Syntheses of Iron-containing Heterometallic Complexes using Tridentate Phosphine Ligands; the Crystal Structure of $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9\{Ph_2PC(CH_2)PPh_2\}]$†

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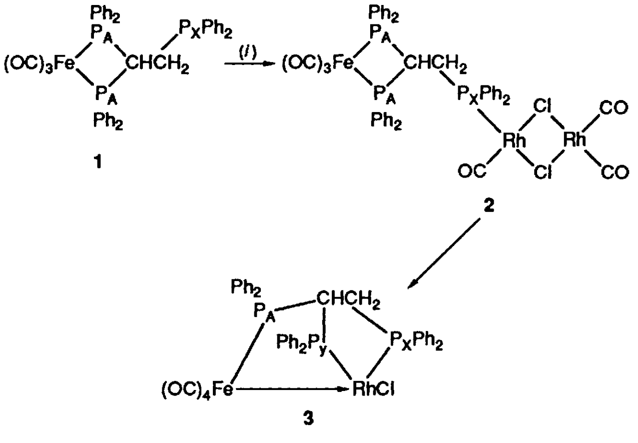
Treatment of $[Fe(CO)_3(dppee)]$ [dppee = 1,1-bis(diphenylphosphino)ethene] with PPh_2H gives the addition product $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ **1**. The unco-ordinated phosphine group of complex **1** reacts with $[\{RhCl(CO)_2\}_2]$ to give $[(OC)_4Fe\{Ph_2PCH(PPh_2)CH_2PPh_2\}RhCl]$ **3** *via* $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Rh(CO)Cl_2Rh(CO)_2]$ **2**. Complex **1** reacts with $[Ru_3(CO)_{10}(dppee)]$ to give the heterometallic complex $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]$ **4** the structure of which has been determined by X-ray crystallography.

We have previously reported the ring-opening reaction of $[Fe(CO)_3(dppee)]$ [dppee = $Ph_2PC(=CH_2)PPh_2$] with $[\{RhCl(CO)_2\}_2]$ which leads to the formation of the complex $[(OC)_4Fe(\mu\text{-dppee})RhCl(CO)]$.[1] This heterobimetallic complex is also formed on treatment of the dangling phosphine-containing complex $[Fe(CO)_4(dppee\text{-}P)]$ with $[\{RhCl(CO)_2\}_2]$.[2] We wished to extend the range of heterometallic complexes involving iron but have found that the ring-opening reaction has limited application. However, it has been reported that the dppee ligand readily undergoes a Michael-type addition reaction with PPh_2H to give the tridentate phosphine ligand $(Ph_2P)_2CHCH_2PPh_2$. This addition reaction occurs both on the uncomplexed dppee[3] and, more readily, on complexed dppee.[4] We have therefore employed this reaction to synthesise $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ **1** and then made use of the dangling phosphine created in this way to synthesise heterometallic complexes. This paper reports the results of the treatment of **1** with $[\{RhCl(CO)_2\}_2]$ and with $[Ru_3(CO)_{10}(dppee)]$.



Scheme 1 (*i*) $[\{RhCl(CO)_2\}_2]$

Results and Discussion

The complex $[Fe(CO)_3(dppee)]$ is prepared in high yield by treatment of $[Fe(CO)_5]$ with dppee in the presence of trimethylamine *N*-oxide. This is a modification of the previously reported synthetic method[5] which maximises the yield of $[Fe(CO)_3(dppee)]$ at the expense of the other product of the reaction, $[Fe(CO)_4(dppee\text{-}P)]$.

The complex $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ **1** is formed in quantitative yield by the base ($KOBu^t$)-catalysed addition of diphenylphosphine to a tetrahydrofuran solution of $[Fe(CO)_3(dppee)]$. The ^{31}P NMR spectrum of **1** consists of a doublet (δ 37.8) due to the two co-ordinated phosphorus atoms and a triplet (δ −21.8) with $^3J(PP) = 11.0$ Hz, due to the unco-ordinated phosphorus atom. Complex **1** is also formed by the direct reaction between $[Fe(CO)_5]$ and $(Ph_2P)_2CHCH_2PPh_2$, but in this reaction several other products are formed.[6]

