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Pt_3Ir cluster complexes: butterfly clusters with iridium at a wingtip

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Abstract—The new coordinatively unsaturated clusters $[Pt_3Ir(\mu\text{-}CO)_3(CO)(\mu\text{-}dppm)_3]^+$ and $[Pt_3Ir(\mu\text{-}CO)_3\{P(OPh)_3\}(\mu\text{-}dppm)_3]^+$ are fluxional, butterfly clusters with iridium at a wingtip position. © 1997 Elsevier Science Ltd

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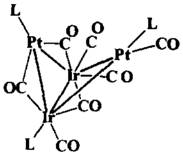
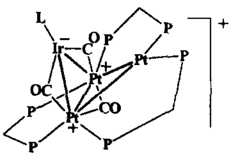
There is current interest in the modelling of bimetallic catalysts, such as Pt–Ir, Pt–Re and Pt–Sn on alumina which are important in petroleum refining, by well characterized heteronuclear cluster complexes [1]. Of the above metal combinations, mixed Pt/Ir cluster complexes are the least developed [1b]. The few crystallographically characterized examples include $[Pt_2Ir_2(\mu\text{-}CO)_3(CO)_4(PPh_3)_3]$ [2], **1**, $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta^5\text{-}C_5Me_5)_3]$ [3], and $[PtIr_4(CO)_9(\mu\text{-}CO)_n]^{2-}$ (n = 3 or 5) [4], and the rarity can be traced to the difficulty of devising planned synthetic routes. For example, cluster **1** was separated from a mixture of compounds formed by reaction of $[Pt_{12}(CO)_{24}]^{2-}$ with $[IrCl(CO)(PPh_3)_2]$ [2]. This article reports the synthesis of the coordinatively unsaturated 58 electron clusters $[Pt_3Ir(\mu\text{-}CO)_3(CO)(\mu\text{-}dppm)_3][PF_6]$, **2**, and $[Pt_3Ir(\mu\text{-}CO)_3\{P(OPh)_3\}(\mu\text{-}dppm)_3][PF_6]$, **3**, dppm = $Ph_2PCH_2PPh_2$; it is shown that they have an unexpected butterfly structure with iridium at a wingtip position.

By analogy with the known reaction of $[Pt_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, **4** with $[Re(CO)_5]^-$ to give the tetrahedral 54-electron Pt_3Re cluster $[Pt_3\{\mu_3\text{-}Re(CO)_3\}(\mu\text{-}dppm)_3]^+$ [5], it was considered that the reaction of **4** with $[Ir(CO)_4]^-$ might give a tetrahedral Pt_3Ir cluster cation. However, the reaction of **4** $[PF_6]_2$ with $[PPN][Ir(CO)_4]$ (PPN = $(PPh_3)_2N^+$) in dry CH_2Cl_2 under N_2 yielded the dark red, air-sensitive cluster $[Pt_3Ir(\mu\text{-}CO)_3(CO)(\mu\text{-}dppm)_3][PF_6]$, **2**, which has an unexpected butterfly structure (Scheme 1).† No further reactions were observed when **2** was treated with an additional equivalent of $[PPN][Ir(CO)_4]$. The terminal carbonyl ligand in **2** was easily replaced by reaction with $P(OPh)_3$ to give the phosphite derivative $[Pt_3Ir(\mu\text{-}CO)_3\{P(OPh)_3\}(\mu\text{-}dppm)_3][PF_6]$, **3**, Scheme



1, L = PCy_3



2, L = CO
3, L = $P(OPh)_3$

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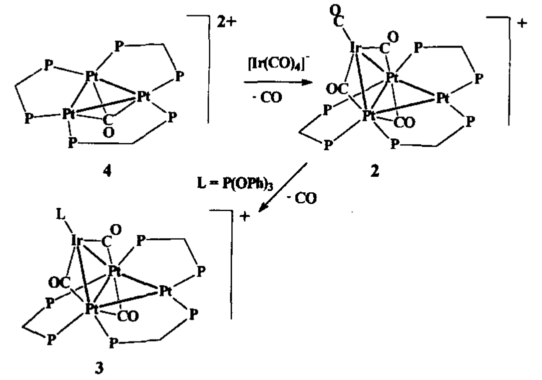
† Spectroscopic data for **2**: IR (Nujol): $\nu(CO)$ = 1982 (m), 1890 (s), 1807 (m), 1765 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6, 23°C): $\delta = -11.9$ [s, $^1J(PtP)$ = 3132 Hz, $^2J(PtP)$ = 134 Hz, $^3J(PP)$ = 194 Hz]. Spectroscopic data for **3**: IR (Nujol): $\nu(CO)$ 1885 (s), 1807 (m), 1765 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6, 23°C): $\delta = -12.4$ [1 : 1 doublet, $^1J(PtP)$ = 3242 Hz, $^2J(PtP)$ = 158 Hz, $^3J(PP)$ = 182 Hz, $^3J(PP)$ = 16 Hz dppm]; δ = 121.9 [1 : 4 : 7 : 4 : 1 quintet of septets, $^2J(PtP)$ = 508, $^3J(PP)$ = 16 Hz, $P(OPh)_3$].



