Synthesis and Reactions of [$(OC)_3Fe(\mu$-dppm$)(\mu$-$CO)Pt(PPh_3)$] with Acetylenes or Allene: Crystal Structures of [$(OC)_3Fe(\mu$-dppm$)(\mu$-$CO)Pt(PPh_3)$], [$(OC)_2Fe(\mu$-dppm$)\{\mu$-$\sigma:\eta^3$-$C(O)C_2H_2\}Pt(PPh_3)$], and [$(OC)_3Fe(\mu$-dppm$)\{\mu$-$CH_2C(=CH_2)\}Pt(PPh_3)$] (dppm = $Ph_2PCH_2PPh_2$)

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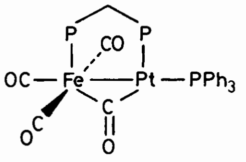
[$(OC)_3Fe(\mu$-dppm$)(\mu$-$CO)PtCl_2$] (dppm = $Ph_2PCH_2PPh_2$) is reduced by $NaBH_4$ in the presence of PPh_3 to give the electron-rich [$(OC)_3Fe(\mu$-dppm$)(\mu$-$CO)Pt(PPh_3)$], which reacts with acetylene(s) or allene under mild conditions to give the title compounds and is protonated to give a hydride.

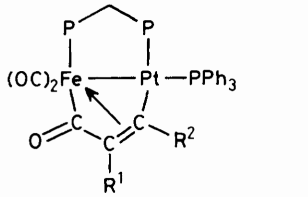
We have shown that [$(OC)_4Fe$(dppm-*P*)], dppm = Ph_2P-CH_2PPh_2, will complex to $PtCl_2$ or $PtBr_2$. In the adducts, both iron and phosphorus are donor atoms to platinum and the crystal structure of [$(OC)_3Fe(\mu$-dppm$)(\mu$-$CO)PtBr_2$] shows, additionally, that one of the CO ligands is weakly semibridging.[1] With compounds of the type [$(OC)_4Fe(PR_3)$] the CO ligands are usually very resistant towards displacement by olefins or acetylenes and in this respect [$(OC)_4Fe$(dppm-*P*)] is no exception: we find that it is recovered unchanged after being heated with an excess of PhC≡CH for 2 h at 80 °C. We reasoned that if we could attach (*i.e.* chelate) [$(OC)_4Fe$(dppm-*P*)] to an electron-rich and labile centre, one which will co-ordinate acetylenes or olefins, then one could promote the iron centre to react with unsaturated organic molecules by an intramolecular process under mild conditions.

Treatment of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})PtCl_2]$ with $NaBH_4$ in CH_2Cl_2–EtOH in the presence of PPh_3 gave the hoped for platinum(0) compound in 75% yield, which, on the basis of microanalytical and spectroscopic studies, was formulated as $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$ (**1**).† This compound (**1**) was also prepared by treating $[(OC)_4Fe(\text{dppm-}P)]$ with $[(Ph_3P)_2Pt(\textit{trans}\text{-stilbene})]$ (yield 70%). We have determined the crystal structure‡ of (**1**), (summarised in Figure 1 and its caption); this shows that the bridging carbonyl is almost symmetrically bridging the metal centres. Treatment of a CH_2Cl_2 solution of (**1**) with acetylene at 20 °C rapidly gave an adduct (**2a**) in 77% yield the crystal structure‡ of which has been determined and is shown in Figure 2, with selected data in the caption. In this structure the C_2H_2CO moiety is σ-bound to platinum and η^3-bound to iron. This mode of bonding is related to that reported in the complex $[Ru_2(CO)(\mu\text{-CO})\{\mu\text{-C(O)}C_2Ph_2\}(\eta^5\text{-}C_5H_5)_2]$.[2]

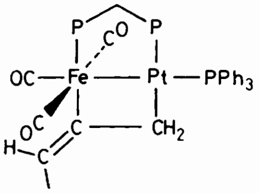
Terminal acetylenes such as $HC{\equiv}CC_6H_4Me\text{-}4$ also react with (**1**) under mild conditions. Thus a solution of (**1**) in



(1)



(2a) $R^1 = R^2 = H$
(2b) $R^1 = H$, $R^2 = C_6H_4Me\text{-}4$
(2c) $R^1 = C_6H_4Me\text{-}4$, $R^2 = H$



