Macropolyhedral boron-containing cluster chemistry. Novel intercluster linkages from the reaction of [Pt(cod)Cl_2] and [PtMe_2(PMe_2Ph)$_2$] with 6,6′-($B_{10}H_{13}$)$_2$O

Jonathan Bould[a] and John D. Kennedy*[b]

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6,6′-($B_{10}H_{13}$)$_2$O with [Pt(cod)Cl_2] gives the [($B_{10}H_{13}OB_{10}H_{11}$)-Pt–{$B_{10}H_{10}OB_{10}H_{12}$)]$^{2-}$ anion in which, uniquely, the units are held together by a B–O–B linkage in combination with a B–B linkage; with [PtMe_2(PMe_2Ph)$_2$] it gives [(PMe_2Ph)$_2$Pt$B_{10}H_{10}$–O,H–$B_{10}H_{11}$Pt(PMe_2Ph)] in which, uniquely, the units are held together by an unsupported hydrogen-to-metal linkage as well as a B–O–B linkage.

The potential chemistries, both pure and applied, of the polyhedral boron-containing cluster compounds are considerably extended by the application of the principle that extended contiguous 'macropolyhedral' structures are available by the fusion, with edges or faces held in common, of smaller cluster building blocks.[1,2] Transferable generic synthetic routes for cluster fusion are, however, lacking. One previously untried approach to cluster fusion is to induce the more intimate cluster bonding required for intercluster fusion starting from a compound in which the clusters are already joined by a simple two-centre σ-bonded linkage. The most readily synthesisable σ-linked double cluster compound is bis(*nido*-decaboranyl) oxide, [6,6′-($B_{10}H_{13}$)$_2$O] (compound **1**), prepared by the treatment of [6,9-(SMe_2)$_2$-*arachno*-$B_{10}H_{12}$] with H_2SO_4;[3] the starting [(SMe_2)$_2$$B_{10}H_{12}$] is readily and quantitatively obtainable from *nido*-$B_{10}H_{14}$ by dissolution in SMe_2.[4] In terms of fusion agents, several metal centres are known to induce intercluster fusion, for example [PdCl_2(PR_3)$_2$],[5] FeCl_2/FeCl_3,[6] NiBr_2,[7] and [Mo(CH_3CN)$_3$(CO)$_3$].[8] Treatment of compound **1** with [PdCl_2(PR_3)$_2$] or its Ni and Pt congeners, however, is known to result in cleavage of the intercluster oxide linkage with the formation of a variety of single-cluster metallaboranes, and no multicluster assemblies are generated.[9] We now report preliminary results from the reaction of compound **1** under milder platination conditions, specifically by using the two organometallic platinum species [PtMe_2(PMe_2Ph)$_2$] (previously shown to be a useful metallation agent in macropolyhedral borane chemistry)[10] and [Pt (cod)Cl_2] (cod = cyclooctadiene) from which double-cluster species with more intimate, and novel, intercluster bonding modes are now isolatable.

Thus, [($B_{10}H_{13}$)$_2$O] **1** (30 mg, 120 μmol), [Pt(cod)Cl_2] (21.7 mg, 120 μmol) and the non-nucleophilic base [$C_{10}H_6$-6,8-(NMe_2)$_2$] (tmnd; 49 mg, 240 μmol) were placed in a round-bottomed flask. The flask was evacuated on a Schlenk line, CH_2Cl_2 (*ca.* 15 ml) was condensed in at 77 K, and then a dinitrogen atmosphere was introduced. The mixture was allowed to warm to ambient temperature and then stirred overnight. A fine yellow precipitate formed (23 mg). The solid was subjected to preparative thin-layer chromatography [silica gel G (Fluka GF_{254}), 100% CH_2Cl_2], giving one mobile component, yellow, R_F 0.05 (trace quantities). Purification attempts by repeated TLC and by crystallisation ultimately resulted in a particular crystallisation by hexane diffusion into a solution in CH_2Cl_2 that gave very small crystals, identified by a single-crystal X-ray diffraction analysis† as the [tmndH]$^+$ salt **2a** of the [($B_{10}H_{13}OB_{10}H_{11}$)Pt–{($B_{10}H_{10}OB_{10}H_{12}$)]$^{2-}$ anion **2** (Fig. 1 and schematic cluster structure **I**).