Scheme 1.

1, whose structure has been determined by X-ray diffraction.†

The structure of the cation **3** is shown in Fig. 1, and it is clear that Pt_3Ir core has a butterfly structure with iridium at one of the wingtip positions. Thus the distance Pt(3)–Ir of 3.002(1) Å is considerably longer than the other Pt–Ir or Pt–Pt distances [range 2.634(1)–2.727(1) Å] and is best considered a non-bonding distance. The hinge angle Ir–Pt(1)–Pt(2)–Pt(3) is typical of butterfly clusters and much larger than the tetrahedral angle of 70.5° [1,2,6]. Each edge of the Pt_3 triangle is bridged by a dppm ligand while each edge of the Pt(1)Pt(2)Ir triangle is bridged by a carbonyl ligand; the atoms of the P(1)IrPt(1)Pt(2)(μ-CO)$_3$ unit are approximately coplanar. The carbonyl-bridged metal–metal distances [Pt(1)–Pt(2) = 2.711(1), Pt(1)–Ir = 2.679(1), Pt(2)–Ir = 2.727(1) Å] are longer than the unbridged ones [Pt(1)–Pt(3) = 2.634(1), Pt(2)–Pt(3) = 2.649(1) Å] [2–4].

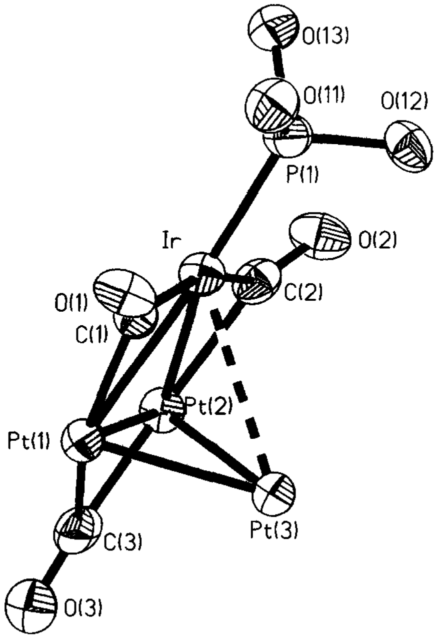


Fig. 1. A view of the inner core of the cluster cation [$Pt_3Ir(\mu$-CO)$_3$\{P(OPh)$_3$\}(μ-dppm)$_3$]$^+$, **3**, illustrating the near planarity of the P(1)IrPt(1)Pt(2)(μ-CO)$_3$ unit. The μ-dppm ligands, which bridge each edge of the Pt_3 triangle, and the phenyl groups of the phosphite ligand, are omitted for clarity. Selected distances: Ir–Pt(1) 2.679(1), Ir–Pt(2) 2.727(1), Ir–Pt(3) 3.002(1), Pt(1)–Pt(3) 2.634(1), Pt(1)–Pt(2) 2.711(1), Pt(2)–Pt(3) 2.649(1) Å; the carbonyl bridges are roughly symmetrical, Ir–C(1)–O(1) 145(2), Pt(1)–C(1)–O(1) 135(2), Ir–C(2)–O(2) 134(2), Pt(2)–C(2)–O(2) 144(2)°. Thermal ellipsoids are drawn at 30% probability.

