(8)	7 704(4)	−1 633(5)	5 626(4)
C(312)	4 109(2)	−1 042(3)	2 214(2)	O(8)	8 112(4)	−2 018(5)	6 106(3)
C(313)	3 415(2)	−638(3)	1 902(2)	C(1s)	109(21)	3 577(30)	4 151(21)
C(314)	3 186(2)	−18(3)	2 252(2)	Cl(1s)	902(6)	3 051(8)	4 367(6)
C(315)	3 651(2)	198(3)	2 915(2)	Cl(2s)	235(6)	4 806(9)	4 259(6)
C(316)	4 345(2)	−206(3)	3 227(2)				

(0.388 g, 1 mmol) was added to a stirred solution of $[Fe(CO)_4(dppm\text{-}P)]$ (1.10 g, 2 mmol) in benzene (15 cm^3). Carbon monoxide was evolved and a solid precipitated. The mixture was refrigerated overnight (5 °C) to give the desired product as orange microcrystals. Yield; 1.30 g (90%).

Complex $[(OC)_4Fe(\mu\text{-vdpp})RhCl(CO)]$ (**2**) was prepared similarly as yellow microcrystals using $[Fe(CO)_4(vdpp\text{-}P)]$. Yield: 80%.

$[Fe_2Rh_2(\mu\text{-dppm})_2(CO)_8]$ (**3**) *from* $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$ (**1**) *and* LiO_2CMe. A solution of LiO_2CMe (0.510 g, 5 mmol) in methanol (3 cm^3) was added to a stirred solution of $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$ (**1**) (0.400 g, 0.577 mmol) in dichloromethane (25 cm^3). After 1 h the solvents were removed under reduced pressure and the residue recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C), to give the desired product as dark green microcrystals. Yield: 0.250 g (69%).

$[Fe_2Rh_2(\mu\text{-vdpp})_2(CO)_8]$ (**4**) *from* $[(OC)_4Fe(\mu\text{-vdpp})RhCl(CO)]$ (**2**) *and methyl-lithium*. A solution of methyl-lithium in diethyl ether (6 mol equiv.) was added to a diethyl ether suspension of $[(OC)_4Fe(\mu\text{-vdpp})RhCl(CO)]$ (**2**) (0.300 g, 0.41 mmol). The mixture was stirred for 1 h, filtered, and the solvent removed from the filtrate under reduced pressure. Recrystallisation from dichloromethane–light petroleum (b.p. 40—60 °C) gave the desired product as dark green microcrystals. Yield: 0.110 g (40%). $[Fe_2Rh_2(\mu\text{-dppm})_2(CO)_8]$ (**3**) was also prepared by this method in 66% yield.

X-Ray Crystallography.—Crystals of (**1**) suitable for single-crystal diffraction analysis were obtained by the diffusion of methylcyclohexane into a solution of compound (**1**) in chlorobenzene while those of compound (**3**) were obtained by diffusion of light petroleum (b.p. 40—60 °C) into a solution of (**3**) in dichloromethane.

All crystallographic measurements were made on a Nicolet *P3/F* diffractometer operating in the ω—2θ scan mode using graphite-monochromatised Mo-K_α radiation (λ = 71.069 pm) following a standard procedure described in detail elsewhere.[13] Both data sets were corrected for absorption empirically once the structures had been solved.[14] Both compounds were solved *via* standard heavy-atom methods and refined by full-matrix [compound (**1**)] or blocked full-matrix [compound (**3**)] least squares using the SHELX program system.[15] All non-hydrogen atoms were assigned anisotropic thermal parameters except for the chlorobenzene [in compound (**1**)] and dichloromethane [in compound (**3**)] solvent molecules which were each assigned an overall isotropic thermal parameter and, in the case of the dichloromethane molecule, refined with an occupancy factor of 0.5. In both complexes methylene and phenyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned to an overall isotropic thermal parameter for each group. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used for both compounds in which the parameter g was included in refinement in order to obtain satisfactory agreement analyses.

Crystal data for compound (**1**)$\cdot C_6H_5Cl$. $C_{30}H_{22}ClFeO_5P_2Rh\cdot C_6H_5Cl$, M = 831.21, monoclinic, a = 1 246.5(2), b = 1 849.0(3), c = 1 612.3(2) pm, β = 110.34(1)°, U = 3.484 nm^3, Z = 4, space group $P2_1/n$, D_c = 1.58 g cm^{-3}, μ = 12.91 cm^{-1}, $F(000)$ = 1 768.

Data collection. Scans running from 1.0° above $K_{\alpha1}$ to 1.0° below $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 5 103 Data collected, 4 053 observed $[I > 2.0\sigma(I)]$, T = 290 K.

Structure refinement. Number of parameters = 330, weighting factor g = 0.0004, R = 0.0481, R' = 0.0568.

The final atomic co-ordinates and their standard deviations are given in Table 5.

Crystal data for compound (**3**)$\cdot 0.5CH_2Cl_2$. $C_{58}H_{44}Fe_2O_8P_4Rh_2\cdot 0.5CH_2Cl_2$, M = 1 304.81, monoclinic, a = 2 074.6(5), b = 1 385.1(3), c = 2 271.6(5) pm, β = 117.48(2)°, U = 5.791 nm^3, Z = 4, space group $P2_1/n$, D_c = 1.50 g cm^{-3}, μ = 11.60 cm^{-1}, $F(000)$ = 2 620.

Data collection. As above. 8 158 Data collected, 6 212 observed $[I > 2.0\sigma(I)]$.

Structure refinement. Number of parameters = 700, weighting factor g = 0.0004, R = 0.0578, R' = 0.0640.

The final atomic co-ordinates and their standard deviations are given in Table 6.

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References

1 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1509.

2 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 13.

3 M. J. Bennet, J. L. Pratt, K. A. Simpson, L. K. K. Lishingham, and J. Takats, *J. Am. Chem. Soc.*, 1976, **98**, 4810.

4 M. King, E. M. Holt, P. Radnia, and J. S. McKennis, *Organometallics*, 1982, **1**, 1718.

5 A. A. Bahsoun, J. A. Osborn, P. H. Bird, D. Nucciarone, and A. V. Peters, *J. Chem. Soc., Chem. Commun.*, 1984, 72.

6 R. J. Haines, N. D. C. T. Steen, and R. B. English, *J. Chem. Soc., Chem. Commun.*, 1981, 407.

7 R. J. Haines, N. D. C. T. Steen, and R. B. English, *J. Chem. Soc., Dalton Trans.*, 1984, 515.

8 R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1972, 200.

9 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134.

10 H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 5285.

11 J. Fischer, A. Mitschler, R. Weiss, J. Dehand, and J. F. Nennig, *J. Organomet. Chem.*, 1975, **91**, C37.

12 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.

13 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.

14 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A.*, 1983, **39**, 158.

15 G. M. Sheldrick, SHELX 76, Program System for *X*-Ray Structure Determination, University of Cambridge, 1976.

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