The Systematic Synthesis of Heterobimetallic Complexes with only One Bridging $Ph_2PCH_2PPh_2$ (dppm) Ligand: Crystal Structures of $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$ and $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtBr_2]$

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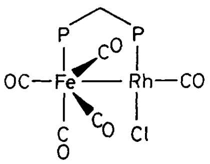
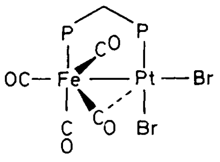
$[(OC)_4Fe(dppm\text{-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) reacts with $[Rh_2Cl_2(CO)_4]$ to give $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$ with an Fe-Rh bond but no bridging carbonyl group; with $[PtBr_2(\text{cyclo-octa-1,5-diene})]$ the product $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtBr_2]$ shows some bridging interaction of one of the carbonyl ligands.

There is a great deal of interest in bimetallic complexes containing bridging $Ph_2PCH_2PPh_2$ [bis(diphenylphosphino)methane, dppm] ligands. By far the most common type contain two such ligands; *i.e.*, the moiety $M^1(\mu\text{-dppm})_2M^2$ where M^1, M^2 can be the same, or different, metals; there are many hundreds of such complexes. In contrast, there are very few bimetallic complexes containing a single, bridging dppm ligand. The few examples include $[(OC)_4Fe(\mu\text{-dppm})Fe(CO)_4]$,[1] $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Fe(CO)_3]$,[2] $[(\eta\text{-}C_5H_5)Fe(\mu\text{-dppm})(\mu\text{-CH}_3)(\mu\text{-CO})Fe(\eta\text{-}C_5H_5)]PF_6$,[3] $[(\eta\text{-}C_5H_5)Rh(\mu\text{-dppm})(\mu\text{-CO})Rh(\eta\text{-}C_5H_5)]$,[4] $[H(dppm\text{-}PP')\text{-}Ru(\mu\text{-dppm})(\mu\text{-H})Rh(1,5\text{-}C_8H_{12})]$,[5] and $[Me_2Si\{\eta^5\text{-}$



(1)



(2)

$C_5H_4Fe\}_2(\mu\text{-}CO)_2(\mu\text{-dppm})]$.[6] With the exception of $[(OC)_4Fe(\mu\text{-dppm})Fe(CO)_4]$, they all contain a metal–metal bond and at least one strongly bridging ligand in addition to dppm; only one of the compounds is a heterobimetallic species.

We reasoned that the known, co-ordinatively saturated, compound $[(OC)_4Fe(\text{dppm-}P)]$[1] might be useful in the systematic synthesis of heterobimetallic compounds containing only one dppm ligand but in which at least one of the carbonyl groups would adopt a bridging mode to the second metal. $[(OC)_4Fe(\text{dppm-}P)]$ was made previously by substituting $Fe(CO)_5$ with dppm photochemically but this method involved a tedious chromatographic separation of various products.[1] We find that on treatment of $[Fe_2(CO)_9]$ with an equimolar quantity of dppm in tetrahydrofuran (THF) the required $[(OC)_4Fe(\text{dppm-}P)]$ is readily formed and is separated by one crystallization from methylcyclohexane in *ca.* 35% yield. It is contaminated with *ca.* 5—10% $[(OC)_4Fe(\mu\text{-dppm})Fe(CO)_4]$ which is inert and interferes negligibly with the reactions or isolations described below.

Treatment of $[(OC)_4Fe(\text{dppm-}P)]$ with a 0.5 mol equiv. of $[Rh_2Cl_2(CO)_4]$ in benzene rapidly gave a single heterobimetallic compound, $[(OC)_4Fe(\mu\text{-dppm})Rh(CO)Cl]$, in 50% isolated yield. The product was characterized by elemental analysis and by ^1H and $^{31}P\{^1H\}$ n.m.r. spectroscopy. Surprisingly, the i.r. spectrum showed the absence of a bridging carbonyl group: ν(CO) (in CH_2Cl_2 solution) 2065s, 2018s, 1992s, 1955m, and 1925s cm^{-1}. In view of this the crystal structure was determined† and is shown in Figure 1. This structure, (**1**), shows a metal–metal distance of 269.9(4) pm, typical of a metal–metal bond and the Rh–C(1) and Rh–C(3) distances, 237.0(8) and 257.8(9) pm respectively, indicate only a very weak bridging interaction of these carbonyl groups. Since the iron in the $[Fe(CO)_4(\text{tertiary phosphine})]$ moiety has an 18 electron configuration we conclude that the iron–rhodium bond is largely of the donor–acceptor type, *viz.* Fe → Rh.‡

