J. CHEM. SOC. DALTON TRANS. 1987 3079

Platinum(II)- and Palladium(II)–Iron(0) Complexes containing One Bridging $Ph_2PCH_2PPh_2$ Ligand. Crystal Structures of $[(OC)_3Fe(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}CO)PtBr_2]$ and $[(OC)_3Fe(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}I)PtI]\cdot CH_2Cl_2$†

Grant B. Jacobsen, Bernard L. Shaw,* and Mark Thornton-Pett
School of Chemistry, University of Leeds, Leeds LS2 9JT

Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) with $[PtX_2(cod)]$ (X = Cl, Br, or Me; cod = cyclo-octa-1,5-diene) gave bimetallics of type $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtX_2]$. The structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtBr_2]$ (**1b**) was established by a single-crystal *X*-ray diffraction study; the crystals are monoclinic, space group $P2_1/n$, with a = 1 256.9(2), b = 1 780.6(2), c = 1 343.6(1) pm, β = 102.352(9)°, and Z = 4; final R factor 0.0271 for 3 386 observed reflections. The structure shows that there is a metal–metal bond [Fe–Pt 264.7(4) pm] formulated as a donor $\longrightarrow$ acceptor bond, *viz.* Fe $\longrightarrow$ Pt; additionally, one of the carbonyl ligands is semi-bridging. Treatment of (**1b**) with MeI gave $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}I)PtI]$ (**2**) quantitatively. Complex (**2**) was also prepared from $[Fe(CO)_4(dppm\text{-}P)]$ and $[PtI_2(cod)]$ and characterised by an *X*-ray diffraction study. Crystals of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}I)PtI]\cdot CH_2Cl_2$ (**2**) are monoclinic, space group $P2_1/c$, with a = 991.3(2), b = 1 398.7(3), c = 2 356.8(4) pm, β = 95.96(1)°, and Z = 4; final R factor 0.0266 for 3 945 observed reflections. The structure shows that there is a metal–metal bond, best formulated as a donor–acceptor bond, *viz.* Fe $\longrightarrow$ Pt, and that one of the iodide ligands symmetrically bridges the two metal centres. Treatment of (**2**) with PPh_3 quantitatively yields a new species, tentatively formulated as $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}I)Pt(PPh_3)I]$. Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ with $[Pt(acac)(cod)]BF_4$ (acac = acetylacetonate) gave $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(acac)]BF_4$ in 75% yield. Attempts to prepare some analogous palladium complexes are described.

In recent publications we have reported the use of the monodentate bis(diphenylphosphino)methane (dppm)–iron complex $[Fe(CO)_4(dppm\text{-}P)]$ in the systematic synthesis of heterobimetallic complexes with Mn^{I},[1] Mo^{0},[1] or Rh^{I},[2] 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) carbonyl with platinum(II) or palladium(II). Aspects of this work have appeared as preliminary communications.[3,4]

Results and Discussion

Treatment of the monodentate dppm complex $[Fe(CO)_4(dppm\text{-}P)]$[1,5] with one mol equivalent of $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) in benzene–dichloromethane gave the iron–platinum complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtCl_2]$ (**1a**) in 80% isolated yield. The corresponding dibromide (**1b**) was similarly prepared using $[PtBr_2(cod)]$. The compounds were characterised by elemental analysis and i.r. spectroscopy (Table 1) and by $^{31}P\text{-}\{^1H\}$ (Table 2) and ^1H (Table 3) n.m.r. spectroscopy; reactions are outlined in the Scheme and preparative details are given in the Experimental section. In addition, the structure of complex (**1b**) has been determined by *X*-ray crystallography (see below). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of (**1a**) and (**1b**) were similar and consisted of two resonances: a low-field doublet (at *ca.* 60 p.p.m.) with satellites due to coupling to ^{195}Pt (J 71 Hz), assigned to the phosphorus atom bonded to iron and a doublet at higher field, also with ^{195}Pt satellites (J 3 386 Hz), assigned to the phosphorus atom bonded to platinum. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of (**1a**) showed a single resonance, with ^{195}Pt satellites, for the PCH_2P protons, at 20 °C. The i.r. spectra of (**1a**) and (**1b**) were very similar in the carbonyl region, showing three bands assigned to terminal carbonyls and a fourth, lower-energy band, at *ca.* 1 860 cm^{-1} indicating a semi-bridging carbonyl ligand.

Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ with $[PtMe_2(cod)]$ in refluxing benzene gave the bimetallic complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtMe_2]$ (**1c**) in 30% isolated yield. This complex was characterised by elemental analysis, i.r. spectroscopy, and $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy; data are in the Tables. The i.r. spectrum of (**1c**) [ν(CO) region] was similar to that of (**1a**) or (**1b**) except that the bands had shifted to lower energy. The band at 1 850 cm^{-1} strongly supported the presence of a semi-bridging carbonyl ligand, *i.e.* similar to (**1a**) and (**1b**).

