

## Communications to the Editor

**Bicluster Oxidative Addition: The Bicapped  
Trigonal Prism in  
[Pt<sub>6</sub>(μ<sub>3</sub>-SnBr<sub>3</sub>)<sub>2</sub>(μ-CO)<sub>6</sub>(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>] and  
Related Clusters**

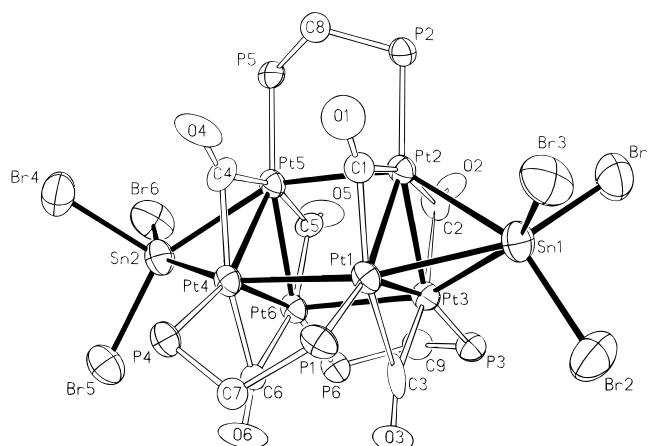
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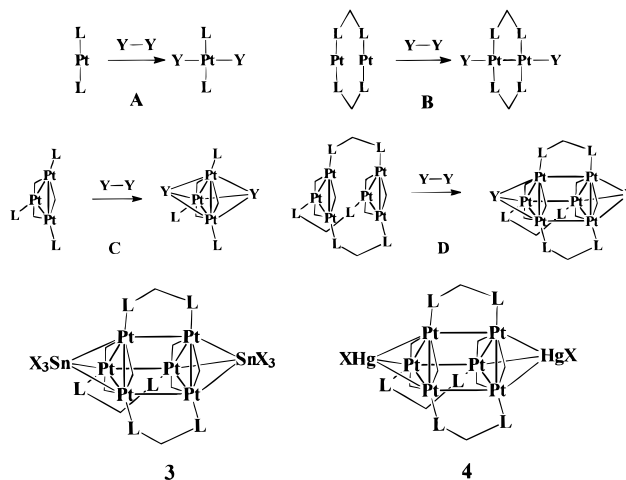
The clusters [Pt<sub>6</sub>(μ-CO)<sub>6</sub>(μ-dppm)<sub>3</sub>] (**1**) and [Pt<sub>6</sub>(CO)<sub>6</sub>(μ-dppm)<sub>3</sub>]<sup>2+</sup> (**2**) (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) have 84- and 82-electron configurations and have 2 × triangular and octahedral stereochemistries respectively.<sup>1</sup> This communication reports new 86-electron clusters, **3** and **4**, with bicapped trigonal prismatic cores, for some of which the formation can be considered to occur by a new type of reaction, termed a bicluster oxidative addition.

In further defining the dependence of structure on electron count in Pt<sub>6</sub> clusters,<sup>1</sup> it was of interest to synthesize derivatives with the 86-electron configuration, but reduction of **1** to the dianion, which would be isoelectronic with the only known trigonal prismatic platinum cluster [Pt<sub>6</sub>(CO)<sub>6</sub>(μ-CO)<sub>6</sub>]<sup>2-</sup>, was unsuccessful.<sup>2</sup> Another approach was therefore required, and a new oxidative addition strategy proved successful as outlined below. To understand this approach, it is useful to draw an analogy with the well-known mononuclear and binuclear oxidative additions, as depicted in **A** and **B** (Scheme 1). Oxidative addition of a reagent Y–Y to [PtL<sub>2</sub>] (L, tertiary phosphine) leads to formation of two new Pt–Y bonds in [PtY<sub>2</sub>L<sub>2</sub>] (**A**) for which each reagent provides two electrons and two orbitals (PtL<sub>2</sub> provides a filled d<sub>z<sup>2</sup></sub> and vacant p<sub>z</sub> orbital). In binuclear oxidative addition to [Pt<sub>2</sub>(μ-L-L)<sub>2</sub>], each platinum atom provides the same orbitals as above, and hence six MOs are formed, of which the lowest three are occupied, so leading to three new bonds, including a Pt–Pt bond, in **B**.<sup>3</sup> A very similar treatment can be used to predict cluster and bicluster oxidative additions, as shown in **C** and **D**, and in each case, the cluster electron count will naturally increase by 2. Case **C** is already known through the reactions of mercury(I) halides, XHg–HgX, with clusters [Pt<sub>3</sub>(μ-CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>]<sup>4</sup> and, at least in a formal sense, through the adducts of X<sub>3</sub>Sn–SnX<sub>3</sub> with [Pt<sub>3</sub>(μ-dppm)<sub>3</sub>].<sup>5</sup> This paper reports the first examples of case **D** by formal oxidative