The unco-ordinated phosphine group of complex **1** reacts with $[\{RhCl(CO)_2\}_2]$ to give an unstable heterobimetallic species which we formulate as $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Rh(CO)Cl_2Rh(CO)_2]$ **2** on the basis of infrared and ^{31}P and ^{13}C NMR spectroscopy, and microanalysis. Thus, the infrared spectrum shows bands due to both $Fe(CO)_3$ and $LRh(CO)(\mu\text{-}Cl)_2Rh(CO)_2$[7] moieties (1980, 1900 and 2077, 2010, 1995 cm^{-1}, respectively). The ^{31}P NMR spectrum shows a resonance at δ 43.5 due to two phosphorus atoms co-ordinated to Fe, and a resonance centred at δ 23.4 [d of t, $J(PRh)$ 126, $J(PP)$ 3.7 Hz] due to the phosphorus atom co-ordinated to Rh, in the ratio of 2:1, as expected. The ^{13}C NMR spectrum in the carbonyl region shows resonances at δ +221.0 due to CO on Fe, and at δ 183.0 due to CO on Rh. Complex **2** is rather unstable and could not be isolated in a pure form. It transforms slowly in solution over a period of a few hours, or immediately on addition of NMe_3O, into $[(OC)_4Fe\{Ph_2PCH(PPh_2)CH_2PPh_2\}RhCl]$ **3**. Again this complex has been characterised by spectroscopic methods. The infrared spectrum is typical of a $Fe(CO)_4$ moiety (2048, 1980 and 1938 cm^{-1}), indicating that a CO group has transferred from rhodium to iron. The ^{31}P NMR spectrum is particularly informative. It shows three resonances of equal intensity, two of which show coupling to rhodium, and the third having a chemical shift typical of a phosphine bonded to a $Fe(CO)_4$ moiety (δ 82.5). The ^{13}C NMR spectrum indicates the absence of CO co-ordinated to rhodium, and consists only of a resonance at δ 214.5, due to the $Fe(CO)_4$ moiety. Complex **3** is therefore formed by carbonyl transfer from rhodium to iron, and phosphine transfer (*via* a ring-opening reaction) from iron to rhodium (Scheme 1).

The unco-ordinated phosphine group of complex **1** also reacts with $[Ru_3(CO)_{10}(dppee)]$ to give the heterometallic complex $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]$ **4**. This complex has been characterised by spectroscopic

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

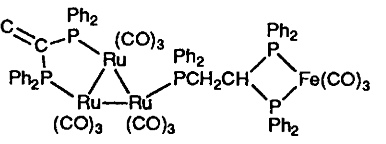
Table 1 Spectroscopic data

Compound	^{31}P NMR [a]	Infrared (cm^{-1}) [b]
1 $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$	37.8 [d, J(PP′) 11.0, P_A] −21.8 [t, J(PP′) 11.0, P_X]	1980s, 1910vs (br)
2 $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Rh(CO)Cl_2Rh(CO)_2]$	43.5 [t, J(PP) 3.7, P_A] 23.4 [d of t, J(PP) 3.7, J(PRh) 126, P_X]	2077m, 2010(sh), 1995s, 1980s, 1900vs (br)
3 $[(OC)_4Fe\{Ph_2PCH(PPh_2)CH_2PPh_2\}RhCl]$	82.5 (m, P_A), 70.1 [br d of t, J(PP) 38, J(PRh) 126, P_X] 58.8 [br d of t, J(PP) 45, J(PRh) 151, P_Y]	2048m, 1980vs, 1938vs
4 $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]$	42.2 [d, J(PP) 2.5, PFe] 23.1 (m, 3PRu)	2052m, 1985vs, 1975s, 1942m, 1915–1900s (br)

[a] In thf–C_6D_6; chemical shifts in δ, coupling constants in Hz. [b] ν(CO), in CH_2Cl_2 solution.