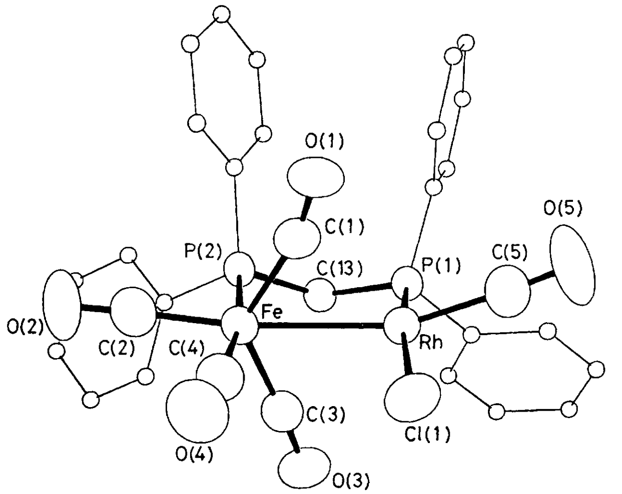


Figure 1. Molecular structure of $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$, (**1**). Selected interatomic distances: Fe–Rh 269.9(4), Rh–C(5) 183.3(9), Rh–Cl 238.6(4), Rh–C(3) 257.8(9), Rh–C(1) 237.0(8), Fe–C(1) 184.7(9), Fe–C(3) 178.9(9) pm. Selected angles: Fe–C(1)–O(1) 163.9(5), Rh–C(1)–O(1) 117.1(6), Fe–C(3)–O(3) 175.3(6), Rh–C(3)–O(3) 110.8(6)°.

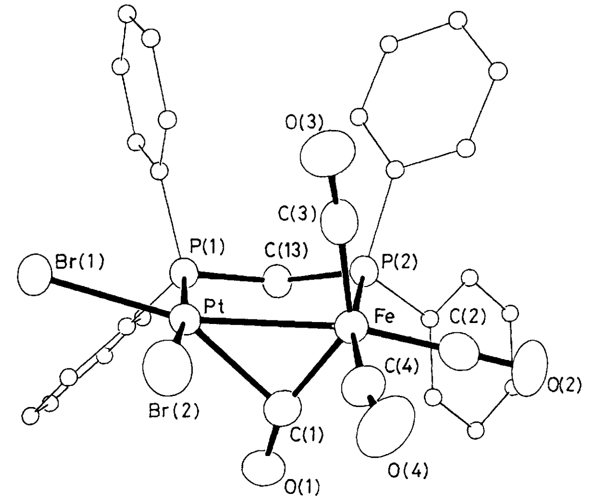


Figure 2. Molecular structure of $[Br_2Pt(\mu\text{-dppm})(\mu\text{-}CO)Fe(CO)_3]$, (**2**). Selected interatomic distances: Pt–Fe 264.7(4), Pt–Br(1) 247.5(3), Pt–Br(2) 247.6(3), Pt–C(1) 221.1(8), Fe–C(1) 185.0(9) pm. Selected angles; Fe–C(1)–O(1) 159.3(5), Pt–C(1)–O(1) 119.9(6)°.