Crystal Structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtBr_2]$ (**1b**).—Complex (**1b**) was crystallised from chlorobenzene–methylcyclohexane (1:3). The structure is shown in Figure 1 and selected intramolecular distances and angles are in Table 4. The Fe and Pt moieties are linked by a single dppm bridge to give a five-membered $\overline{FePCPPt}$ ring. The Fe–Pt distance of 264.7(4) pm indicates a metal–metal bond and is close to those found in other crystallographically characterised compounds of these metals, *viz.* $[Fe_2Pt(CO)_8(cod)]$ (Fe–Pt 256.1 and 255.3 pm)[6] and $[Fe_2Pt(CO)_9(PPh_3)]$ (Fe–Pt 260.5 and 252.6 pm).[7] The Pt–C(1) distance of 221.1(8) pm and the angles Fe–C(1)–O(1) 159.3(5)° and Pt–C(1)–O(1) 119.9(6)° indicate the presence of a semi-bridging carbonyl ligand, as suggested by the solution i.r. spectrum. However, we suggest that the C(1)–O(1)$\cdots$Pt interaction is making only a small contribution to the bonding and that the Fe–Pt bonding is largely of the donor–acceptor type *viz.* Fe $\longrightarrow$ Pt, *i.e.* the Fe atom can be viewed as occupying the fourth co-ordination site of the Pt by electron-pair donation from a filled orbital on Fe to an empty co-ordination position.

---

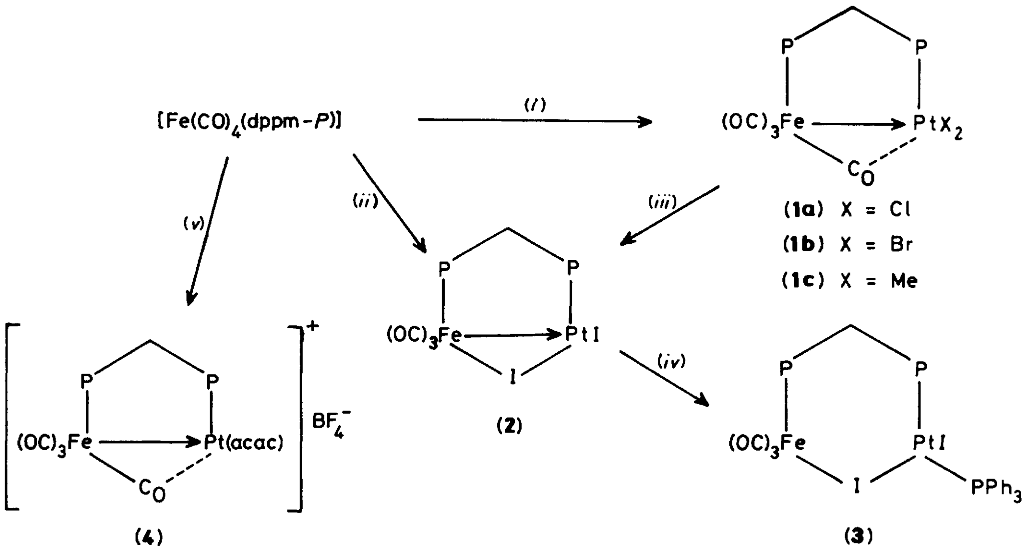
† μ-Bis(diphenylphosphino)methane-1,1-dibromo-μ-carbonyl-2,2,2-tricarbonylplatinum(II)iron(0) (*Pt–Fe*) and μ-bis(diphenylphosphino)methane-2,2,2-tricarbonyl-μ-iodo-1-iodoplatinum(II)iron(0) (*Pt–Fe*)–dichloromethane (1/1) respectively.

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

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

Complex	$\nu(C\equiv O)/cm^{-1}$	Analysis (%) C	H	Halogen
(**1a**)	2 080s, 2 038m, 1 996s, 1 855m	42.25 (42.55)	2.7 (2.7)	8.65 (8.65)
(**1b**)	2 075s, 2 032m, 1 994s, 1 860m	38.10 (38.4)	2.4 (2.45)	17.75 (17.6)
(**1c**)$\cdot$0.2CH_2Cl_2	2 040s, 1 972m, 1 945s, 1 850m	46.55 (47.15)	3.45 (3.6)	1.25 (1.75)
(**2**)$\cdot$0.3CH_2Cl_2	2 040s, 1 988s, br	33.5 (34.0)	2.3 (2.3)	Cl 2.3 (2.15) I 26.0 (25.4)
(**4**)	2 088s, 2 042m, 2 005s, 1 873m	44.8 (44.55)	3.25 (3.55)	—

[a] As solutions in dichloromethane, s = strong, m = medium, and br = broad. [b] Calculated values in parentheses.



