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Unexpected bonding similarities between the bridging metalloligands $[MoCp(CO)_3]^-$ and $[PtI(CO)_2(PPh_3)]^-$ acting as 4-electron donors in metal clusters. Crystal structures of $[Pt_2Mo(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$ and $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}PPh_2)I(PPh_3)_3]$†‡

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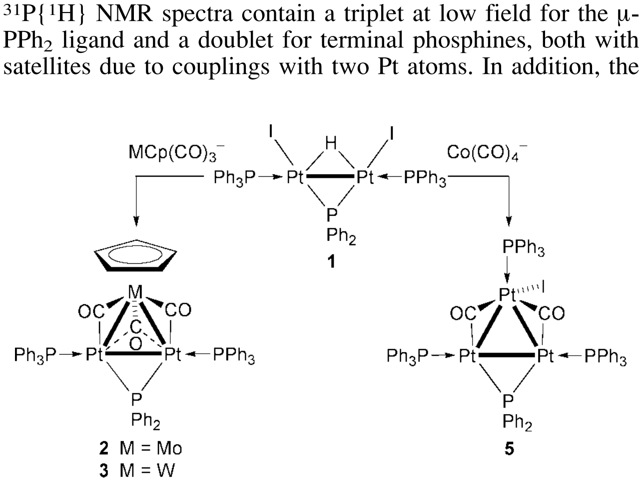
Reactions of the diplatinum complex $[Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)I_2(PPh_3)_2]$ with the carbonylmetalates $[MCp(CO)_3]^-$ (M = Mo, W) or $[Co(CO)_4]^-$ afforded the new 44e clusters $[Pt_2M(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$ (M = Mo, 2; M = W, 3) and $[Pt_3(\mu\text{-}CO)_2(\mu\text{-}PPh_2)I(PPh_3)_3]$ 5, respectively, whose structures can be analysed as formed by a 26e $[Pt_2(\mu\text{-}PPh_2)(PPh_3)_2]^+$ cation and a bridging, 4e donor anion, $[MCp(CO)_3]^-$ in 2 and 3, or the new 18e fragment $[PtI(CO)_2(PPh_3)]^-$ in 5.

In the search for versatile synthetic methods, numerous metal–metal bonded complexes and clusters have been obtained by reaction of carbonylmetalates with mononuclear halide complexes,[1,2] whereas fewer studies have been concerned with dinuclear halide precursors.[3] The reactions of the diplatinum complex $[Pt_2(\mu\text{-}H)(\mu\text{-}PPh_2)I_2(PPh_3)_2]$ **1**, prepared by reaction of $[Pt_2(\mu\text{-}PPh_2)(\mu\text{-}o\text{-}C_6H_4PPh_2)(PPh_3)_2]$[4a] with 2 equiv. of HI in THF,[4b] with three different carbonylmetalates has now afforded clusters whose structures reveal an unexpected bonding similarity between the 18e metalloligands $[MCp(CO)_3]^-$ (M = Mo, W) and $[PtI(CO)_2(PPh_3)]^-$ which are best viewed as 4e donors towards a d^9–d^9 Pt(I)–Pt(I) unit.

