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THE SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF THE HEXANUCLEAR METAL CLUSTER COMPLEX $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$

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Abstract—The compounds $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Pt(C_2H_4)_3]$ in diethyl ether at 0°C react to give the cluster complex $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ in quantitative yield. The structure of the hexanuclear metal species was established by X-ray diffraction. The main feature is a near-planar array of metal atoms with a central triangle of platinum atoms [Pt—Pt (mean), 2.703(3) Å] each edge-bridged by an iridium atom [Ir—Pt (mean) 2.667(3) Å]. The iridium atoms are each ligated by an η^5-C_5Me_5 group and by two CO ligands. Three of the latter are essentially terminally bound to Ir and lie approximately orthogonal to the Ir_3Pt_3 plane, and three bridge between Pt and Ir and lie close to the hexametal plane. The ^{13}C-$\{^1H\}$ NMR data for the cluster reveal that the carbonyl groups and η^5-C_5Me_5 ligands undergo dynamic behaviour in solution and possible mechanisms for ligand site exchange are discussed.

We have reported previously[1] that the unsaturated dirhodium compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$, an inorganic analogue of ethylene,[2] reacts with $[Pt(C_2H_4)_3]$ to give the pentanuclear cluster complex $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$. The iridium analogue of the latter compound cannot at present be prepared by a similar synthesis since the unsaturated diiridium precursor has not as yet been described. We have, therefore, investigated the reaction between $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ and $[Pt(C_2H_4)_3]$ in the expectation that an iridium–platinum cluster species would be formed. No heteronuclear metal complexes of this type appear to have been previously well characterised,[3] apart from (R = H or Ph).[4] Recently we have employed $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ as a reagent for obtaining $(CO)_2(\eta\text{-}C_5Me_5)]$ as a reagent for obtaining heteronuclear clusters containing rhodium,[5] and it seemed probable that $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ would behave in a similar manner.

RESULTS AND DISCUSSION

Addition of a mol equivalent of $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ in diethyl ether to $[Pt(C_2H_4)_3]$ in the same solvent at 0°C gave immediately an intense red-brown solution. Chromatography on an alumina column yielded a brown crystalline product. Since analytical and spectroscopic data for the compound did not establish its nature an X-ray diffraction study was carried out which showed that it was a hexanuclear metal species. There are two crystallographically independent molecules present in the solid-state structure and both are shown in Fig. 1. These two molecules are very similar in terms of their stereochemistry. The central feature of the molecule is a near-planar array of the six metal atoms, a central triangle of platinum atoms, each edge-bridged by an iridium atom. The iridium atoms each carry an η-C_5Me_5 group and are linked to two CO ligands. The latter may be broadly divided into two sets, three lie roughly orthogonal to the Ir_3Pt_3 plane and are essentially terminally bound to the iridium atoms, and three close to the Ir_3Pt_3 plane, bridging alternate outer Ir—Pt edges of the Ir_3Pt_3 core. The $Ir_3Pt_3(\mu\text{-}CO)_3$ unit has approximate C_3-symmetry. The η-C_5Me_5 ligands are well out of the Ir_3Pt_3 plane, one above and two below this plane as viewed in Fig. 1.

The internuclear distances and angles are given in Table 1, from which it will be seen that the Pt_3 triangle is essentially equilateral, with the mean Pt—Pt distance [2.703(3) Å] within the range observed in other species having such triangles, viz.