Table 2 Selected bond lengths (Å) and angles (°) for $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]$ **4**

Ru(1)–Ru(2)	2.846(1)	Ru(3)–C(4)	1.93(2)
Ru(1)–Ru(3)	2.883(1)	P(1)–C(37)	1.86(1)
Ru(2)–Ru(3)	2.852(1)	P(2)–C(37)	1.87(1)
Ru(1)–P(2)	2.332(3)	C(37)–C(38)	1.31(2)
Ru(2)–P(1)	2.309(3)	Fe–P(4)	2.201(3)
Ru(3)–P(3)	2.367(3)	Fe–P(5)	2.206(4)
Ru(1)–C(1)	1.87(2)	P(4)–C(75)	1.90(1)
Ru(1)–C(2)	1.95(1)	P(5)–C(75)	1.89(1)
Ru(1)–C(3)	1.94(1)	C(75)–C(76)	1.56(1)
Ru(2)–C(5)	1.93(1)	P(3)–C(76)	1.85(1)
Ru(2)–C(6)	1.95(2)	Fe–C(10)	1.77(2)
Ru(2)–C(7)	1.87(2)	Fe–C(11)	1.77(2)
Ru(3)–C(8)	1.94(1)	Fe–C(12)	1.75(2)
Ru(3)–C(9)	1.86(2)		
Ru(1)–Ru(2)–Ru(3)	60.79(4)	C(11)–Fe–P(4)	104.2(5)
Ru(2)–Ru(3)–Ru(1)	59.52(4)	C(11)–Fe–P(5)	104.0(6)
Ru(3)–Ru(1)–Ru(2)	59.70(4)	C(11)–Fe–C(10)	101.5(8)
P(1)–C(37)–P(2)	114.2(6)	C(11)–Fe–C(12)	108.1(9)
P(4)–C(75)–P(5)	88.2(4)	P(4)–Fe–C(12)	89.8(5)
P(4)–Fe–P(5)	73.5(1)	P(5)–Fe–C(10)	90.5(6)
		C(10)–Fe–C(12)	91.9(8)



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methods (Table 1) and by a single-crystal X-ray structure determination. The structure is shown in Fig. 1, bond lengths and angles are given in Table 2, and atom parameters in Table 3. The complex is essentially composed of a five-co-ordinate mononuclear iron complex and a triruthenium carbonyl cluster joined by co-ordination to a tridentate phosphine ligand, confirming that the triruthenium moiety has co-ordinated to the dangling phosphine on complex **1**. All the phosphorus atoms co-ordinated to the triruthenium triangle occupy equatorial sites, as expected. The iron atom has a distorted square-pyramidal geometry almost identical to that of $[Fe(CO)_3(dppee)]$,[5] although the Fe–P bond lengths in complex **4** [average 2.203(3) Å] are significantly shorter than in $[Fe(CO)_3(dppee)]$ [average 2.222(3) Å].

Experimental

All reactions were carried out under nitrogen unless otherwise stated, using dry, degassed solvents and standard Schlenk-line techniques. Infrared spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin Elmer 681 spectrometer, NMR spectra on JEOL FX-60 or Bruker WM250 instruments. Chemical shifts are relative to $SiMe_4$ for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P NMR spectra. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. The compounds dppee,[8] $(Ph_2P)_2CHCH_2PPh_2$,[3] and $[Ru_3(CO)_{10}(dppee)]$[5] were prepared according to published procedures.

Preparations.—$[Fe(CO)_3(dppee)]$. The compound $NMe_3O\cdot 2H_2O$ (0.86 g, 7.7 mmol) in methanol (20 cm^3) was added dropwise, over 30 min, to a solution of $[Fe(CO)_5]$ (0.5 cm^3, 3.86 mmol) and dppee (1.53 g, 3.86 mmol) in thf (70 cm^3). The solution was then heated under reflux for 3 h. The resulting red solution was evaporated to dryness under vacuum. Heptane (300 cm^3) was added to the red solid, and the mixture was heated, in air, under reflux for 30 min. The solution was cooled to give a red precipitate of $[Fe(CO)_3(dppee)]$ which was filtered off and dried *in vacuo* (1.44 g, 70%) (Found: C, 64.6; H, 4.0; P, 11.0. $C_{29}H_{22}FeO_3P_2$ requires C, 64.9; H, 4.1; P, 11.6%). The filtrate, upon evaporation to small volume, yielded a small amount of $[Fe(CO)_4(dppee\text{-}P)]$ (0.33 g, 15%).

