

ISOLATION AND STRUCTURE OF $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$. A POSSIBLE PROGNOSTIC FOR NEW GLOBULAR BORANE-BASED CLUSTER ARCHITECTURES

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It is a pleasure for the authors to dedicate this paper to Dr Stanislav Heřmánek on the occasion of his 70th birthday, in recognition of his many imaginative insights and considerable contributions to the field of polyhedral boron-containing cluster chemistry over the final decades of this century.

A novel metallaborane compound, $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$, prepared from $[PdCl_2(PPh_3)_2]$ and $[B_{10}H_{10}]^{2-}$ in EtOH, exhibits a globular cluster architecture consisting of two twelve-vertex *closo* $\{PdB_{11}\}$ cluster units fused to generate a condensed globular $\{PdB_{20}\}$ assembly that has a tetrahedral $\{B_4\}$ borons-only core. There is dynamic bonding between this borane-based assembly and an unusual exopolyhedral palladium-based domain consisting of a $\{(PPh_3)Pd(PPh_2)Pd(PPh_2)Pd(PPh_3)\}$ string. The central tetrahedral borons-only core suggests a new type of globular "megaloborane" architectural principle for higher condensed boron hydrides, which is assessed by *ab initio* studies at the STO-3G level on protonated $[B_{28}H_{18}]^{2-}$ and related structures: results suggest energetic minimisation at neutral $[B_{27}H_{21}]$.

Key words: Boranes; Metallaboranes; Palladium-boron clusters; X-Ray crystallography; NMR spectroscopy; Large "megaloborane" polyhedral clusters; *Ab initio* calculations.

We have jointly been interested for some time in developing the chemistry of multimetal assemblages based around polyhedral boron units¹⁻³. There is also a contemporary general interest in novel cluster chemistry of the Main-Group elements, stimulated somewhat by the populism of fullerene chemistry. Developing on some of our initial work¹, we report here on a

novel metallaborane compound, $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$ (**1**) (Fig. 1), that encompasses interesting elements of both these themes. Compound **1** also offers new implications for future architectural developments in polyhedral boron-containing cluster chemistry, which we assess with *ab initio* calculations.

Reaction between $[PdCl_2(PPh_3)_2]$ (280 mg, 400 μ mol) and $[NEt_4]_2[closo-B_{10}H_{10}]$ (150 mg, 400 μ mol) in refluxing ethanol (75 cm^3) for 68 h under dry dinitrogen, followed by removal of solvent and thence

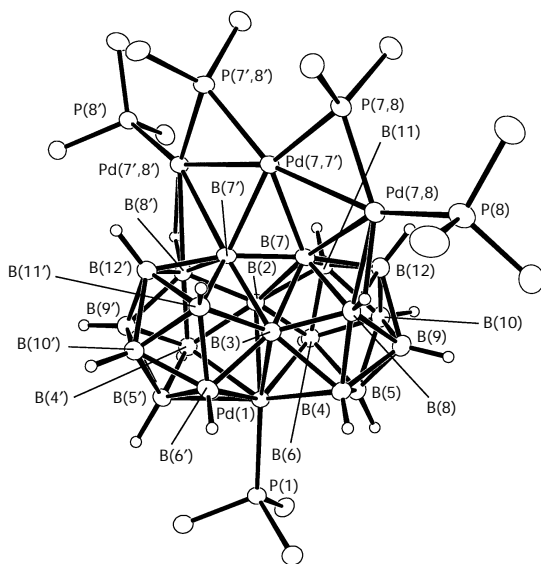
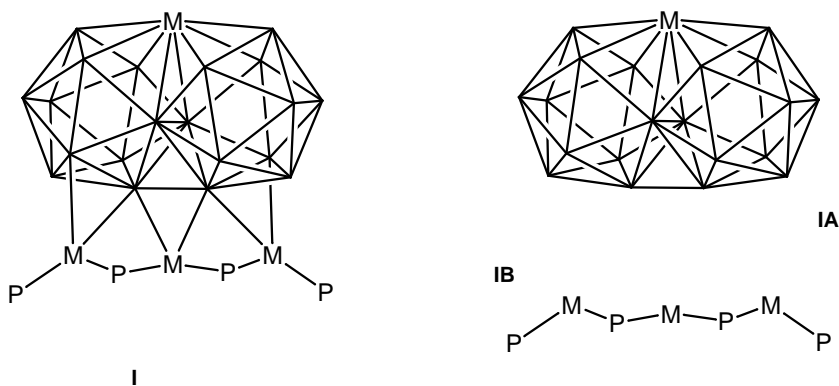