Reaction of 1 equiv. of **1** with 3 equiv. of $[MCp(CO)_3]^-$ in thf afforded the mixed-metal clusters $[Pt_2M(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$ (M = Mo, **2**; M = W, **3**) (Scheme 1).§ Their $^{31}P\{^1H\}$ NMR spectra contain a triplet at low field for the μ-PPh_2 ligand and a doublet for terminal phosphines, both with satellites due to couplings with two Pt atoms. In addition, the pattern of the resonance of the phosphine ligands is typical for a P→Pt–Pt←P chain. An X-ray diffraction study of **2**¶ established that the metal atoms form an isosceles triangle with a Pt–Pt edge bridged by a PPh_2 group (Fig. 1). Two CO ligands occupy a semi-bridging position on the Pt–Mo edges and the third one is semi-triply bridging over the metallic face. This arrangement is reminiscent of that in the tetranuclear cluster $[Pt_2Mo_2(\mu\text{-}CO)_6Cp_2(PEt_3)_2]$ **4**,[5a] its palladium analogue,[5b] or in the trinuclear cluster $[Pd_2Mo(\mu\text{-}Cp)(\mu\text{-}CO)_3Cp(PPr^i{}_3)_2]$.[6] Each Pt atom is ligated by a PPh_3 ligand and the Mo atom by a η^5-cyclopentadienyl ligand. The metal–metal distances in **2** are comparable with those in **4**.[5a] The Pt–(μ-P)–Pt angle (69.55(4)°) is one of the narrowest for a PPh_2 group bridging a metal–metal bond. It is close to that in $[Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ (*ca.* 69.0°)[7] but smaller than in $[Pt_2\{\mu\text{-}Co(CO)_3(PPh_3)\}(\mu\text{-}PPh_2)(PPh_3)_2]$ (72.41(8)°),[8] which is consistent with a longer Pt–Pt bond of 2.664(1) Å in the latter. The three P atoms are almost in the metal plane, at +0.140(2), +0.044(2) and +0.050(2) Å, respectively. The PPh_3 ligands are almost aligned with the Pt atoms.



Scheme 1

The highest yields of clusters **2** and **3** were obtained with a ratio of three $[MCp(CO)_3]^-$ anions for one dinuclear complex **1**. Since one anion enters in the composition of the clusters, the other two are probably eliminated with other ligands of **1**, *i.e.* H and I.

Reaction of 3 equiv. of $[Co(CO)_4]^-$ with 1 equiv. of complex **1** unexpectedly afforded the new homonuclear triplatinum cluster $[Pt_3(\mu\text{-}PPh_2)(\mu\text{-}CO)_2I(PPh_3)_3]$ **5**§ instead of Pt–Co cluster(s). The $^{31}P\{^1H\}$ NMR spectrum contains three signals flanked by ^{195}Pt satellites. The singlet at δ 279.6 is assigned to a PPh_2 group bridging two equivalent Pt atoms and the doublet

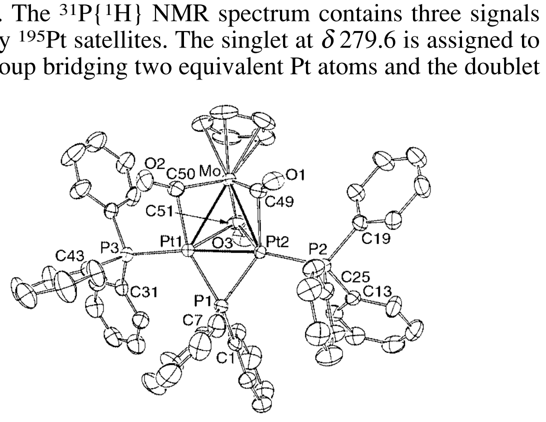


Fig. 1 Molecular structure of $[Pt_2Mo(\mu\text{-}CO)_3(\mu\text{-}PPh_2)Cp(PPh_3)_2]$ **2**. Selected interatomic distances (Å) and angles (°): Pt(1)–Pt(2) 2.6048(3), Pt(1)–Mo 2.7963(5), Pt(2)–Mo 2.8139(6), Pt(1)–P(1) 2.282(2), Pt(1)–P(3) 2.261(2), Pt(2)–P(1) 2.283(2), Pt(2)–P(2) 2.254(2); Pt(1)–Mo–Pt(2) 55.33(1), Mo-Pt(1)–Pt(2) 62.68(1), Mo–Pt(2)–Pt(1) 61.99(1), P(3)–Pt(1)–Pt(2) 174.78(4), P(2)–Pt(2)–Pt(1) 169.72(4), Pt(1)–P(1)–Pt(2) 69.55(4).

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† Electronic supplementary information (ESI) available: preparation of **2**, **3** and **5**. See http://www.rsc.org/suppdata/cc/b1/b101410m/

‡ In memoriam Luigi M. Venanzi, who contributed so much to inorganic and cluster chemistry.

