Macropolyhedral boron-containing cluster chemistry. Synchrotron X-ray structural analysis of [$(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2$] and [$(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)$]: models of intermediates to more condensed metallaboranes from the [$(PMe_2Ph)_2PtB_8H_{12}$] thermolysis system

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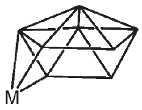
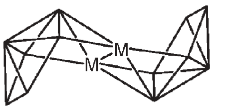
Thermolyses of [$(PMe_2Ph)_2PdB_8H_{12}$] and [$(PMe_2Ph)_2PtB_8H_{12}$] respectively yield eighteen-vertex [$(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2$] and [$(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)$], which exhibit structure models for probable successive precursive intermediates for the more condensed macropolyhedral metallaboranes [$(PMe_2Ph)_4Pt_3B_{14}H_{16}$], [$(PMe_2Ph)_2Pt_2B_{12}H_{16}$] and [$(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)$] that have previously been reported as products from [$(PMe_2Ph)_2PdB_8H_{12}$] thermolyses.

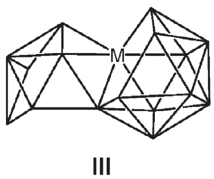
The rich and fertile chemistry of the polyhedral boranes is at present most strongly manifested in the study and manipulation of single-cluster species. The investigation of the manner in which such single-cluster species may interact, either *(a)* covalently to form intimately condensed 'big-borane' assemblies, often dubbed 'macropolyhedral' molecules,[1] or *(b)* by weaker inter-molecular binding modes to form supramolecular aggregations,[2] constitute two ways in which this single-cluster chemistry can be extended beyond the experimental and sometimes intellectual hiatus represented by the stable twelve-vertex single-cluster icosahedron. An additional extension is *(c)* by the expansion of the twelve-vertex icosahedron itself to give single clusters with more than twelve vertices.[3] Of these three areas, the generation of macropolyhedral boron-containing cluster species requires the intimate covalent fusion of single clusters, but at present this has no generally applicable generic synthetic route. Empirically, however, it is found that several *arachno* nine-vertex species are prone to homofusion to generate macropolyhedral molecules on mild thermolysis.[4–6] In this context, the *arachno* {B_8Pt} system, as represented by [$(PMe_2Ph)_2PtB_8H_{12}$] (schematic skeletal structure **I**), is known to give a variety of interesting macropolyhedral compounds upon simple thermolysis.[7] Identified products include [$(PMe_2Ph)_2Pt_2B_{12}H_{18}$], [$(PMe_2Ph)PB_{16}H_{18}(PMe_2Ph)$], [$(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)$] and [$(PMe_2Ph)_4Pt_3B_{14}H_{16}$], of schematic cluster structures **II**, **III**, **IV** and **V** respectively,



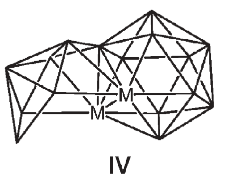
I



II

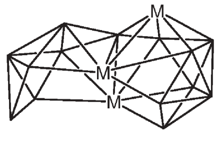


III

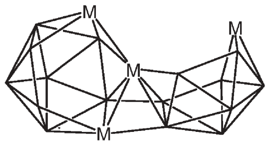


IV

The combined yield of these products is non-trivial,[7] indicating that their skeletal configurations constitute thermodynamic or kinetic sinks among the complex of multi-step reaction coordinates. However, the initial cluster geometry **I** is not traceable in any of these products, and the constitutions of **III** and **V** additionally indicate that intermolecular transfers of platinum and/or boron atoms occur. Similar considerations apply to the related [$(PPh_3)_2PdB_8H_{12}$] system, which, for example, gives [$(PPh_3)_4Pd_4ClB_{16}H_{17}(PPh_3)$] of schematic structure **VI**.[8] The mechanisms associated with these systems are therefore of interest, and further information is valuable: firstly, such information may give clues to the mechanisms within this particular system, and, secondly, it may then give clues for the ultimate design and establishment of general transferable generic routes for intercluster fusion.