$[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ **1**. Diphenylphosphine (0.02 g, 0.11 mmol) and $[Fe(CO)_3(dppee)]$ (0.06 g, 0.22 mmol) in thf (30 cm^3) were stirred at room temperature for 0.5 h in the presence of a catalytic amount of $KOBu^t$. The resulting yellow solution was evaporated to dryness and the yellow residue was washed with three portions (10 cm^3) of pentane and recrystallised from thf to give complex **1** as a yellow solid (0.06 g, 75%) (Found: C, 68.6; H, 4.8. $C_{41}H_{33}FeO_3P_3$ requires C, 68.1; H, 4.6%).

$[(OC)_4Fe\{Ph_2PCH(PPh_2)CH_2PPh_2\}RhCl]$ **3**. The complex $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ (0.16 g, 2.24 × 10^{-4} mol) in thf (10 cm^3) was stirred at room temperature with $[\{RhCl(CO)_2\}_2]$ (0.04 g, 1.12 × 10^{-4} mol). After 10 min the solution was reduced in volume and transferred to an NMR tube. Phosphorus-31 and ^{13}C NMR and infrared spectroscopy showed that the major species present was $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Rh(CO)Cl_2Rh(CO)_2]$ **2**. The solution was evaporated to dryness, and the residue was recrystallised from thf–benzene to give **2** as a yellow solid (0.06 g, 25%) (Found: C, 48.3; H, 3.4. $C_{44}H_{33}Cl_2FeO_6P_3Rh_2$ requires C, 48.8; H, 3.1%).

Complex **2** was redissolved in thf (10 cm^3) and stirred at room temperature for 8 h, after which time NMR spectroscopy showed complete conversion into $[(OC)_4Fe\{Ph_2PCH(PPh_2)CH_2PPh_2\}RhCl]$ **3** had occurred. The yellow solution was evaporated to dryness, and the residue was recrystallised by slow evaporation from thf–benzene (Found: C, 58.2; H, 3.9. $C_{42}H_{33}ClFeO_4P_3Rh$ requires C, 56.7; H, 3.7. $C_{42}H_{33}ClFeO_4P_3Rh\cdot$thf requires C, 57.5; H, 4.3%).

$[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]$ **4**. A mixture of $[Ru_3(CO)_{10}(dppee)]$ (0.114 g, 9.7 × 10^{-5} mol) and $[Fe(CO)_3\{(Ph_2P)_2CHCH_2PPh_2\}]$ (0.07 g, 9.7 × 10^{-5} mol) in

