Chemistry of the Metal Carbonyls. Part 79.[1] Synthesis and X-Ray Crystal Structures of $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, and $[Fe_2Pt(CO)_8(cyclo\text{-}C_8H_{12})]$ †

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Tetraethylammonium or bis(triphenylphosphine)iminium salts of the anion $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]^-$ react with the complex $[Pt(C_2H_4)_2(PPh_3)]$ in tetrahydrofuran to give the di-irondiplatinum compounds $[R][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ $[R = NEt_4^+$ or $N(PPh_3)_2^+]$. The structure of the $N(PPh_3)_2^+$ salt was established by a single-crystal X-ray diffraction study; the crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell with lattice parameters $a = 25.05(3)$, $b = 14.28(1)$, $c = 23.99(2)$ Å, and $\beta = 106.84(7)°$. The structure has been refined to R 0.059 (R' 0.061) for 8 768 independent reflections to $2\theta \leqslant 50°$ [(Mo-K_α) X-radiation] collected at 200 K. The $N(PPh_3)_2^+$ cation is bent [P–N–P 138.1(8)°], while the metal framework of the anion consists of a cluster of Fe_2Pt_2 atoms [Pt–Pt 2.966(1); Pt–Fe 2.756(2), 2.626(2), 2.555(2), and 2.562(2); Fe–Fe 2.522(2) Å], arranged such that a Fe_2Pt triangle, edge-bridged by three CO ligands, is capped by a platinum atom carrying a terminal CO ligand and PPh_3 group. The four remaining CO ligands are terminally bonded in pairs to the two iron atoms, while the platinum atom in the triangle carries a PPh_3 group. Although not located in the X-ray diffraction study, evidence is presented that the hydrido-ligand bridges the longest of the four Fe–Pt separations. Protonation of the salts affords the neutral complex $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, also characterised by an X-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell with lattice parameters $a = 10.83(2)$, $b = 16.00(4)$, $c = 27.88(4)$ Å, and $\beta = 99.40(11)°$. The structure has been refined to R 0.056 (R' 0.060) for 2 474 independent reflections to $2\theta \leqslant 40°$ at 200 K. The structure consists of an Fe_2Pt_2 core [Pt–Pt 2.998(2); Pt–Fe 2.696(3), 2.694(3), 2.631(3), and 2.604(3) Å], with each iron atom bonded to three CO ligands and each platinum atom bonded to a CO and a PPh_3 group. The hydrido-ligands are considered to bridge the two longer Fe–Pt edges. The X-ray studies allow an understanding of the ^1H and ^{31}P n.m.r. data for the two Fe_2Pt_2 species, both of which undergo dynamic behaviour in solution. Reactions of the compound $[Pt(C_2H_4)_2(PPh_3)]$ or $[Pt(cod)(C_8H_{13})][BF_4]$ (cod = cyclo-octa-1,5-diene) with the salt $[NEt_3H][Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]$ afford the compounds $[NEt_3H][Fe_3Pt(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}(PPh_3)]$ and $[Fe_2Pt(CO)_8(cod)]$, respectively. The latter was studied by X-ray crystallography; crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$, in a unit cell of dimensions $a = 12.321(11)$, $b = 9.442(7)$, and $c = 15.707(16)$ Å. The structure has been refined to R 0.050 (R' 0.050) for 1 637 independent reflections to $2\theta \leqslant 55°$ at 200 K. The molecule consists of a triangle of metal atoms [Fe–Pt 2.561(3) and 2.553(3); Fe–Fe 2.704(4) Å]; each iron atom carries four terminally bound CO ligands, and the platinum atom is η^4 bonded to the cod group.

THE formally unsaturated 46-electron triosmium complex $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ reacts with the complexes $[Pt(C_2H_4)_2(PR_3)]$ $[PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3, or $PBu^t{}_2Me]$ or $[Rh(acac)(C_2H_4)_2]$ to afford tetranuclear cluster compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$[2] and $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$[1] (acac = acetylacetonate) respectively. The motivation behind this study was to demonstrate that heteronuclear metal cluster compounds can be obtained by reacting co-ordinatively unsaturated but electron-rich low-valent metal species such as $PtPR_3$ or Rh(acac) with an electron-deficient transition-metal complex. A common feature of these reactions was the transfer of a CO ligand from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to the incoming metal centre; thus both $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ and $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ were shown by X-ray crystallography to contain PtCO and RhCO groups, respectively. This CO ligand transfer achieves two purposes: creation of a vacant co-ordination site on the substrate molecule to which the nucleophilic metal atom can bond, and stabilisation of the resulting complex due to creation of a more usual co-ordination arrangement around the 'naked' incoming metal atom. Formation of new cluster compounds may thus depend on the ease of CO ligand transfer to the electron-rich attacking reagent. Zero-valent platinum species appear to be particularly adept at scavenging carbonyl groups, even to the extent that the latter will displace tertiary phosphine ligands from this metal. Thus the formally unsaturated dirhenium compound $[Re_2(\mu\text{-}H)_2(CO)_8]$ reacts with $[Pt(C_2H_4)(PPh_3)_2]$ to give the triangular cluster $[PtRe_2(\mu\text{-}H)_2(CO)_9(PPh_3)]$, shown by X-ray crystallography to contain a Re–Re bond bridged by a $Pt(CO)(PPh_3)$ group.[3] Moreover, the compounds $[Pt(PPh_3)_4]$ and $[Pt\{P(OPh)_3\}_4]$ react with $[Fe_2(CO)_9]$ to give the complexes $[Fe_2Pt(CO)_9(PPh_3)]$ and $[FePt_2(CO)_5\{P(OPh)_3\}_3]$, both products containing PtCO groups.[4,5] These results suggest that numerous platinum-containing heteronuclear metal cluster compounds might be accessible *via* reactions of the complexes $[Pt(C_2H_4)_2(PR_3)]$[6] or $[Pt(C_2H_4)(PR_3)_2]$[7] with homonuclear metal carbonyl species even if the latter are not electron-deficient and are co-ordinatively saturated, transfer of CO to the platinum furthering the process. In this paper we report some preliminary studies aimed at examining this approach as a method of obtaining heteronuclear metal clusters.

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† Bis(triphenylphosphine)iminium 1,2;1,4;2,4-tri-μ-carbonyl-2,2,3,4,4-pentacarbonyl-2,3-μ-hydrido-1,3-bis(triphenylphosphine)-*tetrahedro*-diplatinumdiferrate(*Pt–Pt*)(4 *Pt–Fe*)(*Fe–Fe*), 1,2,2,2,3,4,4,4-octacarbonyl-1,2;3,4-di-μ-hydrido-1,3-bis(triphenylphosphine)-*tetrahedro*-diplatinumdi-iron(*Pt–Pt*)(4 *Pt–Fe*)-(*Fe–Fe*), and 2,2,2,2,3,3,3,3-octacarbonyl-1-(η-cyclo-octa-1,5-diene)-*triangulo*-platinumdi-iron(2 *Pt–Fe*)(*Fe–Fe*).

RESULTS AND DISCUSSION

An especially well-characterised carbonyldi-iron species is the anion $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]^-$,[8] isostructural with $[Fe_2(CO)_9]$. Reaction in tetrahydrofuran (thf) of the NEt_4^+ or $N(PPh_3)_2^+$ salts of this anion with the complex $[Pt(C_2H_4)_2(PPh_3)]$,[6] in a 1 : 2 molar ratio, afforded dark red-brown crystals of stoicheiometry $[R][Fe_2Pt_2(\mu\text{-}H)(CO)_8(PPh_3)_2]$ [(1a) R = NEt_4^+, (1b) R = $N(PPh_3)_2^+$]. Both salts were stable in air, in remarkable contrast to the pyrophoric precursor $[NEt_4][Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]$. The i.r. spectra of the salts (1) were similar, except that the two distinct low-frequency carbonyl absorptions of (1a) at 1 759 and 1 729 cm^{-1} appeared as one broad band for (1b) at 1 759 cm^{-1}. These absorptions indicated the presence of bridging CO ligands in the anion of (1).

The ^{31}P (^1H-decoupled) n.m.r. spectrum of (1a), measured at −70 °C, showed two resonances with couplings clearly indicating the presence of two inequivalent phosphine ligands bonded to inequivalent platinum atoms {δ (p.p.m.) −42.0 [d, *J*(PP) 9, *J*(PtP) 4 740 and 255] and −19.5 [d, *J*(PP) 9, *J*(PtP) 3 142 and 108 Hz]}. The anion was evidently undergoing dynamic behaviour since at ambient temperatures only a weak broad signal was observed. This was confirmed by the ^1H n.m.r. spectra of (1), the expected hydrido-ligand resonance not being observed for (1a) or (1b) at room temperature, but at −90 °C the spectrum of (1a) showed a broad doublet at τ 21.97 and that of (1b) a similar doublet at τ 22.02, with *J*(PH) 15 Hz in both cases. No ^{195}Pt satellites were observed on either resonance probably due to weak solutions. The highly dynamic nature of the anion is consistent with negative charge on a cluster lowering the barriers for concomitant H and CO site exchange.[9]

Protonation of either (1a) or (1b) with $HBF_4 \cdot 2Et_2O$ afforded a dark red crystalline petrol-soluble complex $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (2). An i.r. spectrum showed no bands in the bridging carbonyl region of the spectrum, whilst the ^{31}P n.m.r. spectrum clearly showed a system with two equivalent phosphorus nuclei, each bound to one equivalent platinum atom {δ (p.p.m.) −33.4 [*J*(PP) 8, *J*(PtP) 2 591 and 168, *J*(PtPt) 3 804 Hz]}. This spectrum, in contrast to that of (1a), was obtainable at ambient temperatures, indicating that any dynamic behaviour in (2) is of higher energy. Interestingly, the ^1H n.m.r. spectrum showed a triplet at τ 20.60 [*J*(PH) 10 Hz] which sharpened on cooling to −60 °C. The ^{195}Pt satellites were also evident [*J*(PtH) 595 Hz]. On lowering the temperature to −90 °C, the triplet began to collapse, but a lower temperature was not attainable due to the $[^2H_6]$acetone solvent used. Some degree of dynamic behaviour is thus indicated.

Profound structural changes obviously occur as a result of the protonation of (1). Since the spectroscopic data for (1) and (2) could not define the structures of these di-irondiplatinum clusters, single-crystal *X*-ray diffraction studies were carried out.