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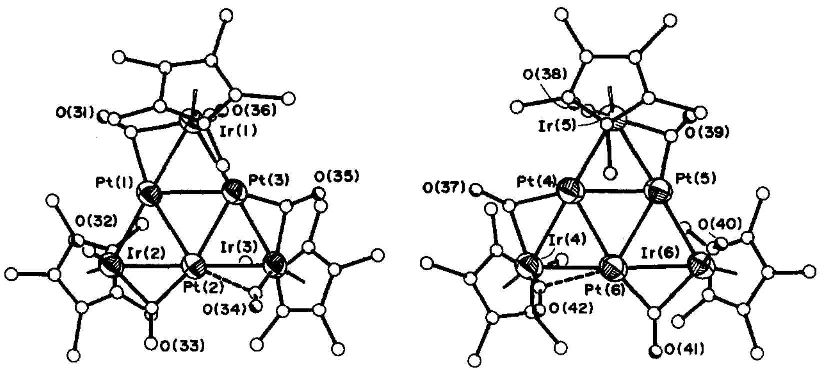

Fig. 1. The molecular structures of the two crystallographically independent molecules of $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ showing the atom numbering scheme.

$[Pt_3(CNBu^t)_6]$ [2.632(2) Å],[6] $[Fe_3Pt_3(CO)_{15}]^{n-}$ [$n = 1$, 2.656(1) Å; $n = 2$, 2.750(1) Å],[7] $[Pt_3(SO_2)_3(PPh_3)_3]$ [2.703(1) Å],[8] and $[Pt_3(CO)_3\{P(C_6H_{11})_3\}_4]$ [2.708(1) Å].[9]

The Ir—Pt separations can be divided into two sets, those bridged by CO groups [av. 2.693(3)Å] and those unbridged [av. 2.640(3) Å], both distances being similar to that observed [2.687(2) Å] in $[IrPt(H)(Ph)(\mu\text{-}H)_2(PEt_3)_4][BPh_4]$.[4] The two sets of carbonyl groups show distinctly different metal–carbon bond lengths. Those bonded in a bridging mode showing the expected longer Ir—CO distance [mean Ir—C 2.06(4) Å] compared with those bonded terminally [mean Ir—C 1.80(4) Å]. There is evidence, however, of platinum–carbon interactions in one member of the latter set of carbonyl groups. This is reflected in the non-linearity of Ir(3)—C(34)—O(34) [155.3(56)°] and Ir(4)—C(42)—O(42) [161.8(46)°]. In the structurally related raft complexes $[Fe_3Pt_3(CO)_{15}]^{n-}$ ($n = 1$ or 2) the three Pt-bonded CO ligands in the 'plane' of the six metal atoms are essentially terminally bound to the platinums [$n = 1$, Pt—C—O av. 173.3°; $n = 2$, Pt—C—O av. 175.3°],[7] and also in contrast the Fe-bonded carbonyl ligands are entirely terminal and linear ($n = 1$, Fe—C—O av. 175.4°, $n = 2$, Fe—C—O av. 173.8°).

As in the Fe_3Pt_3 species, the hexametal Ir_3Pt_3 raft is not exactly planar. Two iridium atoms lie below and one above the Pt_3 plane. The deviations from the 'raft' plane range from 0.1 to 0.6 Å, similar to that in the Fe_3Pt_3 compounds. The dihedral angles between the Ir_2Pt and Pt_3 planes are:

Ir(1)—Pt(1)—Pt(3)	13.4°,
Ir(3)—Pt(2)—Pt(3)	−8.6°
Ir(5)—Pt(5)—Pt(4)	15.8°,
Ir(2)—Pt(1)—Pt(2)	−9.3°,
Ir(4)—Pt(4)—Pt(6)	−9.4°,
Ir(6)—Pt(5)—Pt(6)	−3.0°.

These values compare with the all-positive angles of 8.6 and 16.1° found between the fused Os_3 triangles in $[Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}]$,[10] and the dihedral angles of 12.2, 19.1 and 23.5° between the three Os_3 planes and the Hg_3 plane in $[Hg_3Os_9(CO)_{33}]$.[11] The other osmium raft complex $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ has an approximately planar metal core, showing a maximum deviation of only 0.1 Å.

