MACROPOLYHEDRAL BORON-CONTAINING CLUSTER CHEMISTRY. INTERMOLECULAR COORDINATION VIA HYDROGEN–METAL INTERACTION. THE SOLVENT-FREE SYNTHESIS AND DIMERIC CONSTITUTION OF [Pd$_2$B$_{36}$H$_{40}$(PMe$_2$Ph)$_4$]

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[Pd$_2$B$_{36}$H$_{40}$(PMe$_2$Ph)$_4$], from the solvent-free thermolysis of [(PMe$_2$Ph)$_2$PdB$_8$H$_{12}$] with B$_{10}$H$_{14}$, has a unique dimeric structure in which two novel {PdB$_{18}$H$_{20}$(PMe$_2$Ph)$_2$} nineteen-vertex *arachno*-palladadecaborano-⟨PdB⟩-*nido*-palladaundecaborane units are held together by reciprocal hydrogen-to-metal linkages.
Keywords: Solvent-free synthesis; Boranes; Metallaboranes; Boron clusters; 36-boron cluster compound; X-ray structure; Hydrogen-linked dimerisation; Macropolyhedral metallaborane dimer.

The bulk of modern synthetic molecular chemistry – whether 'organic' or 'inorganic' – involves the joining together of known structural units – ligands, atoms, groups, metal centres – with known types of connectivities. This enables the design and construction of chosen architectures for structure, for functionality and for other effect chemistry. The bulk of molecular synthetic chemistry involves such design and construction using the vast library of carbon hydrides and their derivatives – mostly chains and rings – as structural units. Connectivities include single and multiple bonds, and various π-complexations.

It is necessary to emphasize that there are other structural units and other types of connectivities, both discovered and undiscovered, that can be added to the toolbox of the synthetic chemist. Boron hydrides and the heteroboranes of course form the other potentially vast basis set of structural units – the structural units are now cages and clusters rather than

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chains and rings – and they also exhibit other types of connectivities. Their versatility is at first sight limited, in that it is progressively more difficult to synthesise beyond a single-cluster size of twelve vertices. This barrier is associated with the very high stability of the 12-vertex 26-electron icosahedron.

The expansion of boron-containing cluster chemistry to clusters with more than twelve vertices is an area of very interesting current research activity, of which one fascinating approach is the expansion of twelve-vertex clusters to give larger thirteen-, fourteen- and fifteen-vertex single clusters[1]. The complementary approach is the extension of cluster chemistry beyond the single-cluster horizon by the intimate fusion of borane and/or heteroborane clusters to generate larger contiguous assemblies[2–4], resulting in ar-
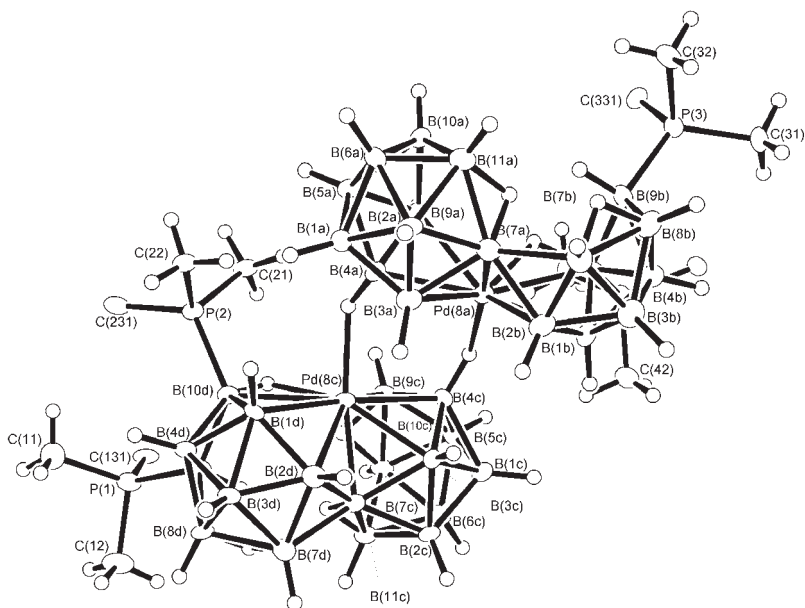