Scheme. (*i*) [PtX_2(cod)] (X = Cl, Br, or Me), (*ii*) [PtI_2(cod)], (*iii*) MeI, (*iv*) PPh_3, (*v*) [Pt(acac)(cod)]BF_4

In this way, the requirements of 18e iron(0) and 16e platinum(II) centres are satisfied.

Treatment of a dichloromethane solution of [$(OC)_3Fe(\mu$-dppm)(μ-CO)$PtBr_2$] (**1b**) with an excess of methyl iodide resulted in a quantitative transformation (^{31}P-{^1H} evidence) to a new bimetallic, formulated as [$(OC)_3Fe(\mu$-dppm)(μ-I)PtI] (**2**). This complex was also prepared by treating [Fe$(CO)_4$(dppm-*P*)] with [PtI_2(cod)]. It was characterised by elemental analysis, i.r. spectroscopy, and ^{31}P-{^1H} and ^1H n.m.r. spectroscopy; data are in the Tables. In addition, the structure of complex (**2**) has been determined by *X*-ray crystallography (see below). The ^{31}P-{^1H} and ^1H n.m.r. spectra of (**2**) were similar to those of (**1a**)—(**1c**) indicating the presence of a Fe(μ-dppm)Pt backbone. The i.r. spectrum [ν(CO) region] indicated the absence of bridging or semi-bridging carbonyl ligands.

Crystal Structure of [$(OC)_3Fe(\mu$-dppm)(μ-I)PtI]$\cdot CH_2Cl_2$ (**2**).—Complex (**2**) was crystallised by slow evaporation of a dichloromethane solution. The structure is shown in Figure 2 and selected intramolecular distances and angles are in Table 5. The Fe and Pt moieties are linked by a single dppm bridge to give a five-membered FePCPPt ring. The Fe–Pt distance of 252.3(4) pm indicates a metal–metal bond and is close to that found in other crystallographically characterised compounds of these metals.[6,7] The Fe–I(1) distance of 261.6(4) pm and Pt–I(1) of 266.4 pm suggest that the iodide ligand is almost symmetrically bridging the metal centres. None of the carbonyl ligands on Fe shows any bridging interaction with the Pt. The metal–metal bonding in (**2**) can be viewed as of the donor–acceptor type as in (**1b**), *viz.* Fe ⟶ Pt. Therefore, the bridging iodide ligand must contribute two electrons to each metal to satisfy an 18e Fe^0 centre and a 16e Pt^{II} centre. However, an alternative view could involve a single metal–metal bond between d^7 Fe^I and d^9 Pt^I centres. The ν(CO) bands of (**2**) (Table 1) tend to support the Fe^0–Pt^{II} description as they are similar to those found for previously characterised Fe^0 compounds containing a $Fe(CO)_3$ fragment, *e.g.* [$Fe(CO)_3(\eta^4$-CH_2=CHCH=CH_2)] [ν(CO) at 2 051 and 1 978 cm^{-1}][8] and [$Fe(CO)_3${η^4-CH=CHCH=CH$(CH_2)_3CH_2$}] [ν(CO) at 2 043, 1 974, and 1 971 cm^{-1}].[9] The structural differences between (**1b**) and (**2**) can presumably be rationalised in terms of the relative size of iodide and bromide ligands. A structure, like that of (**1b**), with a *cis*-dihalide moiety, will be more sterically strained in the case of iodide and this strain can be somewhat relieved by one of the iodide ligands adopting a bridging position, with displacement of CO, as in (**2**). Additionally, iodide is a better bridging group than chloride or bromide for soft metal centres.

Treatment of [$(OC)_3Fe(\mu$-dppm)(μ-I)PtI] (**2**) with one mol equivalent of triphenylphosphine in dichloromethane solution resulted in the quantitative formation of a new bimetallic complex (^{31}P-{^1H} n.m.r. evidence) tentatively formulated as [$(OC)_3Fe(\mu$-dppm)(μ-I)Pt(PPh_3)I] (**3**). It was characterised

Table 2. $^{31}P-\{^1H\}$ N.m.r. data[a]

Complex	$^{31}P-\{^1H\}$ (δ)
(1a)	59.9 [d, P_A, $J(P_AP_B)$ 51, $J(PtP_A)$ 63]
	11.2 [d, P_B, $J(P_AP_B)$ 51, $J(PtP_B)$ 3 442]
(1b)	61.1 [d, P_A, $J(P_AP_B)$ 56, $J(PtP_A)$ 71]
	12.2 [d, P_B, $J(P_AP_B)$ 56, $J(PtP_B)$ 3 386]
(1c)	70.5 [d, P_A, $J(P_AP_B)$ 102, $J(PtP_A)$ 94]
	23.9 [d, P_B, $J(P_AP_B)$ 102, $J(PtP_B)$ 2 029]
(2)	69.0 [d, P_A, $J(P_AP_B)$ 24]
	−14.8 [d, P_B, $J(P_AP_B)$ 24, $J(PtP_B)$ 4 858]
(3)[b]	63.2 [d of d, P_A, J(PP) 31 and 24]
	34.2 [d of d, J(PP) 31 and 17, J(PtP) 3 213]
	−16.5 [d of d, J(PP) 24 and 17, J(PtP) 4 548]
(4)	56.3 [d, P_A, $J(P_AP_B)$ 44, $J(PtP_A)$ 64]
	0.9 [d, P_B, $J(P_AP_B)$ 44, J(PtP) 3 762]