In view of this result we studied the behaviour of $[(OC)_4Fe(\text{dppm-}P)]$ towards the more electronegative *cis*-$PtCl_2$ and *cis*-$PtBr_2$ groups. Treatment of $[PtX_2(\text{cyclo-octa-1,5-diene})]$ (X = Cl or Br) with $[(OC)_4Fe(\text{dppm-}P)]$ gave $[(OC)_4Fe(\mu\text{-dppm})PtX_2]$ (70—75%) both characterized by elemental analysis and n.m.r. and i.r. spectroscopy. The i.r. spectrum of $[(OC)_4Fe(\mu\text{-dppm})PtBr_2]$ (CH_2Cl_2 solution) showed ν(CO) 2075s, 2032m, 1994s, and 1860m cm^{-1}, the lowest frequency band suggesting the possibility of a semi-bridging carbonyl group. We have therefore determined the crystal structure of this compound, (**2**), Figure 2. The Fe–Pt distance of 264.7(4) pm indicates a metal–metal bond and the Pt–C(1) distance 221.1(8) pm and the angles Fe–C(1)–O(1) 159.3(5)° and Pt–C(1)–O(1) 119.9(6)° suggest that the C(1)–O(1) · · · Pt interaction is making a contribution to the bonding, albeit a small one. We suggest that the Fe–Pt bonding is largely of the donor–acceptor type *viz.* Fe → Pt and

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† *Crystal data* for $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]\cdot C_6H_5Cl$, (**1**) M = 821.24, monoclinic, space group $P2_1/n$ (= $P2_1/c$, no. 14), a = 1246.5(2), b = 1849.0(3), c = 1612.3(2) pm, β = 110.34(1)°, U = 3.484(1) nm^3, Z = 4, Mo-K_α radiation, λ = 71.069 pm, $\mu(\text{Mo-}K_\alpha)$ = 10.81 cm^{-1}, $F(000)$ = 1640, $4.0 < 2\theta < 45°$. Final R and R_w values 0.0481 and 0.0568 respectively for 4035 observed reflections.

$[Br_2Pt(\mu\text{-dppm})Fe(CO)_4]$, (**2**) M = 905.22, monoclinic, space group $P2_1/n$ (= $P2_1/c$, no. 14), a = 1256.9(2), b = 1780.6(2), c = 1343.6(1) pm, β = 102.35(1)°, U = 2.937(1) nm^3, Z = 4, Mo-K_α radiation, λ = 71.069 pm, $\mu(\text{Mo-}K_\alpha)$ = 78.37 cm^{-1}, $F(000)$ = 1728, $4.0 < 2\theta < 45°$. Final R and R_w values 0.0271 and 0.0276 respectively for 3386 observed reflections, $[I > 2.0\sigma(I)]$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Other iron–rhodium heterobimetallics with an iron–rhodium bond include $[(OC)_2Rh(\mu\text{-cycloheptatrienyl})Fe(CO)_3]$, Fe· · ·Rh 276.4 pm,[7] $[(\eta\text{-}C_5H_5)Rh\{C_4H_4Fe(CO)_3\}]$, Fe· · ·Rh 255.7 pm,[8] and $[(OC)_2Rh\{\mu\text{-tris(diphenylphosphino)methane}\}Fe(CO)_3]^+$, Fe· · ·Rh 277.6 pm.[9]

is therefore unusual. There does not appear to be another example of a crystal structure on a bimetallic complex with an iron–platinum bond.

We have studied other reactions of [$(OC)_4Fe$(dppm-*P*)] and also of its analogue with $(Ph_2P)_2C{=}CH_2$ (vinylidenediphenylphosphine, vdpp). Treatment of [$(OC)_4Fe$(dppm-*P*)] with [$PdCl_2(PhCN)_2$] gives an intense green product thus far only characterized in solution but it appears to be [$(OC)_4Fe(\mu$-dppm)$PdCl_2$]; this product decomposes on attempted isolation. Treatment of [$(OC)_4Fe$(vdpp-*P*)] with [$Rh_2Cl_2(CO)_4$] gives [$(OC)_4Fe(\mu$-vdpp)RhCl(CO)] which appears to be completely analogous to (**1**), *e.g.* with ν(CO) values of 2065s, 2015s, 1992s, 1955m, and 1927s cm^{-1}.

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