A Macropolyhedral Polymetallaborane Cluster: Molecular Structure of the Seventeen-vertex Triplatinaheptadecaborane [$(PhMe_2P)_4Pt_3B_{14}H_{16}$]†

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The molecular structure of the novel seventeen-vertex macropolyhedral trimetallaborane [$(PhMe_2P)_4Pt_3B_{14}H_{16}$] may be interpreted either in terms of a formal *pentadecahapto* complex of a 7,7′-bi(*arachno*-heptaboranyl)-type ligand co-ordinated η^4, η^5, and η^6 to the three metal centres, or in terms of a *nido*-type 2,7,10-trimetallaundecaborane cluster conjoined to an *iso-arachno*-6,8-dimetallanonaborane cluster with three adjacent vertices PtBPt in common.

Now that the structural patterns for sub-icosahedral boron-containing clusters are becoming well established, increasing attention is being focused on the patterns associated with species that have more than twelve vertices. These constitute (a) the so-called 'supraicosahedral' species, based on *closo* structures with thirteen vertices or more, and (b) the so-called 'macropolyhedral' species based on the fusion of two smaller sub-clusters, usually with two or more vertices in common. Here we report preliminary details of a novel and interesting member in the latter category; this is a seventeen-vertex {Pt_3B_{14}} cluster compound based upon an open nine-vertex cluster and an open eleven-vertex cluster fused with three vertices in common.

Crystals of this dark green compound are monoclinic, space group $P2_1/c$ with a = 1249.0(3), b = 3732.6(8), c = 1072.0(2) pm, β = 104.92(2)° and Z = 4. The structure, based on 4802 independent F_o with $I > 2\sigma(I)$ and corrected for absorption, was solved from Patterson and difference maps and refined to R = 0.049. ORTEP drawings of the structure are given in Figure 1.‡ The cluster structure is seen

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† 2,2,7,10-tetrakis(dimethylphenylphosphine)-2,7(6′),10(8′)-triplatina-*iso-arachno*-nonaborano-[6′,7′,8′ : 7,11,10]-*nido*-undecaborane.

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

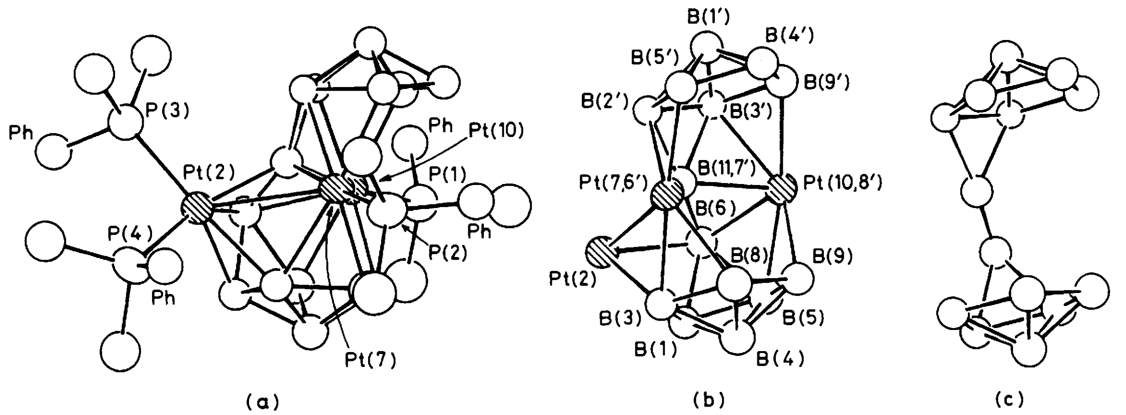


Figure 1. ORTEP drawings of (a) the molecule $[(PhMe_2P)_4Pt_3B_{14}H_{16}]$ (phenyl rings except *ipso* carbons omitted), and (b) a different orientation with the P-organyl groups omitted for clarity; (c) shows the fourteen-vertex 7,7′-bi(*arachno*-heptaboranyl)-type B-frame network. Hydrogen atoms were not located, but B-terminal H atoms are reasonably inferred for all B atoms except B(11). ^1H-$\{^{11}B\}$ N.m.r. spectroscopy indicates that one B atom, presumably B(11), does not have a terminal H atom associated with it, and that there are two bridging H atoms associated with ^{11}B resonances reasonably ascribed to B(4′), B(5′), and B(9′); a third bridging H atom, presumably associated with the Pt(7)B(8)B(9)Pt(10) sub-face, has not been confirmed by n.m.r. spectroscopy, but is inferred from the non-paramagnetic nature of the compound. Distances from Pt(2) are as follows: to Pt(7) 301.2(1), P(3) 234.1(4), P(4) 232.4(4), B(1) 223.3(17), B(3) 230.8(18), B(6) 225.0(16), and B(11) 218.6(17) pm. Distances from Pt(7) are: to Pt(10) 337.6(1), P(2) 231.0(4), B(3) 237.9(17), B(8) 228.6(18), B(11) 212.6(17), B(2′) 227.4(17), and B(5′) 225.7(17) pm. Distances from Pt(10) are: to P(1) 228.8(4), B(5) 226.5(18), B(6) 223.5(17), B(9) 228.1(18), B(11) 212.3(16), B(3′) 228.2(15), and B(9′) 230.4(18) pm.