Fig. 1

ORTEP-3 (ref. [6]) diagram of the crystallographically determined molecular structure of $[Pd_2B_{36}H_{40}(PMe_2Ph)_4]$ (**2**). The two $\{PdB_{18}H_{20}(PMe_2Ph)_2\}$ units are crystallographically independent, but have similar dimensions. Selected representative interatomic distances (in Å) are as follows: Pd(8a)–B(4c) 2.499(6), Pd(8a)–B(3a) 2.208(6), Pd(8a)–B(4a) 2.250(6), Pd(8a)–B(7a) 2.145(7), Pd(8a)–B(9a) 2.319(6), Pd(8a)–B(1b) 2.271(6), Pd(8a)–B(2b) 2.291(7) and Pd(8a)–B(10b) 2.467(6), Pd(8a)–H(8a,10b) 1.73(7), P(1)–B(9d) 1.917(7), P(2)–B(10d) 1.936(6); interboron distances range from 1.728(10) for B(6a)–B(11a) to 1.966(9) for B(10c)–B(11c). Within the Pd(8)–H–B(4) dimer-forming linkages, the crystallographic analysis gave the mean Pd–H and B–H distances as ca. 2.08 and 1.10 Å, respectively, and the mean Pd–H–B angle as ca. 138°

chitectures in which multicentre cluster-bonding properties are an integral part of the intercluster fusion linkage. Such fusions generate so-called 'macropolyhedral' boron-containing cluster compounds of, say, fifteen or more contiguous vertices. Once the intellectual and experimental barriers of the single cluster are transcended, the structural horizons are vast, and expandable further still in combination with the more familiar structural motifs of carbon hydride chemistry. Once fused, the individual subclusters can exhibit new types of single-cluster architecture, either because the constraints of the intercluster fusion linkage block a kinetic cascade to a more conventional cluster type, or because the kinetics of particular multicluster assembly reactions inherently lead to subcluster types not yet realised by single-cluster syntheses. Sometimes it may be the electronics of the intercluster linkage that stabilise a sub-cluster type not seen in isolated single-cluster chemistry. Exploratory work reveals new types of intercluster connectivities that are not experienced in carbon-based frameworks. The properties of such assemblies considerably extend, though do not necessarily mimic[5], those of established smaller single-cluster species.

As yet, however, there are no generic routes for intercluster fusion, which inhibits development of the area. There is consequent interest in exploratory chemistry, not only in terms of new processes which may ultimately lead to generic routes, but also in terms of the elucidation of new architectural features in order to see what Nature may have available[4]. Within this dual context we here report an interesting preliminary result from the solvent-free fusion of *arachno*-type nine-vertex $[(PMe_2Ph)_2PdB_8H_{12}]$ (**1**) with *nido*-type ten-vertex $B_{10}H_{14}$. The identified product, $[Pd_2B_{36}H_{40}(PMe_2Ph)_4]$ (**2**), albeit obtained in low yield, exhibits unprecedented and unanticipated molecular assembly behaviour.

The molecular structure of **2** (Fig. 1 and schematic **I**) is seen to be a dimeric combination **I** of two individual double-cluster $\{PdB_{16}H_{20}(PMe_2Ph_2)_2\}$ units **II**. Mechanistically, the basic cluster structure of each individual double-cluster unit (schematic **II**) is seen to result from an ostensibly


I   II   III   IV
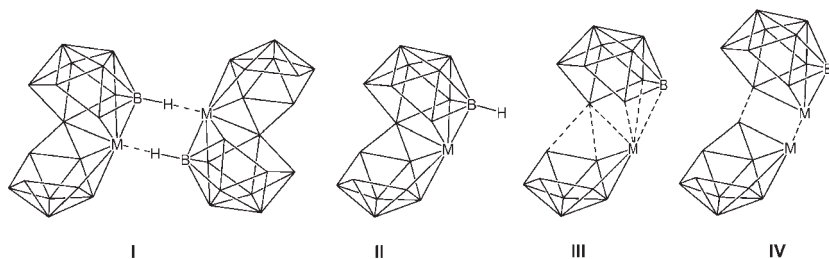
straightforward confluence **III** of the starting *arachno* {PdB$_8$} and *nido* {B$_{10}$} skeletons.

It is, however, evident that there has been an apparent migration of the two PMe$_2$Ph moieties from palladium to boron sites, and, in view of this migration and the low yield, it is prudent to limit mechanistic speculation, even though a simple stoichiometry may be written down as

2 [(PMe$_2$Ph)$_2$PdB$_8$H$_{12}$] (**1**) + 2 B$_{10}$H$_{14}$ → [Pd$_2$B$_{36}$H$_{40}$(PMe$_2$Ph)$_4$] (**2**) + 6 H$_2$ (*1*)
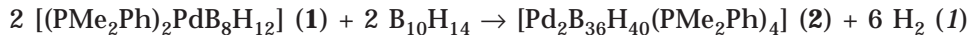
Of most interest is the overall molecular construction itself. It consists of two double-cluster {PdB$_{18}$} units, of which each consists architecturally of a *nido*-type eleven-vertex {PdB$_{10}$} subcluster and an *arachno*-type ten-vertex {PdB$_9$} subcluster fused with a common {PdB} edge. The orientation of the fusion gives a mutually *syn* positioning of the open faces (schematic **IV**). A fusion of a *nido* eleven-vertex with an *arachno* ten-vertex cluster is unprecedented.