[a] Recorded at 40.3 MHz in CD_2Cl_2 solution and 20 °C. Positive shifts to high frequency of external 85% H_3PO_4. Coupling constants in Hz. P_A and P_B refer to the phosphorus atoms bonded to iron and platinum, respectively. The multiplicity, *e.g.* d of d refers to P–P coupling and excludes interactions with ^{195}Pt. [b] Assignments of resonances at δ 34.2 and −16.5 uncertain.

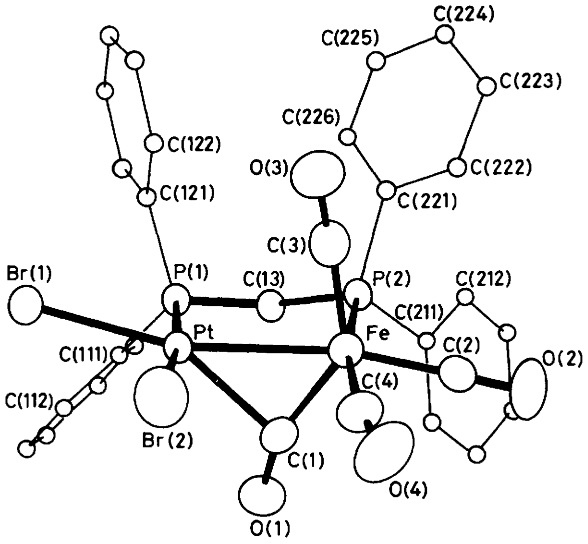


Figure 1. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtBr_2]$ **(1b)**, showing the principal atomic numbering

Table 3. Selected ^1H n.m.r. data*

Complex	^1H (δ)
(1a)	3.29 [2 H, CH_2, J(PtH) 47, J(PH) 11]
(1c)	3.36 [2 H, CH_2, J(PtH) 16, J(PH) 10]
	0.83 [3 H, CH_3, J(PtH) 89, J(PH) 9]
	0.76 [3 H, CH_3, J(PtH) 66, J(PH) 7]
(2)	4.38 [2 H, CH_2, J(PtH) 62, J(PH) 11]
(4)	5.60 [1 H, CH, J(PtH) 7]
	3.84 [2 H, CH_2, J(PtH) 52, J(PH) 12]
	2.05 (3 H, CH_3)
	1.70 [3 H, CH_3 J(PtH) 5]

* Recorded in CD_2Cl_2 solution at 100 MHz and 20 °C. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to $SiMe_4$, coupling constants (J) in Hz (±0.3 Hz).

Table 4. Selected internuclear distances (pm) and angles (°) for $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtBr_2]$ **(1b)***

Fe–Pt	264.7(4)		
Br(1)–Pt	247.5(3)	Br(2)–Pt	247.6(4)
P(1)–Pt	224.0(3)	C(1)–Pt	221.1(8)
P(2)–Fe	227.1(4)	C(1)–Fe	185.0(9)
C(2)–Fe	177.2(9)	C(3)–Fe	181.8(9)
C(4)–Fe	183.6(9)	C(13)–P(1)	183.5(7)
C(13)–P(2)	182.9(7)		
Br(1)–Pt–Fe	163.9	Br(2)–Pt–Fe	89.7
Br(2)–Pt–Br(1)	86.2	P(1)–Pt–Fe	96.6
P(1)–Pt–Br(1)	86.7	P(1)–Pt–Br(2)	172.6
C(1)–Pt–Fe	43.6(2)	C(1)–Pt–Br(1)	152.3(2)
C(1)–Pt–Br(2)	95.7(2)	C(1)–Pt–P(1)	91.5(2)
P(2)–Fe–Pt	94.3	C(1)–Fe–Pt	55.6(3)
C(1)–Fe–P(2)	91.9(3)	C(2)–Fe–Pt	168.4(2)
C(2)–Fe–P(2)	85.3(3)	C(2)–Fe–C(1)	112.9(4)
C(3)–Fe–Pt	81.4(3)	C(3)–Fe–P(2)	92.7(3)
C(3)–Fe–C(1)	136.9(3)	C(3)–Fe–C(2)	110.2(4)
C(4)–Fe–Pt	97.0(3)	C(4)–Fe–P(2)	168.1(2)
C(4)–Fe–C(1)	91.2(4)	C(4)–Fe–C(2)	82.8(4)
C(4)–Fe–C(3)	92.8(4)	C(13)–P(1)–Pt	112.7(3)
C(13)–P(2)–Fe	112.5(3)	Fe–C(1)–Pt	80.8(3)
P(2)–C(13)–P(1)	114.5(4)		

* Where the errors are not shown they are less than 0.1°.

