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Macropolyhedral boron-containing cluster chemistry. Mixed and multiple cluster fusion in platinaborane chemistry and the structure of $[(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]$ as determined by synchrotron X-ray diffraction analysis

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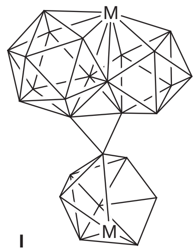
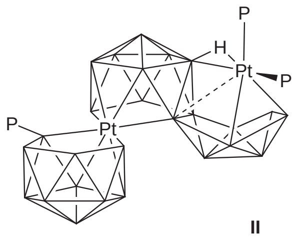
Multiple cluster fusion between $[(PMe_2Ph)_2PtB_8H_{12}]$ and molten $B_{10}H_{14}$ gave the 26-boron species $[(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]$ which exhibits quite different structural and assembly features to the 26-boron species $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ previously prepared from $[(PMe_3)_2(CO)HIrB_8H_{12}]$ and $B_{10}H_{14}$.

Extension of contiguous boron-containing cluster chemistry beyond icosahedral horizons requires intercluster fusion.[1] The structural parameters associated with the intimate subcluster conjunction modes and the reaction parameters associated with the assembly processes, that are both required in order to develop this new area, need to be discovered and explored. Initial experiments show that heteroboranes, particularly, thus far, thiaboranes[2] and metallaboranes,[3,4] have flexible architectures that can expedite this exploration. In this regard, they are much more malleable than the binary boranes themselves. Two-cluster fusion is well-recognised,[1] but more complex subcluster assembly is rare.[5,6] We have recently demonstrated the principle of intimate three-cluster assembly in an iridaborane system by the thermolytic formation of the 26-boron species $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ (structure **I**) from the reaction of $[(PMe_3)_2(CO)HIrB_8H_{12}]$ with molten $B_{10}H_{14}$ as solvent.[6] There is interest in extending this triple-cluster fusion principle to other systems. Here we report its extension to a platinaborane system to give a 26-boron species $[(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]$ (Fig. 1 and structure **II**) that has quite different structural features to that of the iridaborane.

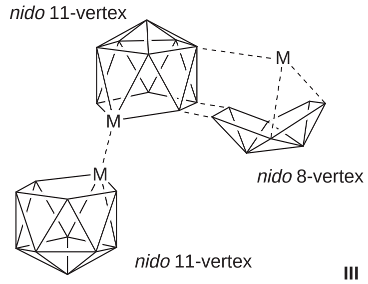
Thermolysis of $[(PMe_2Ph)_2PtB_8H_{12}]$ (290 μmol) in molten $B_{10}H_{14}$ (1400 μmol) at 134 °C for 10 min, followed by repeated TLC and HPLC separation (silica, CH_2Cl_2–hexane mixtures as liquid phases), gave $[(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]$ as an orange crystalline solid (560 μg, 0.50 μmol). The yield was small, but this is to be expected and tolerated in exploratory work delineating new chemistry in an area where both the structural and the assembly principles are unknown.[4] Single crystals (from diffusion of hexane through a benzene layer into a dichloromethane solution) also were small (fine needles of cross-section 10 × 10 μm), and required high-intensity synchrotron radiation to attain sufficient diffraction intensity for structural analysis.* The NMR spectroscopic† and FAB mass spectrometric data were consistent with the crystallographically determined molecular constitution of the platinaborane. The crystal structure showed benzene and hexane of solvation. Additional products from the reaction include known $[(PMe_2Ph)_2Pt\text{-}anti\text{-}B_{18}H_{20}]$ (900 μg, 1.35 μmol), resulting from two-cluster mixed fusion, and known $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (*ca.* 800 μg, 1.41 μmol), presumably resulting from transmetallation, with small quantities of other large platinaboranes which we hope to be able to report upon in due course. None appears so



I



II



III

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* Crystal data for $[(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)]\cdot C_6H_6\cdot 0.5C_6H_{14}$, $M = 1235.1$, monoclinic, space group $P2_1/n$, $a = 14.7903(4)$, $b = 13.0595(3)$, $c = 28.3431(7)$ Å, $\beta = 90.452(2)°$, $U = 5474.4(2)$ Å^3, $Z = 4$, $\lambda = 0.6874$ Å, $\mu = 5.22$ mm^{-1}, $T = 160$ K, $R1 = 0.0375$ for 9491 reflections and $wR2 = 0.0861$ for all 11 734 unique reflections. Methods and programs were as described elsewhere.[7] CCDC reference number 186/1089. See http://www.rsc.org/suppdata/dt/1998/2777/ for crystallographic files in .cif format.

