

**POLYHEDRAL DIPALLADABORANE CHEMISTRY. THE MOLECULAR STRUCTURE AND CLUSTER ELECTRON COUNT OF [7,8-(PPh<sub>3</sub>)<sub>2</sub>-7,8-(μ-PPh<sub>2</sub>)-9,11-(OEt)<sub>2</sub>-*nido*-7,8-Pd<sub>2</sub>B<sub>9</sub>H<sub>8</sub>]**

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[PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and the [NHEt<sub>3</sub>]<sup>+</sup> salt of [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> in refluxing ethanol yield the dipalladundecaborane cluster compound [7,8-(PPh<sub>3</sub>)<sub>2</sub>-7,8-(μ-PPh<sub>2</sub>)-9,11-(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-*nido*-7,8-Pd<sub>2</sub>B<sub>9</sub>H<sub>8</sub>] (**1**). An all-atom single-crystal synchrotron X-ray diffraction study shows a significant difference to four structurally characterised platinum congeners reported in the literature for which revised formulation is now necessary. The importance of taking into consideration the electron count in polyhedral boron-containing cluster systems in the course of their characterisation is emphasised.

**Keywords:** PSEPT; Dimetallaundecaborane; Palladaborane; Metallaborane; Cluster chemistry; electron-counting considerations; Palladium; Boron; Synchrotron X-ray structure.

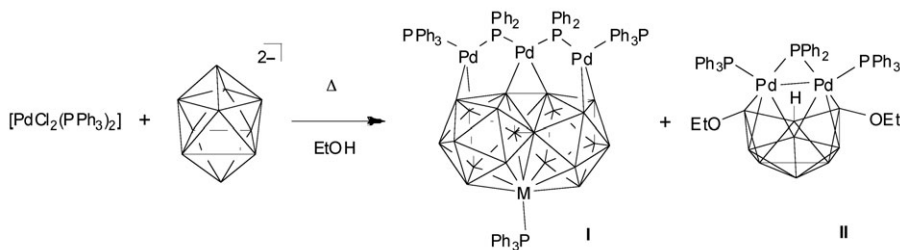
Geometrically *closo* twelve-vertex bimetallic metallaborane clusters containing two Group-10 transition-metal elements, in which the metal atoms are held in adjacent positions by the borane framework – the ‘B-frame’ – of the cluster, are of interest as they have been shown to engender an unusual activity across the metal–metal vector<sup>1–3</sup> that resembles the reactivity found in the well-studied field of ‘A-frame’ compounds<sup>4,5</sup>, and thereby has considerable potential for useful development<sup>3</sup>. Eleven-vertex *nido*-type metallaundecaborane clusters containing Group-10 transition-element centres are

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of interest because their evident *nido* geometry is in conflict with their skeletal electron count<sup>6</sup>, which is one electron pair short of the thirteen required for a *nido* eleven-vertex skeleton by polyhedral skeletal electron pair theories (PSEPTs)<sup>7-9</sup> and thus they may be regarded as belonging to a category of 'disobedient skeletons'<sup>10</sup>. Here we report the isolation of a new eleven-vertex bimetallic metallaundecaborane species that contains two Group-10 metal centres and has *nido* geometry. Although it was obtained only in small yield, compounds in this category are rare and it is useful to have new comparison examples, particularly, in this case, to correct erroneous formulations in the literature.

## RESULTS AND DISCUSSION

The heating at reflux of an equimolar solution of [*cis*-PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and the [NH<sub>4</sub>Et<sub>3</sub>]<sup>+</sup> salt of [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> in ethanol, followed by thin-layer chromatographic separation, afforded a number of coloured components of which one pink species was identified as the known compound [(PPh<sub>3</sub>)<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>Pd<sub>4</sub>B<sub>20</sub>H<sub>16</sub>] (Scheme 1, structure I)<sup>11,12</sup>. Further separation of a second yellow component by high-performance liquid chromatography yielded the title compound [7,8-(PPh<sub>3</sub>)<sub>2</sub>-7,8-(μ-PPh<sub>2</sub>)-9,11-(OEt)<sub>2</sub>-*nido*-7,8-Pd<sub>2</sub>B<sub>9</sub>H<sub>8</sub>] (**1**; Scheme 1, structure II) in 0.8% yield. Single crystals of the compound were obtained by diffusion of hexane into a solution of the compound in CDCl<sub>3</sub>, and an X-ray diffraction study revealed all atoms in the molecular structure; in particular, all of the hydrogen atoms were easily located in the difference map. An illustration of the molecule, including numbering, is given in Fig. 1.