In a second procedure, $CHCl_3$ (*ca.* 5 ml) was condensed onto a mixture of [($B_{10}H_{13}$)$_2$O] (64 mg, 250 μmol) and [PtMe_2(PMe_2Ph)$_2$] (234 mg, 470 μmol) at 77 K. A dinitrogen atmosphere was then

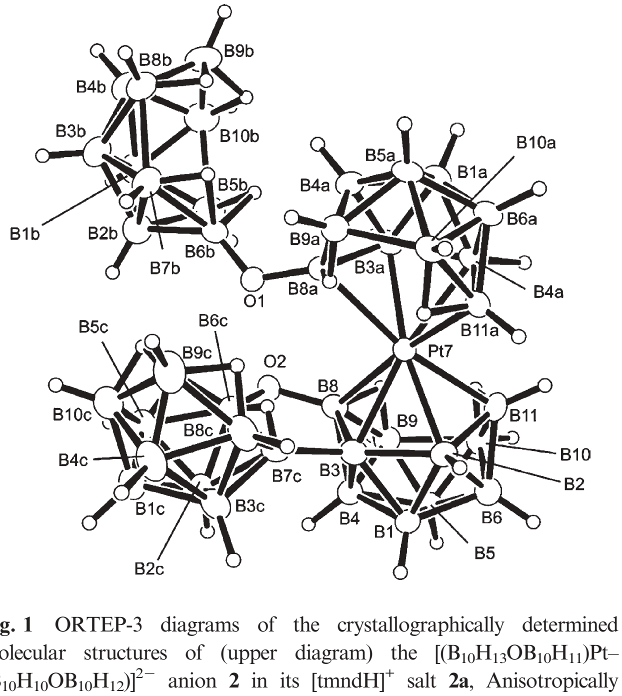

Fig. 1 ORTEP-3 diagrams of the crystallographically determined molecular structures of (upper diagram) the [($B_{10}H_{13}OB_{10}H_{11}$)Pt–($B_{10}H_{10}OB_{10}H_{12}$)]$^{2-}$ anion **2** in its [tmndH]$^+$ salt **2a**, Anisotropically determined atom positions are defined with 50% probability ellipsoids. Selected interatomic distances (in Å) are: from Pt(7) to B(2) 2.211(7), to B(3) 2.234(7), to B(8) 2.366(7), to B(11) 2.261(6), to B(2a) 2.236(6), to B(3a) 2.22.248(6), to B(8a) 2.3346(6), and to B(11a) 2.290(5): the angles B(11a)–O(1)–B(6b) and B(8)–O(2)–B(6c) are 123.5(4) and 109.6(4)°, respectively, with B(8)–Pt(7)–B(8a) and B(11)–Pt(7)–B(11a) 92.3(2) and 84.6(2)°, respectively. See schematics **V** and **VI** for other dimensions.

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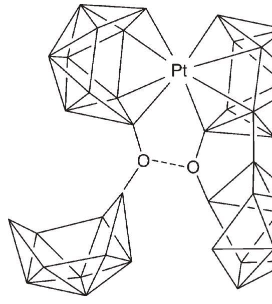
[a] *The School of Chemistry of the University of Leeds, Leeds, UK LS2 9JT. E-mail: jbould@gmail.com; Fax: +44 (0)113 343 6565; Tel: +44 (0)113 343 6449*
[b] *The School of Chemistry of the University of Leeds, Leeds, UK LS2 9JT. E-mail: j.d.kennedy@leeds.ac.uk; Fax: +44 (0)113 343 6401; Tel: +44 (0)113 343 6414*

introduced, the mixture was allowed to warm to ambient temperature and then stirred overnight. TLC analysis showed several coloured components. Repeated separation and purification by TLC and HPLC gave a principal product **3**, identified as [{(7,7-$PMe_2Ph)_2$-7-$PtB_{10}H_{11}$-8-}$_2$O], an assembly of two conventional {*nido*-7-PtB_{10}} structural units, joined by a B–O–B *sigma* link as in the starting substrate **1**, which we would hope to describe later in a full description of these reaction systems. The compound of interest in this present report was a minor product, TLC R_F 0.3 (60 : 40 CH_2Cl_2–C_6H_{14}), faint yellow, which was purified by repeated TLC, and, after a final cleansing by HPLC (Lichosorb SI 60, 25 × 2.12 cm, 60 : 40 CH_2Cl_2–C_6H_{14}), was ultimately isolated as crystals by diffusion of C_6H_{14} through a thin layer of C_6H_6 into a solution of the compound in $CHCl_3$, and identified as [{7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{10}$-μ-8,8′-O-μ-4,7′-H-{7′-PMe_2Ph)-7′-$PtB_{10}H_{11}$}] **4** (*ca.* 1 mg, $\leqslant$*ca.* 0.5%) by a single-crystal X-ray diffraction analysis† (Fig. 2 and schematic cluster structure **II**).