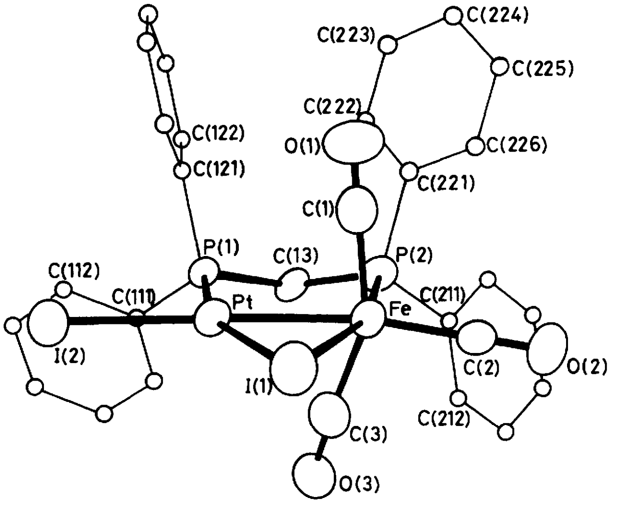


Figure 2. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]\cdot CH_2Cl_2$ **(2)**, showing the principal atomic numbering

only in solution by $^{31}P-\{^1H\}$ n.m.r. spectroscopy (Table 2) as attempts to isolate solid samples resulted in partial decomposition to give uncharacterised products. The $^{31}P-\{^1H\}$ n.m.r. spectrum of **(3)** showed three mutually coupled nuclei, two of which also showed strong coupling to ^{195}Pt, whilst the other showed no resolvable coupling to ^{195}Pt. These data indicated that the PPh_3 ligand was bonded to the platinum centre and that the Fe(μ-dppm)Pt backbone was still intact. Therefore, we propose the structure shown in the Scheme for **(3)** in which the PPh_3 has caused the donor–acceptor Fe $\longrightarrow$ Pt bond to be broken.

We have also examined the action of $[Fe(CO)_4(dppm\text{-}P)]$ on the cationic platinum complex $[Pt(acac)(cod)]BF_4$ (acac = acetylacetonate) to see if an analogue of **(1a)** or **(1b)** could be prepared. Reaction between these species in benzene did indeed give the hoped for complex $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(acac)]BF_4$ **(4)** in 75% isolated yield. Complex **(4)** was characterised by elemental analysis, i.r. spectroscopy, and $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopy; see Tables for data. The $^{31}P-\{^1H\}$ n.m.r. spectrum of **(4)** was similar to those of

Table 5. Selected internuclear distances (pm) and angles (°) for $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]\cdot CH_2Cl_2$ (**2**)*

Fe–Pt	252.3(4)		
I(1)–Pt	266.4	I(2)–Pt	265.6
P(1)–Pt	219.5(3)	C(3)–Pt	259.3(9)
I(1)–Fe	261.6(4)	P(2)–Fe	220.2(3)
C(1)–Fe	183.0(9)	C(2)–Fe	178.0(8)
C(3)–Fe	181.1(8)	C(13)–P(1)	184.1(7)
C(13)–P(2)	183.4(7)		
I(1)–Pt–Fe	60.5	I(2)–Pt–Fe	162.7
I(2)–Pt–I(1)	102.7	P(1)–Pt–Fe	96.3
P(1)–Pt–I(1)	156.7	P(1)–Pt–I(2)	100.2
C(3)–Pt–Fe	41.4(1)	C(3)–Pt–I(1)	70.9(2)
C(3)–Pt–I(2)	141.0(1)	C(3)–Pt–P(1)	93.7(2)
I(1)–Fe–Pt	62.4	P(2)–Fe–Pt	98.2
P(2)–Fe–I(1)	160.5(1)	C(1)–Fe–Pt	83.9(3)
C(1)–Fe–I(1)	84.8(3)	C(1)–Fe–P(2)	91.0(3)
C(2)–Fe–Pt	165.0(2)	C(2)–Fe–I(1)	103.7(3)
C(2)–Fe–P(2)	95.8(3)	C(2)–Fe–C(1)	101.2(4)
C(3)–Fe–Pt	71.4(3)	C(3)–Fe–I(1)	85.1(3)
C(3)–Fe–P(2)	91.1(3)	C(3)–Fe–C(1)	155.3(3)
C(3)–Fe–C(2)	103.1(4)	Fe–I(1)–Pt	57.1
C(13)–P(1)–Pt(1)	111.3(3)	C(13)–P(2)–Fe(1)	109.7(3)
Fe–C(3)–Pt	67.2(3)	P(2)–C(13)–P(1)	113.8(4)