SCHEME 1

The molecular structure of compound **1** is seen to be based on an eleven-vertex {Pd<sub>2</sub>B<sub>9</sub>} cluster structure that has an overall *nido* eleven-vertex cluster geometry that may be schematically derived from the *closo* twelve-vertex icosahedron by the removal of one vertex in accord with the geo-

metrical perceptions of Williams<sup>13,14</sup>. Each cluster boron atom has an *exo*-terminal hydrogen atom associated with it, and there is in addition a single open-face *endo*-terminal hydrogen atom on the B(10) vertex. The two metal atoms are in adjacent positions on the open face; each has a terminal PPh<sub>3</sub> phosphine ligand and the intermetal vector is bridged by a {PPh<sub>2</sub>} moiety. A {PPh<sub>2</sub>} moiety bridging two metal centres is uncommon in metallaborane chemistry, but has precedent, for example in the seven-vertex dimetallaborane cluster compound [(CO)(PPh<sub>3</sub>)(μ-PPh<sub>2</sub>)Os(PPh<sub>3</sub>)PtB<sub>5</sub>H<sub>7</sub>Ph]<sup>15</sup>, in which it bridges the Os–Pt vector, and in [(PPh<sub>3</sub>)<sub>3</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>Pd<sub>4</sub>B<sub>20</sub>H<sub>16</sub>]<sup>11,12</sup> mentioned above, which has two {PPh<sub>2</sub>} units bridging adjacent Pd–Pd vectors within a unique {(Ph<sub>3</sub>P)Pd(μ-PPh<sub>2</sub>)Pd(μ-PPh<sub>2</sub>)Pd(PPh<sub>3</sub>)} exopolyhedral string. A related {PPh<sub>2</sub>} bridge in [(μ-PPh<sub>2</sub>)(PPh<sub>2</sub>)(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)RhB<sub>8</sub>H<sub>9</sub>]<sup>16</sup>, now across a Rh–B vector, rather than across a metal–metal vector, should also be noted.

A much more direct precedent for compound **1** is in four compounds recently reported as having the formulations [(PPh<sub>3</sub>)<sub>2</sub>(μ-PPh<sub>2</sub>)Pt<sub>2</sub>B<sub>9</sub>H<sub>6</sub>(OEt)<sub>3</sub>] (**4**)<sup>17</sup>, [(PPh<sub>3</sub>)<sub>2</sub>(μ-PPh<sub>2</sub>)Pt<sub>2</sub>B<sub>9</sub>H<sub>6</sub>Cl(O<sup>iso</sup>Pr)<sub>2</sub>] (**5**)<sup>18</sup>, [(PPh<sub>3</sub>)<sub>2</sub>(μ-PPh<sub>2</sub>)Pt<sub>2</sub>B<sub>9</sub>H<sub>6</sub>(O<sup>iso</sup>Pr)<sub>3</sub>] (**6**)<sup>18</sup> and [(PPh<sub>3</sub>)<sub>2</sub>(μ-PPh<sub>2</sub>)Pt<sub>2</sub>B<sub>9</sub>H<sub>7</sub>(O<sup>iso</sup>Pr)<sub>2</sub>] (**7**)<sup>19</sup>, of which the general molecular