The results of the study on (1b), which crystallised with two molecules of acetone, are summarised in Tables 1—3; the structures of the anion and the cation, with the atomic numbering scheme, are shown in Figures 1 and 2, respectively. As mentioned above, the ^{31}P n.m.r. spectrum revealed the presence of two non-equivalent $PtPPh_3$ groups in the anion, and this is immediately confirmed because Pt(1) carries one terminal CO ligand whilst Pt(2) is bonded to two bridging CO groups (Figure 1). A third CO ligand bridges the Fe(1)–Fe(2) vector. All three bridging ligands are situated in a plane defined by three [Fe(1), Fe(2), and Pt(2)] of the four metal atoms, a common feature found in several tetranuclear metal carbonyl species, *e.g.* $[Co_4(CO)_{12}]$ [10] and $[Rh_4(CO)_{12}]$.[11] Indeed the arrangement of all the ligands around the Fe_2Pt_2 core of the anion is remarkably similar to that found for the ligands in the isoelectronic 58-electron complex $[Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$.[12] In the latter, the Co–Pt distances [2.579(2)—2 538(2) Å] display less variation than do the Fe–Pt internuclear separations in $[Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]^-$ (Table 2). Rather surprisingly the two Co–Pt edges which are bridged by carbonyl ligands in the dicobaltdiplatinum compound are not significantly shorter than the non-

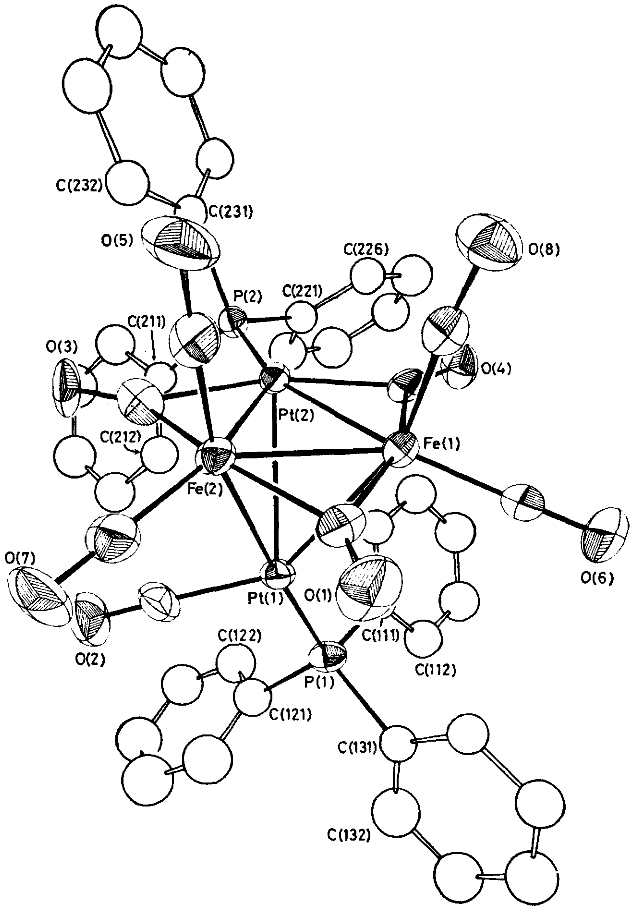


FIGURE 1 Molecular structure of the anion of $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, (1b)

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for the compound $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, (1b)

Atom	*x*	*y*	*z*
Pt(1)	0.789 61(2)	0.146 01(3)	0.055 19(2)
Pt(2)	0.763 39(2)	0.135 34(3)	0.167 87(2)
Fe(1)	0.691 49(8)	0.085 65(12)	0.073 29(7)
Fe(2)	0.720 09(8)	0.255 27(12)	0.088 17(8)
O(1)	0.641 6(5)	0.210 0(7)	−0.027 0(5)
O(2)	0.863 1(5)	0.315 3(9)	0.071 7(5)
O(3)	0.806 4(5)	0.337 6(7)	0.188 6(5)
O(4)	0.730 1(5)	−0.071 1(7)	0.157 4(4)
O(5)	0.629 4(5)	0.333 7(8)	0.126 5(5)
O(6)	0.640 3(5)	−0.057 6(8)	−0.010 3(5)
O(7)	0.732 0(6)	0.422 1(8)	0.025 1(6)
O(8)	0.590 2(5)	0.094 0(8)	0.109 4(5)
C(1)	0.670 4(6)	0.191 3(10)	0.019 4(6)
C(2)	0.832 8(7)	0.253 7(11)	0.064 9(7)
C(3)	0.777 0(7)	0.279 6(11)	0.159 5(7)
C(4)	0.730 2(6)	0.008 1(10)	0.141 4(5)
C(5)	0.667 6(7)	0.302 1(9)	0.112 3(6)
C(6)	0.661 9(6)	−0.002 7(10)	0.022 6(6)
C(7)	0.728 0(7)	0.355 9(11)	0.050 3(7)
C(8)	0.632 1(7)	0.093 1(11)	0.096 9(6)
P(1)	0.843 6(2)	0.045 8(3)	0.020 5(1)
P(2)	0.824 3(1)	0.114 2(2)	0.256 4(1)
P(3)	0.426 9(1)	0.309 7(2)	0.078 9(1)
P(4)	0.462 0(1)	0.223 0(2)	0.195 8(1)
N	0.465 9(5)	0.260 3(7)	0.134 7(4)
C(111)	0.859 6(5)	−0.061 9(7)	0.061 4(3)
C(112)	0.876 0(5)	−0.141 0(7)	0.036 4(3)
C(113)	0.883 8(5)	−0.226 0(7)	0.066 3(3)
C(114)	0.875 2(5)	−0.232 0(7)	0.121 1(3)
C(115)	0.858 8(5)	−0.152 9(7)	0.146 0(3)
C(116)	0.851 0(5)	−0.067 8(7)	0.116 2(3)
C(121)	0.911 1(5)	0.095 4(7)	0.023 3(4)
C(122)	0.958 4(5)	0.071 4(7)	0.068 3(4)
C(123)	1.008 3(5)	0.119 4(7)	0.075 0(4)
C(124)	1.011 0(5)	0.191 6(7)	0.036 7(4)
C(125)	0.963 7(5)	0.215 6(7)	−0.008 3(4)
C(126)	0.913 8(5)	0.167 5(7)	−0.015 0(4)
C(131)	0.814 0(3)	0.005 4(7)	−0.054 4(4)
C(132)	0.846 3(3)	−0.012 2(7)	−0.091 8(4)
C(133)	0.822 1(3)	−0.052 5(7)	−0.146 3(4)
C(134)	0.765 5(3)	−0.075 2(7)	−0.163 3(4)
C(135)	0.733 2(3)	−0.057 5(7)	−0.125 9(4)
C(136)	0.757 4(3)	−0.017 2(7)	−0.071 5(4)
C(211)	0.892 2(4)	0.168 1(7)	0.263 4(3)
C(212)	0.927 7(4)	0.197 5(7)	0.316 8(3)
C(213)	0.980 9(4)	0.230 6(7)	0.320 2(3)
C(214)	0.998 7(4)	0.234 3(7)	0.270 2(3)
C(215)	0.963 2(4)	0.204 9(7)	0.216 9(3)
C(216)	0.909 9(4)	0.171 8(7)	0.213 5(3)
C(221)	0.844 7(3)	−0.005 4(7)	0.282 2(4)
C(222)	0.900 0(3)	−0.035 6(7)	0.297 4(4)
C(223)	0.913 0(3)	−0.128 2(7)	0.314 6(4)
C(224)	0.870 8(3)	−0.190 5(7)	0.316 7(4)
C(225)	0.815 5(3)	−0.160 2(7)	0.301 5(4)
C(226)	0.802 4(3)	−0.067 7(7)	0.284 3(4)
C(231)	0.804 3(4)	0.165 2(6)	0.318 4(3)
C(232)	0.781 4(4)	0.255 0(6)	0.310 9(3)
C(233)	0.763 6(4)	0.296 3(6)	0.355 1(3)
C(234)	0.768 6(4)	0.247 7(6)	0.406 8(3)
C(235)	0.791 4(4)	0.157 9(6)	0.414 3(3)
C(236)	0.809 3(4)	0.116 6(6)	0.370 1(3)
C(311)	0.452 4(3)	0.424 9(6)	0.073 0(4)
C(312)	0.419 4(3)	0.489 1(6)	0.034 2(4)
C(313)	0.440 3(3)	0.577 8(6)	0.027 9(4)
C(314)	0.494 3(3)	0.602 1(6)	0.060 4(4)
C(315)	0.527 4(3)	0.537 8(6)	0.099 1(4)
C(316)	0.506 4(3)	0.449 2(6)	0.105 4(4)
C(321)	0.431 2(3)	0.246 2(6)	0.016 1(3)
C(322)	0.476 8(3)	0.186 7(6)	0.022 5(3)
C(323)	0.483 7(3)	0.138 9(6)	−0.025 6(3)
C(324)	0.445 0(3)	0.150 5(6)	−0.080 2(3)
C(325)	0.399 4(3)	0.210 0(6)	−0.086 6(3)
C(326)	0.392 5(3)	0.257 8(6)	−0.038 5(3)
C(331)	0.355 1(3)	0.324 6(7)	0.076 6(4)
C(332)	0.338 9(3)	0.402 2(7)	0.103 2(4)
C(333)	0.283 3(3)	0.413 2(7)	0.101 9(4)
C(334)	0.243 8(3)	0.346 7(7)	0.074 1(4)
C(335)	0.259 9(3)	0.269 1(7)	0.047 6(4)
C(336)	0.315 6(3)	0.258 0(7)	0.048 9(4)
C(411)	0.431 3(4)	0.108 3(6)	0.192 5(3)
C(412)	0.427 1(4)	0.055 5(6)	0.142 5(3)
C(413)	0.407 6(4)	−0.036 5(6)	0.138 9(3)
C(414)	0.392 4(4)	−0.075 5(6)	0.185 4(3)
C(415)	0.396 6(4)	−0.022 7(6)	0.235 4(3)
C(416)	0.416 1(4)	0.069 3(6)	0.238 9(3)
C(421)	0.532 0(3)	0.209 5(6)	0.242 4(2)
C(422)	0.575 9(3)	0.211 7(6)	0.217 6(2)
C(423)	0.630 0(3)	0.191 3(6)	0.251 5(2)
C(424)	0.640 2(3)	0.168 6(6)	0.310 2(2)
C(425)	0.596 3(3)	0.166 4(6)	0.335 0(2)
C(426)	0.542 2(3)	0.186 8(6)	0.301 1(2)
C(431)	0.426 0(3)	0.303 1(5)	0.229 6(4)
C(432)	0.451 1(3)	0.390 0(5)	0.245 8(4)
C(433)	0.423 3(3)	0.459 1(5)	0.267 6(4)
C(434)	0.370 3(3)	0.441 4(5)	0.273 1(4)
C(435)	0.345 2(3)	0.354 5(5)	0.257 0(4)
C(436)	0.373 0(3)	0.285 3(5)	0.235 2(4)
Solvent			
Acetone molecule A			
O(9)	0.323 0(8)	0.137 5(12)	0.311 8(8)
C(9)	0.285 3(9)	0.119 5(14)	0.330 9(8)
C(10)	0.247 7(13)	0.184 6(21)	0.344 3(12)
C(11)	0.268 1(16)	0.012 7(26)	0.328 6(15)
Acetone molecule B			
O(10)	0.115 0(8)	0.091 0(14)	0.257 5(8)
C(12)	0.091 0(11)	0.018 9(19)	0.270 6(12)
C(13)	0.093 7(14)	−0.001 5(22)	0.328 1(14)
C(14)	0.063 9(17)	−0.034 5(29)	0.220 0(18)

TABLE 2

Internuclear distances (Å) and bond angles (°) for $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, (1b), with estimated standard deviations in parentheses