V



VI

In this context we report the isolation[9] and characterisation[10,11] of two new species. These are of formulation [$(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2$] [compound **1**, Fig. 1 (upper), schematic cluster structure **VII A**] from [$(PMe_2Ph)_2PdB_8H_{12}$] thermal autofusion, and [$(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)$] [compound **2**, Fig. 1 (lower), schematic cluster structure **VIII A**] from [$(PMe_2Ph)_2PtB_8H_{12}$] thermal autofusion. Obtainable crystals of **1** and **2** were small and required synchrotron X-radiation[12] for sufficient diffraction intensity for molecular structure determination.†

Their skeletal configurations are represented in schematic cluster structures **VII A** and **VIII A** respectively. In each of these, the skeletal pattern **I** of the {B_8M} starting substrate is now readily traced. The simple reaction stoichiometries of eqn. (1) and (2) thence suggest that the structures may represent initial steps in the

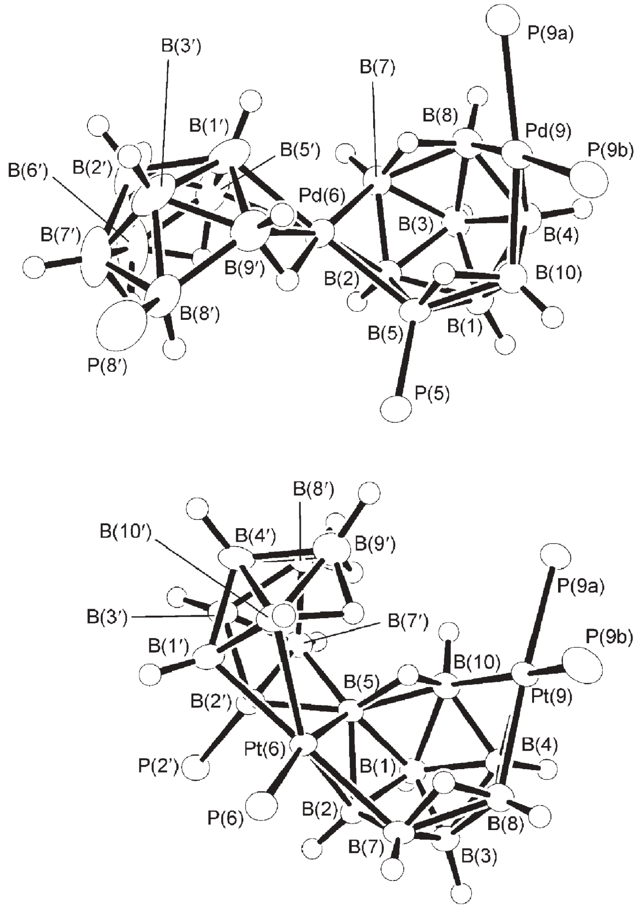


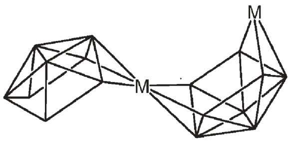
Fig. 1 ORTEP-3[16] diagrams of the crystallographically determined[10] cluster structures of (upper diagram) $[(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2]$ (compound **1**) (schematics **VII**) and (lower diagram) $[(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)]$ (compound **2**) (schematics **VIII**), with P-organyl group atoms omitted for clarity; ellipsoid probability 70%. For **1**, unbridged palladium–boron distances are in the range 2.205(3)–2.298(3) Å, and hydrogen-bridged Pd(6)–B(9′) is 2.365(3) Å; the palladium–phosphorus distances are 2.3364(7) and 2.3329(7) Å; B(5)–P(5) is 1.919(3) Å , B(8′)–P(8′) is 1.916(3) Å, and interboron distances are in the range 1.730(4)–1.882(5) Å; diagram and data are for one of four similar but crystallographically independent molecules. For **2**, platinum–boron distances are in the range 2.204(4)–2.340(5) Å; Pt (9)–P(9a) is 2.319(1) Å, Pt (9)–P(9b) is 2.297(1) Å and Pt(6)–P(6) is 2.284(1), Å; B(2′)–P(2′) is 1.918(4) Å and interboron distances are in the range 1.705(7)–1.883(7) Å.

complex fusion-condensation processes that ultimately engender skeletons such as **II**, **III**, **IV**, **V** and **VI**.