Table 3 Atom parameters for $[(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)]\cdot thf$ **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.1222(1)	0.1764(1)	0.3374(1)	C(34)	0.4802(7)	0.2698(6)	0.2547(5)
Ru(2)	−0.0478(1)	0.2713(1)	0.2828(1)	C(35)	0.3897(7)	0.2195(6)	0.2577(5)
Ru(3)	0.0256(1)	0.2793(1)	0.4434(1)	C(36)	0.2754(7)	0.2108(6)	0.2062(5)
Fe	0.6202(2)	0.3183(1)	0.7892(1)	C(37)	0.0248(11)	0.1401(7)	0.1360(7)
P(1)	−0.0742(2)	0.2148(1)	0.1540(2)	C(38)	−0.0093(15)	0.0822(8)	0.0760(8)
P(2)	0.1625(2)	0.1470(1)	0.2180(2)	C(39)	0.0375(10)	0.4171(6)	0.6247(5)
P(3)	0.1200(2)	0.2805(1)	0.5728(2)	C(40)	−0.0093(10)	0.4687(6)	0.6744(5)
P(4)	0.5020(3)	0.2373(2)	0.6870(2)	C(41)	−0.0133(10)	0.4568(6)	0.7450(5)
P(5)	0.4650(3)	0.3761(2)	0.7452(2)	C(42)	0.0295(10)	0.3933(6)	0.7658(5)
C(1)	0.2130(13)	0.1135(8)	0.3887(8)	C(43)	0.0763(10)	0.3417(6)	0.7161(5)
C(2)	0.2492((13)	0.2592(8)	0.3868(8)	C(44)	0.0803(10)	0.3536(6)	0.6456(5)
C(3)	−0.0164(12)	0.1012(8)	0.2964(7)	C(45)	0.1454(8)	0.1346(6)	0.5827(6)
C(4)	−0.0595(12)	0.1834(8)	0.4306(7)	C(46)	0.1047(8)	0.0642(6)	0.5871(6)
C(5)	0.0947(12)	0.3388(7)	0.2912(7)	C(47)	−0.0046(8)	0.0534(6)	0.6034(6)
C(6)	−0.1828(13)	0.2087(7)	0.2882(7)	C(48)	−0.0731(8)	0.1130(6)	0.6153(6)
C(7)	−0.1491(14)	0.3460(8)	0.2717(8)	C(49)	−0.0323(8)	0.1834(6)	0.6110(6)
C(8)	0.1244(13)	0.3704(8)	0.4531(7)	C(50)	0.0769(8)	0.1941(6)	0.5947(6)
C(9)	−0.1053(14)	0.3311(9)	0.4553(9)	C(51)	0.4120(10)	0.5030(5)	0.8409(6)
C(10)	0.7087(15)	0.4056(10)	0.8358(10)	C(52)	0.3752(10)	0.5402(5)	0.9043(6)
C(11)	0.5883(14)	0.2918(9)	0.8676(9)	C(53)	0.3217(10)	0.4994(5)	0.9433(6)
C(12)	0.7449(14)	0.2751(9)	0.7710(10)	C(54)	0.3049(10)	0.4214(5)	0.9191(6)
O(1)	0.2656(11)	0.0713(7)	0.4174(7)	C(55)	0.3417(10)	0.3842(5)	0.8557(6)
O(2)	0.3311(9)	0.3014(6)	0.4134(7)	C(56)	0.3952(10)	0.4250(5)	0.8167(6)
O(3)	−0.0907(9)	0.0536(5)	0.2727(6)	C(57)	0.3743(8)	0.4766(6)	0.6600(6)
O(4)	−0.1142(9)	0.1300(6)	0.4299(5)	C(58)	0.3814(8)	0.5354(6)	0.6142(6)
O(5)	0.1729(10)	0.3743(5)	0.2909(6)	C(59)	0.4882(8)	0.5386(6)	0.5959(6)
O(6)	−0.2675(9)	0.1763(6)	0.2888(6)	C(60)	0.5879(8)	0.5031(6)	0.6233(6)
O(7)	−0.2186(11)	0.3892(7)	0.2624(8)	C(61)	0.5808(8)	0.4543(6)	0.6690(6)
O(8)	0.1747(11)	0.4273(6)	0.4629(6)	C(62)	0.4740(8)	0.4411(6)	0.6874(6)
O(9)	−0.1849(12)	0.3618(8)	0.4597(8)	C(63)	0.3977(10)	0.1352(5)	0.7436(6)
O(10)	0.7657(13)	0.4628(8)	0.8662(8)	C(64)	0.3734(10)	0.0641(5)	0.7529(6)
O(11)	0.5756(13)	0.2758(8)	0.9212(7)	C(65)	0.4184(10)	0.0029(5)	0.7135(6)
O(12)	0.8269(11)	0.2463(8)	0.7589(9)	C(66)	0.4876(10)	0.0128(5)	0.6649(6)
C(13)	−0.3132(9)	0.2064(5)	0.0701(6)	C(67)	0.5119(10)	0.0839(5)	0.6556(6)
C(14)	−0.4337(9)	0.1767(5)	0.0445(6)	C(68)	0.4669(10)	0.1451(5)	0.6949(6)
C(15)	−0.4673(9)	0.1079(5)	0.0556(6)	C(69)*	0.6342(20)	0.2809(11)	0.5982(10)
C(16)	−0.3804(9)	0.0687(5)	0.0923(6)	C(70)*	0.6687(20)	0.2735(11)	0.5307(10)
C(17)	−0.2598(9)	0.0984(5)	0.1178(6)	C(71)*	0.6122(20)	0.2159(11)	0.4656(10)
C(18)	−0.2262(9)	0.1673(5)	0.1067(6)	C(72)*	0.5211(20)	0.1656(11)	0.4680(10)
C(19)	−0.0638(10)	0.2387(4)	0.0120(6)	C(73)*	0.4866(20)	0.1729(11)	0.5355(10)
C(20)	−0.0531(10)	0.2828(4)	−0.0376(6)	C(74)	0.5431(20)	0.2306(11)	0.6006(10)
C(21)	−0.0370(10)	0.3606(4)	−0.0109(6)	C(75)	0.3642(9)	0.2901(5)	0.6784(6)
C(22)	−0.0318(10)	0.3945(4)	0.0656(6)	C(76)	0.2861(9)	0.2907(6)	0.5962(6)
C(23)	−0.0425(10)	0.3505(4)	0.1152(6)	C(77)	0.1929(17)	0.2181(10)	0.8493(11)
C(24)	−0.0585(10)	0.2726(4)	0.0884(6)	C(78)	0.2491(13)	0.2173(8)	0.9250(8)
C(25)	0.1822(9)	−0.0040(6)	0.2137(5)	C(79)	0.1193(28)	0.1073(16)	0.8828(17)
C(26)	0.2165(9)	−0.0746(6)	0.1875(5)	C(80)	0.2309(27)	0.1416(16)	0.9368(16)
C(27)	0.2828(9)	−0.0857(6)	0.1339(5)	C(81)*	0.5286(18)	0.2635(10)	0.5467(11)
C(28)	0.3149(9)	−0.0262(6)	0.1065(5)	C(82)*	0.5716(18)	0.2506(10)	0.4820(11)
C(29)	0.2806(9)	0.0444(6)	0.1327(5)	C(83)*	0.6318(18)	0.1881(10)	0.4638(10)
C(30)	0.2142(9)	0.0555(6)	0.1863(5)	C(84)*	0.6490(18)	0.1384(10)	0.5105(11)
C(31)	0.2517(7)	0.2524(6)	0.1516(5)	C(85)*	0.6061(18)	0.1513(10)	0.5752(11)
C(32)	0.3422(7)	0.3026(6)	0.1486(5)	O(13)	0.1112(8)	0.1541(5)	0.8214(5)
C(33)	0.4565(7)	0.3114(6)	0.2001(5)				