(*a*) Distances *

Pt(1)–Pt(2)	2.966(1)	O(6)–C(6)	1.13(2)
Pt(1)–Fe(1)	2.756(2)	O(7)–C(7)	1.14(2)
Pt(1)–Fe(2)	2.626(2)	O(8)–C(8)	1.17(2)
Pt(2)–Fe(1)	2.555(2)	P(1)–C(111)	1.81(1)
Pt(2)–Fe(2)	2.562(2)	P(1)–C(121)	1.82(1)
Fe(1)–Fe(2)	2.522(2)	P(1)–C(131)	1.83(1)
Fe(1)–C(1)	1.96(1)	P(2)–C(211)	1.83(1)
Fe(2)–C(1)	1.98(1)	P(2)–C(221)	1.84(1)
Pt(1)–C(2)	1.86(2)	P(2)–C(231)	1.85(1)
Pt(2)–C(3)	2.11(2)	P(3)–C(311)	1.786(9)
Fe(2)–C(3)	1.92(1)	P(3)–C(321)	1.789(9)
Pt(2)–C(4)	2.02(1)	P(3)–C(331)	1.80(1)
Fe(1)–C(4)	1.98(1)	P(4)–C(411)	1.800(9)
Fe(2)–C(5)	1.72(2)	P(4)–C(421)	1.797(9)
Fe(1)–C(6)	1.76(1)	P(4)–C(431)	1.790(9)
Fe(2)–C(7)	1.74(2)	P(3)–N	1.58(1)
Fe(1)–C(8)	1.74(2)	P(4)–N	1.59(1)
Pt(1)–P(1)	2.285(4)	O(9)–C(9)	1.19(3)
Pt(2)–P(2)	2.249(3)	O(9)–C(10)	2.34(4)
O(1)–C(1)	1.17(2)	O(9)–C(11)	2.36(4)
O(2)–C(2)	1.14(2)	O(10)–C(12)	1.28(4)
O(3)–C(3)	1.19(2)	O(10)–C(13)	2.33(4)
O(4)–C(4)	1.19(2)	O(10)–C(14)	2.24(4)
O(5)–C(5)	1.19(2)		

(*b*) Angles

(*i*) About Pt(1)

Pt(2)–Pt(1)–Fe(1)	52.9(1)	Pt(2)–Pt(1)–P(1)	127.6(1)
Pt(2)–Pt(1)–Fe(2)	54.1(1)	Fe(1)–Pt(1)–P(1)	120.7(1)
Pt(2)–Pt(1)–C(2)	101.7(6)	Fe(2)–Pt(1)–C(2)	83.3(6)
Fe(1)–Pt(1)–Fe(2)	55.8(1)	Fe(2)–Pt(1)–P(1)	175.1(1)
Fe(1)–Pt(1)–C(2)	138.9(6)	P(1)–Pt(1)–C(2)	100.4(6)

Table 2 (*continued*)

(*ii*) About Pt(2)

Pt(1)–Pt(2)–Fe(1)	59.3(1)	Fe(2)–Pt(2)–C(4)	108.7(4)
Pt(1)–Pt(2)–Fe(2)	56.1(1)	C(3)–Pt(2)–C(4)	155.8(5)
Fe(1)–Pt(2)–Fe(2)	59.1(1)	Pt(1)–Pt(2)–P(2)	126.8(1)
Pt(1)–Pt(2)–C(3)	77.2(5)	Fe(1)–Pt(2)–P(2)	155.9(1)
Fe(1)–Pt(2)–C(3)	106.2(4)	Fe(2)–Pt(2)–P(2)	145.1(1)
Fe(2)–Pt(2)–C(3)	47.2(4)	P(2)–Pt(2)–C(3)	97.9(4)
Pt(1)–Pt(2)–C(4)	86.5(4)	P(2)–Pt(2)–C(4)	106.3(4)
Fe(1)–Pt(2)–C(4)	49.6(4)		

(*iii*) About Fe(1)

Pt(1)–Fe(1)–Pt(2)	67.8(1)	Pt(2)–Fe(1)–C(6)	149.3(5)
Pt(1)–Fe(1)–Fe(2)	59.5(1)	Fe(2)–Fe(1)–C(6)	146.3(5)
Pt(2)–Fe(1)–Fe(2)	60.6(1)	C(1)–Fe(1)–C(6)	96.8(6)
Pt(1)–Fe(1)–C(1)	74.7(5)	C(4)–Fe(1)–C(6)	100.2(6)
Pt(2)–Fe(1)–C(1)	111.0(4)	Pt(1)–Fe(1)–C(8)	156.5(5)
Fe(2)–Fe(1)–C(1)	50.5(4)	Pt(2)–Fe(1)–C(8)	98.2(5)
Pt(1)–Fe(1)–C(4)	93.4(5)	Fe(2)–Fe(1)–C(8)	97.5(5)
Pt(2)–Fe(1)–C(4)	51.1(4)	C(1)–Fe(1)–C(8)	94.4(7)
Fe(2)–Fe(1)–C(4)	111.7(4)	C(4)–Fe(1)–C(8)	91.5(7)
C(1)–Fe(1)–C(4)	161.8(6)	C(6)–Fe(1)–C(8)	92.3(7)
Pt(1)–Fe(1)–C(6)	109.4(6)		

(*iv*) About Fe(2)

Pt(1)–Fe(2)–Pt(2)	69.7(1)	Pt(1)–Fe(2)–C(1)	77.6(5)
Pt(1)–Fe(2)–Fe(1)	64.7(1)	Pt(2)–Fe(2)–C(1)	110.0(4)
Pt(2)–Fe(2)–Fe(1)	60.3(1)	Fe(1)–Fe(2)–C(1)	49.8(4)
Pt(1)–Fe(2)–C(3)	89.4(5)	C(3)–Fe(2)–C(5)	94.1(7)
Pt(2)–Fe(2)–C(3)	53.8(5)	Pt(1)–Fe(2)–C(7)	98.5(6)
Fe(1)–Fe(2)–C(3)	114.1(5)	Pt(2)–Fe(2)–C(7)	148.6(5)
C(1)–Fe(2)–C(3)	162.6(6)	Fe(1)–Fe(2)–C(7)	142.1(5)
Pt(1)–Fe(2)–C(5)	166.4(5)	C(1)–Fe(2)–C(7)	94.9(6)
Pt(2)–Fe(2)–C(5)	102.0(5)	C(3)–Fe(2)–C(7)	98.6(7)
Fe(1)–Fe(2)–C(5)	102.0(5)	C(5)–Fe(2)–C(7)	94.0(8)
C(1)–Fe(2)–C(5)	95.9(7)		

(*v*) About the carbonyl carbon atoms

Fe(1)–C(1)–Fe(2)	79.7(5)	Pt(2)–C(4)–Fe(1)	79.3(5)
Fe(1)–C(1)–O(1)	141(1)	Pt(2)–C(4)–O(4)	142(1)
Fe(2)–C(1)–O(1)	139(1)	Fe(1)–C(4)–O(4)	139(1)
Pt(1)–C(2)–O(2)	174(2)	Fe(2)–C(5)–O(5)	177(1)
Pt(2)–C(3)–Fe(2)	79.0(6)	Fe(1)–C(6)–O(6)	177(2)
Pt(2)–C(3)–O(3)	136(1)	Fe(2)–C(7)–O(7)	179(2)
Fe(2)–C(3)–O(3)	146(1)	Fe(1)–C(8)–O(8)	175(1)

(*vi*) About P(1)

Pt(1)–P(1)–C(111)	113.5(4)	C(121)–P(1)–C(111)	104.7(5)
Pt(1)–P(1)–C(121)	112.7(4)	C(131)–P(1)–C(111)	103.2(5)
Pt(1)–P(1)–C(131)	116.2(3)	C(131)–P(1)–C(121)	105.4(5)

(*vii*) About P(2)

Pt(2)–P(2)–C(211)	112.9(3)	C(221)–P(2)–C(211)	101.5(4)
Pt(2)–P(2)–C(221)	119.3(3)	C(231)–P(2)–C(211)	102.8(4)
Pt(2)–P(2)–C(231)	116.0(3)	C(231)–P(2)–C(221)	102.0(5)

(*viii*) About P(3)

N–P(3)–C(311)	109.4(5)	C(321)–P(3)–C(311)	106.8(5)
N–P(3)–C(321)	108.3(5)	C(331)–P(3)–C(311)	105.5(4)
N–P(3)–C(331)	116.6(6)	C(321)–P(3)–C(331)	109.8(4)

(*ix*) About P(4)

N–P(4)–C(411)	113.8(5)	C(421)–P(4)–C(411)	104.9(4)
N–P(4)–C(421)	107.5(5)	C(431)–P(4)–C(411)	109.7(4)
N–P(4)–C(431)	112.2(5)	C(421)–P(4)–C(431)	108.4(4)

(*x*) About N

P(3)–N–P(4)	138.1(8)

(*xi*) About the bonded phenyl carbon atoms

C(112)–C(111)–P(1)	120.3(7)	C(312)–C(311)–P(3)	120.1(5)
C(116)–C(111)–P(1)	119.5(8)	C(316)–C(311)–P(3)	119.8(6)
C(122)–C(121)–P(1)	120.3(8)	C(322)–C(321)–P(3)	117.6(5)
C(126)–C(121)–P(1)	119.0(8)	C(326)–C(321)–P(3)	122.3(7)
C(132)–C(131)–P(1)	123.0(6)	C(332)–C(331)–P(3)	120.0(6)
C(136)–C(131)–P(1)	116.7(8)	C(336)–C(331)–P(3)	120.0(7)
C(212)–C(211)–P(2)	122.6(8)	C(412)–C(411)–P(4)	117.1(7)
C(216)–C(211)–P(2)	117.2(6)	C(416)–C(411)–P(4)	122.7(6)
C(222)–C(221)–P(2)	122.2(7)	C(422)–C(421)–P(4)	118.7(4)
C(226)–C(221)–P(2)	117.7(6)	C(426)–C(421)–P(4)	120.9(7)
C(232)–C(231)–P(2)	117.0(6)	C(432)–C(431)–P(4)	116.7(6)
C(236)–C(231)–P(2)	122.9(7)	C(436)–C(431)–P(4)	123.1(6)

Table 2 (*continued*)

(*xii*) In the solvent molecules

Acetone molecule A

C(10)–C(9)–O(9)	127(2)	C(10)–C(9)–C(11)	116(3)
C(11)–C(9)–O(9)	116(2)		

Acetone molecule B

C(13)–C(12)–O(10)	122(3)	C(14)–C(12)–C(13)	127(3)
C(14)–C(12)–O(10)	111(3)		

* The phenyl rings were refined as rigid hexagons with the C–C distance = 1.395 Å.

bridged Co—Pt distances. However, in the di-irondiplatinum anion the Fe–Pt edges bridged by the CO ligands are discernably shorter than the other two Fe–Pt interatomic distances. This contraction of metal–metal separations by bridging CO groups is commonly observed.[13,14]

The disparity of over 0.1 Å found in the two apparently unbridged internuclear Fe—Pt distances [2.756(2) and 2.626(2) Å] in (1b) immediately suggests that the longer of these two vectors [Fe(1)–Pt(1)] is associated with a bridging hydrido-ligand,[15,16] the presence of this ligand being known from the ^{1}H n.m.r. spectrum. However, although calculations[17] based on potential energy minima reveal a feasible site for the hydrido-ligand on the Fe(1)–Pt(1) edge, there is a terminal site on Pt(1), *trans* to the Pt(1)–Pt(2) vector, which has lower

Table 3

Some least-squares planes * for the anion of (1b); distances (Å) of atoms from the planes are given in square brackets

Plane (*a*): Pt(2), Fe(2), C(3)

$$-21.764x + 3.003y + 16.343z = 8.299$$

[Pt(2) 0.0, Fe(2) 0.0, C(3) 0.0, O(3) 0.009]

Plane (*b*): Pt(2), Fe(1), C(4)

$$-22.384x + 2.572y + 15.665z = 8.274$$

[Pt(2) 0.0, Fe(1) 0.0, C(4) 0.0, O(4) 0.504]