The compound $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ is stable in air in the solid state, although solutions in organic solvents decompose slowly giving $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ and a black residue presumed to be platinum. In the IR spectrum CO bands occur at 1959 and 1768 cm^{-1}, corresponding to terminal and bridging modes, as established in the X-ray diffraction study. Examination of the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the cluster revealed that it undergoes dynamic behaviour in solution. Although in the structure found in the solid state one $\eta\text{-}C_5Me_5$ ligand lies above the Ir_3Pt_3 plane and two below, and also there are terminal and bridging CO groups, at ambient temperatures in the 50.1-MHz spectrum there are only three resonances at 178.1 (CO), 99.1 ($\eta\text{-}C_5Me_5$) and 9.6 ppm ($\eta\text{-}C_5Me_5$). The observation of a single resonance for the carbonyl carbons indicates that these are undergoing a rapid exchange between the different bonding sites shown by the crystal structure, and the observation of single resonances for the $\eta\text{-}C_5Me_5$ groups indicates that they are undergoing exchange between sites on either side of the metal atoms.

The resonance at 178.1 ppm also shows satellite peaks due to coupling to ^{195}Pt nuclei. There are two sets of satellite peaks, a sharper pair [$J(PtC) = 35$ Hz] and a very broad pair [$J(PtC) \sim 300$ Hz]. That some of the broadening of the latter pair is due to platinum relaxation caused by chemical shift anisotropy is proved by the fact that when the spectrum was measured at 22.5 MHz these lines became somewhat sharper. However, the main cause

Table 1. Bond distances (Å) and angles (°) for the complex $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$