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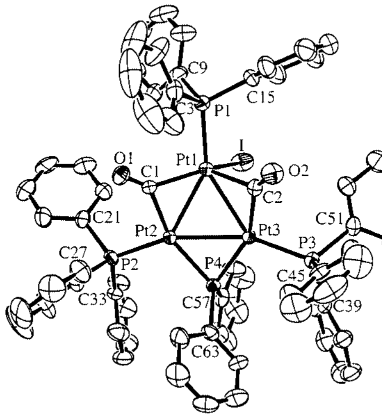

Fig. 2 Molecular structure of $[Pt_3(\mu\text{-}PPh_2)(\mu\text{-}CO)_2I(PPh_3)_3]$ **5**. Selected interatomic distances (Å) and angles (°): Pt(1)–Pt(2) 2.6832(13), Pt(1)–Pt(3) 2.694(2), Pt(2)–Pt(3) 2.736(2), Pt(1)–I 2.8165(17), Pt(1)–P(1) 2.268(3), Pt(2)–P(2) 2.238(3), Pt(3)–P(3) 2.256(3), Pt(2)–P(4) 2.279(3), Pt(3)–P(4) 2.273(3), Pt(2)–Pt(1)–Pt(3) 61.17(4), P(1)–Pt(1)–I 99.72(8), Pt(1)–Pt(2)–Pt(3) 59.62(5), P(2)–Pt(2)–Pt(3) 160.76(7), P(3)–Pt(3)–Pt(2) 159.33(7), Pt(3)–P(4)–Pt(2) 73.90(8).

at δ 33.8 to the phosphine ligands in the $Ph_3P{\rightarrow}Pt{-}Pt{\leftarrow}PPh_3$ moiety. These phosphines are coupled with a third phosphorus, which resonates as a triplet at δ 75.2. From the intensities of its ^{195}Pt satellites, it is deduced that this phosphine is coordinated to a Pt atom, which is itself linked to two equivalent Pt atoms. Cluster **5** should contain a triangle of Pt atoms, each bearing a phosphine ligand, with two Pt atoms being bridged by a PPh_2 group. An X-ray diffraction study¶ established the structure of **5** in which the shortest edge of the metal triangle, Pt(2)–Pt(3), is bridged by a PPh_2 group and the other two are each symmetrically bridged by a CO group (Fig. 2). A PPh_3 ligand is coordinated to each Pt atom and an iodine atom is bonded to Pt(1). The P(1)Pt(1)C(1)C(2)I atoms form the apices of a trigonal pyramid with P(1) in an apical position. The P(1)–Pt(1) bond makes angles of *ca.* 100° with the three basal bonds Pt(1)–I, Pt(1)–C(1) and Pt(1)–C(2).

Formation of **5** implies a complex reaction mechanism, where carbonyl groups have exchanged between cobalt and platinum, probably *via* a mixed Pt–Co complex. Fragmentation of the Pt_2 entity of complex **1** is required to form the Pt_3 framework and iodine could either remain on one of the Pt atoms or I^- attack an intermediate species. Complex reactions between Pt(II) halide complexes and $[Co(CO)_4]^-$ have been described from which heterometallic Pt–Co clusters with diverse Pt/Co compositions were isolated[9] and when the isoelectronic metalates $[Mn(CO)_5]^-$ or $[Fe(CO)_3(NO)]^-$ were used instead, no Pt–Mn or Pt–Fe clusters were observed, respectively, but rather $[Pt_5(CO)_6(PR_3)_4]$ which resulted from selective reductive carbonylation of the Pt(II) precursor complex.[10]

The 44e clusters **2** and **3** can formally be viewed as formed of two fragments, the cationic, 26-valence electrons (VE) entity $[Pt_2(\mu\text{-}PPh_2)(PPh_3)_2]^+$, which possesses two vacant fragment orbitals (2a′ and 2a″ in C_s symmetry)[11] and a bridging, 18-VE carbonylmetalate $[MCp(CO)_3]^-$. The HOMOs of the latter ($1a_1$ + 1e) can formally donate 4e to the dinuclear cation,[12] so that each Pt atom achieves its usual 16 VE count. The 44e count in cluster **5** is not unusual for Pt_3 clusters (with two 16e and one 18e metal centres), although the 42e alternative is more frequently encountered.[13] By analogy with the bonding behaviour of $[MCp(CO)_3]^-$, one can view the fragment $[PtI(CO)_2(PPh_3)]^-$ as a bridging group formally donating 4e to the $[Pt_2(\mu\text{-}PPh_2)(PPh_3)_2]^+$ cation, through two Pt–Pt bonds and two bridging CO groups, *i.e.* 2e to each Pt atom. In terms of electron counting, this makes these metalates behave remarkably similar to bridging halides or $\mu\text{-}PR_2^-$. To our knowledge, the anionic 18e complex $[PtI(CO)_2(PPh_3)]^-$ has not been isolated previously.