Plane (*c*): Fe(1), Fe(2), C(1)

$$23.101x - 2.648y - 14.216z = 8.396$$

[Fe(1) 0.0, Fe(2) 0.0, C(1) 0.0, O(1) −0.057]

Plane (*d*): Pt(2), Fe(1), Fe(2), C(3), C(4), P(2)

$$-22.237x + 2.657y + 15.852z = 8.266$$

[Pt(2) 0.0158, Fe(1) −0.0167, Fe(2) 0.0338, C(3) −0.0365, C(4) −0.0048, P(2) 0.0084]

Plane (*e*): Pt(1), Fe(1), Fe(2), C(2), P(1)

$$5.413x - 3.483y + 20.212z = -0.542$$

[Pt(1) 0.010, Fe(1) 0.055, Fe(2) −0.0803, C(2) 0.0642, P(1) −0.0489]

Relevant angles (°) between the least-squares planes

(*a*)–(*b*)	3.1	(*b*)–(*c*)	175.6	(*c*)–(*e*)	94.4
(*a*)–(*c*)	172.9	(*b*)–(*d*)	0.7	(*d*)–(*e*)	80.7
(*a*)–(*d*)	2.4	(*b*)–(*e*)	81.3		
(*a*)–(*e*)	79.3	(*c*)–(*d*)	174.9		

Torsion angles (°) in the metal cluster

Fe(2)–Pt(1)–Pt(2)–Fe(1)	71.2
Fe(2)–Pt(2)–Fe(1)–Pt(1)	66.4
Pt(2)–Pt(1)–Fe(1)–Fe(2)	68.0
Pt(1)–Pt(2)–Fe(2)–Fe(1)	71.7
Fe(1)–Pt(1)–Fe(2)–Pt(2)	65.9
Pt(2)–Fe(1)–Fe(2)–Pt(1)	80.1

* *x*, *y*, and *z* are fractional crystal co-ordinates.

energy. Nevertheless, further evidence for an edge-bridging location of the hydrido-ligand is offered by the observed widening of the *cis* Pt(1)–Fe(1)–C(6) angle to 109.4(6)°, which is significantly larger than the other *cis* M–M–C angles which range from 83.3(6) to 102.0(5)°.

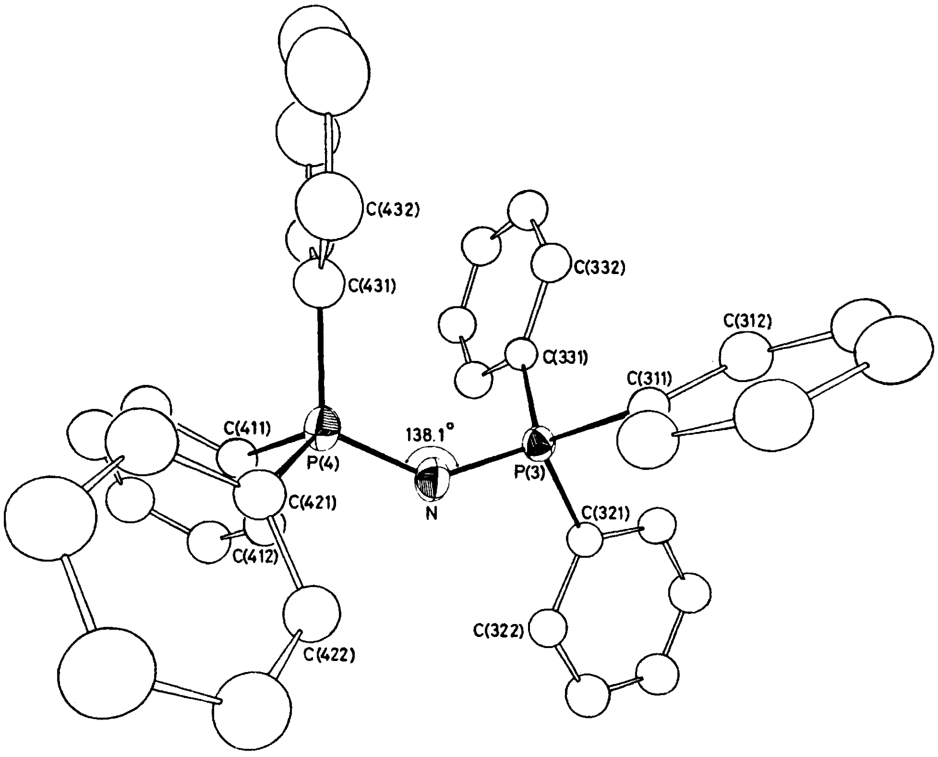


FIGURE 2 Molecular structure of the cation of $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, (1b)

Intuitively, a bridge-bonding mode for the hydride suggests itself, since this form of co-ordination is by far the most commonly observed in transition metal cluster systems.[15,16] The presence of two low-energy sites for possible hydrido-ligand location might present some rationale for the observed highly dynamic nature of the anion, which must involve both H and CO site exchange.

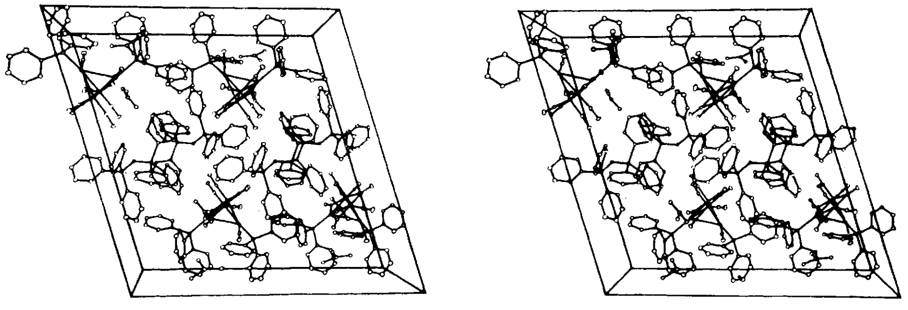


FIGURE 3 Stereoscopic view of the contents of the unit cell for complex (1b)

The Fe(1)–Fe(2) separation [2.522(2) Å] in (1b) is identical within experimental error to that found (2.52 Å) in $[Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]^-$.[8] By comparison, the non-bridged Fe–Fe distance found in $[Fe_2Pt(CO)_8(cod)]$ [2.704(3) Å] is *ca.* 0.2 Å longer, as discussed below.

The bridging carbonyl ligands show no serious deviations from coplanarity with the Fe_2Pt ring, but are slightly asymmetrically bonded on the Fe–Pt edges. Hence the average Pt–C (bridge) internuclear distance is 2.06 Å, whilst the average Fe–C(bridge) distance is 1.96 Å. For the Fe(μ-CO)Fe group the two Fe–C distances are the same.

The terminal CO ligands all have near-linear geometry [M–C–O angles range from 174(1) to 179(2)°], with C–O distances of 1.13(2)—1.19(2) Å.

The geometry about the two platinum atoms shows only minor deviations from planarity. The two triphenylphosphine ligands display the usual geometry with a slight but consistent ' bending back ' of the phenyl rings away from the metal centres [Pt–P–C angles range from 119.3(3) to 112.7(4)°, whilst C–P–C angles are in the range 105.4(5) to 101.8(3)°]. The Pt–P bonding distances of 2.285(4) and 2.249(3) Å are similar to those found in [$Fe_2Pt(CO)_9(PPh_3)$] [2.30(1) Å],[18] [$Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2$] [2.310(3) Å],[19] and [$Pt_4(CO)_5(PPhMe_2)_4$] [2.30—2.26(3) Å].[20] The stereoscopic view of the unit cell given in Figure 3 shows with unusual clarity the mode of packing of the anion with the cation, and the stereochemical relationships of the phenyl rings of the phosphine ligands.

The configuration of the cation $N(PPh_3)_2^+$ in (1b) is of

TABLE 4

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for the compound [$Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2$], (2)

Atom	*x*	*y*	*z*
Pt(1)	0.915 37(7)	0.185 30(3)	0.096 31(2)
Pt(2)	0.927 12(7)	0.349 68(3)	0.148 45(2)
Fe(1)	0.994 0(2)	0.321 8(1)	0.061 42(6)
Fe(2)	1.127 0(2)	0.261 7(1)	0.138 97(6)
H(1)	1.051 9	0.161 3	0.139 9
H(2)	0.921 6	0.402 8	0.091 6
C(01)	0.779 4(11)	0.188 8(7)	0.050 4(4)
O(01)	0.689 1(10)	0.187 2(5)	0.019 1(3)
C(02)	0.951 9(15)	0.323 4(7)	0.213 0(4)
O(02)	0.955 7(10)	0.309 0(5)	0.254 1(3)
C(11)	1.090 7(16)	0.249 4(8)	0.037 9(5)
O(11)	1.137 6(12)	0.200 7(6)	0.015 3(3)
C(12)	1.077(2)	0.411 1(9)	0.046 9(5)
O(12)	1.124 5(11)	0.469 1(6)	0.034 7(3)
C(13)	0.880(2)	0.339 5(8)	0.013 9(5)
O(13)	0.795 4(12)	0.348 9(6)	−0.018 5(3)
C(21)	1.174 1(16)	0.242 4(8)	0.199 0(5)
O(21)	1.212 1(11)	0.230 4(6)	0.241 6(3)
C(22)	1.180(2)	0.356 4(9)	0.136 1(5)
O(22)	1.261 6(11)	0.415 5(6)	0.136 4(3)
C(23)	1.251(2)	0.204 1(8)	0.123 4(5)
O(23)	1.327 6(13)	0.159 9(6)	0.108 1(4)
P(1)	0.878 5(4)	0.052 3(2)	0.122 5(1)
C(31)	0.746 4(15)	0.006 6(7)	0.093 4(4)
C(32)	0.736 9(16)	−0.062 1(7)	0.062 0(4)
C(33)	0.626(2)	−0.097 5(8)	0.040 8(5)
C(34)	0.518(2)	−0.067 1(9)	0.049 0(5)
C(35)	0.502(2)	−0.000 1(9)	0.084 9(5)
C(36)	0.627 7(15)	0.033 6(7)	0.102 2(4)
C(41)	0.999 0(15)	−0.015 2(7)	0.105 9(4)
C(42)	1.061 1(16)	−0.000 2(7)	0.070 7(4)
C(43)	1.154(2)	−0.052 6(8)	0.057 3(5)
C(44)	1.185 5(16)	−0.129 7(8)	0.082 8(5)
C(45)	1.128(2)	−0.144 6(9)	0.124 0(5)
C(46)	1.032 4(16)	−0.092 8(8)	0.136 2(5)
C(51)	0.870 0(14)	0.040 1(6)	0.190 0(4)
C(52)	0.924 5(15)	0.102 3(7)	0.216 8(4)
C(53)	0.922(2)	0.094 6(9)	0.265 6(5)
C(54)	0.869(2)	0.025 3(8)	0.284 4(5)
C(55)	0.823 2(15)	−0.036 4(7)	0.253 2(4)
C(56)	0.818 3(15)	−0.029 6(7)	0.205 3(4)
P(2)	0.761 7(4)	0.443 4(2)	0.146 3(1)
C(61)	0.630(2)	0.417 2(9)	0.100 8(5)
C(62)	0.608(2)	0.330 8(9)	0.091 8(5)
C(63)	0.490(2)	0.308 1(10)	0.060 3(6)
C(64)	0.410(2)	0.368 1(9)	0.039 2(5)
C(65)	0.444(2)	0.450 8(9)	0.046 0(6)
C(66)	0.545(2)	0.476 6(8)	0.077 3(5)
C(71)	0.703(2)	0.460 3(6)	0.202 3(4)
C(72)	0.786 1(15)	0.484 0(7)	0.244 8(4)
C(73)	0.735(2)	0.503 4(7)	0.285 0(4)
C(74)	0.611(2)	0.502 0(8)	0.286 7(5)
C(75)	0.517(2)	0.474 1(11)	0.241 1(7)
C(76)	0.570(2)	0.457 8(8)	0.203 2(5)
C(81)	0.799 3(16)	0.550 1(8)	0.131 7(5)
C(82)	0.869(2)	0.559 2(8)	0.093 5(5)
C(83)	0.902(2)	0.641 0(10)	0.075 0(5)
C(84)	0.868(2)	0.709 4(9)	0.099 0(5)
C(85)	0.794(2)	0.698 8(9)	0.136 6(5)
C(86)	0.765(2)	0.616 7(9)	0.153 5(5)

