Use of the Monomeric η^2-Phospha-alkyne Complex $[Pt(PPh_3)_2(Bu^tCP)]$ in Heterometallic Cluster Synthesis. Crystal and Molecular Structure of the Novel Pentametallic Complex $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$

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Treatment of the η^2-phospha-alkyne complex $[Pt(PPh_3)_2(Bu^tCP)]$ with $[Pd(PPh_3)_4]$ affords the pentametallic complex $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$ whose structure is that expected on the basis of the cluster condensation generalisation.

Transition metal cluster chemistry is an area of current activity and a variety of synthetic routes to both homo- and heterometallic systems have been developed. The addition of metal fragments to unsaturated species such as metal–metal multiple bonds and to metal–carbene and metal–carbyne compounds has been particularly fruitful.[1]

We have previously[2] drawn attention to the isolobal relationship RC $\underset{\circ}{\longleftrightarrow}$ P $\underset{\circ}{\longleftrightarrow}$ $W(CO)_2(\eta^2\text{-}C_5H_5)$ $\underset{\circ}{\longleftrightarrow}$ $Co(CO)_3$ and reported the use of the phospha-alkyne $Bu^tC{\equiv}P$ in the synthesis of mononuclear {*e.g.* $[Pt(PPh_3)_2(Bu^tCP)]$[3]}, dinuclear {*e.g.* $[Co_2(CO)_6(Bu^tCP)]$,[3] $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(Bu^tCP)]$[4]}, and trinuclear {*e.g.* $[Fe_2Pt(Ph_2PCH_2CH_2PPh_2)(CO)_6(Bu^tCP)]$[2]} complexes as well as in compounds in which clusters are interlinked {*e.g.* $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(Bu^tCP)\{M_3(CO)_{11}\}]$, (M = Ru, Os)[5]}.

We now report that the η^2-phospha-alkyne complex $[Pt(PPh_3)_2(Bu^tCP)]$ reacts readily with $[Pd(PPh_3)_4]$ in toluene at *ca.* 60 °C to give the novel deep-red pentametallic compound $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$, (**1**).† A single crystal

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† *Added in proof:* The analogous $[Pd_5(PPh_3)_5(Bu^tCP)_3]$ complex has also been synthesised and is isomorphous with (**1**).

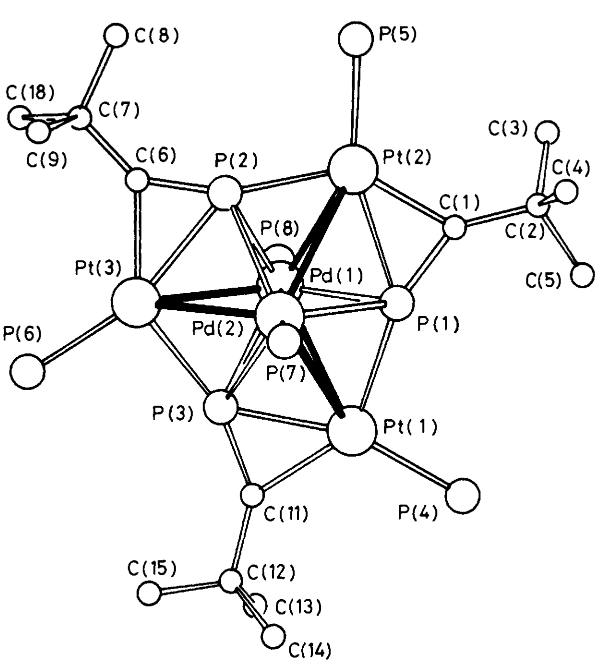
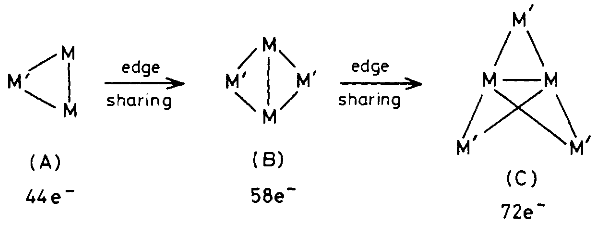


Figure 1. Structure of $[Pd_2Pt_3(PPh_3)_5(Bu^tCP)_3]$, (**1**).