* Atom with site occupancy factor of 0.5.

thf (30 cm^3) was heated to 50 °C with stirring for 2 h. The resulting red solution was evaporated to dryness and the residue recrystallised from thf–benzene to yield red crystals of complex 4 (0.085 g, 50%) (Found: C, 54.4; H, 3.9. $C_{76}H_{55}FeO_{12}P_5Ru_3\cdot C_4H_8O$ requires C, 55.0; H, 3.6%).

Crystal Structure Determination of $[(OC)_3Fe\{(Ph_2P)_2CH-CH_2PPh_2\}Ru_3(CO)_9(dppee)]\cdot thf$ 4.—Crystals of complex 4 were grown by slow evaporation of a thf–benzene mixture, and a suitable red single crystal of dimensions 0.4 × 0.3 × 0.3 mm was sealed in a Lindemann tube.

Crystal data. $C_{80}H_{63}FeO_{13}P_5Ru_3$, $M = 1745.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.596(5)$, $b = 18.512(3)$, $c = 18.621(2)$ Å, $\alpha = 103.848(11)$, $\beta = 105.141(30)$, $\gamma = 92.407(30)°$, $U = 3723.32$ Å^3 (by least-squares refinement of angles from 25 reflections), Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $Z = 2$, $D_c = 1.56$ g cm^{-3}, $F(000) = 1760$, $\mu = 9.428$ cm^{-1}.

Data collection and processing. Nonius CAD-4 diffractometer (Queen Mary College, London), ω–2θ scan mode, 10 928 unique reflections recorded, reduced to 8291 by removing those with $F < 2\sigma(F)$ using the program FIX[9] ($\theta_{max} = 25°$, *h* 0–12, *k* −20 to 20, *l* −20 to 20), of which 6951 with $F_o > 8\sigma(F_o)$ were used in refinement. Empirical absorption correction based on azimuthal scans applied (transmission factor range 1–0.868). Three standard reflections showed no significant intensity variation during data collection.