† NMR data, with chemical shifts δ in ppm (CD_2Cl_2 at 300 K), are as follows. The ^{11}B NMR spectrum (9.5 T, 128 MHz) features a region between *ca.* −2 and +15 ppm containing fairly broad, overlapping, and hence poorly resolved resonances arising from 18 of the 26 boron atoms, such that the individual peaks cannot yet be unequivocally distinguished. The data are presented in the order: relative ^{11}B intensity [$\delta(^{11}B)$ {$\delta(^1H)$ of directly attached hydrogen atoms}]: *ca.* 4B [*ca.* +15, +12.7, *ca.* +11 {+3.00, +2.89, +2.71, +2.62}], *ca.* 14B [+7.1 (probable *conjuncto* site with no terminal ^1H or ^{31}P coupling), *ca.*+7, +6.0, +2.4, 0.0, −1.5, −2.6 {+4.04, +3.90, +3.82, +3.60, +3.75, +3.78, +3.00, +2.80, +2.49, +2.35}], 1B [-6.9 {+2.08}], 1B [-9.7 {+1.99}], 1B [-15.6 {+1.24}], 1B [-19.1 {+1.54}], 1B [-20.1 {+1.44}], 1B [-25.6 {+1.56}], 1B [-26.7 {+1.64}], 1B [-36.0 {+0.85}]; additionally $\delta(^1H)$-(μ-H) −1.14, −1.16 (2H), −1.70(2), −3.72, −8.69 {d, $^2J(^{31}P\text{–}^1H)$ 71 Hz}, $\delta(^1H)(PMe_3)$ +2.28 and +2.23 {overlapping d, each with $^2J(^{31}P\text{–}^1H)$ 11 Hz}, +1.92 and +1.82 {doublets, each with $^2J(^{31}P\text{–}^1H)$ 12 Hz}, +1.43 {d, $^2J(^{31}P\text{–}^1H)$ 11 Hz}, $\delta(^{31}P)$[P(8)] −5.57 (br), $\delta(^{31}P)$[P(71) and P(72)] −10.3 {$^1J(^{195}Pt\text{–}^{31}P)$ 3746 Hz} and −11.3 {$^1J(^{195}Pt\text{–}^{31}P)$ 2660 Hz}, any $^2J(^{31}P\text{–}^{31}P)$ coupling not resolved (<*ca.* 3 Hz).