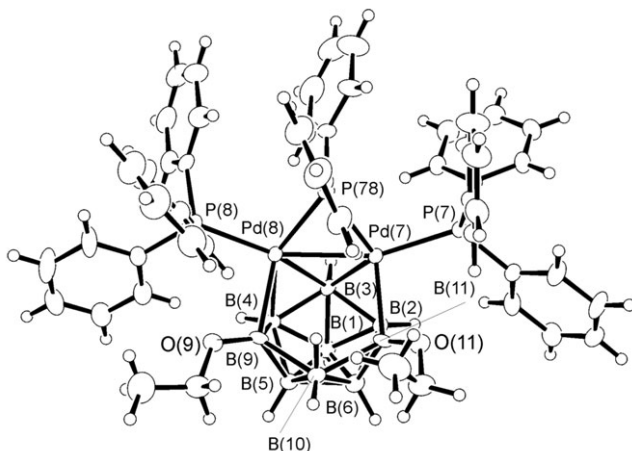


FIG. 1

ORTEP-3<sup>34</sup> diagram of the crystallographically determined molecular structure of [7,8-(PPh<sub>3</sub>)<sub>2</sub>-7,8-(μ-PPh<sub>2</sub>)-9,11-(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-*nido*-7,8-Pd<sub>2</sub>B<sub>9</sub>H<sub>8</sub>] (compound **1**). All hydrogen atoms were clearly locatable. Selected dimensions (in Å) are: from Pd(7) to Pd(8) 2.6666(4), to P(7) 2.3467(11), to P(78) 2.2782(11), to B(2) 2.256(5), to B(3) 2.236(5) and to B(11) 2.296(5); from Pd(8) to P(8) 2.3292(11), to P(78) 2.3010(12), to B(3) 2.283(5), to B(4) 2.290(5) and to B(9) 2.287(4); B(9)–O(9) 1.380(6), B(11)–O(11) 1.366(6). Selected angles (in °) are: Pd(7)–P(78)–Pd(8) 71.22(3), P(7)–Pd(7)–P(78) 104.14(4), P(8)–Pd(8)–P(78) 54.79(3)

constructions are also established by single-crystal X-ray diffraction analyses. These are in principle close analogues of the present dipalladium species  $[(PPh_3)_2(\mu-PPh_2)Pd_2B_9H_8(OEt)_2]$  (**1**), except that each of the reported formulations for compounds **4–7** implies one cluster electron fewer than for compound **1**. In the reports of compounds **4** to **7** the location of cluster hydrogen atoms is not addressed, and no cluster  $^{11}B$  and  $^1H$  NMR data are presented<sup>17–19</sup>. The formulations  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_6(OEt)_3]$ ,  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_6X(O^{iso}Pr)_2]$  ( $X = H, Cl$ ) and  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_6(O^{iso}Pr)_3]$  imply paramagnetic odd-electron species, which in turn may imply intense UV/VIS absorptions, but in the reports on **4**, **5**, **6** and **7** their colours were not recorded. Further, the reported  $^1H$  and  $^{13}C$  NMR chemical shifts for the OEt,  $PPh_3$  and  $PPh_2$  groupings in these compounds are within normal ranges for diamagnetic species, whereas a paramagnetism implied by the formulations would engender broader line-widths and anomalous extreme ranges of  $^1H$  and  $^{13}C$  nuclear shieldings<sup>20,21</sup>, contrary to the observations in the reports<sup>17–19</sup> on compounds **4–7**.

The apparent paradox is resolved by the present crystallographically determined molecular structure of compound **1**, in which all atoms, particularly the cluster hydrogen atoms, are unequivocally located. As mentioned above, in addition to the seven BH(*exo*) hydrogen atoms associated with the metallaborane cluster, there is additionally an *endo*-terminal hydrogen atom on B(10), equivalent to and chemically consistent with the open face *endo*-terminal hydrogen atom on the binary borane *nido* eleven-vertex model, the  $[B_{11}H_{14}]^-$  anion itself<sup>22</sup>. The conclusion is that compounds **4–7** also have this *endo*-terminal hydrogen atom at the B(10) position, and should thence be formulated as  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_7(OEt)_3]$ ,  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_7Cl(O^{iso}Pr)_2]$ ,  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_7(O^{iso}Pr)_3]$  and  $[(PPh_3)_2(\mu-PPh_2)Pt_2B_9H_8(O^{iso}Pr)_2]$ , respectively. The importance of taking into consideration the electron count in polyhedral boron-containing cluster systems in the course of their characterisation is thereby emphasised.

An additional factor of interest and interpretation for these compounds, in terms of classical cluster electron-count associated with the PSEPT theories<sup>8,9</sup>, is the contribution of the two palladium centres to the cluster bonding scheme and thence to the cluster electron-count. Some of the confusion in the characterisation of these compounds may also arise, in simple terms, from the propensity of platinum and palladium to adopt 16-electron configurations rather than 18-electron ones. A referee has emphasised that apparent exceptions to borane-based PSEPT electron-counting rules will be expected for transition-element systems in which metals use fewer than nine of their available valence orbitals.