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Notes and references

§ *Selected data*: **2**: IR (KBr) ν(CO)/cm^{-1}: 1830s, 1788s. FAB-MS (NBA matrix): *m/z* 1099.1 ($[Pt_2(\mu\text{-}PPh_2)(PPh_3)_2]^+$ = [M − $MoCp(CO)_3]^+$). $^{31}P\{^1H\}$ NMR (THF–C_6D_6): δ 283.3 (t, ^2J(P–P) 42, ^1J(Pt–P) 2738 Hz), 42.8 (d, ^2J(P–P) 42, ^1J(Pt–P) 4780, ^2J(Pt–P) 50, ^3J(P–P) 88 Hz).

3: IR (KBr) ν(CO)/cm^{-1}: 1830s, 1788s. FAB-MS (NBA matrix): *m/z* 1099.1 ($[Pt_2(\mu\text{-}PPh_2)(PPh_3)_2]^+$ = [M − $WCp(CO)_3]^+$). $^{31}P\{^1H\}$ NMR (THF–C_6D_6): δ 312.4 (t, ^2J(P–P) 43, ^1J(Pt–P) 2631 Hz), 44.1 (d, ^2J(P–P) 43, ^1J(Pt–P) 4832, ^2J(Pt–P) 87, ^3J(P–P) 87 Hz).

5: IR (KBr) ν(CO)/cm^{-1}: 1831s, 1789vs. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 279.6 (s, ^1J(Pt–P) 2511 Hz), 75.2 (t, ^3J(P–P) 44, ^1J(Pt–P) 5809, ^2J(Pt–P) 505 Hz), 33.8 (d, ^3J(P–P) 44, ^1J(Pt–P) 4382, ^2J(Pt–P) 70, ^3J(P–P) 81 Hz).

¶ *Crystal data*: for **2**: single crystals were obtained by slow diffusion of diethyl ether into a solution of **2** in dichloromethane. $C_{56}H_{45}MoO_3P_3Pt_2 \cdot H_2O$, M = 1363.04, triclinic, space group $P\bar{1}$, a = 12.053(1), b = 13.690(1), c = 17.292(3) Å, α = 109.271(6), β = 92.541(6), γ = 106.169(6)°, V = 2557.5(5) Å^3, Z = 2, D_c = 1.77 g cm^{-3}, μ = 5.886 mm^{-1}, T = 173 K, λ(Mo-Kα) = 0.70930 Å, 8988 data collected, 7078 data with $I > 3\sigma(I)$, θ min./max. = 2.5/24.92°, $R(F)$ = 0.023, $R_w(F)$ = 0.034, GOF = 1.095.

For **5**: single crystals were obtained by slow diffusion of hexane into a solution of **5** in toluene. $C_{68}H_{55}IO_2P_4Pt_3$, M = 1740.17, triclinic, space group $P\bar{1}$, a = 13.564(12), b = 14.954(6), c = 17.948(8) Å, α = 69.64(3), β = 75.44(4), γ = 63.98(4)°, V = 3046(3) Å^3, Z = 2, D_c = 1.897 g cm^{-3}, μ = 7.528 mm^{-1}, T = 253 K, λ(Mo-Kα) 0.71073 Å, 11189 data collected, 10693 data with $I > 2\sigma(I)$, R_1 = 0.0397, wR_2 = 0.0913. CCDC 158327 and 158328. See http://www.rsc.org/suppdata/cc/b1/b101410m/ for crystallographic data in .cif or other electronic format.

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