**Figure 1.** View of the structure of **3c**. The eclipsed conformations of the two Pt<sub>3</sub> triangles and SnBr<sub>3</sub> groups are indicated by the dihedral angles typeified by P1–Pt1–Pt4–P4 and Br1–Sn1–Sn2–Br6 which fall in the ranges 1.5–6.1° and 7.2–10.7°, respectively. In the idealized structure, these should be zero. The Pt–Sn distances are in the range 2.745(3)–2.950(3) Å.

**Scheme 1<sup>a</sup>**



<sup>a</sup> L, phosphine; L-L, dppm. Only the position of the carbon atom of μ-carbonyl ligands are shown. In the cluster reactions, Y = HgX. addition to **1**, which is regarded as consisting of two [Pt<sub>3</sub>(μ-CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>] units held together by the three bridging dppm ligands.<sup>1,6</sup>

The clusters [Pt<sub>6</sub>(μ<sub>3</sub>-SnX<sub>3</sub>)<sub>2</sub>(μ-CO)<sub>6</sub>(μ-dppm)<sub>3</sub>] (**3**; X = F, **3a**; Cl, **3b**; Br, **3c**) were formed on reaction of either **1** or **2** with SnX<sub>3</sub><sup>-</sup>, formed *in situ* from SnX<sub>2</sub> and NaX or KX (the iodide derivative decomposed in solution and is only partially characterized).<sup>6</sup> Similarly, the clusters [Pt<sub>6</sub>(μ<sub>3</sub>-HgX)<sub>2</sub>(μ-CO)<sub>6</sub>(μ-dppm)<sub>3</sub>] (**4**; X = Cl, **4a**; Br, **4b**; I, **4c**) were formed on reaction of either **1** or **2** with Hg<sub>2</sub>X<sub>2</sub>.<sup>6</sup> Stoichiometry requires that **3** be formed from **2** and **4** from **1**, but in practice, either combination is possible. Indeed, **4** can also be prepared from **1** or **2** with HgX<sub>2</sub>, though the yields are much lower than with Hg<sub>2</sub>X<sub>2</sub>. Clearly, **3** and **4** are thermodynamically stable, and when necessary, additional redox reactions occur to allow their formation. For example, in the reaction of **1** with HgCl<sub>2</sub>, a major byproduct is [PtCl<sub>2</sub>(dppm)], formed by oxidative degradation of **1**.

(6) Analytical and spectroscopic data for the new clusters are given as supporting information.

(1) Hao, L.; Spivak, G. J.; Xiao, J.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 7011.

(2) (a) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225. (b) Underwood, D. J.; Hoffmann, R.; Tatsumi, K.; Nakamura, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5968.

(3) See, for example: (a) Balch, A. L. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L., Ed.; Plenum Press: New York, 1983. (b) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99. Note that most Pt(0) complexes exist as [PtL<sub>3</sub>] or [Pt<sub>2</sub>(μ-L-L)<sub>2</sub>] but often dissociate one ligand prior to oxidative addition; Scheme 1 is simplified for clarity. Preorganization of the metal centers by bridging ligands is generally necessary to promote binuclear (and bicluster) oxidative additions.

(4) (a) Albinati, A.; Dahmen, K.-H.; Demartin, F.; Forward, J. M.; Longley, C. J.; Mingos, D. M. P.; Venanzi, L. M. *Inorg. Chem.* **1992**, *31*, 2223. (b) Imhof, D.; Venanzi, L. M. *Chem. Soc. Rev.* **1994**, 185. Note that in the cluster reactions, an MO derived from combination of three d or p orbitals takes the place of the individual orbitals in mononuclear oxidative addition.

(5) Jennings, M. C.; Schoettel, G.; Roy, S.; Puddephatt, R. J.; Douglas, G.; Jennings, M. C.; Manojlović-Muir, Lj.; Muir, K. W. *Organometallics* **1991**, *10*, 580.