* Where the errors are not shown they are less than 0.1 pm or 0.1°.

complexes (**1a**)—(**1c**) and (**2**) suggesting the presence of a Fe(μ-dppm)Pt backbone. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum of (**4**), as well as showing a resonance due to the PCH_2P protons, also showed resonances due to the co-ordinated acac ligand. Coupling with the ^{195}Pt isotope was observed for the resonances at 5.60 [*J*(PtH) 7] and 1.70 p.p.m. [*J*(PtH) 5 Hz] due to the CH and one of the CH_3 resonances of the acac ligand respectively. The i.r. spectrum of (**4**) [ν(CO) region] shows three bands assigned to terminal carbonyl ligands and a single band at 1 873 cm^{-1} assigned to a semi-bridging carbonyl ligand. We therefore suggest that the structure of (**4**) is analogous to those of the neutral complexes (**1a**)—(**1c**).

Palladium Complexes.—Treatment of $[Fe(CO)_4(dppm\text{-}P)]$ with $[PdCl_2(NCPh)_2]$ in dichloromethane gave an intensely dark green solution which on the basis of $^{31}P\text{-}\{^1H\}$ n.m.r. evidence contained a single iron–palladium bimetallic complex, as well as other unidentified minor species [*viz.* AX spin system, δ_P(Fe) 59.9, δ_P(Pd) 29.9 p.p.m., *J*(PP) 59 Hz]. However, this solution and the dark green solid which could be isolated from it were both extremely air-sensitive and we were not able to characterise this species. It may be an analogue of (**1a**) but it is not clear why it is so intensely coloured.

We also attempted to prepare a palladium analogue of (**4**) by treating $[Fe(CO)_4(dppm\text{-}P)]$ with $[Pd(acac)(cod)]BF_4$ in benzene. We obtained a dark red-brown microcrystalline solid, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of which showed the expected AX pattern, *viz.* δ_P(Fe) 55.0, δ_P(Pd) 28.7 p.p.m., *J*(PP) 51 Hz. However, we were unable to obtain analytically pure samples of this material.

Experimental

General methods were as previously described in recent papers from this laboratory.[10] The complexes $[M(acac)(cod)]BF_4$ (M = Pd or Pt)[11] and $[Fe(CO)_4(dppm\text{-}P)]$[1] were prepared by published procedures. The complexes $[PtX_2(cod)]$ (X = Br or I) were prepared by metathesis from the dichloride in acetone using KBr or NaI.

Table 6. Atom co-ordinates (× 10^4) for compound (**1b**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt	1 217.7(2)	1 637.3(1)	3 266.9(2)
Fe	−105(1)	1 677.6(4)	4 557(1)
Br(1)	2 154(1)	1 911.7(4)	1 864(1)
Br(2)	−283(1)	1 132.6(4)	1 934(1)
P(1)	2 654(1)	2 164(1)	4 309(1)
P(2)	1 093(1)	2 303(1)	5 782(1)
C(1)	889(5)	919(4)	4 510(4)
O(1)	1 361(4)	366(3)	4 708(3)
C(2)	−859(5)	1 533(3)	5 515(5)
O(2)	−1 371(4)	1 429(3)	6 125(4)
C(3)	−551(5)	2 535(4)	3 855(5)
O(3)	−813(4)	3 068(3)	3 382(4)
C(4)	−1 210(5)	1 120(4)	3 785(5)
O(4)	−1 954(4)	784(3)	3 447(4)
C(111)	3 943(2)	1 655(2)	4 482(3)
C(112)	4 090(2)	1 096(2)	3 797(3)
C(113)	5 064(2)	694(2)	3 958(3)
C(114)	5 892(2)	851(2)	4 804(3)
C(115)	5 744(2)	1 411(2)	5 489(3)
C(116)	4 770(2)	1 813(2)	5 328(3)
C(121)	2 853(3)	3 128(2)	3 947(3)
C(122)	1 975(3)	3 506(2)	3 343(3)
C(123)	2 086(3)	4 255(2)	3 079(3)
C(124)	3 075(3)	4 627(2)	3 420(3)
C(125)	3 952(3)	4 248(2)	4 024(3)
C(126)	3 841(3)	3 499(2)	4 288(3)
C(13)	2 500(4)	2 208(3)	5 635(4)
C(211)	1 236(3)	1 949(2)	7 077(2)
C(212)	1 419(3)	2 438(2)	7 906(2)
C(213)	1 607(3)	2 154(2)	8 896(2)
C(214)	1 612(3)	1 380(2)	9 056(2)
C(215)	1 429(3)	890(2)	8 227(2)
C(216)	1 241(3)	1 174(2)	7 237(2)
C(221)	793(3)	3 292(2)	5 884(3)
C(222)	−258(3)	3 468(2)	5 992(3)
C(223)	−533(3)	4 211(2)	6 149(3)
C(224)	243(3)	4 778(2)	6 198(3)
C(225)	1 294(3)	4 602(2)	6 089(3)
C(226)	1 569(3)	3 858(2)	5 932(3)