Structure analysis and refinement. The Ru and Fe atoms were located by heavy-atom methods using SHELX 86[10] and other

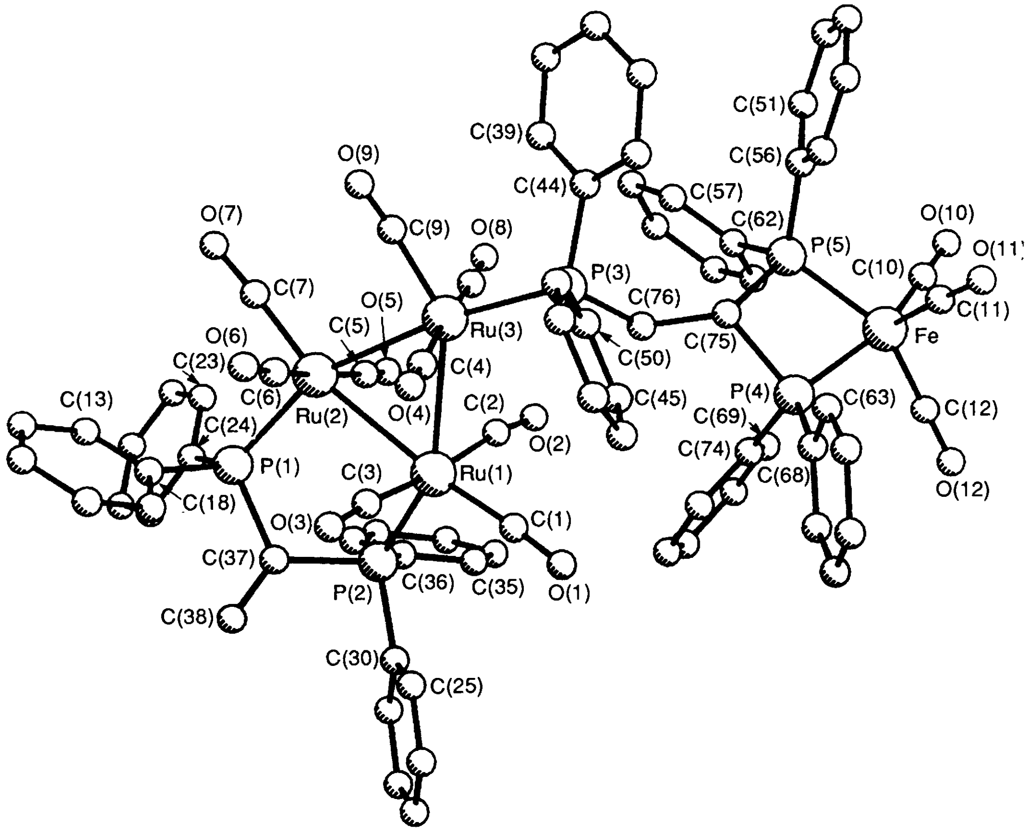

Fig. 1 The molecular structure of [$(OC)_3Fe\{(Ph_2P)_2CHCH_2PPh_2\}Ru_3(CO)_9(dppee)$] 4, showing the atom numbering scheme. Hydrogen atoms have been omitted

non-hydrogen atoms by Fourier techniques (SHELX 76[11]). Examination of the electron-density map indicated that one of the phenyl rings of the dppee ligand was disordered. All phenyl rings were constrained to regular hexagons (C–C 1.395 Å, 120°) with hydrogen atoms placed in calculated positions (C–H 1.08 Å). All phenyl carbon atoms were given a fixed thermal parameter, $U = 0.07$ Å^2. The two orientations of the disordered phenyl ring were entered into least-squares refinement, each given an occupancy factor of 0.5, with the pivot atom C(74) entered for each orientation. Blocked least-squares refinement (anisotropic Ru, Fe, P, O, all non-phenyl carbons), with a weighting scheme, $w = 7.0852/[\sigma^2(F) + 0.000\,368(F_o)^2]$, gave satisfactory agreement analyses, and converged to $R = 0.065$, $R' = 0.071$. Atom scattering factors were taken from ref. 12. Diagrams were produced using PLUTO.[13] A list of fractional atomic coordinates is given in Table 3.

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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