TABLE 5

Internuclear distances (Å) and bond angles (°) for [$Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_2)_2$], (2), with estimated standard deviations in parentheses

(*a*) Distances

Pt(1)–Pt(2)	2.998(2)	C(02)–O(02)	1.16(2)
Pt(1)–Fe(1)	2.604(3)	C(11)–O(11)	1.17(3)
Pt(1)–Fe(2)	2.696(3)	C(12)–O(12)	1.14(3)
Pt(2)–Fe(1)	2.694(3)	C(13)–O(13)	1.18(3)
Pt(2)–Fe(2)	2.631(3)	C(21)–O(21)	1.21(3)
Fe(1)–Fe(2)	2.567(4)	C(22)–O(22)	1.29(4)
Pt(1)–C(01)	1.79(2)	C(23)–O(23)	1.22(3)
Pt(2)–C(02)	1.82(2)	Pt(1)–P(1)	2.307(4)
Fe(1)–C(11)	1.74(3)	Pt(2)–P(2)	2.329(4)
Fe(1)–C(12)	1.75(3)	P(1)–C(31)	1.79(2)
Fe(1)–C(13)	1.70(3)	P(1)–C(41)	1.81(3)
Fe(2)–C(21)	1.70(2)	P(1)–C(51)	1.91(2)
Fe(2)–C(22)	1.63(3)	P(2)–C(61)	1.79(3)
Fe(2)–C(23)	1.74(3)	P(2)–C(71)	1.80(3)
C(01)–O(01)	1.20(3)	P(2)–C(81)	1.82(2)

Mean C–C (phenyl) = 1.39

(*b*) Angles

(*i*) About Pt(1)

Pt(2)–Pt(1)–Fe(1)	57.0(1)	Pt(2)–Pt(1)–P(1)	130.7(7)
Pt(2)–Pt(1)–Fe(2)	54.7(1)	Fe(1)–Pt(1)–P(1)	169.0(8)
Pt(2)–Pt(1)–C(01)	106.5(8)	Fe(2)–Pt(1)–C(01)	147.5(8)
Fe(1)–Pt(1)–Fe(2)	57.9(1)	Fe(2)–Pt(1)–P(1)	117.2(8)
Fe(1)–Pt(1)–C(01)	89.8(9)	P(1)–Pt(1)–C(01)	95.2(9)

(*ii*) About Pt(2)

Pt(1)–Pt(2)–Fe(1)	54.2(1)	Pt(1)–Pt(2)–P(2)	125.5(7)
Pt(1)–Pt(2)–Fe(2)	56.8(1)	Fe(1)–Pt(2)–P(2)	113.8(9)
Pt(1)–Pt(2)–C(02)	105.3(7)	Fe(2)–Pt(2)–C(02)	89.1(7)
Fe(1)–Pt(2)–Fe(2)	57.6(1)	Fe(2)–Pt(2)–P(2)	169.6(8)
Fe(2)–Pt(2)–C(02)	89.1(9)	P(2)–Pt(2)–C(02)	99.3(9)

(*iii*) About Fe(1)

Pt(1)–Fe(1)–Pt(2)	68.9(1)	Pt(1)–Fe(1)–C(12)	167.6(9)
Pt(1)–Fe(1)–Fe(2)	62.8(1)	Pt(2)–Fe(1)–C(12)	107.1(9)
Pt(2)–Fe(1)–Fe(2)	60.0(1)	Fe(2)–Fe(1)–C(12)	106.2(9)
Pt(1)–Fe(1)–C(11)	80.6(9)	Pt(1)–Fe(1)–C(13)	100.0(9)
Pt(2)–Fe(1)–C(11)	135.4(8)	Pt(2)–Fe(1)–C(13)	112.9(9)
Fe(2)–Fe(1)–C(11)	78.1(9)	Fe(2)–Fe(1)–C(13)	139.2(9)

(*iv*) About Fe(2)

Pt(1)–Fe(2)–Pt(2)	68.5(1)	Pt(1)–Fe(2)–C(22)	133.0(8)
Pt(1)–Fe(2)–Fe(1)	59.3(1)	Pt(2)–Fe(2)–C(22)	78.8(12)
Pt(2)–Fe(2)–Fe(1)	62.4(1)	Fe(1)–Fe(2)–C(22)	75.9(10)
Pt(1)–Fe(2)–C(21)	116.7(9)	Pt(1)–Fe(2)–C(23)	106.4(9)
Pt(2)–Fe(2)–C(21)	96.8(10)	Pt(2)–Fe(2)–C(23)	171.4(10)
Fe(1)–Fe(2)–C(21)	158.7(9)	Fe(1)–Fe(2)–C(23)	109.1(9)

(*v*) About the carbonyl carbon atoms

Pt(1)–C(01)–O(01)	177(1)	Pt(2)–C(02)–O(02)	173(2)
Fe(1)–C(11)–O(11)	168(2)	Fe(2)–C(21)–O(21)	177(2)
Fe(1)–C(12)–O(12)	176(2)	Fe(2)–C(22)–O(22)	167(3)
Fe(1)–C(13)–O(13)	177(2)	Fe(2)–C(23)–O(23)	178(2)

(*vi*) About the phosphorus atoms

Pt(1)–P(1)–C(31)	115.1(4)	Pt(2)–P(2)–C(61)	112.7(6)
Pt(1)–P(1)–C(41)	107.5(5)	Pt(2)–P(2)–C(71)	116.9(5)
Pt(1)–P(1)–C(51)	116.4(4)	Pt(2)–P(2)–C(81)	114.3(6)
C(31)–P(1)–C(41)	102.0(7)	C(61)–P(2)–C(71)	107.2(9)
C(31)–P(1)–C(51)	104.8(7)	C(61)–P(2)–C(81)	104.1(7)
C(41)–P(1)–C(51)	110.1(6)	C(71)–P(2)–C(81)	100.2(6)

(*vii*) About the bonded phenyl carbon atoms

P(1)–C(31)–C(36)	120(2)	P(2)–C(61)–C(66)	124(2)
P(1)–C(31)–C(32)	128(2)	P(2)–C(61)–C(62)	117(2)
P(1)–C(41)–C(46)	118(2)	P(2)–C(71)–C(76)	120(2)
P(1)–C(41)–C(42)	124(2)	P(2)–C(71)–C(72)	120(2)
P(1)–C(51)–C(56)	119(2)	P(2)–C(81)–C(86)	125(2)
P(1)–C(51)–C(52)	113(2)	P(2)–C(81)–C(82)	116(2)

(*viii*) Torsion angles in the metal cluster

Pt(2)–Fe(1)–Fe(2)–Pt(1)	80.1
Fe(2)–Pt(1)–Pt(2)–Fe(1)	71.5
Pt(2)–Pt(1)–Fe(1)–Fe(2)	66.1
Fe(1)–Pt(1)–Fe(2)–Pt(2)	69.9
Fe(2)–Pt(2)–Fe(1)–Pt(1)	70.0
Pt(1)–Pt(2)–Fe(2)–Fe(1)	65.6

interest, because both bent and linear P–N–P structures for this species have been observed in its salts. The bent arrangement is much more common, for example as found in $[N(PPh_3)_2][Cr_2(\mu\text{-}H)(CO)_{10}]$ [21] and $[N(PPh_3)_2][CoFe(CO)_8]$; [22] the P–N–P group is, however, linear in $[N(PPh_3)_2][V(CO)_6]$.[23] In (1b) (Figure 2) P(4)–N–P(3) = 138.1°, with P–N (average) = 1.585(10) Å. These values fall within the limits found in several structures containing the cation in a bent configuration, *viz.* 134.6(3)—139.0(7)°, with N–P distances 1.56(2)—1.59(2) Å.[21-23]

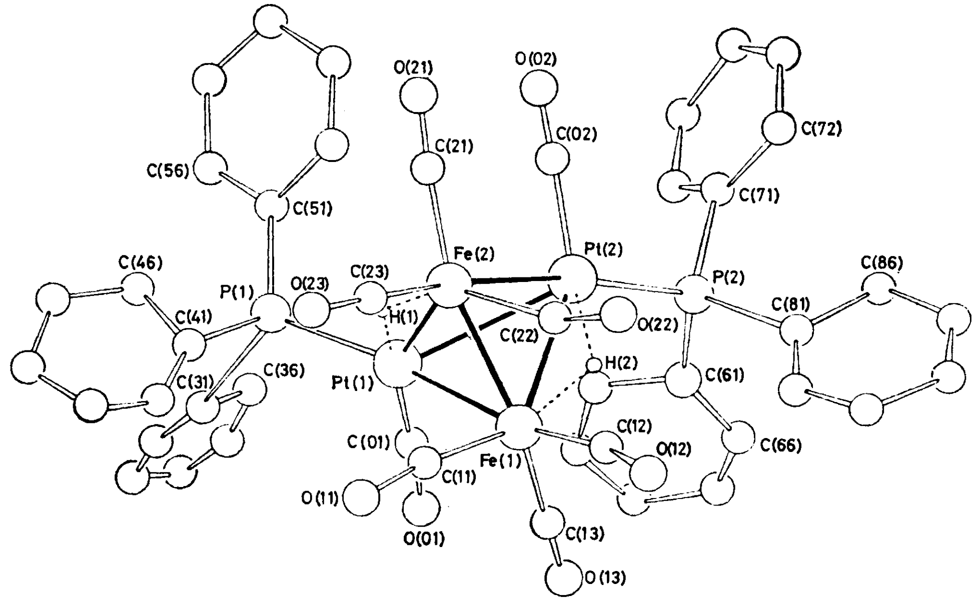


FIGURE 4 Molecular structure of the complex $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (2)

The molecular structure of the dihydrido-complex $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ (2) is shown in Figure 4, together with the atomic numbering scheme. Data from the *X*-ray diffraction study are summarised in Tables 4 and 5. It is immediately apparent that all the carbonyl ligands are terminally bound, as was indicated by the i.r. spectrum. Moreover, each platinum atom carries a CO ligand, as well as a PPh_3 group.