Preparations.—$[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ (**1a**). Solid $[PtCl_2(cod)]$ (0.75 g, 2 mmol) was added to a solution of $[Fe(CO)_4(dppm\text{-}P)]$ (1.10 g, 2 mmol) in benzene (15 cm^3) and dichloromethane (3 cm^3). The mixture was stirred for 1 h and then refrigerated (5 °C) overnight to give the desired product as yellow microcrystals. Yield: 1.31 g (80%). The dibromide was similarly prepared, in 70% yield, as yellow-orange microcrystals using $[PtBr_2(cod)]$.

$[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtMe_2]$ (**1c**). $[Fe(CO)_4(\mu\text{-dppm-}P)]$ (0.55 g, 1 mmol) and $[PtMe_2(cod)]$ (0.33 g, 1 mmol) were refluxed together in benzene (20 cm^3) for 0.5 h. The resultant solution was cooled to *ca.* 20 °C and the solvent removed under reduced pressure. The residue was recrystallised from dichloromethane–diethyl ether to give the desired product as yellow microcrystals. Yield: 0.23 g (30%).

$[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]$ (**2**) *from* $[Fe(CO)_4(dppm\text{-}P)]$ *and* $[PtI_2(cod)]$. $[Fe(CO)_4(dppm\text{-}P)]$ (1.10 g, 2 mmol) and $[PtI_2(cod)]$ (1.12 g, 2 mmol) were stirred together in dichloromethane (20 cm^3) for 2 h. The solvent was removed under reduced pressure and the residue recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give the desired product as dark brown microcrystals. Yield: 1.32 g (68%).

$[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-I})PtI]$ (**2**) *from* (**1b**) *and* MeI. A solution of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtBr_2]$ (**1b**) (0.025 g, 0.028 mmol) in dichloromethane (1 cm^3) was treated with

Table 7. Atom co-ordinates (× 10^4) for compound **(2)** with e.s.d.s in parentheses

Atom	x	y	z
Pt	5 514.0(2)	2 815.5(1)	3 165.8(1)
Fe	4 655(1)	3 318(1)	4 091.3(3)
I(1)	7 222.6(4)	2 870.9(3)	4 115.7(2)
I(2)	7 047.0(4)	2 111.5(3)	2 405.6(2)
P(1)	3 548(2)	2 890(1)	2 645(1)
P(2)	2 502(1)	3 508(1)	3 775(1)
C(1)	4 399(6)	2 035(5)	4 185(3)
O(1)	4 235(5)	1 248(3)	4 255(2)
C(2)	4 503(6)	3 749(4)	4 792(3)
O(2)	4 362(5)	4 018(4)	5 243(2)
C(3)	5 112(6)	4 379(5)	3 715(3)
O(3)	5 379(5)	5 090(3)	3 510(2)
C(111)	3 536(4)	3 432(2)	1 943(1)
C(112)	3 745(4)	2 852(2)	1 479(1)
C(113)	3 837(4)	3 259(2)	944(1)
C(114)	3 721(4)	4 247(2)	874(1)
C(115)	3 512(4)	4 827(2)	1 338(1)
C(116)	3 419(4)	4 420(2)	1 873(1)
C(121)	2 751(3)	1 735(2)	2 514(2)
C(122)	1 450(3)	1 662(2)	2 229(2)
C(123)	851(3)	766(2)	2 133(2)
C(124)	1 555(3)	−57(2)	2 321(2)
C(125)	2 856(3)	16(2)	2 606(2)
C(126)	3 454(3)	912(2)	2 703(2)
C(13)	2 326(5)	3 618(4)	2 995(2)
C(211)	1 655(3)	4 574(2)	4 012(2)
C(212)	2 361(3)	5 437(2)	4 070(2)
C(213)	1 715(3)	6 258(2)	4 242(2)
C(214)	363(3)	6 215(2)	4 356(2)
C(215)	−343(3)	5 352(2)	4 298(2)
C(216)	303(3)	4 531(2)	4 125(2)
C(221)	1 417(3)	2 537(2)	3 970(1)
C(222)	600(3)	2 006(2)	3 568(1)
C(223)	−152(3)	1 237(2)	3 743(1)
C(224)	−88(3)	999(2)	4 320(1)
C(225)	729(3)	1 530(2)	4 722(1)
C(226)	1 482(3)	2 299(2)	4 547(1)
C(1S)	7 885(9)	4 074(6)	1 140(3)
Cl(1S)	7 415(3)	3 878(2)	406(1)
Cl(2S)	9 569(3)	3 696(2)	1 326(1)

methyl iodide (100 μl, 1.60 mmol). After 24 h the ^{31}P-{^{1}H} n.m.r. spectrum of the solution indicated the formation of a single new heterobimetallic complex identified as **(2)**.