X-ray diffraction study‡ on (**1**) reveals that the molecular structure (Figure 1) consists of a trigonal bipyramidal arrangement of the metal atoms with the two Pd atoms, which are bonded [Pd–Pd 2.679(2) Å], occupying axial positions and the platinum atoms in equatorial sites. Each metal is co-ordinated to one PPh_3 ligand and the P–Pd–Pd–P framework is essentially linear. The three phospha-alkynes act as bridging ligands and are symmetrically placed so that there is a C_3 rotation axis lying along the P–Pd–Pd–P vector. Each Bu^tCP ligand remains η^2- to one platinum [Pt–P 2.437(6) Å] and is σ-to another [Pt–P 2.329(6) Å]. Likewise each phospha-alkyne is asymmetrically disposed with respect to the Pd–Pd bond [Pd–P 2.444(6) and 2.525(6) Å respectively]. The P–C bond length of the co-ordinated Bu^tCP is 1.62(2) Å which is considerably larger than in the free ligand, but similar to that in $[Pt(PPh_3)_2(Bu^tCP)]$.[3]

The structure of (**1**) can also be considered as being tristellated about the central Pd–Pd bond and interestingly the propeller-like structure adopted by the five metal atoms is in accord with predictions based on the cluster condensation generalisation.[6–8] Thus if we consider the triangular metal system (A) containing 44 electrons {*e.g.* M = M′ = Pt; as in $[Pt_3(CO)_3(PR_3)_4]$[9–11] (R = C_6H_{11})}, then edge sharing produces the 58 electron butterfly structure (B) {*e.g.* M = M′ = Pt; as in $[Pt_4(CO)_5(PMe_2Ph)_4]$[12]}. Further edge sharing in



(B) then leads to the 72 electron 'propeller' type structure (C) (M = Pd, M′ = Pt), exemplified by complex (**1**), if the Bu^tCP ligands are regarded as 4e donors. Another example of structure (C), although not previously discussed within the cluster condensation generalisation, is the recently reported[13] pentametallic complex $[Pt_2(PPh_3)_2\{Sn(acac)_2\}_3]$(Hacac = $MeCOCH_2COMe$).

An alternative approach using the isolobal relationship also suggests that (**1**) represents the first example of a hexagonal bipyramidal *closo*-cluster. The equatorial plane is defined by the three platinum and three phosphorus atoms and the palladium atoms lie in the axial sites. If the Bu^tC– ligands are viewed as three electron bridging ligands then the observed electron count of 84 is consistent with the electron counting rules for *closo*-deltahedra.[6] The short Pd–Pd distance 2.679(2) Å can be viewed as a geometric consequence of attempting to equalise the equatorial–equatorial and equatorial–axial bond lengths in a hexagonal bipyramid. A similar short axial distance (Au–Au 2.58 Å) has been reported for the pentagonal bipyramidal $[Au_7(PPh_3)_7]^+$ cluster.[14]

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‡ *Crystal data* for (**1**): $C_{105}H_{102}Pd_2P_8Pt_3$, M = 2409.9, monoclinic, space group $P2_1/c$, a = 14.952(4), b = 24.029(10), c = 28.628(16) Å, β = 90.60(4)°, U = 10282.0 Å^3, Z = 4, D_c = 1.56 g cm^{-3}. The structure was solved by heavy atom methods and refined to R = 0.069 by least squares. 10,353 Reflections were measured on an Enraf-Nonius CAD 4 diffractometer with Mo-K_α radiation, and 6271 with $|F^2|>\sigma|F^2|$ were used in the refinement.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

1 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 89, and references therein.
2 S. I. Al-Resayes, P. B. Hitchcock, M. F. Meidine, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1984, 1080.
3 J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1981, 1141.
4 J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, M. F. Meidine, and J. F. Nixon, *J. Organomet. Chem.*, 1981, **238**, C82.
5 R. Bartsch, P. B. Hitchcock, M. F. Meidine, and J. F. Nixon, *J. Organomet. Chem.*, 1984, **266**, C41.
6 D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706; *Acc. Chem. Res.*, 1984, **17**, 311.
7 D. G. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **240**, 321.
8 D. M. P. Mingos and D. G. Evans, *J. Organomet. Chem.*, 1983, **251**, C13.
9 F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33, and references therein.
10 A. Albinati, G. Carturan, and A. Musco, *Inorg. Chim. Acta*, 1976, **16**, L3.
11 A. Albinati, *Inorg. Chim. Acta*, 1977, **22**, L31.
12 R. G. Vranka, L. F. Dahl, P. Chini, and J. Chatt, *J. Am. Chem. Soc.*, 1969, **91**, 1574.
13 G. W. Bushnell, D. T. Eadie, A. Pidcock, A. R. Sam, R. D. Holmes-Smith, S. R. Stobart, E. T. Brennan, and T. S. Cameron, *J. Am. Chem. Soc.*, 1982, **104**, 5837.
14 J. W. A. van der Velden, P. T. Beurskens, J. J. Bour, W. P. Bosman, J. H. Noordik, M. Kolenbrander, and J. A. K. M. Buskes, *Inorg. Chem.*, 1984, **23**, 146.