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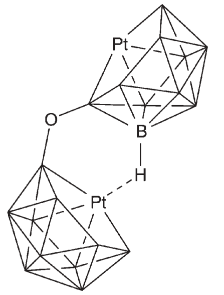

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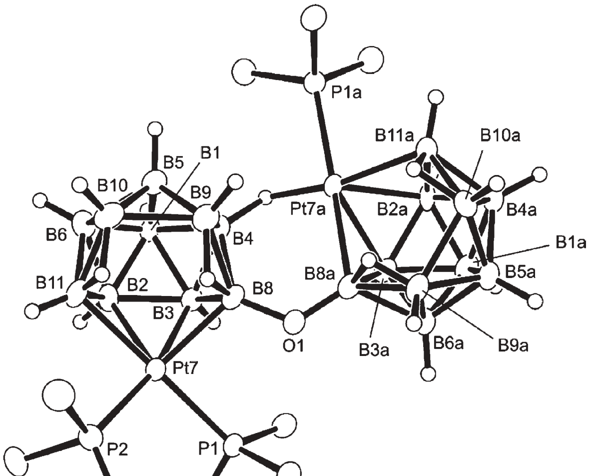
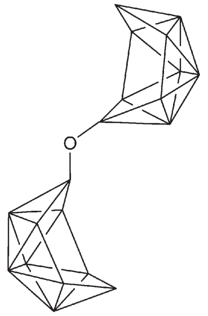


Fig. 2 ORTEP-3 diagram of the crystallographically determined molecular structure of [{$(PMe_2Ph)_2PtB_{10}H_{10}$}–μ-O-μ-H–{$(PMe_2Ph)$Pt–$B_{10}H_{11}$}] **4** in its $CHCl_3$ solvate (selected P-organyl atoms omitted for clarity). Anisotropically determined atom positions are defined with 50% probability ellipsoids. Selected interatomic distances (in Å) are: from Pt(7) to B(2) 2.228(6), to B(3) 2.225(6), to B(8) 2.209(7), to B(11) 2.298(7), to P(1) 2.3345(14) and to P(2) 2.3642(15). From Pt(7a): to B(4) 2.573(6), to B(2a) 2.164(6), to B(3a) 2.226(6), to B(8a) 2.330(6), to B(11a) 2.235(6) and to P(1a) 2.3294(13); Selected angles are P(1)–Pt(7)–P(2) 96.35(5), P(1a)–Pt(7a)–H(4) 83.2(14) and B(8)–O(1)–B(8a) 122.9(4)°. See schematic **VII** for other distances and angles.

For both **2** and **4** the very small quantities of pure compound so far available have precluded definitive NMR characterisation, but each of the all-atom molecular structures derived from the crystallographic analyses is self-consistent and chemically logical. In the structures of both species, the architecture of the starting substrate **1** (schematic **III**) can clearly be traced. The particular interest resides in the novel detail of their intercluster interactions (schematics **V–VII** below). For anion **2**, in addition to the starting B–O–B intercluster linkage, an additional B–B intercluster two-electron–two-centre σ bond has been induced (schematics **I** and **V**). This combination is unique. An additional interesting feature in anion **2** derives from the conformation of the two {(B_{10})–O–(B_{10})} units about the metal atom. Although the platinum-to-η^4-decaboranyl linkage is fluxional with a relatively low activation energy,[11] anion **2** in the solid state has chosen to adopt a conformation in which the two electronegative and lone-pair-containing oxygen atoms [B–O–B angles 109.6(4) and 123.5(4)°] are close in space [2.819(8) Å, schematic **VI**]. This is also unique.



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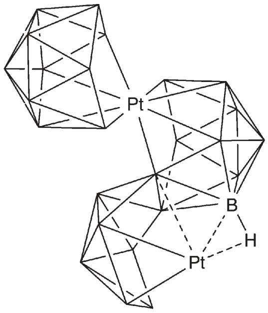
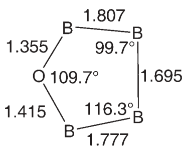