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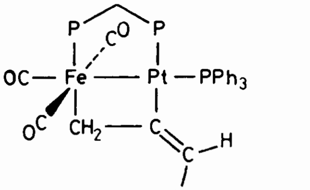

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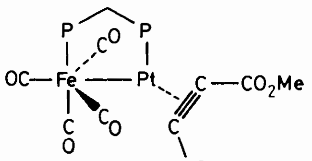

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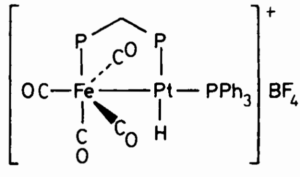

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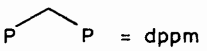

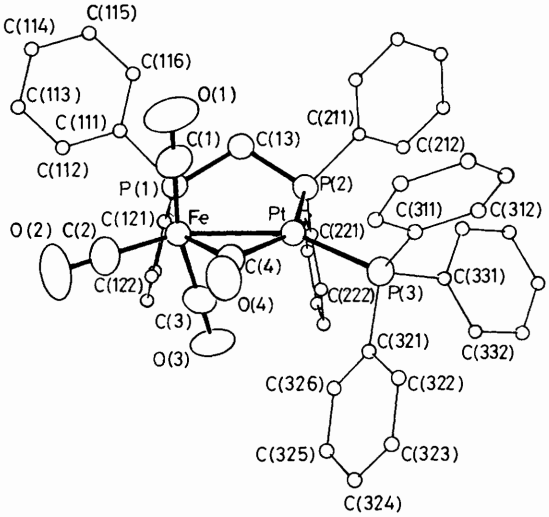

Figure 1. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$, (**1**). Selected interatomic distances: Fe–Pt 257.9(4), Fe–C(4) 201.2(7), Pt–C(4) 199.2(7), Pt–P(3) 226.9(3) pm. Selected angles: Fe–C(4)–O(4) 137.1(4), Pt–C(4)–O(4) 142.6(4)°.

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† This and other complexes discussed in the communication were characterised by elemental analysis, and by i.r. and n.m.r. (^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$) spectroscopy, *e.g.* the spectroscopic data, are (i.r. in CH_2Cl_2, $^1H\{^{31}P\}$ n.m.r. in $CDCl_3$, $^{31}P\{^1H\}$ n.m.r. in CD_2Cl_2, δ values in p.p.m., *J* values in Hz): (**2b**), ν(CO) at 1965s, 1915s, and 1687m cm^{-1}, $^1H\{^{31}P\}$ n.m.r., δ 5.05 [s, *J*(PtH) 202, CH], 4.85 (br, CH_2), 4.45 (br, CH_2), and 2.10 (s, Me), $^{31}P\{^1H\}$ n.m.r., δ 62.6 [dd, *J*(PP) 59, 34, *J*(PtP) 130, PFe], 34.8 [dd, *J*(PP) 34, 7, *J*(PtP) 3336, PPh_3], and 8.9 [dd, *J*(PP) 59, 7, *J*(PtP) 2560, CH_2PPt]; (**2c**), ν(CO), at 1965s, 1916s, and 1692m cm^{-1}, $^1H\{^{31}P\}$ n.m.r., δ 9.00 [s, *J*(PtH) 28, CH], 4.76(CH_2), 4.69(CH_2), and 2.05 (s, Me), $^{31}P\{^1H\}$ n.m.r., δ 60.1 [dd, *J*(PP) 60, 37, *J*(PtP) 139, PFe], 33.6 [dd, *J*(PP) 37, 4, *J*(PtP) 3440, PPh_3], and 8.0 [d, br., *J*(PP) 60, *J*(PtP) 2680, CH_2PPt]. (**4**), ν(CO) at 1986s, 1918s, and 1884s cm^{-1}, $^1H\{^{31}P\}$ n.m.r., δ 5.23 [s, *J*(PtH) 72, *J*(HH) 1.5, $C{=}CH_2$], 4.33 [s, *J*(PtH) 37, *J*(HH) 1.5, $C{=}CH_2$], 3.68 [s, *J*(PtH) 41, $FeCH_2$], and 3.55 [s, *J*(PtH) 26, PCH_2P], $^{31}P\{^1H\}$ n.m.r., δ 56.2 [dd, *J*(PP) 102, 10, *J*(PtP) 100, PFe], 26.0 [dd, *J*(PP) 10, 9, *J*(PtP) 3210, PPh_3], and 17.9 [dd, *J*(PP) 102, 9, *J*(PtP) 1880, CH_2PPt]; (**5**), ν(CO) at 2062s, 2018s, 1964s, 1944s, and 1695s cm^{-1}, $^1H\{^{31}P\}$ n.m.r., δ 3.83 [s, *J*(PtH) 39, CH_2], 3.81 (s, Me), and 3.69 (s, Me), $^{31}P\{^1H\}$ n.m.r., δ 74.5 [d, *J*(PP) 125, *J*(PtP) 126, PFe], and 24.2 [d, *J*(PP) 125, *J*(PtP) 1990, PPt]; (**6**), ν(CO) at 2078s, 2024m, 1988m, and 1948m cm^{-1}, $^1H\{^{31}P\}$ n.m.r., δ 3.50 [s, *J*(PtH) 22, CH_2], and −5.53 [s, *J*(PtH) 713, PtH], $^{31}P\{^1H\}$ n.m.r., δ 70.3 [dd, *J*(PP) 86, 12, *J*(PtP) 80, PFe], 29.5 [d, br, *J*(PP) 86, *J*(PtP) 2150, CH_2PPt], and 26.6 [dd, *J*(PP) 12, 11, *J*(PtP) 3850, PPh_3].

