Macropolyhedral boron-containing cluster chemistry: isolation and characterization of twenty-one-vertex [$(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)$]

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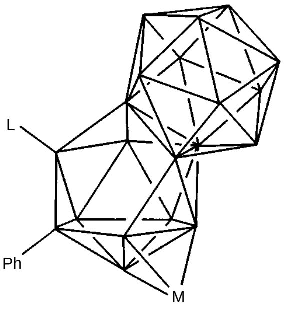
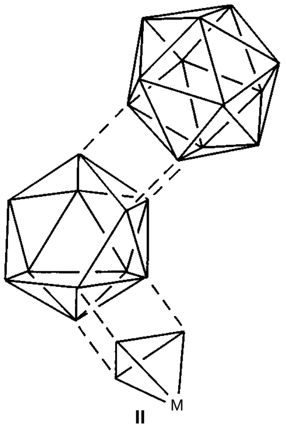
Reaction of $B_{20}H_{16}$ with [$ReH_5(PMe_2Ph)_3$] yields the twenty-one-vertex metallaborane [$(PMe_2Ph)_3HReB_{20}H_{15}Ph$-($PHMe_2$)] which consists of a *closo* twelve-vertex {B_{12}} unit and a *nido* eleven-vertex {B_{11}} unit fused with a common triangular face, with the {$(PMe_2Ph)_3HRe$} moiety capping *exo* to the *nido* {B_{11}} unit with three Re–H–B bonds; an unusual reductive P-phenyl cleavage of a PMe_2Ph moiety to give B-pendant *exo* $PHMe_2$ and *exo* Ph moieties on the open face of the eleven-vertex subcluster is also apparent.

The extension of the contiguous cluster chemistry of polyhedral boron-containing compounds beyond about fourteen vertices into the so-called 'macropolyhedral' area requires either fusion chemistry of smaller clusters[1] or Aufbau chemistry on preformed macropolyhedral species. Aufbau reactions to incorporate metal centres into the two accessible isomers of $B_{18}H_{22}$ yield nineteen- and twenty-vertex metallaboranes,[2,3] but to use this approach for even bigger clusters requires bigger contiguous starting substrates. The next highest known contiguous binary borane, $B_{20}H_{16}$,[4] is very difficult to come by. Its bis(ligand) adduct formation was investigaterd some 30 years ago,[5,6] as well as some related hydrolysis and alcoholysis behaviour,[6] but any further chemistry is unexamined since then. We have now isolated small quantities of $B_{20}H_{16}$ from crude $B_{10}H_{14}$,[7] and here report preliminary results from its reaction with [$ReH_5(PMe_2Ph)_3$] to generate the large, twenty-one-vertex, contiguous metallaborane [$(PMe_2Ph)_3HReB_{20}H_{15}Ph$-($PHMe_2$)].

Reaction of [$ReH_5(PMe_2Ph)_3$] (83 mg; 138 μmol) and $B_{20}H_{16}$ (32 mg; 138 μmol) in solution in C_6H_6 (7 cm^3) at reflux for 60 min, followed by chromatographic separation, revealed several coloured reaction products. Of these, two are identifiable as rhenaborane products in yields that are viable for further examination on this reaction scale. Repeated thin-layer chromatography [silica gel G (Fluka GF_{254}), CH_2Cl_2–C_6H_{14} mixtures] and repeated recrystallization has now ultimately given one of these, [$(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)$], as a pure, yellow, crystalline solid [4 mg; 5.5 μmol; 4% (R_f 0.46, CH_2Cl_2–C_6H_{14} 80 : 20)]. Crystals suitable for single-crystal X-ray work have been exceedingly difficult to grow. Ultimately (eleven months) one was obtained of suitable size for CCD work (Fig. 1 and schematic cluster structure **I**).‡ The results from the X-ray structural analysis are consistent with the results from NMR spectroscopy of the bulk material.§ The basic cluster structure is based on a *nido* eleven-vertex subcluster and a *closo* twelve-vertex subcluster fused with a common triangular three-boron face (schematics **I** and **II**). This twenty-vertex geometry is similar to those (*a*) of the bis(ligand) adducts of $B_{20}H_{16}$ such as [$B_{20}H_{16}(MeCN)_2$][5] and (*b*) of [$(PMe_2Ph)_4Pt_2B_{18}H_{16}$][2] formed *via* oxidative Aufbau from $B_{18}H_{22}$. These three incidences may suggest a particular stability of this twelve-vertex: eleven-vertex *closo* : *nido* structural format. In [$(PMe_2Ph)_3$-$HReB_{20}H_{15}Ph(PHMe_2)$] the twenty-first vertex is provided by the capping of a closed triangular three-boron face of the *nido*