Thus, in this present set of compounds, **1**, **4**, **5**, **6** and **7**, if each of the palladium centres is formally square-planar palladium(II), then the overall cluster electron-count for each of compounds is eleven electron pairs, i.e. two electron pairs fewer than is formally required for an eleven-vertex *nido* cluster. There is consequently an apparent paradox between this formal *pileo*  $2n$  electron-pair count, which might imply a capped-*closo* geometry, and the observed *nido* geometry that closely mimics that of the *nido* eleven-vertex model  $[B_{11}H_{14}]^-$ . This type of apparent dichotomy is addressed elsewhere<sup>6,10,24–26</sup>, and arises because the PSEPT theories originated with, and apply most effectively to, basic binary boranes and closely related species such as the carbaboranes<sup>7,13</sup>. In the simple boranes, for example, the PSEPT rules apply because each vertex is based on a boron atom with four valence orbitals and three electrons available for bonding. As boron atoms are replaced by non-boron atoms then the cluster may begin to deviate from the classical binary borane polyhedral shapes and conventionally required PSEPT electron counts. With boron, most commonly, one valence orbital and one electron are occupied in bonding to an *exo*-terminal hydrogen atom thus leaving three orbitals and two electrons to be involved in bonding directly to the other cluster atoms. However, in the case of the  $\{BH_2\}$  vertex in  $[B_{11}H_{14}]^-$  (corresponding to B(10) in compound **1**), the *endo*- and *exo*-terminal hydrogen atoms remove two orbitals and two electrons from the direct bonding to the other cluster atoms, leaving this vertex to contribute only two orbitals and one electron to the cluster bonding proper. In the basic PSEPT counting conventions, the pair of electrons in the B-H(*endo*) bond is credited to the counting scheme. However, when such a position is occupied and subrogated by a formal square-planar Group-10 transition-element atom, the metal centre lacks the extra pair of *endo*-terminal electrons to credit to the counting scheme, although it nevertheless does supply two electrons and two orbitals to bind to the other cluster atoms. Thus, such a cluster compound is able to attain the classical eleven-vertex *nido*-undecaboranyl cluster shape although it is ostensibly one pair of electrons short of a formal PSEPT requirement of thirteen electron pairs. This is seen, for example, in the observed *nido* geometry for  $[(PMe_2Ph)_2MB_{10}H_{12}]$  (M = Pd, Pt)<sup>27,28</sup> where the metal centre can be regarded as subrogating the formal  $\{BH_2\}^-$  vertex of the  $[B_{11}H_{14}]^-$  anion. Compound **1**, by contrast, does possess a  $\{BH_2\}$  group and here, therefore, the  $\{(PPh_3)_2(\mu-PPh_2)Pd_2\}$  unit would formally take the place of the  $\{(H_{exo}B-\mu-H_{bridge})_2\}^-$  unit in the  $[B_{11}H_{14}]^-$  eleven-vertex *nido* cluster model. This  $\{(H_{exo}B-\mu-H_{bridge})_2\}^-$  unit would classically involve a donation of seven cluster electrons to the cluster electron-count. However, the presence of the

odd-electron ( $\mu$ -PPh<sub>2</sub>) group, effectively subtracts one electron from direct cluster bonding, making the metal–metal unit overall a four-orbital three-electron, contributor, four electrons fewer than the seven electrons donated by the  $\{(H_{\text{exo}}B-\mu-H_{\text{bridge}})_2\}^-$  unit. Thus, in comparison to the *nido*-shaped cluster in the monometallic species [L<sub>2</sub>PdB<sub>10</sub>H<sub>12</sub>], where the cluster count is one electron-pair short of the PSEPT requirement for eleven-vertex *nido*, the *nido*-shaped bimetallic cluster in compound **1** is now two pairs short of the PSEPT requirement.