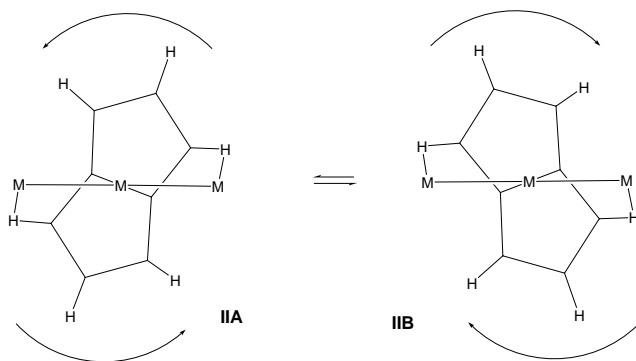
FIG. 1

Molecular structure of $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$ (**1**) with P-phenyl group atoms, apart from the *ipso* carbon ones, omitted for clarity. Distances from Pd(1) to the eight adjacent boron atoms are in the range 2.165(4)–2.290(5) Å, and from Pd(1) to P(1) 2.369(1) Å. Distances within the central four-boron tetrahedron are: B(2)–B(3) long at 2.017(6), B(7)–B(7') short at 1.706(6), B(2)–B(7) 196.0(6), B(3)–B(7) 1.850(6), B(2)–B(7') 1.853(6) and B(3)–B(7') 1.949(6) Å, and metal–phosphorus distances along the $\{P(8)Pd(7,8)P(7,8)Pd(7,7')P(7',8')Pd(7',8')P(8')\}$ string are successively 2.286(1), 2.212(1), 2.250(1), 2.268(1), 2.209(1) and 2.267(1) Å. The two hydrogen-bridged palladium-to-boron distances Pd(7,8)–B(8) and Pd(7',8')–B(8') are 2.399(4) and 2.407(4) Å, respectively, and the remaining palladium-to-boron contact distances are: Pd(7,8)–B(7) 2.686(4), Pd(7,7')–B(7) 2.225(4), Pd(7,7')–B(7') 2.223(4) and Pd(7',8')–B(7') 2.585(4) Å, with distances from Pd(1) being as follows to: B(2) 2.165(4), B(3) 2.166(4), B(4) 2.232(4), B(5) 2.215(4), B(6) 2.250(5), B(4') 2.215(5), B(5') 2.218(4) and B(6') 2.290(5) Å. The intermetal distances Pd(7,7')–Pd(7,8) and Pd(7,7')–Pd(7',8') are 2.7316(4) and 2.7362(4) Å, respectively.

thin-layer chromatography of the residue on silica G (Merck 60G) using CH_2Cl_2 as liquid phase, gave an interesting red component (*ca* 40 mg). An aliquot of this (*ca* 10 mg) was subjected to further chromatographic separation (silica; CH_2Cl_2 -hexane mixtures), which revealed three substances. The predominant compound was colourless [*closo*- $\text{B}_{10}\text{H}_8(\text{PPh}_3)_2$], predominantly the 2,6- and/or 2,7-isomers² (*ca* 9 mg, 14 μmol). The other two were red and air-stable. One was only in trace quantities (*<* *ca* 80 μg), and is as yet unidentified, but the number of resonances in its ^{11}B NMR spectrum⁴, of which some are at quite low field, suggests a macropolyhedral fused-cluster species with more than two metal centres. The third is a quite novel macropolyhedral species (**1**) of formulation $[(\text{PPh}_3)_3(\text{PPh}_2)_2\text{Pd}_4\text{B}_{20}\text{H}_{16}]$ (*ca* 850 μg , 0.47 μmol), identified as such by single-crystal X-ray diffraction analysis⁵ (Fig. 1 and schematic structure I) and corroborative NMR spectroscopy⁶.



