

Molecular Structure of the 17-Vertex *conjuncto*-Platinaheptadecaborane [(PMe₂Ph) {PtB₁₆H₁₈ (PMe₂Ph)}]: a 16-Vertex η^6 -Hexadecaboranyl Ligand

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The compound [7-(PMe₂Ph) {7-PtB₁₆H₁₈-9'-(PMe₂Ph)}] is a complex of a macropolyhedral 16-vertex borane ligand based on the structure of an as yet unknown B₆-B₁₀ *conjuncto*-borane; it is the first example of a contiguous 17-vertex cluster species, and has a number of other interesting features.

There are few examples of contiguous open seven- and eight-vertex cluster species in polyhedral boron chemistry, and it is important to synthesize examples in order to establish

structural behavioural patterns. We now report that *arachno*-[(PMe₂Ph)₂(PtB₈H₁₂)]¹ when heated, yields a 17-vertex compound which not only contains a *nido*-eight-vertex structural

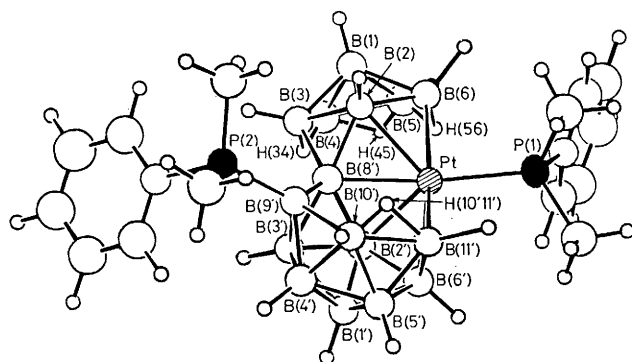
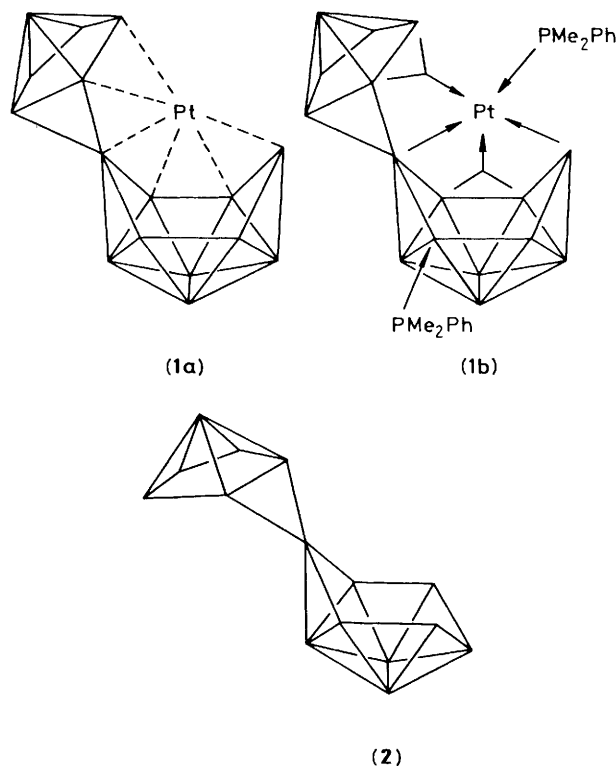


Figure 1. ORTEP drawing of the molecular structure of $[(\text{PMe}_2\text{Ph})\{\text{PtB}_{16}\text{H}_{18}(\text{PMe}_2\text{Ph})\}]$. Methyl and phenyl groups, with their hydrogen atoms, were refined as rigid groups with $\text{C}-\text{C}=139.5$ and $\text{C}-\text{H}=108$ pm. Borane hydrogens were located from a difference map and refined with fixed temperature factors $U_{180} = 700$ pm². Distances from the Pt atom are as follows: to B(2) 223.9(8), to B(6) 227.4(11), to B(8) 223.0(12), to B(2') 223.7(11), to B(6') 224.7(20), to B(11') 229.4(11), and to P(1) 232.2(4) pm. All B-B distances are within the range 173.6(20)–190.7(15) pm except for B(8)–B(9') which is shorter at 163.1(15) pm. B(9')–P(2) is 191.8(11) pm. The compound is numbered as a *nido*-undecaborano-(7', 8': 7, 8)-*nido*-octaborane.



subunit, $\{\text{PtB}_7\}$, but also has additional structural features of greater novelty, interest, and implication.