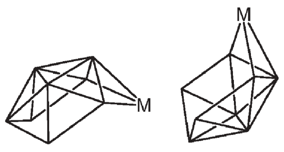
$$2\ [(PMe_2Ph)_2PdB_8H_{12}] \rightarrow [(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2]\ \mathbf{1} + 2\ H_2 \qquad (1)$$

$$2\ [(PMe_2Ph)_2PtB_8H_{12}] \rightarrow [(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)]\ \mathbf{2} + 3\ H_2 \qquad (2)$$

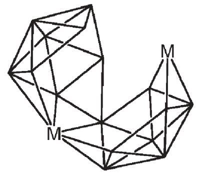
Mechanistically, the formation of $[(PMe_2Ph)_2Pd_2B_{16}H_{20}(PMe_2Ph)_2]$ (schematic **VII A**) can be envisaged as the simple confluence of two starting-material *arachno* $\{B_8M\}$ geometries (schematic **VII B** below). As such it can be in turn envisaged as an initial step of cluster fusion. This initially formed *spiro*-type structure **VII A** is related to that invoked in the initial stages of autofusion of the *arachno* nine-vertex thiaborane $[SB_8H_{12}]$ to give $[S_2B_{16}H_{16}]$ isomers.[13] There is also a parallel with a similar *spiro*-type connection established for neutral $[S_2B_{18}H_{20}]$.[14]



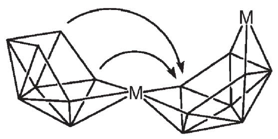
VII A



VII B



VIII A



VIII B

The more condensed platinum compound $[(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)]$ (schematic **VIII A**) hence could represent a second step. Cluster fusion and subsequent condensation to increase the intimacy of the fusion are oxidative processes. This is implicit in eqn. (1) and (2), which show the loss of two and three dihydrogen molecules respectively. Mechanistically, the basic skeletal type **VIII A** derives from a simple skeletal closure from a *spiro*-type structure **VIII B** related to that exhibited by the $\{Pd_2B_{16}H_{20}\}$ species (schematic **VII A**). There are again some parallels with thiaborane chemistry, in that the two-electron oxidative closure from **VIII B** to **VIII A** together with the concomitant subcluster swing resemble the characteristics of the two-electron oxidative closure of the $[S_2B_{17}H_{18}]^-$ anion to form neutral $S_2B_{17}H_{17}$.[15]

In conclusion, it seems reasonable to postulate that condensations such as **VII B** → **VII A** and **VIII B** → **VIII A** will typify successive initial steps in at least one of the pathways that ultimately lead to more severely modified species represented by configurations **II**, **III**, **IV**, **V** and **VI**. The link between these two initially formed $\{B_{16}M_2\}$ frameworks and the more condensed and rearranged skeletons is, however, not yet made. It is to be hoped that the continued isolation of species from these and related reaction systems will continue to give clues for the further understanding of the overall mechanism. Any understanding here will aid the development of generic cluster fusion routes.

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Notes and references

† CCDC 198684 and 198685. See http://www.rsc.org/suppdata/cc/b4/b419242g/ for crystallographic data in .cif or other electronic format.

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9 $[(PMe_2Ph)_2PdB_8H_{12}]$ (197 mg, 410 μmol) was heated for 60 min in refluxing toluene (20 ml), the toluene evaporated, and preparative TLC (silica G, CH_2Cl_2/n-C_6H_{12} 80:20) thence gave a number of coloured bands, including a red component (R_F 0.2) which was further purified by HPLC [silica (Lichrosorb Si60, 7 μm), 25 × 2.1 cm; CH_2Cl_2/n-C_6H_{12} 40:60 at 20 ml min^{-1}] to give pure red **1** (R_T 18 min; 1.5 mg, 3.5 μmol, *ca.* 1%). An exactly analogous procedure starting with $[(PMe_2Ph)_2PtB_8H_{12}]$ (194 mg, 340 μmol) gave pure red **2** (TLC R_F 0.2; HPLC R_T 12 min; 2 mg, 3.5 μmol, *ca.* 1%).