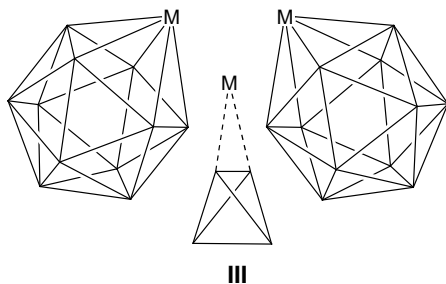
The basic $\{\text{PdB}_{20}\text{H}_{16}\}$ unit of compound **1** (schematic structure IA) obviously derives from the palladium-mediated fusion of two $\{\text{B}_{10}\}$ units. Fusions of borane-based clusters induced by transition-element halides are well known⁷, but, in compound **1**, the incorporation of palladium into the resulting larger cluster, and the very large twenty-one-vertex assembly (schematic IA), are both novel. This latter $\{\text{PdB}_{20}\}$ unit has an additional interesting feature in that it supports, *via* a combination of metal-boron and metal-hydrogen-boron interactions (Fig. 1), an unusual tripalladium string, $\{(\text{PPh}_3)\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_3)\}$ (schematic IB). The $\{\text{PPh}_2\}$ units must derive from phosphorus-to-phenyl bond cleavage, recognised in palladium chemistry⁸, and for which there is also precedent in metallaborane systems⁹.



The $^{31}\text{P}\{-^1\text{H}(\text{broadband})\}$ NMR spectrum of compound **1** is consistent with the solid-state structure, with an $[\text{AX}]_2$ pattern from the $\{\text{PPh}_3\}\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_3)\}$ string and a singlet from the lone $\{\text{Pd}(\text{PPh}_3)\}$ group. The $^1\text{H}\{-^{11}\text{B}(\text{broadband})\}$ spectrum at low temperatures shows an eight-resonance $2 : 2 : 2 : 2 : 2 : 2 : 2 : 2$ pattern for the $\{\text{PdB}_{20}\text{H}_{16}\}$ unit in accord with a solution-state C_2 symmetry as suggested by the solid-state structure of Fig. 1. At higher temperatures, three pairs of these coalesce to give a $2 : 4 : 2 : 4 : 4$ five-resonance pattern, demonstrating a fluxionality. The ^{11}B spectra are also in accord with fluxional behaviour. Because of broad lines, unsurprising in view of the large molecular size, and because of accidentally coincident resonances, the ^{11}B spectra do not analyse by simple inspection. However, with the aid of $^1\text{H}\{-^{11}\text{B}(\text{selective})\}$ spectroscopy and a recognition of the fluxional process, ten positions of equal intensity can be established at lower temperatures, with three pairs of these each coalescing at higher temperatures to give a $4 : 2 : 2 : 2 : 2 : 4 : 4$ relative intensity distribution. These observations imply a time-average C_{2v} symmetry for the fluxional process, which is reasonably accounted for by a rapid positional exchange of each of the terminal Pd atoms of the $\{\text{PPh}_3\}\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_3)\}$ string, between BH(8) and BH(11') for Pd(7,8), and between BH(8') and BH(11) for Pd(7',8') (schematics **IIA** and **IIB**). Coalescence temperatures in the ^1H and ^{11}B spectra give values of *ca* 37 kJ mol^{-1} for the activation energy ΔG^\ddagger for the fluxional process in the temperature region 185–230 K. Related fluxionalities in non-borane poly-palladium systems are recognised¹⁰.

In terms of cluster architectural principles, as opposed to synthetic ones, the twenty-one-vertex cluster is based on the fusion of two icosahedral twelve-vertex *closo* $\{\text{PdB}_{11}\}$ units with a common triangular face, $\{\text{Pd}(1)\text{B}(2)\text{B}(3)\}$, together with an intercluster fusion link, $\{\text{B}(7)\text{B}(7')\}$. This