Whereas the hydrido-ligand site in (1b) was not clearly defined, the situation is much more satisfactory for (2). The angles Pt(2)–Fe(1)–C(13) and Pt(1)–Fe(2)–C(21) are widened to 112.9(9) and 116.7(9)°, respectively, and these are markedly larger than the other *cis* M–M–C angles which range from 76 to 109° (Table 5). The relatively large Pt(2)–Fe(1)–C(13) and Pt(1)–Fe(2)–C(21) angles suggest the presence of hydrido-ligands along the Fe(1)–Pt(2) and Fe(2)–Pt(1) edges, and in accord with this, these are the longer Fe–Pt separations (Table 5). Moreover, calculations [17] indicated potential energy minima for hydrido-ligand co-ordination on these edge sites. Still further evidence for the location of the hydrido-ligands derives from projection of the structure onto the $\overline{\text{Fe(1), Pt(1), Pt(2)}}$ and $\overline{\text{Fe(2), Pt(1), Pt(2)}}$ planes which show that the CO ligands on Fe(2) and Fe(1), respectively, are staggered relative to the M–M bonds.[15]

With the hydrido-ligands in the position indicated (Figure 4), the molecule has an approximate C_2 axis passing through the midpoints of Fe(1)–Fe(2) and Pt(1)–Pt(2). The equivalence of the phosphine ligands in the ^{31}P n.m.r. spectrum is thus explained.

Apart from differences which may be attributed to the bridging ligands, there is a strong resemblance between corresponding metal–metal separations in (1b) and (2), summarised in Table 6. The usual lengthening of metal–metal distances by μ-hydrido-ligands and shortening by μ-carbonyl groups is apparent. The Pt–Pt separations in (1b) and (2) are seen to be very similar, and compare closely with that [2.987(4) Å] found [12] in $[Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$. In the trimetal complex $[FePt_2(CO)_5\{P(OPh)_3\}_3]$ the Pt–Pt distance [2.633(1) Å] is significantly less. The compound $[Co_2Pt_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$ is considered to have a ' butterfly ' structure, and it is tempting to give this description to the two di-irondiplatinum species (1b) and (2), which are also 58-electron complexes. Moreover, the dihedral

TABLE 6

Comparison of the corresponding internuclear separations (Å) for the metal atom frameworks of $[Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]^-$, (1b), and $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (2)

Complex (1b)		Complex (2)	
Pt(1)–Pt(2)	2.966(1)	2.998(2)	Pt(1)–Pt(2)
Fe(1)–Pt(2)	2.555(2) [a]	2.604(3)	Fe(1)–Pt(1)
Fe(2)–Pt(2)	2.562(2) [a]	2.696(3) [b]	Fe(2)–Pt(1)
Fe(1)–Pt(1)	2.756(2) [b]	2.694(3) [b]	Fe(1)–Pt(2)
Fe(2)–Pt(1)	2.626(2)	2.631(3)	Fe(2)–Pt(2)
Fe(1)–Fe(2)	2.522(2) [a]	2.567(4)	Fe(1)–Fe(2)

[a] Bridging CO ligand. [b] Bridging H ligand.

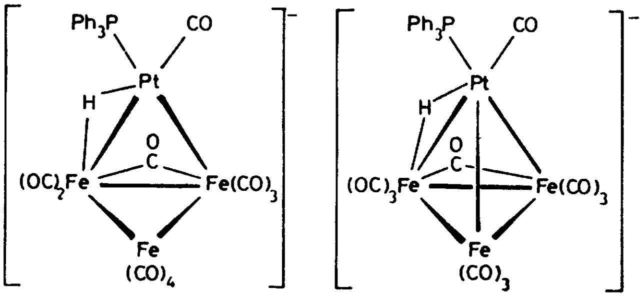
angles between the planes Pt(1), Fe(1), Fe(2) and Pt(2), Fe(1), Fe(2) in (1b) and (2) are 80.1°, indicating a 10° distortion from regular tetrahedral geometry. However, it may not be correct to assume that there is no direct Pt–Pt bonding on the basis of the observed Pt–Pt separations even though these are greater than the sum (2.6 Å) of the covalent radii of platinum. In the related 58-electron complex [Os$_2$Pt$_2$(μ-H)$_2$(CO)$_8$(PPh$_3$)$_2$] the Pt–Pt distance [3.206(1) Å] is significantly longer.[24] As direct metal–metal bonding interactions gradually become weaker, there seems no reason to expect a clear demarcation between a *closo* tetrahedral structure on the one hand and an open butterfly structure on the other. Indeed, in some instances dynamic behaviour observed in solution may be facilitated by flexing of the metal framework between tetrahedral and butterfly structures of similar energies, thereby allowing site exchange of peripheral ligands *via* edges or faces.

Although the structures of the anion of (1b) and of the neutral complex (2) as depicted in Figures 1 and 4 are derived from different enantiomers, the conversion of the former into the latter by protonation can be represented as in the Scheme, where both structures are shown with the same chirality.[*]

A synchronous rotation of the three bridging carbonyls and the one terminal ligand [C(7)O(7) of Figure 1, this group being close to the basal plane defined by Fe(1), Fe(2), Pt(2)], in the direction indicated by the arrows, can be seen to transform the arrangement of CO ligands observed in the anion into that found in (2). This movement is rather similar to that proposed to account for the dynamic behaviour of [Co$_4$(CO)$_{12}$].[25]

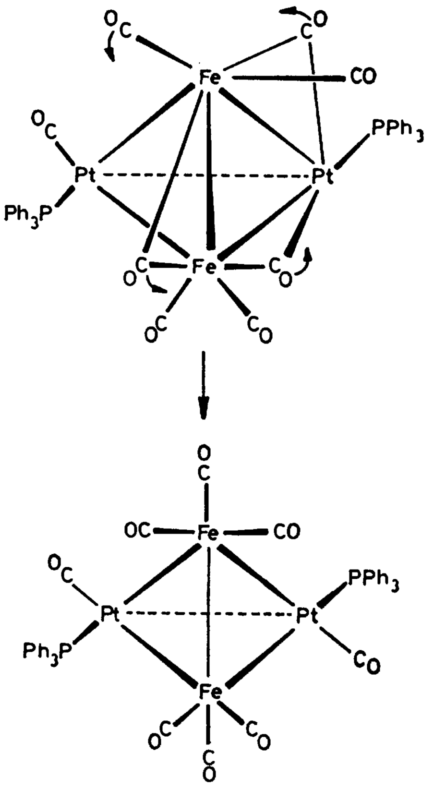
The successful addition of two PtPPh$_3$ groups to [Fe$_2$(μ-H)(μ-CO)$_2$(CO)$_6$]$^-$ prompted a study of the reaction of [Pt(C$_2$H$_4$)$_2$(PPh$_3$)] with the 48-electron tri-iron anion [Fe$_3$(μ-H)(μ-CO)(CO)$_{10}$]$^-$. Even though the latter is electronically saturated, in contrast to [Os$_3$(μ-H)$_2$(CO)$_{10}$], it was anticipated that transfer of a CO ligand from iron to the incoming platinum atom would provide an electron-deficient vacant site on the iron triangle, enabling formation of a tetranuclear Fe$_3$Pt cluster.

Reaction of [Pt(C$_2$H$_4$)$_2$(PPh$_3$)] with the salt [NEt$_3$H][Fe$_3$(μ-H)(μ-CO)(CO)$_{10}$] in diethyl ether at room temperature afforded black crystals which can be formulated as [NEt$_3$H][Fe$_3$Pt(μ-H)(μ-CO)(CO)$_{10}$(PPh$_3$)], (3), on the basis of microanalysis, an i.r. band at 1 637 cm^{-1}, corresponding to a bridging CO group, and a resonance in the ^{1}H n.m.r. spectrum at τ 25.90 [d, J(PH) 4] indicative of a hydrido-ligand. The high-field resonance had ^{195}Pt satellites, and the magnitude of the coupling (465 Hz) showed that the hydride was attached to the platinum atom. A ^{13}C n.m.r. spectrum of (3) at −90 °C revealed only one resonance for the CO ligands, demonstrating dynamic behaviour *via* a low energy exchange process. In the absence of confirmation through an X-ray crystallographic study, the most likely structures for the anion are (3a) or (3b). The related 60-electron complex [Os$_3$Pt(μ-H)$_2$(CO)$_{11}${P(cyclo-C$_6$H$_{11}$)$_3$}] almost certainly has a butterfly arrangement of the metal atoms with an Os(μ-H)Pt bridge, because such a structure has been established by X-ray diffraction for its analogue [Os$_3$Pt(μ-H)$_2$(CO)$_{10}$(PPh$_3$)$_2$].[19] In these circumstances structure (3a) seems most probable for the tri-iron-platinum anion.



(3)

In an attempt to prepare a neutral tri-ironmonoplatinum complex, a reaction between the salts [NEt$_3$H][Fe$_3$(μ-H)(μ-CO)(CO)$_{10}$] and [Pt(cod)(C$_8$H$_{13}$)][BF$_4$] [26] (cod = cyclo-octa-1,5-diene) was investigated. Unfortunately, no Fe$_3$Pt species was isolated; extensive decomposition occurred accompanied by formation of



SCHEME Possible mode for conversion of the anion of (1) into the metal complex (2) on protonation. Hydrido-ligands are omitted

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[*] As both structures belong to centrosymmetric space groups, the crystals comprise both enantiomers present in equal numbers.

the complex [$Fe_2Pt(CO)_8$(cod)], (4), which was fully identified *via* an *X*-ray crystallographic study.

The molecular structure and atomic numbering scheme are shown in Figure 5, and the results are summarised in Tables 7—9. The *X*-ray diffraction study established a triangular array of two iron atoms and one platinum atom, and the molecule is thus closely related to the previously prepared complexes [$Fe_2Pt(CO)_8L_2$] and [$Fe_2Pt(CO)_9L$] (L = PPh_3, PPh_2Me, $PPhMe_2$, or PMe_3),[4] one of which, [$Fe_2Pt(CO)_9(PPh_3)$], has had its structure determined by *X*-ray diffraction methods.[18]

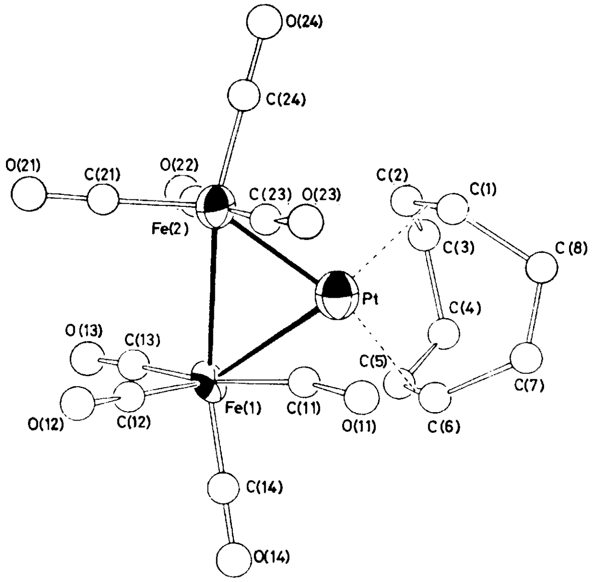

FIGURE 5 Molecular structure of the complex [$Fe_2Pt(CO)_8(cyclo\text{-}C_8H_{12})$], (4)

The geometry about the iron atoms in both (4) and in [$Fe_2Pt(CO)_9(PPh_3)$] is very similar, *i.e.* approximately octahedral, whilst that of the platinum atoms tends towards square planar. The intermetallic distances in (4) (Table 8) are very similar to those found [18] in [$Fe_2Pt(CO)_9(PPh_3)$] [Fe–Fe 2.780, Fe–Pt 2.605 and 2.526 Å]. It is rather surprising that in both compounds the Fe–Fe separations are longer than the Fe–Pt distances, but nevertheless they are similar to that found [22] [2.787(2) Å] in the dianion [$Fe_2(CO)_8$]$^{2-}$.