## EXPERIMENTAL

A stirred suspension of [cis-PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (280 mg, 400  $\mu$ mol) and the [NHEt<sub>3</sub>]<sup>+</sup> salt of [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> (129 mg, 400  $\mu$ mol) in EtOH (75 ml) was heated at reflux overnight under a nitrogen atmosphere. The cooled mixture was then filtered through silica gel (Fluka, GF254), reduced to dryness on a rotary evaporator (ca. 30 °C), taken up in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) and then subjected to thin-layer chromatographic separation (TLC) (Fluka silica gel GF254, CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 70:30). A number of coloured bands were evident but with three dominant bands: A, yellow,  $R_F$  0.8; B, pink,  $R_F$  0.5; C, orange,  $R_F$  0.4. With further TLC separation (CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 80:20) band C afforded two further bands: C1, pink,  $R_F$  0.6, identified as the known<sup>11,12</sup> metallamegaloborane [(PPh<sub>3</sub>)<sub>3</sub>( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Pd<sub>4</sub>B<sub>20</sub>H<sub>16</sub>] (850  $\mu$ g, 0.47  $\mu$ mol, 0.47%) and C2, yellow,  $R_F$  0.5. HPLC separation (silica, Knauer, Lichrosorb Si60, 7  $\mu$ m, CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 45:55, 10 ml min<sup>-1</sup>) of band C2 afforded three significant peaks for which one, with  $R_T$  43 min, yielded, by the layering of hexane over a solution of the compound in CDCl<sub>3</sub>, [7,8-(PPh<sub>3</sub>)<sub>2</sub>-7,8-( $\mu$ -PPh<sub>2</sub>)-9,11-(OEt)<sub>2</sub>-*nido*-7,8-Pd<sub>2</sub>B<sub>9</sub>H<sub>8</sub>] (**1**; 177  $\mu$ g, 1.6  $\mu$ mol, 0.8%). Measured cluster NMR data for compound **1** at 300 K in CDCl<sub>3</sub> solution,  $\delta(^{11}\text{B})/\text{ppm}$  (with calculated shieldings in brackets): B(3) +57.3 [+69.4], B(9,11) +48.5 [+52.2], B(1) +7.2 [+16.0], B(5,6) -14.2 [-11.0], B(10) -19.2 [-18.2], B(2,4) -21.2 [-16.4]; with  $\delta(^1\text{H})/\text{ppm}$ : +7.60, +4.57, +2.87, +2.24, +2.24, +1.86, +1.25 and +1.07; with  $\delta(^{31}\text{P})/\text{ppm}$  for P(7) and P(8) +22.3, for P( $\mu$ -7,8) +247.8. Tentative assignments for the <sup>11</sup>B chemical shifts are made on the basis of DFT/GIAO chemical shielding calculations for the molecule using the Gaussian-03 package<sup>29</sup>. Although for some sites the quantitative agreement between experimental and calculated <sup>11</sup>B nuclear magnetic shielding is not as good as for borane cluster species that do not contain transition-element centres, nevertheless the qualitative sequencing confirms assignments; the principal discrepancies arise mainly at the sites adjacent to the metal–metal vector.

## X-ray Crystallography

Single crystals of **1** were small and required synchrotron radiation to achieve sufficient diffraction intensity. C<sub>52</sub>H<sub>58</sub>B<sub>9</sub>O<sub>2</sub>P<sub>3</sub>Pd<sub>2</sub>,  $M = 1117.98$ ; monoclinic,  $0.32 \times 0.02 \times 0.01$  mm, purple prism, space group  $C2/c$ ,  $a = 58.128(3)$ ,  $b = 9.9627(6)$ ,  $c = 21.0138(12)$  Å,  $\beta = 110.825(2)^\circ$ ,  $Z = 4$ ,  $\lambda = 0.6942$  Å (wiggler-generated from 2-GeV electrons at 150–250 mA, station 9.8, CCLRC, Daresbury, U.K.)<sup>30–32</sup>,  $\mu = 0.753$  mm<sup>-1</sup>,  $T = 150(2)$  K;  $R_1 = 0.0671$ ,  $wR_2 = 0.1074$ . The data were solved by direct methods and refined by full-matrix least-squares methods on all measured  $F^2$  values using the standard SHELX programme system. Hydrogen atoms were located in the difference map but were modelled in calculated positions. Disordered hexane

solvent molecules were incorporated in the model using PLATON SQUEEZE<sup>33</sup>. CCDC 198879 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](http://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). Methods and programs were standard<sup>34-37</sup>.

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