Platinum Cluster Compounds: *X*-Ray Structures of Phosphido-bridged Bi- and Tri-nuclear Complexes with Strong Metal–Metal Bonds Derived from $[Pt(PPh_3)_4]$

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Summary Binuclear $[(Pt_2(PPh_3)_2(PPh_2)_2]$ and trinuclear $[Pt_3(PPh_3)_2(PPh_2)_3Ph]$ cluster compounds of platinum have been prepared from $[Pt(Ph_3P)_4]$ and characterised by *X*-ray crystal structure analyses of their benzene solvates.

THE complexes $[Pt(PPh_3)]_n$ (n = 2—4) have assumed significance as models for chemisorption on metals and as precursors for an extensive range of inorganic derivatives.[1] Certain aspects of their chemistry are, however, ill defined and contentious. In particular, the mechanistically important[2] compound $[Pt(PPh_3)_2]$[3] unlike $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$ which have been unambiguously characterised,[4,5] requires further elucidation and the nature of several coloured polynuclear derivatives prepared from $[Pt(PPh_3)_n]$[6] or $[Pt(PPh_3)_2(C_2H_4)]$[7] appears uncertain. We observed, as have others,[5] the production of red solutions on heating $[Pt(PPh_3)_4]$ in benzene for extended periods. The *X*-ray crystal structures of two crystalline red complexes $[Pt_2(PPh_3)_2(PPh_2)_2],C_6H_6$ (I) and $[Pt_3(PPh_3)_2(PPh_2)_3(Ph)],C_6H_6$ (II) obtained from these solutions have now been determined. The results are significant in the context of previously postulated cluster structures and the general solution chemistry of $[Pt(PPh_3)_n]$.

On refluxing $[Pt(PPh_3)_4]$ in benzene under argon or nitrogen for several days deep red solutions result.† Orange red crystals of (I)‡ are obtained after solvent removal, extraction with n-hexane, and recrystallisation of the solid residue from benzene–diethyl ether. Needles of (I) are monoclinic, space group $P2_1/n$ with $a = 21{\cdot}533(11)$, $b = 16{\cdot}933(16)$, $c = 15{\cdot}870(10)$ Å; $\beta = 97{\cdot}34(6)°$; $Z = 4$; $D_m = 1{\cdot}58$ g cm^{-3}; $D_c = 1{\cdot}577$ g cm^{-3}. Anisotropic least-squares refinement gave $R = 0{\cdot}067$ for 3694 independent diffractometry data $[I \geqslant 2\sigma(I)]$. The structure consists of a binuclear molecule with a strong Pt–Pt bond, bridging diphenylphosphide groups, and two terminal triphenylphosphine ligands. The Pt_2P_4 skeleton shows only a small deviation from idealised D_{2h} symmetry (Figure). The following stereochemical features are evident from a comparison with related molecules: (i) The Pt–Pt distance [2·604(1) Å] is distinctly shorter than the Pt–Pt bond length [2·647(2) Å] in $[Pt_2S(CO)(PPh_3)_3]$[8] and the average intra-triangular Pt–Pt distance (2·66 Å) in the anions $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n^{2-}$ (n = 2,3,5)[9] suggesting a Pt–Pt bond order somewhat greater than one. Heavy metal bond orders of two have been invoked for M–M distances of 2·551(1) and 2·629(1) Å in $[Ir(CO)(PPh_3)(\mu\text{-}PPh_2)]_2$[10] and $[Ru(NO)(PPh_3)(\mu\text{-}PPh_2)]_2$[11] respectively. (ii) The stereochemistry of the Pt_2P_2 ring, with acute Pt–P–Pt angles (av. 69·0°) closely resembles other M_2P_2 rings where metal–metal interactions are present.[10,11] Orange rectangular blocks of (II),§ obtained from the same reaction mixture after further refluxing are orthorhombic, space group *Pbcn*, $a = 22{\cdot}411(8)$, $b = 17{\cdot}940(7)$, $c = 18{\cdot}359(8)$, $Z = 4$, $D_m = 1{\cdot}67$ g cm^{-3}; $D_c = 1{\cdot}638$ g cm^{-3}. Least-squares refinement with anisotropic temperature coefficients for P and Pt gave $R = 0{\cdot}079$ for 2808 reflections $[I \geqslant 1{\cdot}5\sigma(I)]$. The structure of (II) is based on an open Pt_3 cluster with two Pt–Pt bonds and