This constitution for the individual {PdB$_{18}$} units **II** would leave each with an exposed and coordinatively unsaturated 'naked' palladium atom at the point of conjunction. In the overall {PdB$_{18}$}$_2$ skeletal unit **I** this otherwise coordinatively unsaturated site in each {PdB$_{18}$} subunit **II** is filled by the acceptance of coordination from a hydrogen atom of an exo-terminal {BH} group in the other {PdB$_{18}$} subunit: the hydrogen atom will be negatively polarised due to the polarity of the B–H bond. The two reciprocal B–H–Pd interactions, with derived Pd–H distances of 2.01 Å in one case and 2.14 Å in the other, result in the observed large overall dimeric assembly.

V   **VI**
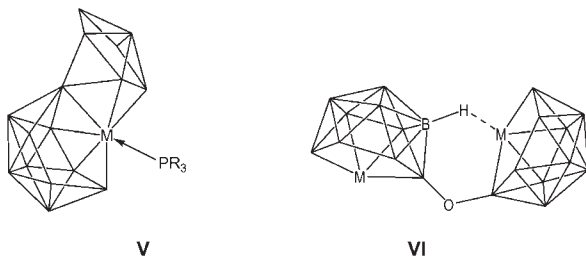
A related {PtB$_{16}$} single-unit cluster configuration is exhibited by previously reported monomeric [(PMe$_2$Ph)PtB$_{16}$H$_{18}$(PMe$_2$Ph)] (**3**) (schematic **V**)[7], in which a *nido* eleven-vertex {PtB$_{10}$} subcluster and an *arachno* eight-vertex {PtB$_7$} subcluster fuse together with a common {PtB} edge, but with a mutual *anti* positioning of the two open faces, in contrast to the mutual *syn* orientation of compound **2**. In compound **3**, however, the equivalent of

the {BH} hydrogen-to-metal coordination in **2** is taken up by the more conventional PMe_2Ph two-electron ligand on the metal centre, and hydrogen-bonded dimeric behaviour is not observed. This mode of inter-cluster assembly in dimer **2** is, as far as we are aware, quite unique. Although the recently reported species $[(PMe_2Ph)_2PtB_{10}H_{10}-O,H-B_{10}H_{11}Pt(PMe_2Ph)]$ (**4**) also exhibits a related type of BH-to-metal coordination (schematic **VI**)[8], this has additonal and strong intercluster support, as the two single-cluster units in **4** are joined also by a conventional ether-like B–O–B sigma-bonded linkage.
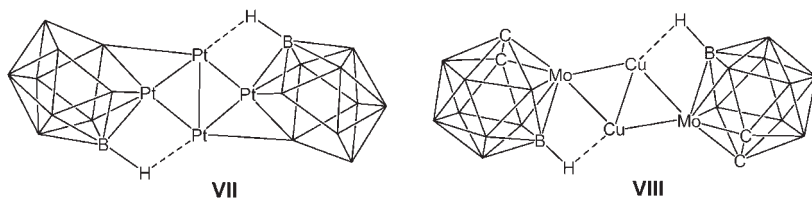
the atachment of single metal centres to single cluster units via BH(*exo*)-to-metal interactions has long been recognised[9], in terms of the present unique double boron-hydride hydrogen-to-metal interaction, the nearest precedent is perhaps in the dimeric species $[\{(PPh_3)_2Pt_2B_{10}H_{10}-(OCMe_3)\}_2]$ [10], of which the structure (schematic **VII**) in turn is related somewhat to that of $[\{(CO)_3HMoCuC_2B_9H_{10}\}_2]$ (schematic **VIII**)[11]. Each of these two tetrametal species, however, has a much more complex intercluster nexus, in which the linkage between the subclusters has strong, direct, metal-to-boron and metal-to-metal bonding, as well as exhibiting hydrogen-to-metal linkages. The simpler, intimate assembly of compound **2**, via two M–H–B interactions only, is without direct precedent. Mechanistically, this type of coordination, together with subsequent dihydrogen loss, may have importance as being representative of steps towards the currently elusive target of very condensed fusion, as observed, for example, in the formation of the {PdB_{20}} and {IrB_{18}} cores of $[(PPh_3)_2(PPh_2)_2Pd_3B_{20}H_{16}-Pd(PPh_3)]$ [12] and $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$ [13].