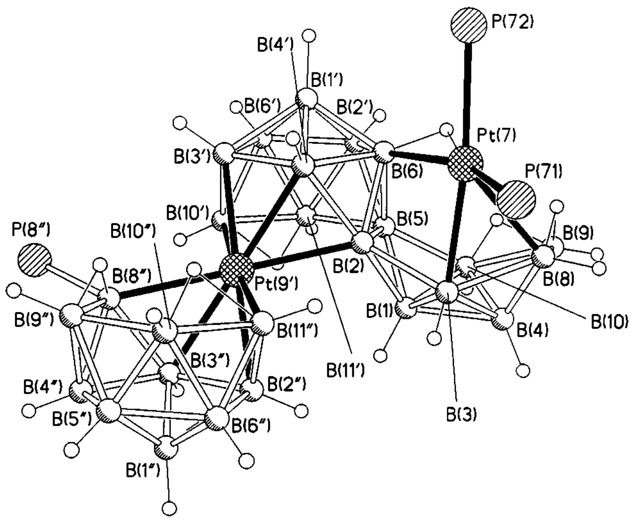

Fig. 1 Drawing of the crystallographically determined molecular structure of [$(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)$], with P–organyl groups omitted for clarity. Selected interatomic distances (Å) are as follows: Pt(7)–B(8) 2.299(7), Pt(7)–B(3) 2.321(6), Pt(7)–B(6) 2.357(6), Pt(7)–H(6) 1.84(6), Pt(7)···B(2) 2.602(6), Pt(7)–P(71) 2.2652(15), Pt(6)–P(72) 2.3327(14), Pt(9′)–B(4′) 2.198(6), Pt(9′)–B(2″) 2.228(6), Pt(9′)–B(3′) 2.231(6), Pt(9′)–B(3″) 2.233(6), Pt(9′)–B(2) 2.275(6), Pt(9′)–B(11″) 2.277(6), Pt(9′)–B(10′) 2.278(7), Pt(9′)–B(8″) 2.298(6), P(8″)–B(8″) 1.939(7)

far to identify with known products[3] resulting from the *thermolytic autofusion of* [$(PMe_2Ph)_2PtB_8H_{12}$] in benzene or toluene solvents.

Structurally, [$(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)$] at first sight appears as a three-cluster assembly, based on two classical[8,9] *nido* eleven-vertex {MB_{10}} clusters and a *nido*-shaped ten-vertex {PtB_9} cluster. In this work it is formally numbered as such, *viz.* as 7,7,8″-tris(dimethylphenylphosphine)-*nido*-7″-platinaundecaborano-(7″:9′)-*nido*-9′-platinaundecaborano-(8′,7′,3′:2,5,6)-*nido*-7-platinadecaborane. The {PtB_9} unit is, however, not of true *nido* character, as discussed below.

The two *nido* eleven-vertex {PtB_{10}} units are conjoined with a common platinum atom. A basic model for this double unit is the [$Pt(B_{10}H_{12})_2$]$^{2-}$ dianion.[8,10] With a formal $PMe_2Ph \longleftrightarrow$ hydride-ion replacement, this first subcluster (double-primed in the numbering system) would therefore have no net negative charge associated with it. The neutral two-cluster analogue, [$Pt\{B_{10}H_{11}(PMe_2Ph)_2\}_2$] has not been reported. The second {PtB_{10}} unit, *i.e.* the central (single-primed) subcluster in the molecule, is also of relatively straightforward constitution, with one of the two bridging hydrogen positions of a [$Pt(B_{10}H_{12})_2$]$^{2-}$ subcluster model being occupied by one bridging hydrogen atom and the other by the elements of what at first sight resembles a fused B(2)B(5)B(6) three-borons-in-common triangular link to the final *nido*-shaped ten-vertex {5-PtB_9} subcluster.

Although this latter {PtB_9} subcluster approximates to the ten-vertex *nido* shape, the platinum–boron distance Pt(7)–B(2) is essentially non-bonding at 2.602(6) Å (hatched line in structure **II**). This subcluster is thus better regarded as based on a *nido* eight-vertex {B_8} subcluster which is fused to the central {PtB_{10}} unit with a common two-boron edge B(2)–B(5) (structure **III**). The platinum centre Pt(7) is then regarded as bridging the B(3)–B(8) position, but it is also linked in turn to the B(6) atom in the central {PtB_{10}} subcluster *via* an unusual type of Pt–H–B bridging hydrogen atom.[11] This latter link is unsupported by additional platinum bonding to boron atoms adjacent to the B–H (*exo*) site in question. This B–H (*exo*) $\longrightarrow$ Pt interaction may throw useful light on contemporary considerations of 'agostic' interaction between square-planar transition-element centres and B–H or C–H bonds that happen to be close by in solid-state structures.[12] Inter-subcluster bridging links related to this are an increasingly recognised feature in macropolyhedral borane compounds, and the incidence of sulfur-bridged subclusters in [$S_2B_{16}H_{14}(PPh_3)$] and [$(PPh_3)NiS_2B_{16}H_{12}(PPh_3)$],[13] and of iridium-bridged subclusters in [$(PMe_3)_2(CO)IrB_{16}H_{14}Ir(CO)(PMe_3)_2$],[4] are to be noted in this context.

Acknowledgements

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