I



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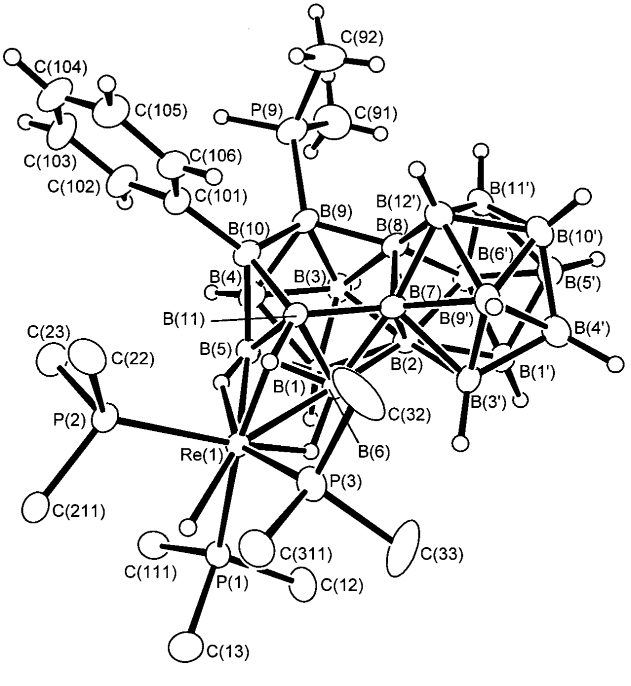

Fig. 1 ORTEP-type diagram of the molecular structure of [$(PMe_2Ph)_3$-$HReB_{20}H_{15}Ph(PHMe_2)$]. Selected distances (in Å) are as follows: from Re(1) to P(1) 2.3533(14), to P(2) 2.351(2), to P(3) 2.374(2), to B(5) 2.376(6), to B(6) 2.3561(7) and to B(11) 2.447(6); interboron B(2)–B(7) 1.800(9), B(2)–B(8) 1.772(9), B(7)–B(8) 1.841(10), B(8)–B(9) 1.756(9), B(9)–B(10) 1.736(9), B(10)–B(11) 1.748(9), B(7)–B(11) 1.755(9); B(2)–B(3) is long at 1.991(9), with the other interboron distances in the range 1.712(9)–1.914(9) for the *nido* subcluster and 1.729(11)–1.819(10) for the *closo* subcluster; shorter intercluster distances are B(3)–B(6′) 2.409(10) and B(3′)–B(6) 2.367(9); B(9)–P(9) is 1.888(7) and B(10)–C(101) 1.589(8). Selected angles (in °) at Re(1) are P(1)–P(2) 100.90(5), P(2)–P(3) 104.14(6), P(1)–P(3) 108.52(6), P(1)–H(12) 68.17(4), P(2)–H(12) 64.09(4) and P(3)–H(12) 65.61(4).

eleven-vertex subcluster by a {$(PMe_2Ph)_3HRe$} centre *via* three B–H(*exo*)–Re linkages. This latter type of linkage has predecent in $[(PPh_3)_2ClRuB_{12}H_{11}(NEt_3)]$,[8] and, in Group VII chemistry, $[(CO)_3MnB_8H_{14}]$ and $[(CO)_3MnB_3H_8]$.[9] In sum, the twenty-one-vertex contiguous cluster structure is based upon a triple-cluster unit consisting of a central eleven-vertex {B_{11}} *nido* subcluster conjoined by a common three-boron triangular face to a *closo* twelve-vertex {B_{12}} subcluster and by a second common three-boron triangular face to a *nido*-type four-vertex {ReB_3} subcluster (schematic **II**).