‡ *Crystal data* for (**1**)·C_6H_6; orange solvent dependent prisms, $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]\cdot C_6H_6$, M = 1087.77, triclinic, space group $P\bar{1}$, a = 1177.3(2), b = 1198.4(1), c = 1776.5(1) pm, α = 103.34(1), β = 107.81(1), γ = 91.76(1)°, U = 2.305 nm^3, Z = 2, μ = 33.36 cm^{-1}, $F(000)$ = 1092. (**2a**): $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}\sigma:\eta^3\text{-C(O)}C_2H_2\}Pt(PPh_3)]$, M = 1007.69, orthorhombic, space group $Pbca$, a = 1898.9(4), b = 1828.3(3), c = 2414.4(5) pm, U = 8.3839 nm^3, Z = 8, μ = 36.64 cm^{-1}, $F(000)$ = 4000. (**3**): $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}CH_2C({=}CH_2)\}Pt(PPh_3)]$, M = 1021.71, monoclinic, space group $P2_1/n$, a = 1195.1(2), b = 2258.5(3), c = 1673.9(4) pm, β = 108.15(2)°, U = 4.483 nm^3, Z = 4, μ = 34.26 cm^{-1}, $F(000)$ = 2012. Scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$, scan speeds 2.0—29.3° min^{-1}, and $4.0 < 2\theta < 45.0°$ for all three compounds. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[3] The data sets were corrected for absorption empirically.[4] All three structures were solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX76.[5] Refinement was the same in all three cases with all non-hydrogen atoms refined anisotropically, all phenyl- and methylene-hydrogen atoms being included in calculated positions (C–H = 108 pm) and refined with an overall isotropic temperature factors. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used in all cases at the end of refinement. Final R and R_w values are as follows: 0.0257 and 0.0264 (443 parameters, 5422 observed data) for (**1**); 0.0381 and 0.0327 (426 parameters, 4163 observed data) for (**2a**); and 0.0286 and 0.0295 (451 parameters, 4835 observed data) for (**3**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