EXPERIMENTAL

$[(PMe_2Ph)_2PdB_8H_{12}]$ (**1**) was made in 92% yield from the [*arachno*-B_9H_{14}]⁻ anion and $[PdCl_2(PMe_2Ph)_2]$ in an analogous manner to that published for its platinum analogue $[(PMe_2Ph)_2PtB_8H_{12}]$ from $[PtCl_2(PMe_2Ph)_2]$ [1,14]. Thence, in a modification of the 'boranes as solvent' synthetic approach[3,13], pale yellow **1** (160 mg, 340 µmol) and a ten-fold molecular excess of $B_{10}H_{14}$ (400 mg, 3.4 mmol) were intimately ground together in air. A colour

change to deep yellow was observed. The mixture was transferred to a dry dinitrogen atmosphere, and progressively heated to 100 °C (oil bath). Liquefaction and effervescence occurred, and, after 15 min at 100 °C, a colour change from yellow to deep red-brown had occurred. Cooling, removal of excess $B_{10}H_{14}$ by sublimation, extraction with CH_2Cl_2, evaporation of the extract, and TLC separation of the residue (Silica G, Fluka GF_{254}, CH_2Cl_2:n-C_6H_{14} 80:20) thence yielded unreacted **1** (pale yellow, R_F ca. 0.8), and smaller quantities of two species: known[14] *nido* eleven-vertex [$(PMe_2Ph)_2PdB_{10}H_{12}$] (yellow, R_F ca. 0.7) and a red component, [$Pd_2B_{36}H_{40}(PMe_2Ph)_4$] (**2**) (Fig. 1) ($R_F$ ca. 0.25, crude yield 8 mg, 6.4 μmol, ca. 2%). After purification by repeated TLC followed by HPLC (R_T 28 min; silica (Knauer, Lichrosorb Si60), 21 mm × 25 cm, n-C_6H_{14}:CH_2Cl_2 60:40, 20 ml min^{-1}), compound **2** was identified by an all-atom molecular structure derived from a single-crystal X-ray diffraction analysis (Fig. 1), a small quantity of suitable crystals for this, in the form of very thin red needles, ultimately being obtained, after several attempts, by diffusion of n-C_6H_{14} through a layer of C_6H_6 into a solution of **2** in CH_2Cl_2. The measured NMR data, that we were able to obtain on this small amount of pure compound, were entirely consistent with this molecular structure.

X-ray Diffraction Data

Compound **2**: $C_{36.5}H_{86.5}B_{36}Cl_{0.5}P_4Pd_2$ (includes partial occupancy of disordered solvent molecules), M = 1269.35, rhombohedral (0.12 × 0.02 × 0.02 mm, red needle from CH_2Cl_2/C_6H_6/n-C_6H_{14}), space group $R3$, a = b = 36.6540(2) Å, c = 29.2571(12) Å, $α$ = $β$ = 90°, $γ$ = 120°, U = 34041(2) Å^3, D_{calc} = 1.115 Mg m^{-3}, Z = 18, $λ$ = 0.71073 Å (MoKα), μ = 0.603 mm^{-1}, T = 150(2) K, R_1 = 0.0533 for 8143 reflections with $I > 2σ(I)$, and wR_2 = 0.1585 for all 12669 independent reflections. Methods and programs were standard[6,15,16]. CCDC 657374 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

NMR Data

Compound **2**: $CDCl_3$, 295–300 K, δ in ppm: ^{11}B resonances (rel. $BF_3(OEt_2)$ in $CDCl_3$) at +27.0, ca. +21.0, ca. +20.0, +17.9, +12.7, ca. +10.0, +9.1, ca. +1.0, +0.8, ca. +0.6, –3.4, –14.9, –18.8, –20.3, –26.2, ca. –29.5, ca. –29.1 and –40.1; cluster ^1H resonances (rel. TMS) at ca. +5.25, ca. +5.15, +4.33, +4.18, +3.92, +3.53, ca. +3.15, ca. +3.05, ca. +2.77, ca. +2.70, ca. +2.63, +1.83, ca. +1.24, ca. +1.14, ca. +0.04, ca –0.06, –1.30, –1.57, –2.42 and –2.56; $δ(^{31}P)$ resonances (rel. 85% H_3PO_4) at ca. +0.4 and –0.7. Although constrained to be crystallographically independent in the solid state, the individual $\{PdB_{18}\}$ units are equivalent in solution.

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