The compound has several other interesting features: (*a*) at twenty-one vertices it is the largest molecular contiguous boron-containing cluster yet characterized; (*b*) the twelve-vertex-*closo* : eleven-vertex-*nido* double-subcluster format with three-atoms-in-common appears to be a stable one; (*c*) the rhenium centre bonds *exo*–*nido*, rather than *endo* to form a *closo* cluster (there is contemporary interest[10] in this type of boron-to-metal bonding and the factors that may influence it); (*d*) the reductive P–phenyl cleavage of a PMe_2Ph moiety and (*e*) the concomitant phenyl transfer to boron are both very unusual, and the compound may therefore model intermediates for the formation of $[(PH_3)_2(Ph_2PC_6H_4)IrB_9H_7(PPh_3)]$ *via* a so-far unique complete reductive $PAr_3 \rightarrow PH_3$ cleavage,[11] and for the formation of $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ *via* a phosphorus-to-boron phenyl-group transfer.[12] There is clearly much interesting chemistry to be revealed by the further examination of this and other related twenty-boron systems, and we currently attempt to do this.

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Footnotes

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‡ *Crystal data* for $[(PMe_2Ph)_3HReB_{20}H_{15}Ph(PHMe_2)]\cdot CHCl_3$: $C_{33}H_{62}B_{20}Cl_3P_4Re$, $M = 1091.58$ (includes solvent), triclinic, space group $P\bar{1}$, $a = 12.8286(9)$, $b = 14.2985(10)$, $c = 15.4090(10)$ Å, $\alpha = 113.369(2)°$, $\beta = 99.955(2)°$ $\gamma = 93.486(2)°$, $U = 2529.2(3)$ Å^3, $Z = 2$, $D_c = 1.43$ Mg m^{-3}, $F(000) = 1092$, $\mu = 2.577$ mm^{-1}, $T = 160$ K; crystal size 0.40 × 0.10 × 0.10 mm. 15960 reflections were measured on a Siemens SMART CCD area detector using graphite-monochromated Mo-Kα radiation and narrow ω-rotation frames. Data were corrected for absorption empirically using redundant and symmetry equivalent data. The structure was solved by heavy-atom methods[13] and was refined by full-matrix least-squares analysis on F^2 using all 11092 unique reflections ($R_{int} = 0.0421$).[14] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.1001$ for all data, conventional R [on F values of 9360 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0485, goodness of fit $S = 1.134$ on all F^2 for 610 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl, phenyl and methine hydrogen atoms were constrained to idealised positions with fixed isotropic displacement parameters of nU_{eq} of the parent carbon atom (where $n = 1.5$ for methyl and 1.2 for phenyl and methine). All other hydrogen atoms were located on Fourier difference syntheses and were freely refined apart from those hydrogen atoms bonded to rhenium which were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/312.

§ Measured NMR data ($CDCl_3$) as follows (294–297 K) {ordered as $\delta(^{11}B)$ (in ppm rel. F_3BOEt_3) [$\delta(^1H)$ (in ppm rel. $SiMe_4$) of directly bound *exo* hydrogen atoms in square brackets]: +23.6 [no *exo*-H], +7.1 [+3.43], *ca.* +0.5 [+2.37], *ca.* +0.5 [+4.08], −1.5 [+2.50], −4.2 [+2.79], −4.7 [−6.53, ReHB bridge], −6.3 [+2.13], −8.0 [+1.96], −11.2 [no *exo*-H], −14.2 [+1.38], −15.0 [+1.54], −17.6 [+2.08], *ca.* −18.0 [no *exo*-H], *ca.* −18.5 [+1.55], *ca.* −18.6 [no *exo*-H], −19.2 [−8.30, ReHB bridge], −28.4 [no *exo*-H], −33.3 [+1.02], −36.2 [−5.66, ReHB bridge]; additionally $\delta(^1H)$(ReH) −6.27 [1 : 2 : 1 t, $^2J(^{31}P–^1H)$(mean) 60 Hz of 1 : 1 d, $^2J(^{31}P–^1H)$ 46 Hz], $\delta(^1H)$(PH) + 4.94 [d, $^1J(^{31}P–^1H)$ 394 Hz of m, $^3J(^1H–C–P–^1H)$(mean) 6 Hz], $\delta(^1H)(PMe)(PHMe_2)$ + 1.23 and +1.38 [for both, $^2J(^{31}P–^1H)$ *ca.* 13 Hz, $^3J(^1H–P–C–^1H)$ *ca.* 6 Hz], $\delta(^1H)(PMe)(PMe_2Ph)$ + 2.07, +1.91, +1.90, +1.77, +1.76 and +1.72 [one tentative, all $^2J(^{31}P–^1H)$ *ca.* 9–10 Hz], $\delta(^{31}P)$ (in ppm rel. 85% H_3PO_4) (223 K) −18.3 (sharp), −20.0 (sharp), −20.3 (sharp) and −30.9 (br, $PHMe_2$ group).

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