Ir(1)-Pt(1)	2.686(3)	Ir(1)-Pt(3)	2.643(3)
Ir(1)-C(31)	2.073(47)	Ir(1)-C(36)	1.773(43)
Pt(1)-Pt(3)	2.711(3)	Pt(1)-Ir(2)	2.644(3)
Pt(1)-Pt(2)	2.710(3)	Pt(1)-C(31)	2.056(48)
Pt(3)-Ir(3)	2.702(3)	Pt(3)-Pt(2)	2.700(3)
Pt(3)-C(35)	1.714(41)	Pt(5)-Pt(6)	2.708(3)
Pt(5)-Ir(5)	2.678(3)	Pt(5)-Ir(6)	2.646(3)
Pt(5)-Pt(4)	2.691(3)	Pt(5)-C(39)	1.752(35)
Ir(4)-Pt(6)	2.645(3)	Ir(4)-Pt(4)	2.701(3)
Ir(4)-C(42)	1.853(40)	Ir(4)-C(37)	2.074(47)
Pt(6)-Ir(6)	2.708(3)	Pt(6)-Pt(4)	2.702(3)
Pt(6)-C(41)	1.882(47)	Pt(6)-C(42)	2.610(53)
Ir(2)-Pt(2)	2.683(3)	Ir(2)-C(32)	1.823(43)
Ir(2)-C(33)	2.053(39)	Ir(5)-Pt(4)	2.641(3)
Ir(5)-C(39)	2.012(36)	Ir(5)-C(38)	1.780(39)
Ir(3)-Pt(2)	2.625(3)	Ir(3)-C(34)	1.764(45)
Ir(3)-C(35)	2.058(35)	Ir(6)-C(40)	1.805(47)
Ir(6)-C(41)	2.124(35)	Pt(2)-C(33)	1.901(45)
Pt(2)-C(34)	2.326(61)	Pt(4)-C(38)	2.739(53)
Pt(4)-C(37)	1.924(60)	C(32)-O(32)	1.156(58)
C(31)-O(31)	1.124(57)	C(33)-O(33)	1.180(66)
C(34)-O(34)	1.162(65)	C(35)-O(35)	1.210(55)
C(36)-O(36)	1.113(65)	C(39)-O(39)	1.169(59)
C(40)-O(40)	1.161(62)	C(38)-O(38)	1.148(56)
C(41)-O(41)	1.176(56)	C(42)-O(42)	1.189(60)
C(37)-O(37)	1.172(61)		
Pt(1)-Ir(1)-Pt(3)	61.1(1)	Pt(1)-Ir(1)-C(31)	49.1(13)
Pt(3)-Ir(1)-C(31)	106.5(13)	Pt(1)-Ir(1)-C(36)	98.5(21)
Pt(3)-Ir(1)-C(36)	77.7(22)	C(31)-Ir(1)-C(36)	91.1(27)
Ir(1)-Pt(1)-Pt(3)	58.6(1)	Ir(1)-Pt(1)-Ir(2)	175.8(1)
Pt(3)-Pt(1)-Ir(2)	119.3(1)	Ir(1)-Pt(1)-Pt(2)	117.1(1)
Pt(3)-Pt(1)-Pt(2)	59.8(1)	Ir(2)-Pt(1)-Pt(2)	60.1(1)
Ir(1)-Pt(1)-C(31)	49.7(13)	Pt(3)-Pt(1)-C(31)	104.7(13)
Ir(2)-Pt(1)-C(31)	133.6(13)	Pt(2)-Pt(1)-C(31)	163.5(15)
Ir(1)-Pt(3)-Pt(1)	60.2(1)	Ir(1)-Pt(3)-Ir(3)	175.0(1)
Pt(1)-Pt(3)-Ir(3)	117.7(1)	Ir(1)-Pt(3)-Pt(2)	119.0(1)
Pt(1)-Pt(3)-Pt(2)	60.1(1)	Ir(3)-Pt(3)-Pt(2)	58.2(1)
Ir(1)-Pt(3)-C(35)	130.7(12)	Pt(1)-Pt(3)-C(35)	159.0(14)
Ir(3)-Pt(3)-C(35)	49.6(12)	Pt(2)-Pt(3)-C(35)	103.0(12)
Pt(6)-Pt(5)-Ir(5)	117.2(1)	Pt(6)-Pt(5)-Ir(6)	60.8(1)
Ir(5)-Pt(5)-Ir(6)	169.1(1)	Pt(6)-Pt(5)-Pt(4)	60.1(1)
Ir(5)-Pt(5)-Pt(4)	58.9(1)	Ir(6)-Pt(5)-Pt(4)	120.7(1)
Pt(6)-Pt(5)-C(39)	162.9(13)	Ir(5)-Pt(5)-C(39)	48.7(12)
Ir(6)-Pt(5)-C(39)	135.2(12)	Pt(4)-Pt(5)-C(39)	103.5(12)
Pt(6)-Ir(4)-Pt(4)	60.7(1)	Pt(6)-Ir(4)-C(42)	68.3(16)
Pt(4)-Ir(4)-C(42)	89.4(16)	Pt(6)-Ir(4)-C(37)	103.6(18)
Pt(4)-Ir(4)-C(37)	45.2(17)	C(42)-Ir(4)-C(37)	92.6(27)
Pt(5)-Pt(6)-Ir(4)	119.7(1)	Pt(5)-Pt(6)-Ir(6)	58.5(1)
Ir(4)-Pt(6)-Ir(6)	169.1(1)	Pt(5)-Pt(6)-Pt(4)	59.7(1)
Ir(4)-Pt(6)-Pt(4)	60.7(1)	Ir(6)-Pt(6)-Pt(4)	118.1(1)
Pt(5)-Pt(6)-C(41)	107.3(11)	Ir(4)-Pt(6)-C(41)	132.9(11)