10 Crystal and X-ray data (synchrotron X-radiation, Station 9.8, Daresbury, UK,[12] λ = 0.6942 Å, SHELX solution and refinement methods)[17]: compound **1**, $C_{32}H_{64}B_{16}P_4Pd_2$: $M = 958.47$, triclinic (orange needle, 0.60 × 0.06 × 0.03 mm^3, from dichloromethane/hexane), space group $P\bar{1}$, $a = 9.5388(4)$, $b = 30.0590(14)$, $c = 33.0514(15)$ Å, $\alpha = 84.051(2)°$, $\beta = 83.8669(2)°$, $\gamma = 81.165(2)°$, $V = 9270.8(7)$ Å^3, $Z = 8$, $\mu = 0.938$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0389$ for 36747 reflections with $I > 2\sigma(I)$ and $wR2 = 0.0864$ for all 92143 unique reflections, CCDC reference number 198684: compound **2**, $C_{32}H_{62}B_{16}P_4Pt_2$: $M = 1133.84$, monoclinic (red plate 0.40 × 0.10 × 0.02 mm^3, from $C_6H_{12}/C_6H_6/CDCl_3$), space group $P2_1/c$, $a = 25.3975(11)$, $b = 10.2760(5)$, $c = 18.4033(8)$ Å, $\beta = 106.0630(10)°$, $V = 4615.5(4)$ Å^3, $Z = 4$, $\mu = 6.218$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0348$ for 10418 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0768$ for all 29614 unique reflections, CCDC reference number 198685.

11 Selected NMR data for $[(PMe_2Ph)_3Pt_2B_{16}H_{18}(PMe_2Ph)]$ **2** are as follows: $\delta(^{11}B)$/ppm [with $\delta(^1H)$/ppm for directly bound H(*exo*) atoms in square brackets] (CD_2Cl_2 solution) +31.0 [+4.96], +30.3 [+5.10], +7.5 [+2.70], +6.1 [no *exo*-H, probably B(5) on the basis that ^{11}B coupling to the ^1H bridging resonance at −2.39 was removed upon selective irradiation of this ^{11}B resonance in ^1H-$\{^{11}B\}$ experiments], *ca.* +2.0 [+3.98], *ca.* +1.2 [+2.32], *ca.* +0.5 [+4.17], *ca.* −5.5 [+1.61], *ca.* −5.5 [+1.38], −7.0 [+2.78], *ca.* −13.5 [no *exo*-H, probably B(2′) on the basis that no ^{11}B coupling to any ^1H resonances in the BHB-bridging region was definitively removed upon selective irradiation of this ^{11}B resonance in ^1H-$\{^{11}B\}$ experiments], *ca.* −14.0 [+1.19], *ca.* −14.3 [+1.96], −15.8 [+3.19], −23.0 [+1.49] and −34.5 [+0.80], with $\delta(^1H)(\mu H)$ at −1.41, −2.39, −2.50 and −3.82 ppm, and with $\delta(^{31}P)$/ppm ($CDCl_3$ solution) at *ca.* −25 with $^1J(^{31}P–^{11}B)$ *ca.* 135 Hz, at −4.3 with $^1J(^{195}Pt–^{31}P)$ 3325 Hz, at −5.7 with $^1J(^{195}Pt–^{31}P)$ 2945 Hz, and at −9.9 with $^1J(^{195}Pt–^{31}P)$ 2675 Hz; ^{31}P couplings are given ±10 Hz. Because of overlapping resonances, cluster $\delta(^{11}B)$ and $\delta(^1H)$ data for $[(PMe_2Ph)_2$-$Pd_2B_{16}H_{20}(PMe_2Ph)_2]$ **1** were less well defined. Tentative ^{11}B resonance positions are: +28.0. +24.7, +20.2, +8.0, +3.1, ca. +1.0, *ca.* −12.4, *ca.* −13.5, −18.1, −20.0, −27.0 −33.0 and −45.8 ppm, plus two other resonances in the region +10 to −5 ppm; tentative ^1H resonance positions are +5.83, +5.59, +5.20, +4.83, +4.33, +4.10, + 3.63, +3.40, +2.76, +2.75, +2.68, +2.60, +2.17, +1.77, +1.04, +0.10, −0.38, −2.07, −2.17 and −5.17 ppm; with ^{31}P resonances ($CDCl_3$ solution) at $\delta(^{31}P)$ −10.9 and −8.5 [both sharper, two doublets, $^2J(^{31}P–^{31}P)$ *ca.* 50 Hz], and −1.6 (broader) and −5.2 ppm (broader).

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