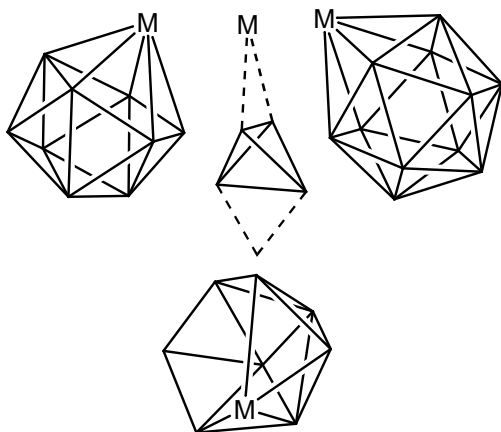
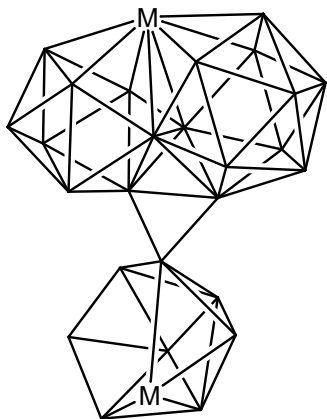
effectively generates a $\{B(2)B(3)B(7)B(7')\}$ borons-only tetrahedral four-atom core (schematic **III**). This feature is also seen in $[(CO)(PMe_3)_4Ir_2B_{26}H_{24}]$ (schematic **IV**) (ref.¹¹), and related tetrahedral architectural cores can also be discerned in $[(C_5Me_5)_3HIr_3B_{18}H_{14}(OH)]$ (schematic **V**) (ref.¹²) and



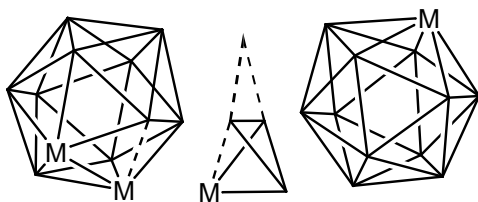
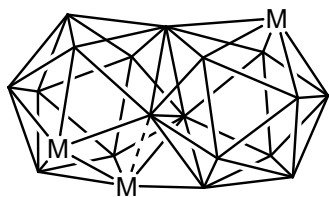
$[(PMe_2Ph)_4Pt_2B_{18}H_{16}]$ (schematic **VI**) (ref.¹³). The observation of these four-atom inner cores in these very condensed species leads to a general concept that novel series of big-cluster boron-hydride species may be available, based on the structural principle of borons-only cores surrounded by boron-hydride sheaths. One manifestation would be clusters with central borons-only cores fused to a number of surrounding more conventional boron-hydride units, which themselves may be mutually fused. These new “megaloboranes” would be “filled-cage” cluster compounds, previously unconsidered for boranes. They are quite distinct from the concept of “hollow-cage” species, such as $B_{32}H_{32}$, which have been the subject of theoretical calculations¹⁴, but which are more akin to the alternative hollow-cage fullerene architectural principle.

The majority of molecular cluster compounds can be visualised as domains of elemental or ceramic lattices with peripheral valencies occupied by ligands or other chemical features. In this context the central tetrahedral unit of compound **1** is strongly reminiscent of the tetrahedral four-boron unit that resides at the centre of the C_{3v} $\{B_{28}\}$ representation that is commonly used to depict a $\{B_{27}\}$ unit of elemental boron itself in its β -rhombohedral allotrope¹⁵. In β -rhombohedral boron this tetrahedral $\{B_4\}$ unit fuses three icosahedra. In compound **1** it fuses two. These considerations have led us to the idea that this $\{B_{28}\}$ unit is a promising starting point for the investigation for possible stabilities within these new types of larger megaloborane aggregates. This we have assessed initially by *ab initio* calculations at the STO-3G level¹⁶, which is adequate enough to explore possibilities for purposes of initial survey.