Ir(6)-Pt(6)-C(41)	51.4(11)	Pt(4)-Pt(6)-C(41)	161.8(13)
Pt(5)-Pt(6)-C(42)	125.6(12)	Ir(4)-Pt(6)-C(42)	41.3(9)
Ir(6)-Pt(6)-C(42)	149.4(9)	Pt(4)-Pt(6)-C(42)	75.7(11)
C(41)-Pt(6)-C(42)	106.9(16)	Pt(1)-Ir(2)-Pt(2)	61.1(1)
Pt(1)-Ir(2)-C(32)	76.2(15)	Pt(2)-Ir(2)-C(32)	99.5(16)
Pt(1)-Ir(2)-C(33)	99.7(12)	Pt(2)-Ir(2)-C(33)	44.9(12)
C(32)-Ir(2)-C(33)	87.8(20)	Pt(5)-Ir(5)-Pt(4)	60.8(1)
Pt(5)-Ir(5)-C(39)	40.9(10)	Pt(4)-Ir(5)-C(39)	98.0(10)
Pt(5)-Ir(5)-C(38)	99.5(19)	Pt(4)-Ir(5)-C(38)	73.7(18)
C(39)-Ir(5)-C(38)	95.7(22)	Pt(3)-Ir(3)-Pt(2)	60.9(1)
Pt(3)-Ir(3)-C(34)	95.1(20)	Pt(2)-Ir(3)-C(34)	60.3(20)
Pt(3)-Ir(3)-C(35)	39.4(11)	Pt(2)-Ir(3)-C(35)	96.3(12)
C(34)-Ir(3)-C(35)	100.0(23)	Pt(5)-Ir(6)-Pt(6)	60.8(1)
Pt(5)-Ir(6)-C(40)	74.5(15)	Pt(6)-Ir(6)-C(40)	95.2(16)
Pt(5)-Ir(6)-C(41)	102.2(13)	Pt(6)-Ir(6)-C(41)	43.8(13)
C(40)-Ir(6)-C(41)	93.9(21)	Pt(1)-Pt(2)-Pt(3)	60.1(1)
Pt(1)-Pt(2)-Ir(2)	58.7(1)	Pt(3)-Pt(2)-Ir(2)	118.2(1)
Pt(1)-Pt(2)-Ir(3)	120.5(1)	Pt(3)-Pt(2)-Ir(3)	60.9(1)
Ir(2)-Pt(2)-Ir(3)	164.6(1)	Pt(1)-Pt(2)-C(33)	101.6(12)
Pt(3)-Pt(2)-C(33)	155.9(13)	Ir(2)-Pt(2)-C(33)	49.7(12)
Ir(3)-Pt(2)-C(33)	137.1(12)	Pt(1)-Pt(2)-C(34)	134.7(15)
Pt(3)-Pt(2)-C(34)	83.4(14)	Ir(2)-Pt(2)-C(34)	151.8(12)
Ir(3)-Pt(2)-C(34)	41.2(12)	C(33)-Pt(2)-C(34)	103.2(18)
Pt(5)-Pt(4)-Ir(4)	118.3(1)	Pt(5)-Pt(4)-Pt(6)	60.3(1)
Ir(4)-Pt(4)-Pt(6)	58.6(1)	Pt(5)-Pt(4)-Ir(5)	60.3(1)
Ir(4)-Pt(4)-Ir(5)	173.9(1)	Pt(6)-Pt(4)-Ir(5)	118.7(1)
Pt(5)-Pt(4)-C(38)	78.9(11)	Ir(4)-Pt(4)-C(38)	147.4(9)
Pt(6)-Pt(4)-C(38)	134.6(12)	Ir(5)-Pt(4)-C(38)	38.6(9)
Pt(5)-Pt(4)-C(37)	165.0(18)	Ir(4)-Pt(4)-C(37)	49.9(14)
Pt(6)-Pt(4)-C(37)	106.0(16)	Ir(5)-Pt(4)-C(37)	130.3(14)
C(38)-Pt(4)-C(37)	116.1(21)	Ir(2)-C(32)-O(32)	175.4(48)
Ir(1)-C(31)-Pt(1)	81.2(16)	Ir(1)-C(31)-O(31)	144.7(41)
Pt(1)-C(31)-O(31)	134.0(40)	Ir(2)-C(33)-Pt(2)	85.4(17)
Ir(2)-C(33)-O(33)	139.1(39)	Pt(2)-C(33)-O(33)	135.5(37)
Ir(3)-C(34)-Pt(2)	78.5(20)	Ir(3)-C(34)-O(34)	155.3(56)
Pt(2)-C(34)-O(34)	119.9(45)	Pt(3)-C(35)-Ir(3)	91.0(15)
Pt(3)-C(35)-O(35)	141.2(36)	Ir(3)-C(35)-O(35)	127.0(35)
Ir(1)-C(36)-O(36)	178.0(72)	Pt(5)-C(39)-Ir(5)	90.4(15)
Pt(5)-C(39)-O(39)	136.0(40)	Ir(5)-C(39)-O(39)	125.3(39)
Ir(6)-C(40)-O(40)	170.6(44)	Ir(5)-C(38)-Pt(4)	67.7(15)
Ir(5)-C(38)-O(38)	175.4(46)	Pt(4)-C(38)-O(38)	116.7(40)
Pt(6)-C(41)-Ir(6)	84.8(15)	Pt(6)-C(41)-O(41)	141.2(33)
Ir(6)-C(41)-O(41)	134.0(36)	Ir(4)-C(42)-Pt(6)	70.4(16)
Ir(4)-C(42)-O(42)	161.8(46)	Pt(6)-C(42)-O(42)	121.6(38)
Ir(4)-C(37)-Pt(4)	84.9(18)	Ir(4)-C(37)-O(37)	135.0(49)
Pt(4)-C(37)-O(37)	138.5(49)		