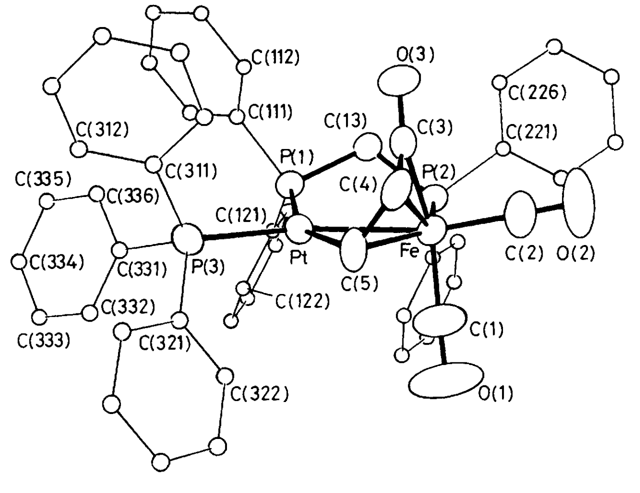

Figure 2. Molecular structure of $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}C(O)C_2H_2\}Pt(PPh_3)]$, (**2a**). Selected interatomic distances: Fe–Pt 259.7(4), Pt–C(5) 202.2(9), Fe–C(5) 211.4(9), C(4)–C(5) 140.8(12), C(4)–C(3) 145.1(12), Fe–C(3) 191.3(9), Fe–C(4) 209.5(9), C(3)–O(3) 121.3(10), Pt–P(3) 226.8(4) pm. Selected angles: Pt–C(5)–Fe 77.8(4), Pt–C(5)–C(4) 111.5(6), C(5)–C(4)–C(3) 110.7(7), Fe–C(3)–O(3) 148.3(6)°.

CH_2Cl_2 is converted at 20 °C almost quantitatively into a product which, on the basis of microanalytical and spectroscopic data,† is formulated as (**2b**). However, in CH_2Cl_2 solution (**2b**) slowly isomerises, over a period of 48 h at 20 °C to give (**2c**), which was also fully characterised.†

Treatment of a benzene solution of (**1**) with allene at 80 °C for 15 min gives (**3**) the crystal structure‡ of which is summarised in Figure 3 and its caption. In this structure allene is bridging the metals to give a novel dimetallacyclobutane ring with an exocyclic methylene group. Interestingly, treatment of a CH_2Cl_2 solution of (**1**) with allene at 20 °C gives, after several days, a different product which, on the basis of spectroscopic evidence, is tentatively formulated as (**4**). Surprisingly (**4**), on heating in benzene, is not converted into (**3**) but gives another, as yet uncharacterised, product. (**1**) also reacts with ethylene, slowly however, (at 20 °C) and not cleanly, to give a mixture of products.

Preliminary work shows that (**1**) reacts with a number of electrophilic reagents to give products, some of which have been characterised. Treatment with $MeO_2CC{\equiv}CCO_2Me$ displaces PPh_3 to give $[(OC)_4Fe(\mu\text{-dppm})\text{-}Pt(MeO_2CC{\equiv}CCO_2\text{-}Me)]$ (**5**). (**1**) is protonated, when treated with $HBF_4{\cdot}Et_2O$, to give the hydride (**6**) in 83% isolated yield. The ^1H spectrum of (**6**) (CD_2Cl_2 solution) shows a hydride resonance at δ −5.53 p.p.m. with $^1J(PtH)$ 713 Hz. Selective decoupling experiments show $^2J(P_APtH)$ 179 Hz, *i.e.* clearly the hydride is in a *trans*-position to P_A.

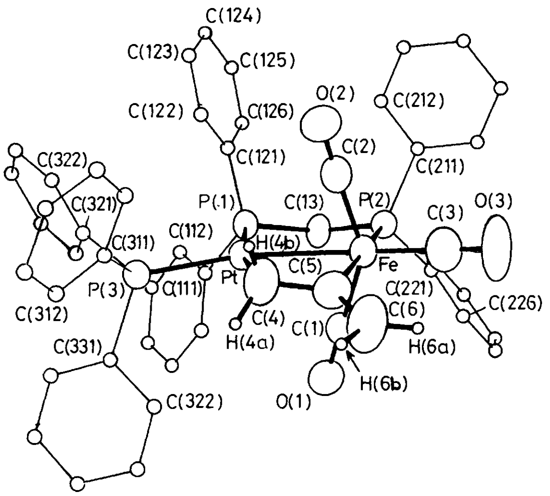

Figure 3. Molecular structure of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}CH_2C(=CH_2)\}Pt(PPh_3)]$, (**3**). Selected interatomic distances: Fe–Pt 263.4(4), Pt–C(4) 209.3(8), Pt–C(5) 284.1(8), Fe–C(5) 208.8(7), Pt–P(1) 232.6(3), Pt–P(3) 232.8(3), Fe–P(2) 224.3(3), C(4)–C(5) 145.0(11), C(5)–C(6) 135.0(9) pm. Selected angles: Pt–C(4)–C(5) 105.1(6), Fe–C(5)–C(4) 106.8(5), C(4)–C(5)–C(6) 123.9(7)°.

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