The air-stable flame-red compound $[(\text{PMe}_2\text{Ph})\{\text{PtB}_{16}\text{H}_{18}(\text{PMe}_2\text{Ph})\}]$, m.p. 94–96 °C, was isolated in *ca.* 2% yield from the thermal disproportionation of $[(\text{PMe}_2\text{Ph})_2(\text{PtB}_8\text{H}_{12})]$ in boiling toluene for 1.5 h. Crystals are monoclinic, space-group $P2_1$, with $a = 992.7(3)$, $b = 1067.2(2)$, $c = 1378.7(3)$ pm, $\beta = 95.08(2)^\circ$, $Z = 2$, and the structure, based on 1992 independent F_o , was refined to $R = 0.0216$. A drawing of the molecular structure is given in Figure 1.†

The compound may be viewed as an edge-fused *conjuncto*-borane consisting of a *nido*- $\{\text{PtB}_7\}$ cluster and a *nido*- $\{\text{PtB}_{10}\}$ cluster conjoined with a Pt–B vector as the common edge. The eight-vertex $\{\text{PtB}_7\}$ cluster has the expected *nido*-geometry as typified by B_8H_{12} itself,² and the *nido*- $\{\text{PtB}_{10}\}$ cluster topography is like that in the known *nido*-7-platinaundecaboranes.³

The compound may also usefully be regarded as a complex between the $\{\text{B}_{16}\text{H}_{18}(\text{PMe}_2\text{Ph})\}^{4-}$ ligand and a $\{\text{Pt}(\text{PMe}_2\text{Ph})\}^{4+}$ metal centre. The borane ligand is a phosphine-substituted 16-vertex boron skeleton [see (1a)] formally derived from the as yet unknown *conjuncto*-borane $\text{B}_{16}\text{H}_{24}$; its overall geometry and structural principles are similar to those suggested for the known⁴ macropolyhedral borane $\text{B}_{15}\text{H}_{23}$ (2), but with an *arachno*-ten-vertex subunit rather than an *arachno*-nine-vertex subunit for the larger cluster. In (1) the subunit is that of *arachno*- $\text{B}_{10}\text{H}_{12}\text{L}_2$ whereas in (2) it is that of *iso-arachno*- $\text{B}_9\text{H}_{13}\text{L}$. In the platinum compound the *arachno*-ten-vertex sub-cluster can be regarded as formally η^4 tridentate to the metal atom and the remaining *nido*-six-vertex sub-cluster η^2 monodentate, as indicated in (1b). In these terms, the metal atom contributes four electrons to the seventeen-vertex

cluster bonding and may thus be regarded as platinum(IV) as is often the case in polyhedral platinaboranes.

That the ligand geometry of the macropolyhedral borane ligand can in fact be rationalized in terms of the structure of the known borane $\text{B}_{15}\text{H}_{23}$ is of wider significance. Firstly, it indicates that derivatives such as $\text{B}_{10}\text{H}_{12}\text{L}_2$, where $\text{L} = \text{B}_6\text{H}_{10}$, may well be stable and be readily synthesised from $\text{B}_{10}\text{H}_{14}$ and B_6H_{10} . Secondly, although in the present case the reaction, starting from an eight-boron cluster to give a sixteen-boron species, is probably very complex and the yield correspondingly modest, it nevertheless shows that two initially separate borane ligands about metal centres can be induced to conjoin. This emphasizes the important possibility that suitable low-coordinate or labile transition-metal species may readily act as suitable catalysts for borane oligomerisation in a similar manner to those well established for hydrocarbon species.

Finally, we report that the thermolysis of $[(\text{PMe}_2\text{Ph})_2(\text{PtB}_8\text{H}_{12})]$ also leads to additional higher metallaborane species which from multinuclear n.m.r. spectroscopy appear to be further complexes of macropolyhedral borane ligands which contain >12 B atoms; we hope to report more conclusively on these elsewhere.

We thank the SERC for support.

Received, 1st March 1982; Com. 219

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† 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.