of the broadening is chemical exchange, since a spectrum run at +60°C showed these lines to be considerably sharper. Also, on the 22.5-MHz spectrum, a further sharp pair of satellite peaks is observed [J(PtC) = 616 Hz]. Their intensity (approximately one-quarter of that of the peaks with $J = 35$ Hz] corresponds to the expected abundance of molecules with two ^{195}Pt nuclei, and their sharpness indicates that chemical shift anisotropy cannot be the cause of the broadness of the satellites with $J \sim 300$ Hz.

At −90°C, the spectrum at 50.1 MHz is more complicated. The ring and methyl carbon signals are now both split into two resonances, at δ 100.5 and 100.2 ppm (ring carbons, intensity ratio 1 : 2) and at 11.0 and 10.8 ppm (methyl carbons, intensity ratio 1 : 2). The splitting of these signals indicates that the location of the η-C_5Me_5 rings relative to the plane of the metal atoms indicated by the crystal structure (one above, two below) now has a sufficiently long lifetime for the separate signals to be observed. In the −90°C spectrum there are also three CO peaks at δ 181.2, 180.9 and 179.6 ppm. The observation of three, rather than six separate signals, together with the fact that two of the rings are equivalent, indicates that there is still an apparent C_s-symmetry in the molecule, as shown in Fig. 2.

The close similarity of the chemical shifts of all the carbonyls suggests that no distinction can be made in solution between bridging and terminal environments, though the observation of three signals shows that there is only slow exchange between different positions on each iridium atom, e.g. $B \rightleftharpoons C$ or $B' \rightleftharpoons C'$ (Fig. 2). This is confirmed by the platinum satellite signals, which, though very broad, show a value of J(PtC) of approximately 600 Hz. The

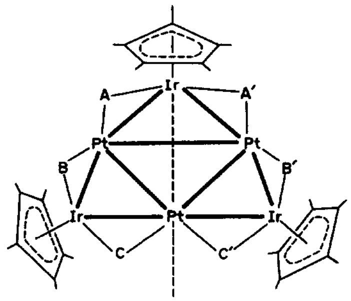

Fig. 2. Apparent structure of $[Ir_3Pt_3(CO)_6(\eta\text{-}C_5Me_5)_3]$ as indicated by $^{13}C\text{-}\{^1H\}$ NMR studies at −90°C. Symmetry plane indicated by dotted line, one η-C_5Me_5 group above the metal plane, two below. At ambient temperatures slipping of the C_5Me_5 groups equilibrates chemical shifts of all CO groups and ^{195}Pt coupling information also indicates a rapid pairwise exchange $A \rightleftharpoons A'$, $B \rightleftharpoons C$ and $B' \rightleftharpoons C'$ (see cursive text).