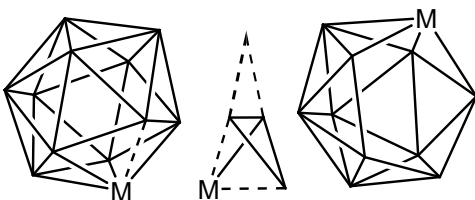
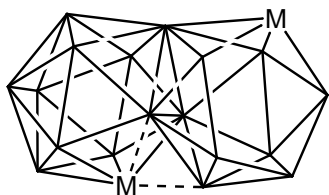
Initial siting calculation at the semi-empirical AM-1 level¹⁶ was based on the coordinates of the C_{3v} geometry of the $\{B_{28}\}$ core of β -rhombohedral boron, with the eighteen most prominent vertices bonded to hydrogen to yield $[B_{28}H_{18}]$. This assembly minimised energetically at a mirror plane structure that was geometrically close to the starting C_{3v} unit. Important



IV



V



VI

features of the resulting MO scheme showed that (i) the LUMO was low-lying and centred in the core of the molecule and (ii) there was an exposed HOMO on the periphery of the molecule associated with a triangular unit of three very exposed boron atoms that were not bound in BH(*exo*) entities. Feature (i) suggested that an additional two electrons might readily be accommodated to enhance cluster stability in the production of a stable anionic $[\text{B}_{28}\text{H}_{18}]^{2-}$ species. Feature (ii) suggested that the exposed triangular $\{\text{B}_3\}$ unit might favour protonation to enhance compound stability. We examined for variations in both these aspects. The effect of LUMO occupancy was assessed by establishing energy minimisations for the evenly charged ions around $[\text{B}_{28}\text{H}_{18}]^{2-}$ to engender the sequence $[\text{B}_{28}\text{H}_{18}]^{2+}$, $[\text{B}_{28}\text{H}_{18}]$, $[\text{B}_{28}\text{H}_{18}]^{2-}$ and $[\text{B}_{28}\text{H}_{18}]^{4-}$. The effects of protonation of the exposed $\{\text{B}_3\}$ unit was assessed by minimising structures for the $[\text{B}_{28}\text{H}_{21}]^+$ cation. The corresponding species based on protonations of neutral $[\text{B}_{28}\text{H}_{18}]$ and of the $[\text{B}_{28}\text{H}_{18}]^{4-}$ tetraanion were also examined in order better to define the multi-dimensional geometry–energy–charge minimum in question. Consolidations were achieved with similar gross geometries to that of the initial $\{\text{B}_{28}\text{H}_{18}\}$ unit, confirming the inherent stability for the gross three-fused-icosahedra geometry in this particular system. Principal differences were associated with the opening and closing of linkages in the exposed $\{\text{B}_3\}$ triangle. The most satisfactory minimum was around $[\text{B}_{28}\text{H}_{21}]^+$, but this exhibited very close distances among the three extra hydrogen positions on the exposed $\{\text{B}_3\}$ triangle, much closer than a Van-der-Waals radius sum. Calculations at the *ab initio* STO-3G level, starting with this AM-1 $[\text{B}_{28}\text{H}_{21}]^-$ geometry, removed this crowded feature but generated a $\{\text{BH}\}$ bridge between borons in this triangular region. Intuitively this is chemically unrealistic, but removal of the $\{\text{BH}\}$ unit and replacement by $\{\text{H}\}^-$ gave a hydrogen bridge in this position, and gave a nicely minimised structure for the resulting neutral $[\text{B}_{27}\text{H}_{21}]$ species as in Fig. 2. This is based on two *closo* $\{\text{B}_{12}\}$ units and a *nido* $\{\text{B}_{11}\}$ unit fused about the central tetrahedral core, with an additional longer interboron connectivity generating a second tetrahedron. The overall result exhibits good augury for the ultimate isolation of compounds based on these structural principles.

More complex megaloborane units can readily be envisaged. One example can be based on the $\{\text{B}_{84}\}$ unit of β -rhombohedral boron. If each of the twelve effective *nido* hexaboranyl faces on the periphery of this unit is bound with four *endo*/bridging hydrogen atoms, as in B_6H_{10} itself, then the $[\text{B}_{84}\text{H}_{48}]^{2-}$ anion is generated. The double anionic charge would arise on the basis that the megaloborane assembly is effectively icosahedral $[\text{B}_{12}\text{H}_{12}]^{2-}$ with the twelve two-centre two-electron B–H *exo* bonds replaced by twelve

two-electron two-centre bonds to the apical positions of twelve mutually linked neutral *nido* hexaboranyl units. From this starting point, again at the AM-1 level, we assessed for charge variation and for variation of hydrogen-atom incidence, and these currently minimise around the neutral $[B_{84}H_{54}]$ species as in Fig. 3. In contrast to the $[B_{27}H_{21}]$ species, which would have a surface predominantly of fixed *exo* hydrogen atoms, $[B_{84}H_{54}]$ would have a