The high symmetry of **3** and **4** is indicated by the NMR spectra,<sup>6</sup> which contain single resonances for the six dppm CH<sub>2</sub> protons, the six  $\mu$ -CO groups, and the six dppm phosphorus atoms in the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra, respectively. These data are consistent with, but do not prove, a trigonal prismatic structure, as expected for the 86-electron configurations.<sup>2</sup>

The structure of **3c** was determined by X-ray crystallography (Figure 1).<sup>7</sup> The cluster has approximately *D*<sub>3h</sub> symmetry, and the metal core can be described as a trigonal prism of platinum atoms, with each triangular face capped by a SnBr<sub>3</sub> group. Thus, both the Pt<sub>3</sub> triangles and the SnBr<sub>3</sub> groups are eclipsed.<sup>7</sup> The Pt–Pt bond lengths within each Pt<sub>3</sub> triangle range from 2.656(2) to 2.681(2) Å, slightly longer than in [Pt<sub>3</sub>( $\mu$ -SnF<sub>3</sub>)<sub>2</sub>( $\mu$ -dppm)<sub>3</sub>] (2.609(2)–2.639(1) Å) and related complexes.<sup>5</sup> The intertriangle Pt–Pt distances in **3c** (2.929(2)–2.946(2) Å) are longer, as is also found in the anionic cluster [Pt<sub>6</sub>( $\mu$ -CO)<sub>6</sub>(CO)<sub>6</sub>]<sup>2-</sup>.<sup>2</sup> The intertriangle Pt–Pt distances are expected to be shorter than in **1** according to the formalism **D**. The structure of **1** has not been determined, but it is significant that the analogous Pd–Pd distances (2.948(3)–3.030(2) Å) in the palladium analog of **1** are longer than the Pt–Pt distances in

(7) X-ray data for **3c**: C<sub>81</sub>H<sub>66</sub>O<sub>6</sub>P<sub>6</sub>Br<sub>6</sub>Sn<sub>2</sub>Pt<sub>6</sub>; fw = 3208.54; monoclinic, space group *P*2<sub>1</sub>/*c*; *a* = 16.831(3) Å, *b* = 18.588(3) Å, *c* = 33.575(6) Å,  $\beta$  = 90.20(2)°, *V* = 10 504(3) Å<sup>3</sup>, *Z* = 4, *R*<sub>1</sub> = 0.0772, *wR*<sub>2</sub> = 0.1705 for 6769 observations with *F* ≥ 4σ(*F*).

**3c**.<sup>8</sup> Thus, the hypothesis that bicluster oxidative addition to **1** should lead to intertriangle Pt–Pt bonding to give a trigonal prismatic Pt<sub>6</sub> cluster core appears to be upheld and leads to a new bicapped trigonal prism structure.<sup>9</sup>

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**Supporting Information Available:** Spectroscopic and analytical data for the clusters, details of the X-ray structure determination, and tables of X-ray crystallographic data (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(8) Holah, D. G.; Hughes, A. N.; Krysa, E.; Magnuson, V. R. *Organometallics* **1993**, *12*, 4721. The covalent radii of Pd and Pt are very similar. EHMO calculations on the model compounds [Pt<sub>6</sub>( $\mu$ -CO)<sub>6</sub>(PH<sub>3</sub>)<sub>6</sub>] and [Pt<sub>6</sub>( $\mu$ -CO)<sub>6</sub>(PH<sub>3</sub>)<sub>6</sub>( $\mu$ -3-MX<sub>n</sub>)<sub>2</sub>] predict enhanced intertriangle Pt–Pt bonding when the ( $\mu$ -3-MX<sub>n</sub>)<sub>2</sub> groups (M = Sn, X = Br, *n* = 3; M = Hg, X = Cl, *n* = 1) are present.

(9) The bicapped trigonal prism is also uncommon for other transition metal clusters. The closest analogy appears to be in the carbide-centered, 90-electron cluster [Rh<sub>6</sub>C(CO)<sub>15</sub>( $\mu$ -3-CuCNMe)<sub>2</sub>]. Albano, V. G.; Braga, D.; Martinengo, S.; Chini, P.; Sansoni, M.; Strumolo, D. *J. Chem. Soc., Dalton Trans.* **1980**, 52.