exchange observed at ambient temperatures within pairs, A $\rightleftharpoons$ A′, B $\rightleftharpoons$ C and B′ $\rightleftharpoons$ C′, then results in the broad platinum satellites observed at approximately 300 Hz, i.e. one half of J(PtC). If both platinum nuclei in an $IrPt_2(CO)_2$ fragment are ^{195}Pt, then exchange will leave the resonance unchanged, with the satellite separation equal to ^1J(PtC) + ^2J(PtC) (observed at 616 Hz). The observation of the second coupling to ^{195}Pt (J = 35 Hz) shows that even at ambient temperatures the carbonyls remain associated with two platinums and one iridium, *i.e.* there is no exchange of the type A $\rightleftharpoons$ B, C $\rightleftharpoons$ C′ or B′ $\rightleftharpoons$ A′, although the chemical shifts are equilibrated by the flipping of the η-C_5Me_5 groups.

The structure of $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ is of interest in view of a recent theoretical analysis[12] of bonding in raft clusters. The electronic requirements for triangulated rafts are evidently flexible since the total number of cluster valence electrons (CVEs) varies from 84 for the Ir_3Pt_3 species, through 85 in $[Fe_3Pt_3(CO)_{15}]^-$, 86 in $[Fe_3Pt_3(CO)_{15}]^{2-}$ to 90 in $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ and $[Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}]$. Evans and Mingos have postulated that there exists a low-lying empty metal-based orbital in the 90 CVE clusters which is anti-bonding with respect to the metal–metal interactions within the central triangle.[12] The electron count of 84 in $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ can be related to the 90 CVEs in the Os_6 clusters if it is assumed that one valence orbital on each platinum is empty, and not involved in bonding, i.e. the platinums are 16 e centres. The $[Fe_3Pt_3(CO)_{15}]^{n-}$ (n = 1 or 2) anions are then also analogous to the Os_6 rafts with the low-lying orbital half and fully occupied for n = 1 and 2, respectively. An alternative view of the electronic structure of the three triplatinum species depends on an appreciation that the groups $Ir(CO)(\eta\text{-}C_5Me_5)$, $Fe(CO)_4$, CR_2, SO_2, and less exactly CO and CNR, are isolobal. This allows the stoichiometry of the Ir_3Pt_3 species and the Fe_3Pt_3 carbonyl anions to be related to the known compounds $[Pt_3(CNBu^t)_6]$, $[Pt_3(SO_2)_3(PPh_3)_3]$, $[Pt_3(CO)_3(PR_3)_3]$ and $[Pt_3(CR_2)_3(PR_3)_3]$, and also to the dianion $[Pt_3(CO)_6]^{2-}$, due allowance being made for any negative charge. For $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ the bridging CO ligands render the closeness of the analogy arguable.

EXPERIMENTAL

The compounds $[Pt(cod)_2]$[13] and $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$[14] were prepared as described previously. Preparative work was carried out under oxygen-free nitrogen employing Schlenk tube techniques. Light petroleum refers to the fraction with b.p. 40–60°C. The NMR spectra were measured with JEOL FX90Q and FX200 instruments. Chemical shifts are positive to a high frequency of $SiMe_4$ (^{13}C-{^{1}H}) and ^{195}Pt [Ξ (^{195}Pt) 21.4 MHz].