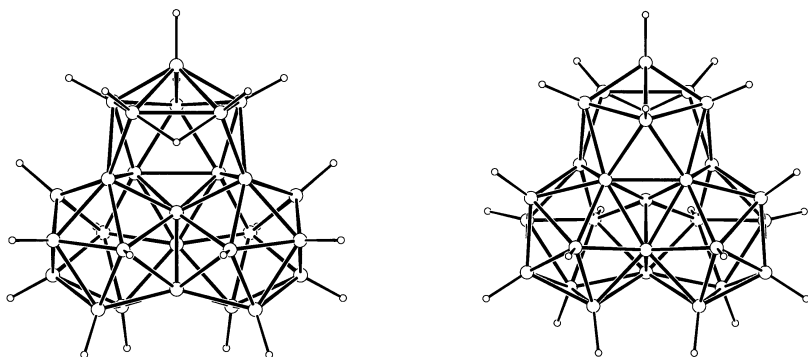


FIG. 2

Representations, from opposing sides of the molecule, of the STO-3G *ab initio* structure of neutral $[B_{27}H_{21}]$, energy-minimised with a C_s symmetry constraint. The $\{B_{27}\}$ unit has many similarities with the $\{B_{27}\}$ unit of β -rhombohedral boron. It fuses two closed twelve-vertex icosahedra and one eleven-vertex *nido* unit together to generate a central tetrahedral $\{B_4\}$ core in a reasonable extension of the fusion principles observed in compound **1** (schematics **III**), in which a central tetrahedral $\{B_4\}$ unit fuses two rather than three deltahedra. There are twenty peripheral boron atoms bound to *exo* hydrogen atoms and there is one bridging hydrogen atom in an *endo* position on the open face of the *nido* eleven-vertex subunit

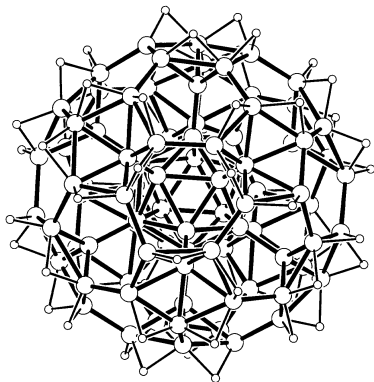


FIG. 3

Representation of the AM-1 semi-empirical energy-minimised structure of neutral $[B_{84}H_{54}]$, optimised within the constraints of D_3 symmetry, constraint of position, and of *endo versus* bridging character of the hydrogen atoms, results in energy minima of very similar magnitude, with only minor flexing of the basic $\{B_{84}\}$ cage. The species would therefore probably be highly fluxional with respect to hydrogen-atom exchange over the surface. This contrasts to $[B_{27}H_{21}]$ (Fig. 2), which would have a surface predominantly of fixed *exo*-terminal hydrogen atoms

surface of more mobile bridging/*endo* hydrogen atoms. Parallels with B_6H_{10} suggest that these could be fluxional, possibly over the whole surface, and the compound would also be likely to be much more reactive. This type of surface represents one extreme of surface hydrogen behaviour. The other extreme would consist of $BH(exo)$ hydrogens only, which $[B_{27}H_{21}]$ nearly achieves, and which is exhibited by smaller, neutral, $[B_{20}H_{16}]$ (ref.¹⁸), the only known binary borane to belong to this class. The $[B_{27}H_{21}]$ species may well prove to be typical in that experimentally achievable megaloborane cluster molecules could well have mixed domains of both surface types, most likely with a predominance of *exo* hydrogen atoms.

These metallaborane experimental results and ensuing theoretical considerations therefore support the possibility of higher boron hydrides based on boron-hydride units assembled around borons-only cores to give "filled-cage" cluster species. One experimental possibility, until rational *Aufbau* syntheses can be developed, is the high-energy ablation of elemental boron in a dilute hydrogen atmosphere. Here it is of interest that higher boron hydrides have been tentatively identified in the products of laser work in this area¹⁸. It will be of obvious high interest (i) to see detailed analyses of products from such systems, as well as (ii) to examine for other possible metal-containing megaloborane species from the palladium system reported here.