The IR spectra* of **2** and **3** each contain three bands due to the μ-CO ligands in the range 1890–1765 cm^{-1} and **2** also gives a terminal carbonyl band at 1982 cm^{-1}. The similarity of the IR and NMR (*vide infra*) data for **2** and **3** clearly indicate that they have the same skeletal structure. The observation of a butterfly structure is not unexpected since **2** and **3** have 58-electron configurations as in the Pt_2Ir_2 cluster **1** and in several homonuclear Pt_4 clusters [2,6,7]. Such clusters are electron-precise and the wingtip and hinge atoms have 16-electron and 18-electron configurations respectively. Since iridium has a greater tendency than platinum to adopt an 18-electron configuration, iridium is expected to have a preference for the hinge positions and this is what is found in the cluster **1** [2]. Indeed, in all known electron-precise Pt–Ir clusters, namely in **1**, the raft cluster [$Pt_3Ir_3(C_5Me_5)_3(CO)_3(\mu$-CO)$_3$] and in [$PtIr_2$(indenyl)$_2(CO)_3(PCy_3)$], the platinum and iridium atoms have 16- and 18-electron configurations respectively [2,3,8]. It is therefore remarkable that in **2** and **3** the iridium atom is in a wingtip position with a 16-electron configuration. The reason for this unusual situation is clearly the presence of the inert $Pt_3(\mu$-dppm)$_3$ unit which does not allow a structure with two platinum atoms in wingtip positions. Note that electron-counting for **2**, supported by EHMO calculations for the model cluster [$Pt_3Ir(\mu$-CO)$_3$(CO)(μ-$H_2PCH_2PH_2$)]$^{2+}$,‡ requires a negative charge on iridium and positive charges on the two platinum atoms in the hinge positions and so, if formation of **2** is considered to occur by combination of [$Ir(CO)_3$]$^-$ and [$Pt_3(\mu$-CO)(μ-dppm)$_3$]$^{2+}$ fragments, little net electron transfer occurs.

The clusters **2** and **3** are highly fluxional. Thus, in the room temperature ^{31}P NMR spectrum, **3** gives only one doublet resonance for the phosphorus atoms of the μ-dppm ligands indicating that they are equivalent on the NMR time scale. In agreement, the

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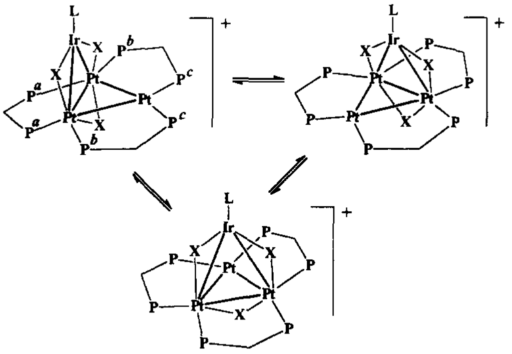
† Crystal data for **3**, $C_{96}H_{81}F_6IrO_6P_8Pt_3$, monoclinic, $P2_1/c$, a = 15.016(1), b = 34.618(2), c = 19.615(1) Å, β = 106.662(1)°, V = 9768(1) Å^3, Z = 4, d(calc.) = 1.679 g cm^{-3}, R_1(F) [$I > 2\sigma(I)$] = 0.00680, $wR_2(F^2)$ = 0.1747.

‡ The computed charges on the Ir(CO)(μ-CO)$_2$ and [$Pt_3(\mu$-CO)(μ-$H_2PCH_2PH_2$)$_3$] fragments respectively were −1.5 e and +2.5 e, respectively, using an idealized structure based on the structure of **3** and standard parameters supplied with the program CACAO.

phosphite resonance appears as a septet due to long range coupling $^3J(PP) = 16$ Hz, indicating effective equivalence of the six dppm phosphorus atoms, and also gave a 1 : 4 : 7 : 4 : 1 multiplet due to the coupling $^2J(PtP) = 508$ Hz, characteristic of coupling to three effectively equivalent platinum atoms [8]. In the ^{31}P NMR spectrum of **3** at −90°C the dppm resonance split into three very broad resonances ($\delta = -7, -9$ and -19) attributed to the non-equivalent phosphorus atoms P^a, P^b and P^c in **3**, and the $P(OPh)_3$ resonance was also very broad. Similarly, the dppm resonance of **2** at $\delta = -11.9$ at room temperature split into three broad resonances ($\delta = -1.5, -11.5$ and -21.5) at −90°C. The spectra indicate that the '$Ir(\mu\text{-}CO)_2L$' group can migrate very easily about one side of the Pt_3 face with the $Pt_2(\mu\text{-}CO)$ ligand migrating about the other side, thus leading to effective three-fold symmetry (Scheme 2). The observation of the long-range coupling $^3J(Pt\text{–}P(OPh)_3)$ under conditions of fast fluxionality clearly eliminates the alternative mechanism involving reversible dissociation of the $[Ir(CO)_2L]^-$ group from the cluster.

In summary, the clusters **2** and **3** are of considerable interest as models for Pt/Ir catalysts since each contains a coordinatively unsaturated 16-electron iridium and platinum centre. We suggest that the presence of the 16-electron iridium centre is, at least in part, responsible for the particularly easy fluxionality and for the high reactivity of the clusters compared to related butterfly clusters [6,8].



Scheme 2. X = μ-CO; L = CO or $P(OPh)_3$

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