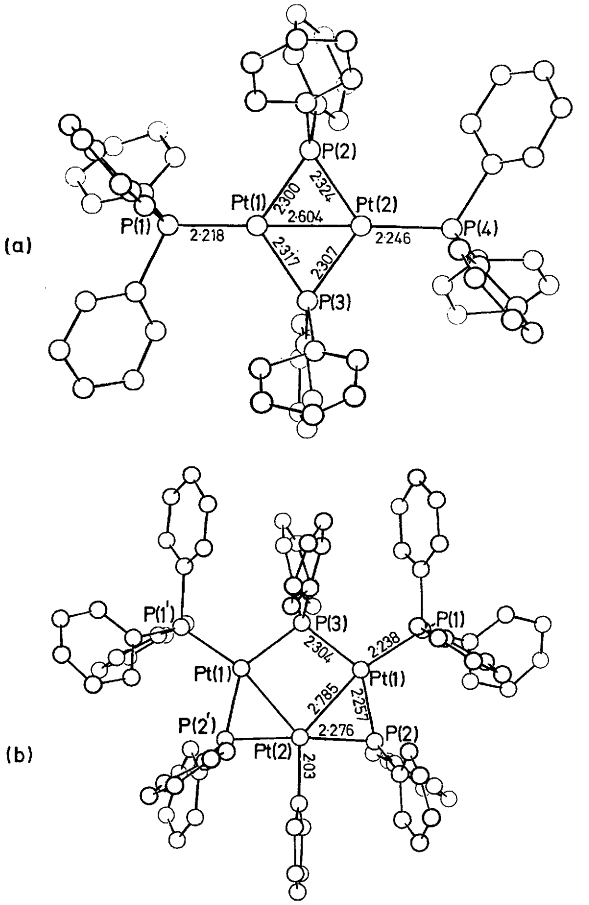

FIGURE. The molecular structures of (a) $[Pt_2(PPh_3)_2(PPh_2)_2],C_6H_6$ and (b) $[Pt_3(PPh_3)_2(PPh_2)_3Ph],C_6H_6$ as drawn by ORTEP. The non-bonding Pt(1)–Pt(1′) distance is 3·630(1) Å in (b).

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† Complex (I) was initially prepared at the University of Sussex in attempted reactions of $[Hg\{(Me_3Si)_2CH\}_2]$ with $[Pt(Ph_3P)_4]$.

‡ Different crystallisation conditions give different crystalline forms, which appear to be identical compounds from *X*-ray measurements.

§ Since (I) and (II) have very similar colours they are best distinguished by a morphological examination under a microscope. Careful examination of i.r. data also revealed significant differences in frequencies and intensities in the region 400—800 cm^{-1} which can be used diagnostically.

three bridging phosphido groups. The Pt–Pt bond length [2·785(1) Å] is longer than in (I) but comparable to Pt–Pt distances of 2·75 and 2·79 Å in $[Pt_4(PR_2R')_4(\mu_2\text{-}CO)_5]$ ($R =$ Me, $R' =$ Ph).[12] The unique Pt atom is co-ordinated to two phosphido groups, Pt(1) and Pt(1′) and the carbon atom of a σ-bonded phenyl group [Pt–C 2·03(2) Å]. The presence of a Pt–C(phenyl) bond is not unexpected since formation of PPh_2 bridges from PPh_3 ligands implies P–C bond cleavage. Numerous other examples of facile P–C bond cleavage in reactions of phosphines with low-valent metals are known,[13] a particularly notable example being the synthesis of phenyl and benzyne complexes from $[Os_3(CO)_{12}]$ and PPh_3.[14]

The structural relationship of (I) and (II) to other so-called clusters of platinum derived from Pt^0 or Pt^{II} precursors is clearly of some importance. Brown or red clusters originally assigned[6] tri- or tetra-meric structures with no bridging ligands have been reformulated as orthometallated species.[7] Reported physical data for these compounds are insufficient to permit comparison with (I) and (II).

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