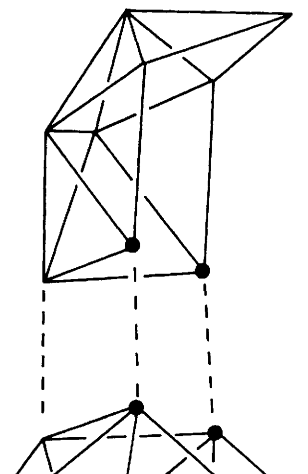
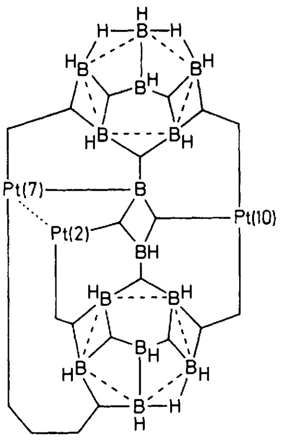
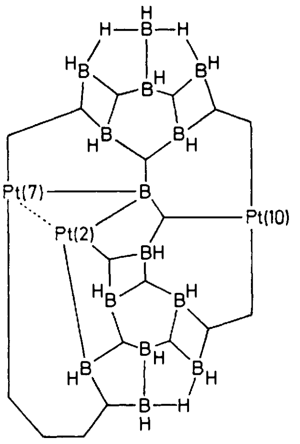


Figure 2. Schematic diagram of the two subclusters which conjoin to form the macropolyhedral Pt_3B_{14} cluster: the *arachno*-type nine-vertex subcluster $\{6',8'\text{-}Pt_2B_7\}$ has its 6′,7′,8′-PtBPt atoms in common with the 7,11,10-PtBPt atoms of the *nido*-type eleven-vertex subcluster $\{2,7,10\text{-}Pt_3B_8\}$.

to have a seventeen-vertex polyhedral configuration with a seven-membered $\overline{PtB_3PtB_2}$ open face, 10(8′),9′,4′,5′,6′(7),8,9, but with an otherwise deltahedral framework. It may be interpreted in terms of two sub-clusters: (i) an *arachno*-type nine-vertex $\{6',8'\text{-}Pt_2B_7\}$ moiety which has its 6′,7′,8′-PtBPt atoms in common with the 7,11,10-PtBPt atoms of (ii) a *nido*-type eleven-vertex $\{2,7,10\text{-}Pt_3B_8\}$ moiety distorted somewhat from the idealised $\{B_{11}H_{14}\}^-$ configuration by the accommodation of the larger Pt atoms and the longer Pt(2)–Pt(7) distance of *ca.* 301 pm. These two sub-clusters are illustrated in Figure 2.



(I)



(II)

The ^{11}B n.m.r. properties of the molecule suggest that the two pentagonal pyramidal $\{B_6\}$ sub-clusters [Figure 1(c) and broken lines in structure I] largely retain a *nido*-hexaboranyl electronic cluster character, which enables straightforward contributory valence-bond structures such as I and II to be written down. In I all metal atoms are formally platinum(II), square planar, with $\{(PhMe_2P)Pt(7)\}$ and $\{(PhMe_2P)Pt(10)\}$ each contributing three orbitals, and $\{(PhMe_2P)_2Pt(2)\}$ two orbitals, to the cluster bonding. In II, $\{(PhMe_2P)_2Pt(2)\}$ has a three-orbital platinum(IV)-type configuration, in accord with its geometric similarities to species such as $[(PhMe_2P)_2PtB_{10}H_{12}]$. In terms of structure II the complex may be regarded formally as a complex of a 7,7′-bi(*arachno*-heptaboranyl)-type ligand $\{(B_7H_8)_2\}^{8-}$, co-ordinating η^4, η^5, and η^6 to the atoms Pt(2), Pt(7), and Pt(10) respectively. In isolobal terms, the overall molecular structure then has the gross configuration that may be expected for the (as yet hypothetical) binary borane species $\{B_{17}H_{20}\}^-$ (from structure I) and $\{B_{17}H_{19}\}^{2-}$ (from structure II).

The compound is obtained in a yield of *ca.* 6% (based on platinum content) from the thermolysis of the nine vertex *arachno*-type compound $[(PhMe_2P)_2PtB_8H_{12}]$ in boiling toluene solution. Two other macropolyhedral species have already been identified from this reaction {[$(PhMe_2P)PtB_{16}H_{18}(PMe_2Ph)$][1] and [$(PhMe_2P)_2Pt_2B_{12}H_{18}$][2]}, and n.m.r. spectroscopy shows that others, as yet uncharacterised, are also present as reaction products. This behaviour of [$(PhMe_2P)_2PtB_8H_{12}$] is in sharp contrast to that of its iridium analogue [$(Me_3P)_2(CO)HIrB_8H_{12}$], which upon heating degrades smoothly and quantitatively by H_2 elimination to give the *nido*-species [$(Me_3P)_2(CO)IrB_8H_{11}$],[3] but may have some similarities to related osmium systems, in which cluster fusion to give the eighteen vertex macropolyhedral species {$B_{18}H_{22}$} occurs.[4]

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