Reaction of [(OC)$_3$Fe(μ-dppm)(μ-I)PtI] **(2)** *with* PPh$_3$. A solution of [(OC)$_3$Fe(μ-dppm)(μ-I)PtI] **(2)** (0.10 g, 0.10 mmol) in dichloromethane (3 cm^3) was treated with triphenylphosphine (0.03 g, 0.11 mmol). The ^{31}P-{^{1}H} n.m.r. spectrum of the solution indicated the formation of a single new heterobimetallic complex tentatively formulated as [(OC)$_3$Fe(μ-dppm)(μ-I)-Pt(PPh$_3$)I] **(3)**.

[(OC)$_3$Fe(μ-dppm)(μ-CO)Pt(acac)]BF$_4$ **(4)**. [Fe(CO)$_4$-(dppm-*P*)] (0.33 g, 0.60 mmol) and [Pt(acac)(cod)]BF$_4$ (0.24 g, 0.50 mmol) were refluxed together in benzene (15 cm^3) for 1.5 h. The solution was cooled to *ca.* 20 °C and the solid isolated by filtration. Recrystallisation from dichloromethane–diethyl ether gave the desired product as yellow microcrystals. Yield: 0.35 g (75%).

X-Ray Crystallography.—Crystals of compound **(1b)**, suitable for single-crystal diffraction analysis, were obtained by diffusion of methylcyclohexane into a chlorobenzene solution of **(1b)**, while those of compound **(2)** were obtained by the slow evaporation of a dichloromethane solution of **(2)**.

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.[12] Both data sets were corrected for absorption empirically once the structures had been solved.[13] Both structures were solved *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[14] In both cases all non-hydrogen atoms were assigned anisotropic thermal parameters including the dichloromethane molecule in compound **(2)**. All phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). For both structures the hydrogen atoms were included in calculated positions (C–H 108 pm) and assigned to an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used in both cases with the parameter g included in refinement so as to give satisfactory agreement analyses. Final atomic co-ordinates are given in Tables 6 and 7.

Crystal data for compound **(1b)**. $C_{29}H_{22}Br_2FeO_4P_2Pt$, M = 907.17, monoclinic, a = 1 256.9(2), b = 1 780.6(2), c = 1 343.6(1) pm, β = 102.352(9)°, U = 2.937 nm^3, Z = 4, space group $P2_1/n$(= $P2_1/c$, no. 14), D_c = 2.05 g cm^{-3}, μ = 78.37 cm^{-1}, and F(000) = 1 728.

Data collection. Scans running from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 4 101 Data collected, 3 386 observed [$I > 2.0\sigma(I)$], T = 290 K.

Structure refinement. Number of parameters = 235, weighting factor g = 0.0003, R = 0.0271, R' = 0.0276.

Crystal data for compound **(2)**. $C_{28}H_{22}FeI_2O_3P_2Pt \cdot CH_2Cl_2$, M = 1 086.11, monoclinic, a = 991.3(2), b = 1 398.7(3), c = 2 356.8(4) pm, β = 95.96(1)°, U = 3.250 nm^3, Z = 4, space group $P2_1/c$, D_c = 2.21 g cm^{-3}, μ = 66.08 cm^{-1}, and F(000) = 2 040.

Data collection. As above. 4 560 Data collected, 3 945 observed [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 315, weighting factor g = 0.0007, R = 0.0266, R' = 0.0323.

Acknowledgements

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

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., Dalton Trans.*, 1987, 2751.
3 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 13.
4 G. B. Jacobsen, B. L. Shaw, and M. Thornton-Pett, *Inorg. Chim. Acta*, 1986, **121**, L1.
5 P. A. Wegner, L. F. Evans, and J. Haddock, *Inorg. Chem.*, 1975, **14**, 192.
6 L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134.
7 R. Mason, J. Zubieta, A. T. T. Hseih, J. Knight, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1972, 200.
8 B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 642.
9 A. J. Deeming, S. S. Ulah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1974, 2093.
10 S. W. Carr, B. L. Shaw, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2131.
11 D. A. White, *Inorg. Synth.*, 1972, **13**, 55.
12 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.
13 N. Walter and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
14 G. M. Sheldrick, SHELX 76, Program System for *X*-Ray Structure Determination, University of Cambridge, 1976

Received 19*th January* 1987; *Paper* 7/092