Synthesis of the compound $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$

Ethylene was bubbled into a solution of $[Pt(cod)_2]$ (0.5 g, 1.2 mmol) in diethyl ether (30 cm^3) at 0°C in order to generate $[Pt(C_2H_4)_3]$ *in situ*. This reagent was then treated with $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$ (0.46 g, 1.2 mmol) in the same solvent (30 cm^3). The mixture became dark brown and after stirring for 30 min the solvent was removed *in vacuo*. The residue was transferred to the top of an alumina column (15 × 2 cm) and chromatographed, eluting initially with light petroleum to remove trace amounts of $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$. Subsequent elution with diethyl ether-light petroleum (1:1) gave an orange-brown band. Removal of solvent *in vacuo* and crystallisation of the product from dichloromethane-light petroleum (1:2) afforded dark brown *crystals* of $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ (0.66 g, *ca* 100%). Found: C, 24.8; H, 2.6%. $C_{36}H_{45}Ir_3O_6Pt_3$ requires C, 24.9; H, 2.6%. M.p. 234°C (with decomp.); ν_{CO} (tetrahydrofuran) at 1959s(br) and 1768s cm^{-1}. NMR: ^{1}H ($CDCl_3$), δ 2.15 [Me, J(PtH) 7 Hz]; ^{13}C-{^{1}H} (CD_2Cl_2-CH_2Cl_2), δ 179.0 (*br*, CO), 100.1 (C_5Me_5) and 10.7 ppm (C_5Me_5); ^{195}Pt-{^{1}H} ($CDCl_3$), δ −874.9 ppm.

Crystal structure determination

A suitable crystal (0.4 × 0.25 × 0.15 mm) was grown from dichloromethane-light petroleum. Data were collected at 293 K on a Nicolet *P*3*m* diffractometer.

Crystal data. $C_{36}H_{45}Ir_3O_6Pt_3$, M = 1639.7, monoclinic, a = 41.811(34), b = 9.183(6), c = 21.892(14) Å, β = 90.99(6)°, U = 8404(10) Å^3, Z = 8, D_c = 2.59 g cm^{-3}, F(000) = 5694, space group $P2/n$, Mo-$K\alpha$ X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.71069 Å, μ(Mo-$K\alpha$) = 130.9 cm^{-1}.

The structure was solved by direct methods, which located the 12 independent metal atoms; the remaining carbon and oxygen atoms being located from difference Fourier syntheses. Absorption effects were corrected by an empirical method via a six-parameter fit to 348 azimuthal scan data. Transmission coefficients varied between 0.013 and 0.002. Of 11,307 intensities measured in a unique quadrant of reciprocal space for $4 \leqslant 2\theta \leqslant 45°$, 9740 unique data remained after averaging of repeat measurements, and deletion of mismeasured reflections. Of these data, 6549 with $I \geqslant 2\sigma(I)$ were retained for use in the structure solution and refinement. The C—C separations within the η-C_5Me_5 rings were fixed at 1.42 Å, and exocyclic C—C distances were constrained to be close to a common value which refined to 1.52(1) Å. Similar constraints were applied to the iridium–carbon distances of the bridging and terminal CO groups. The common values refined to 2.06(2) and 1.79(2) Å, respectively. The C—O bonds were constrained to average 1.15 Å. Final residuals were $R = 0.0903$ ($R' = 0.0915$) [$R = \sum||F_o|-|F_c||/\sum|F_o|$; $R' = \sum w^{1/2}||F_o|-|F_c||/\sum w^{1/2}|F_o|$; $w = (\sigma^2(F_o)+0.002F_o^2)$]*. The weighting scheme adopted accounted satisfactorily for the variance in $|F_o|$ as shown by examination of $\sum w(|F_o|-|F_c|)^2$ as a function of sin θ and $|F_o|$. All computations were carried out on an Eclipse (Data General) computer with the SHELXTL system of programs.[15] Complex neutral atom scattering factors were from Ref. 16.

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*The atomic positional and thermal parameters, together with lists of F_o/F_c values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.