The cyclo-octa-1,5-diene ligand in (4) adopts its customary bidentate tub-like configuration, similar to that found in many other platinum complexes.[27,28] The midpoints of the co-ordinated olefinic bonds are almost coplanar with the Fe_2Pt triangle, and the angle between the planes Pt, C(1), C(2) and Pt, C(5), C(6) is 94.7°. Since Fe(1)–Pt–Fe(2) is only 63.8(1)°, the geometry about the platinum is rather distorted square-planar.

TABLE 7

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for [$Fe_2Pt(CO)_8$(cod)], (4)

Atom	*x*	*y*	*z*
Pt	0.262 84(4)	0.243 73(6)	0.782 79(3)
Fe(1)	0.349 9(2)	0.297 6(2)	0.927 2(1)
Fe(2)	0.317 4(2)	0.029 6(2)	0.872 3(1)
C(1)	0.143(2)	0.165(2)	0.688 3(11)
C(2)	0.237(2)	0.157(2)	0.653 3(8)
C(3)	0.299 8(14)	0.254(2)	0.591 4(10)
C(4)	0.281(2)	0.410(2)	0.611 7(12)
C(5)	0.275(2)	0.441(2)	0.707 4(9)
C(6)	0.183(2)	0.453(2)	0.751 7(10)
C(7)	0.073(2)	0.411(2)	0.722 7(14)
C(8)	0.059 6(15)	0.290(2)	0.665 5(12)
C(11)	0.204 4(15)	0.318(2)	0.931 1(9)
O(11)	0.113 7(8)	0.345 6(12)	0.942 7(7)
C(12)	0.371 0(12)	0.254(2)	1.039 4(8)
O(12)	0.379 9(9)	0.230(2)	1.110 5(7)
C(13)	0.491 8(15)	0.272(2)	0.889 0(8)
O(13)	0.576 2(7)	0.265 9(15)	0.868 2(8)
C(14)	0.371 9(14)	0.482(2)	0.927 1(9)
O(14)	0.383 1(10)	0.603 8(11)	0.930 1(7)
C(21)	0.191 1(15)	0.037(2)	0.928 6(9)
O(21)	0.104 4(12)	0.029 3(13)	0.958 5(10)
C(22)	0.404 7(15)	−0.039(2)	0.950 5(9)
O(22)	0.462 0(9)	−0.092 6(13)	1.003 6(7)
C(23)	0.411 7(14)	0.064(2)	0.787 6(9)
O(23)	0.472 4(9)	0.069 1(12)	0.732 1(7)
C(24)	0.272 9(15)	−0.129(2)	0.823 5(9)
O(24)	0.244 5(8)	−0.231 6(11)	0.788 8(7)

TABLE 8

Internuclear distances (Å) and bond angles (°) for [$Fe_2Pt(CO)_8$(cod)], (4)

(*a*) Distances

Pt–Fe(1)	2.561(3)	C(1)–C(2)	1.29(3)
Pt–Fe(2)	2.553(3)	C(2)–C(3)	1.54(2)
Fe(1)–Fe(2)	2.704(4)	C(3)–C(4)	1.52(3)
		C(4)–C(5)	1.53(2)
Pt–C(1)	2.22(2)	C(5)–C(6)	1.33(3)
Pt–C(2)	2.22(2)	C(6)–C(7)	1.48(4)
Pt–C(5)	2.21(2)	C(7)–C(8)	1.46(3)
Pt–C(6)	2.26(2)	C(8)–C(1)	1.60(3)
Fe(1)–C(11)	1.80(2)	C(11)–O(11)	1.16(2)
Fe(1)–C(12)	1.83(1)	C(12)–O(12)	1.14(2)
Fe(1)–C(13)	1.87(2)	C(13)–O(13)	1.09(2)
Fe(1)–C(14)	1.77(2)	C(14)–O(14)	1.15(2)
Fe(2)–C(21)	1.79(2)	C(21)–O(21)	1.17(2)
Fe(2)–C(22)	1.76(2)	C(22)–O(22)	1.20(2)
Fe(2)–C(23)	1.80(2)	C(23)–O(23)	1.15(2)
Fe(2)–C(24)	1.77(2)	C(24)–O(24)	1.16(2)
Pt–C(11)	2.54(2)		
Pt–C(3)	2.50(2)		

(*b*) Angles

Fe(1)–Pt–Fe(2)	63.83(8)	C(13)–Fe(1)–C(14)	89.2(7)
Pt–Fe(1)–Fe(2)	57.95(7)	C(21)–Fe(2)–C(22)	101.6(7)
Pt–Fe(2)–Fe(1)	58.22(8)	C(21)–Fe(2)–C(24)	88.7(8)
		C(22)–Fe(2)–C(23)	100.8(8)
Pt–Fe(1)–C(11)	68.6(4)	C(22)–Fe(2)–C(24)	100.3(8)
Pt–Fe(1)–C(12)	150.3(6)	C(23)–Fe(2)–C(24)	91.8(7)
Pt–Fe(1)–C(13)	94.6(4)		
Pt–Fe(1)–C(14)	105.0(5)	Fe(1)–C(11)–O(11)	170(1)
		Fe(1)–C(12)–O(12)	177(1)
Pt–Fe(2)–C(21)	90.8(5)	Fe(1)–C(13)–O(13)	175(1)
Pt–Fe(2)–C(22)	147.0(6)	Fe(1)–C(14)–O(14)	177(1)
Pt–Fe(2)–C(23)	67.7(5)	Fe(2)–C(21)–O(21)	172(1)
Pt–Fe(2)–C(24)	110.5(5)	Fe(2)–C(22)–O(22)	177(1)
		Fe(2)–C(23)–O(23)	172(1)
C(11)–Fe(1)–C(12)	97.7(6)	Fe(2)–C(24)–O(24)	178(1)
C(11)–Fe(1)–C(14)	92.7(7)	C(8)–C(1)–C(2)	122(1)
C(12)–Fe(1)–C(13)	98.5(6)	C(1)–C(2)–C(3)	133(2)
C(12)–Fe(1)–C(14)	101.7(7)	C(2)–C(3)–C(4)	111(1)
C(1)–Pt–C(2)	33.7(7)	C(3)–C(4)–C(5)	114(1)
C(5)–Pt–C(6)	34.5(7)	C(4)–C(5)–C(6)	125(2)
		C(5)–C(6)–C(7)	126(2)
		C(6)–C(7)–C(8)	120(2)
		C(7)–C(8)–C(1)	111(1)

However, if Fe(1)–Pt–Fe(2) were larger the already long Fe–Fe separation would need to increase still further.

The reaction which produced complex (4) was obviously a complicated one, since the starting anion was an Fe_3 species. An attempt to prepare (4) by a more orthodox route, *viz.* from $[Fe_2(CO)_9]$ and $[Pt(cod)_2]$, failed, extensive decomposition taking place.

TABLE 9

Some least-squares planes * for compound (4); distances (Å) of atoms from the planes are given in square brackets

(*a*) Pt, Fe(1), Fe(2)

$$11.136x + 0.027y - 6.720z = 4.393$$

[C(1) −0.706, C(2) 0.579, C(5) 0.643, C(6) −0.670]

(*b*) Pt, C(1), C(2)

$$-1.140x + 8.761y - 5.601z = 3.000$$

[Fe(1) − 0.454]

(*c*) Pt, C(5), C(6)

$$6.189x + 4.105y + 11.704z = 0.077$$

[Fe(2) 0.510]

(*d*) C(1), C(2), C(5), C(6)

$$5.230x - 3.402y + 13.047z = -3.852$$

[C(3) −0.774, C(7) −0.780]

(*e*) C(3), C(4), C(7), C(8)

$$5.069x - 3.530y + 13.057z = -4.897$$

[C(1) 0.967, C(2) 1.016, C(5) 0.910, C(6) 0.986]

The dihedral angle between planes (*b*) and (*c*) is 94.7°

* *x*, *y*, and *z* are fractional crystal co-ordinates.

EXPERIMENTAL

N.m.r. (^1H, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$) were recorded on JEOL PFT and PS 100 spectrometers, with ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.) and ^{31}P shifts relative to H_3PO_4 (external) taken as positive to low frequency (high field). Infrared spectra were measured with Perkin-Elmer 257 and 457 spectrophotometers. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction b.p. 40—60 °C. The compound $[Pt(C_2H_4)_2(PPh_3)]$ was prepared as described previously.[6]

Synthesis of Salts of the Anion $[Fe_2Pt_2(\mu-H)(\mu-CO)_3(CO)_5(PPh_3)_2]^-$.—(*a*) To a solution of $[NEt_4][Fe_2(\mu-H)(\mu-CO)_2(CO)_6]$ (0.45 g, 1 mmol) in thf (20 cm^3) was added a solution of $[Pt(C_2H_4)_2(PPh_3)]$ (1.03 g, 2 mmol) in the same solvent (20 cm^3). After 0.5 h, the dark red-brown mixture was filtered, and diethyl ether added to the solution, affording red-brown *crystals* of $[NEt_4][Fe_2Pt_2(\mu-H)(\mu-CO)_3(CO)_5(PPh_3)_2]$, (1a) (1.0 g, 70%), m.p. 130—136 °C (decomp.) (Found: C, 45.4; H, 4.0; N, 1.0. $C_{52}H_{51}Fe_2NO_8P_2Pt_2$ requires C, 45.2; H, 3.7; N, 1.0%); $\nu_{max.}$(CO) (Nujol) at 2 032m, 1 967s, 1 926s, 1 895m, 1 874m, 1 796m, 1 757s, and 1 729s cm^{-1}. N.m.r.: ^1H ([$^2H_6$]acetone, −90 °C), τ 2.74 (m, 30 H, Ph), 6.61 [q, 8 H, CH_2, *J*(HH) 7], 8.89 [t, 12 H, Me, *J*(HH) 7], and 21.97 [d, 1 H, Fe(μ-H)Pt, *J*(PH) 15 Hz]; ^{31}P ([$^2H_6$]acetone, −70 °C), δ −42.0 [d, PPt, *J*(PP) 9, *J*(PtP) 4 740 and 255] and −19.5 p.p.m. [d, PPt, *J*(PP) 9, *J*(PtP) 3 142 and 108 Hz].

(*b*) In an analogous manner $[N(PPh_3)_2][Fe_2(\mu-H)(\mu-CO)_2(CO)_6]$ (0.87 g, 1 mmol) and $[Pt(C_2H_4)_2(PPh_3)]$ (1.03 g, 2 mmol) gave, after crystallisation from acetone–diethyl ether, red-brown plate-like *crystals* of the diacetone solvate $[N(PPh_3)_2][Fe_2Pt_2(\mu-H)(\mu-CO)_3(CO)_5(PPh_3)_2]\cdot 2Me_2CO$, (1b) (1.2 g, 63%), m.p. 110—115 °C (decomp.) (Found: C, 52.9; H, 4.2; N, 0.7. $C_{80}H_{61}Fe_2NO_8P_4Pt_2\cdot C_6H_{12}O_2$ requires C, 54.2; H, 3.9; N, 0.7%); $\nu_{max.}$(CO) (Nujol) at 2 040m, 1 969s, 1 923s, 1 899s, 1 880m, 1 803m, and 1 759s, br cm^{-1}. ^1H n.m.r. ([$^2H_6$]acetone, −90 °C), τ 2.40 and 2.80 (m, 60 H, Ph) and 22.02 [d, 1 H, Fe(μ-H)Pt, *J*(PH) 15 Hz].