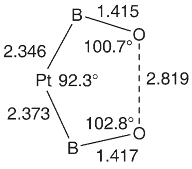
IV

In compound **4**, the {$(PMe_2Ph)_2PtB_{10}H_{11}$} subcluster [simply numbered cluster in the numbering scheme (Fig. 2)] has close parallels with the well-recognised single-cluster model [$(PMe_2Ph)_2PtB_{10}H_{12}$].[11,12] The {$(PMe_2Ph)PtB_{10}H_{11}$} subcluster (cluster 'a' in the numbering scheme), however, although otherwise analogous, has only one phosphine ligand on the metal centre, with the resulting coordination vacancy occupied by a hydrogen atom from a {B–H(*exo*)} unit in the other subcluster, with a close Pt–H approach of 1.64 Å (schematics **II** and **VII**). Whether this may be described as an agostic interaction may be subject to discussion.[13] In what is perhaps the nearest analogy, [$(PMe_2Ph)_2PtB_{16}H_{17}PtB_{10}H_{11}(PMe_2Ph)$] **5** (schematic **IV**),[1] there is also a {B–H(*exo*)} intercluster interaction with an otherwise vacant platinum coordination site, but in **5** the two subclusters are held in position because the two-borons-in-common conjunction in **5** rigidly gives the basic B-frame skeleton the necessary conformation. Although a number of other Pt–H–B agostic or quasi-agostic bonding interactions are recognised, principally from the work of Stone and co-workers,[14,15] in all cases the relevant Pt and BH units are similarly held in position by other bonding features. In **4**, by contrast, there is no additional bonding support, and the two skeletal subclusters could otherwise potentially swing out of the way of each other by rotation about one or both of the B–O bonds.

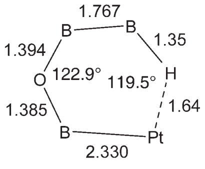
A referee has pertinently pointed out that there are interesting variations of dimensions among the B–O–B linkages. For example, there seems to be a differential effect on the boron-to-oxygen bonding occasioned by the metallation of the individual {B_{10}}



V



VI



VII

subclusters, but this seems not to be reciprocated in any significant changes within the subclusters. There is, however, a lack of sufficient data for meaningful comparison, these being the only examples of metallated [$(B_{10}H_{13})_2O$] species that have so far been established, but we would intend to address this deficiency with further experimentation on the incorporation of metal centres into the [$(B_{10}H_{13})_2O$] matrix.

The two new intercluster interaction modes exhibited by compounds **1** and **2** add interestingly and potentially usefully to the ultimate stock of cluster building materials available for future designed big-molecule architectures. We plan attempts to enhance yields of these low-yield products in order to permit examination of further chemistry of these interesting species, in particular to induce further increases in the intimacies of intercluster fusion, and in order to extend this principle of increasing the intimacy of intercluster fusion to other pre-linked clusters.

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Notes and references

† Single-crystal X-ray diffraction data. Compound **2a**: $C_{28}H_{84}B_{40}N_4O_2Pt$, M = 1136.48, triclinic (yellow block, 0.04 × 0.03 × 0.02 mm, from CH_2Cl_2–C_6H_{14}), $P\bar{1}$, a = 10.7721(4), b = 13.7551(5), c = 20.785(7) Å, α = 90.619(2), β = 95.784(2), γ = 104.140(2)°, U = 2985.83(18) Å^3, Z = 2, Brüker-Nonius FR591 rotating anode, λ = 0.71073 Å (Mo-Kα), μ = 2.383 mm^{-1}, T = 120(2) K, $R1$ = 0.0505 for 10380 reflections with $I > 2.0\sigma(I)$, $wR2$ = 0.1052 for all 13589 independent data, CCDC 655718. Compound **4**: ($CHCl_3$ solvate) $C_{24}H_{55}B_{20}OP_3Pt_2{\cdot}CHCl_3$, M = 1178.34, triclinic (yellow plate, 0.40 × 0.10 × 0.06 mm, from $CHCl_3$–C_6H_6–C_6H_{14}), $P\bar{1}$, a = 10.63360(10), b = 14.8948(2), c = 15.7371(2) Å, α = 66.7610(10), β = 83.475(2), γ = 86.483(2)°, U = 2275.09(5) Å^3, Z = 2, Nonius fine-focus sealed tube, λ = 0.71073 Å (Mo-Kα), μ = 6.448 mm^{-1}, T = 150(2) K, $R1$ = 0.0520 for 8881 reflections with $I > 2.0\sigma(I)$, $wR2$ = 0.1428 for all 10403 independent data, CCDC 655719. Methods and programmes were standard (COLLECT, DENZO-SMN, SHELXS-97, SHELXL-97, ORTEP-3). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712084b

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