Crystallographic data for the structure of $[(PPh_3)_3(PPh_2)_2Pd_4B_{20}H_{16}]$ (**1**) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-111909. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk. Coordinates for the calculated structures of $B_{27}H_{21}$ and $B_{84}H_{54}$, as depicted in Figs 2 and 3, respectively, are available from authors.

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4. $\delta(^{11}\text{B})$ at *ca* +75 (1B), +43 (1B), +8 (1B) and +3 ppm (1B), with a larger resonance agglomerate centred around $\delta(^{11}\text{B})$ *ca* -24 ppm (*ca* 16B) with peaks $\delta(^{11}\text{B})$ (max) at *ca* -18, -22, -25 and -28 ppm.
5. Crystal data for $[(\text{PPh}_3)_3(\text{PPh}_2)_2\text{Pd}_4\text{B}_{20}\text{H}_{16}] [\text{CH}_2\text{Cl}_2]_{1.5}$, $\text{C}_{79.50}\text{H}_{84}\text{B}_{20}\text{Cl}_3\text{P}_5\text{Pd}_4$, $M = 1\,942.47$, monoclinic, space group $P2_1/n$, $a = 13.2653(3)$, $b = 24.8824(8)$, $c = 26.0008(8)$ Å, $\beta = 90.0850(16)^\circ$, $U = 8582.1(4)$ Å³, $Z = 4$, $\text{MoK}\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.054$ mm⁻¹, $T = 190(2)$ K, $R1 = 0.0424$ for 14 675 reflections with $F^2 > 2.0\sigma(F^2)$, and $wR2 = 0.1113$ for all 16 815 unique reflections. CCDC No. 111909.
6. Results of the analysis of the cluster ^{11}B and ^1H NMR data for compound **1** {ordered as peak designator (relative intensity) $\delta(^{11}\text{B})$ in ppm [$\delta(^1\text{H})$ in ppm]}, CD_2Cl_2 solution: (i) at 193 K: A (2BH) *ca* +4.5 [+3.31], B (2BH) *ca* +4.5 [+2.66], C (2BH) +0.9 [+2.47], D (2B) *ca* +1.0 [no terminal hydrogen], E (2BH) *ca* -7.7 [+4.20], F (2B) *ca* +8.0 [no terminal hydrogen], G (2BH) -11.3 [+2.16], H (2BH) *ca* -16.5 [+1.47], I *ca* -16.5 [+0.54], and J (2BH) -38.9 [-1.67]; (ii) at 273 K: AB (4BH) +6.4 [+3.08], C (2BH) *ca* +2.5 [+2.52], D (2B) *ca* +2.5 [no terminal hydrogen], E (2BH) *ca* -6.0 [+4.20], F (2B) *ca* -6.0 [no terminal hydrogen], GH (4BH) -12.5 [+1.85], and IJ (4BH) -26.5 [-0.48]. Coalescence temperatures in K: in the 500 MHz ^1H spectrum: 213 ± 5 for IJ, with AB and GH both 188 ± 4 ; in the 128 MHz ^{11}B spectrum: 210.5 ± 2.5 for GH and 225.5 ± 2.5 for IJ. These give calculated values for ΔG^\ddagger within the range 34.9 to 38.9 kJ mol⁻¹. Phenyl proton resonances occurred between $\delta(^1\text{H})$ +6.5 and +7.9 ppm. Additionally ^{31}P - $\{^1\text{H}\}$ spectrum (294 K): $\delta(^{31}\text{P})$ [1P, singlet, P(1)] at +27.3 ppm plus an [AX]₂ pattern with $\delta(^{31}\text{P})$ [2P, P(7,8;7',8')] at +262.8 ppm (PPh₂ units) and [2P, P(8,8')] at +26.7 ppm (PPh₃ units), with $N = [^2J(^{31}\text{P}(7,8)^{31}\text{P}(7',8')) + ^4J(^{31}\text{P}(8)^{31}\text{P}(8'))] = 135$ Hz; some broadening of the PPh₂ ^{31}P resonance was apparent at 183 K.
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