Synthesis of the Complex $[Fe_2Pt_2(\mu-H)_2(CO)_8(PPh_3)_2]$.—Three drops of $HBF_4\cdot 2Et_2O$ were added to a stirred diethyl ether (20 cm^3) suspension of the salt (1a) (0.5 g, 0.36 mmol), which rapidly dissolved to give a dark red solution. Solvent was removed *in vacuo*, and the residue extracted with light petroleum (50 cm^3). Reduction in volume, and cooling, gave black *crystals* of $[Fe_2Pt_2(\mu-H)_2(CO)_8(PPh_3)_2]$, (2) (0.25 g, 55%) (Found: C, 42.2; H, 2.7. $C_{44}H_{32}Fe_2O_8P_2Pt_2$ requires C, 42.2; H, 2.6%); $\nu_{max.}$(CO) (cyclohexane) at 2 033s, 2 015s, 1 983m, 1 955s, 1 945m (sh), and 1 929w cm^{-1}. N.m.r.: ^1H ([$^2H_6$]acetone), τ 2.48 (m, 30 H, Ph) and 20.60 [t, 2 H, Fe(μ-H)Pt, *J*(PH) 10, *J*(PtH) 595 Hz]; ^{31}P ([$^2H_6$]acetone), δ −33.4 p.p.m. [s, PPt, *J*(PP) 8, *J*(PtP) 2 591 and 168, *J*(PtPt) 3 804 Hz].

Preparation of the Salt $[NEt_3H][Fe_3Pt(\mu-H)(\mu-CO)(CO)_{10}(PPh_3)]$.—The compound $[Pt(C_2H_4)_2(PPh_3)]$ (0.40 g, 0.78 mmol) was added to a stirred diethyl ether (60 cm^3) solution of $[NEt_3H][Fe_3(\mu-H)(\mu-CO)(CO)_{10}]$ (0.42 g, 0.78 mmol). After 0.5 h, black crystals were deposited. Removal of solvent and washing the residue with light petroleum (3 × 5 cm^3) gave black *microcrystals* of the salt $[NEt_3H][Fe_3Pt(\mu-H)(\mu-CO)(CO)_{10}(PPh_3)]$, (3) (0.54 g, 52%) (Found: C, 40.6; H, 3.3; N, 1.3. $C_{35}H_{32}Fe_3NO_{11}PPt$ requires C, 40.6; H, 3.1; N, 1.3%); $\nu_{max.}$(CO) (Nujol) at 2 049m, 2 000s, 1 957vs, 1 938s, 1 915s, 1 898s, and 1 637m, br cm^{-1}. N.m.r.: ^1H ([$^2H_6$]acetone), τ 2.73 (m, 15 H, Ph), 6.16 (s, 1 H, NH), 6.56 [q, 6 H, CH_2, *J*(HH) 8], 8.60 [t, 9 H, Me, *J*(HH) 8], and 25.90 [d, 1 H, Fe(μ-H)Pt, *J*(PH) 4, *J*(PtH) 465 Hz]; ^{31}P ([$^2H_6$]acetone), δ −20.5 p.p.m. [s, PPt, *J*(PtP) 2 734 Hz]; ^{13}C (−90 °C) {[$^2H_2$]dichloromethane–[$^2H_1$]chloroform, in the presence of $[Cr(acac)_3]$}, δ 210.4 (br, CO), 132.8, 130.7, 128.2 [br, Ph], 62.9 (CH_2), and 17.6 p.p.m. (Me).

Preparation of the Complex $[Fe_2Pt(CO)_8(cod)]$.—A dichloromethane (20 cm^3) solution of $[NEt_3H][Fe_3(\mu-H)(\mu-CO)(CO)_{10}]$ (0.57 g, 1 mmol) was treated with $[Pt(cod)(C_8H_{13})][BF_4]$ (0.48 g, 1 mmol) in the same solvent (10 cm^3). After stirring (15 h), the solvent was removed *in vacuo*, and the dark residue extracted with light petroleum (2 × 20 cm^3). The red solution was concentrated and cooled (−70 °C) to give black *crystals* of $[Fe_2Pt(CO)_8(cod)]$, (4) (0.15 g, 23%), m.p. 94—98 °C (decomp.) (Found: C, 30.3; H, 2.1. $C_{16}H_{12}Fe_2O_8Pt$ requires C, 30.1; H, 1.8%); $\nu_{max.}$(CO) (cyclohexane) at 2 065m, 2 013s, 1 995w, 1 981m, 1 969m, and 1 945w cm^{-1}. ^1H n.m.r. ([$^2H_1$]chloroform), τ 4.70 [s br, 4 H, CH, *J*(PtH) 66 Hz], 7.70 and 7.84 (s, 8 H, CH_2).

Crystal-structure Determinations of (1b), (2), *and* (4).—$[N(PPh_3)_2][Fe_2Pt_2(\mu-H)(\mu-CO)_3(CO)_5(PPh_3)_2]$, (1b). Crystals of (1b) grow as very thin, red-brown plates. Diffracted intensities were recorded at 200 K for a crystal of dimensions 0.35 × 0.35 × 0.05 mm. Of the 14 555 independent intensities measured for $2\theta \leqslant 50°$ on a Syntex $P2_1$ four-circle diffractometer, 8 768 for which $|F| > 5.0\sigma(F)$ were used for the solution and refinement of the structure. Check reflections 1 1 0 and 2 0 0 were remeasured every 50 reflections, and showed some 12% decay over the 398 h of data collection. Correction was made for this decay, and also for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data for (1b). $C_{80}H_{61}Fe_2NO_8P_4Pt_2\cdot C_6H_{12}O_2$, $M =$ 1 906, Monoclinic, $a = 25.05(3)$, $b = 14.28(1)$, $c = 23.99(2)$ Å, $\beta = 106.84(7)°$, $U = 8\ 218.8$ Å^3, $Z = 4$, $D_c = 1.49$ g cm^{-3}, $F(000) = 3\ 784$. Space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å (throughout), μ(Mo-K_α) = 37.0 cm^{-1}.

The structure was solved by heavy-atom methods for all non-hydrogen atoms. Electron density difference maps revealed also the presence of two crystallographically independent molecules of acetone, whose atom co-ordinates have been included in Table 1. On the final difference map a further peak *ca.* 1.7 e Å^{-3} appeared on the centre of inversion at 0 0 $\frac{1}{2}$, with other similar ill defined peaks in the neighbourhood. The ^{1}H n.m.r. spectrum of (1b) had given evidence for the presence of diethyl ether as well as of acetone in the crystalline sample; if this interpretation is correct, the molecules of diethyl ether must be disordered and are, of course, thermally active. Inclusion of a single oxygen atom at 0 0 $\frac{1}{2}$ in the final refinement gave a population parameter of 0.36, suggesting that on average about three-quarters of the sites 0 0 $\frac{1}{2}$ are occupied by ether molecules. Refinement of the structure was by blocked-matrix least squares, using the SHELX [29] system of programs on the South Western Universities' Computer Network. It was not possible to include the contributions of the 73 hydrogen atoms in the structure-factor calculations; all H atoms have therefore been omitted. All phenyl rings were refined as rigid regular hexagons with a C–C bond length of 1.395 Å and with isotropic thermal parameters. Weights were optimised according to the scheme $w = 1.719$ $[\sigma^2(F) + 0.001\ 4|F|^2]^{-1}$. Refinement converged at R 0.059 (R' 0.061). Scattering factors were from ref. 30; those for Pt and Fe were also corrected for the effects of anomalous dispersion.[31] Interatomic distances and bond angles are in Table 2, and the equations of relevant least-squares planes in Table 3.

$[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (2). Crystals of (2) grow as deep red (nearly black) prisms. Conditions of data collection as for (1b), and as described earlier,[32,33] except for the following: 3 952 independent intensities were measured for $2\theta \leqslant 40°$, and above 40° no significant diffraction occurred; a fast scan rate was used to minimise crystal decomposition; only those intensities for which $I \geqslant 3\sigma(I)$ were used in the solution and refinement of the structure (2 474).

Crystal data for (2). $C_{44}H_{32}Fe_2O_8P_2Pt_2$, $M = 1\ 252.6$, Monoclinic, $a = 10.83(2)$, $b = 16.00(4)$, $c = 27.88(4)$ Å, $\beta = 99.40(11)°$, $U = 4\ 766(15)$ Å^3, $Z = 4$, $D_c = 1.75$ g cm^{-3}, $F(000) = 2\ 392$. Space group $P2_1/c$ (no. 14), μ(Mo-K_α) = 66.8 cm^{-1}.

The structure was solved by heavy-atom methods, but the quality of the crystal, and hence of the intensity data, was poor, so that standard deviations are correspondingly large. Corrections for *X*-ray absorption led to A^* values (the reciprocal of the transmission factor) ranging from 1.8 to 4.6. There was no possibility of locating directly the bridging hydrides, but the probable locations are evident from the stereochemical relationships (see Discussion section). Phenyl hydrogen atoms were incorporated at calculated positions; both their positional and thermal parameters were kept invariant. Only the metal atoms were given anisotropic thermal parameters; all other non-hydrogen atoms were refined isotropically. Refinement by blocked-matrix least squares [29] converged at R 0.056 (R' 0.060). Scattering factors and other corrections were as for (1b); [30,31] those for hydrogen were from ref. 34. Atomic positional parameters for (2) are in Table 4, and bond lengths, angles, and some dihedral angles are in Table 5.

$[Fe_2Pt(CO)_8(cod)]$, (4). Crystals of (4) grow as deep red (nearly black) prisms. Data collection was from a crystal 0.20 × 0.20 × 0.10 mm to $2\theta = 55°$ at 200 K. Check reflections $\bar{1}$ 0 2 and 0 3 $\bar{2}$ were monitored every 50 reflections, and of the total 2 646 measured independent intensities 1 637 had $I \geqslant 2.0\sigma(I)$ and were used to solve and refine the structure. There was no significant crystal decay.

Crystal data for (4). $C_{16}H_{12}Fe_2O_8Pt$, $M = 639$, Orthorhombic, $a = 12.321(11)$, $b = 9.442(7)$, $c = 15.707(16)$ Å, $U = 1\ 827(4)$ Å^3, D_m(flotation) = 2.10, $Z = 4$, $D_c = 2.12$ g cm^{-3}, $F(000) = 1\ 124$. Space group $P2_12_12_1$ (no. 19), μ(Mo-K_α) = 96.6 cm^{-1}.

The structure was solved for all non-hydrogen atoms by heavy-atom methods. Corrections for *X*-ray absorption led to A^* values ranging from 3.3 to 5.9. Refinement by blocked-matrix least squares [29] led to R 0.050 (R' 0.050) after incorporation of hydrogen atoms at calculated positions. All non-hydrogen atoms were given anisotropic thermal parameters. Scattering factors were from refs. 30, 31, and 34 with the usual corrections for anomalous dispersion. Atomic positional parameters for (4) are in Table 7, bond lengths and angles in Table 8, and some least-squares planes in Table 9. For all three structures, observed and calculated structure factors, all thermal parameters and, where appropriate, hydrogen atom co-ordinates, are listed in Supplementary Publication No. SUP 23007 (35 pp).†

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