

**POLYHEDRAL AZAPLATINABORANE CHEMISTRY. REACTION OF MEMBERS OF THE *hypho*-TYPE FAMILY  $R'H_2NB_8H_{11}NHR$  WITH  $[PtCl_2(PMe_2Ph)_2]$  AND  $[PtCl_2(PPh_3)_2]$ . FORMATION OF MEMBERS OF THE FAMILY OF OPEN SEVEN-BORON SPECIES  $[3,3-(PMe_2Ph)_2-3-PtB_7H_{10}-\mu-5,6-(NHR)]$**

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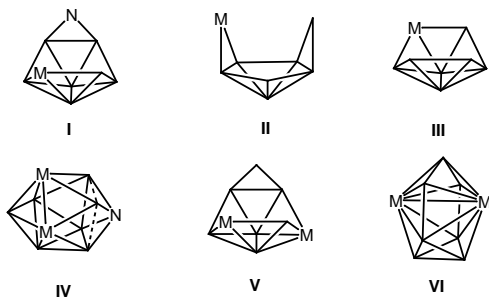
*It is a pleasure for the authors to dedicate this paper to Dr Stanislav Heřmánek on the occasion of his 70th birthday, in recognition not only of personal acquaintance and friendship, but also of his considerable insights and contributions to the field of polyhedral boron-containing cluster chemistry over the final decades of this century.*

$[PtCl_2(PMe_2Ph)_2]$  and  $[(R'NH_2)NB_8H_{11}NHR]$  (where both  $R'$  and  $R = Et$  or  $i-Pr$  and where  $R' = i-Pr$ ,  $R = t-Bu$ ) with  $NaH$  and air-exposure gives the series  $[3,3-(PMe_2Ph)_2-3-PtB_7H_{10}-\mu-5,6-(NHR)]$  (33–44%) of which the structures are closely related to those of the open eight-boron *hypho*-type starting compounds  $[(R'NH_2)B_8H_{11}NHR]$  by interchange of  $\{BH(NH_2R')\}$  and  $\{Pt(PMe_2Ph)\}$  vertices, with structural similarities to the rare *arachno* nine-vertex "normal"  $B_9H_{15}$  geometry. Related compounds from related reactions are  $[(PPh_3)_2PtB_7H_{10}NHet]$  and  $[(PMe_2Ph)_2PtB_7H_{10}NMe_2]$ .

**Key words:** Boranes; Metallaboranes; Azametallaboranes; Platinaheteroboranes; X-Ray diffraction; Boron clusters; NMR spectroscopy, <sup>1</sup>H, <sup>11</sup>B, <sup>31</sup>P.

Study of metallaborane clusters of low metal-atom content that contain seven or eight boron atoms is difficult because suitable borane substrates that contain these numbers of boron atoms are generally tedious and/or difficult to synthesise from the available five-boron and ten-boron starting materials  $B_5H_9$  and  $B_{10}H_{14}$  (ref.<sup>1</sup>). The few seven- and eight-boron metallaboranes that are known are obtained, often serendipitously, by cluster-dismantling or cluster-*Aufbau* reactions<sup>2</sup>. A series of eight-boron *hypho*-species  $[(R'H_2N)B_8H_{11}NHR]$ , where  $R', R = Et$  (**1a**);  $R', R = i-Pr$  (**1b**) and  $R' = i-Pr, R = t-Bu$  (**1c**) (Fig. 1 and cluster schematic **I**), is now prepared readily from

$B_{10}H_{14}$  (refs<sup>3-6</sup>). These compounds in principle are good entries into the chemistry of clusters that contain eight boron atoms and, *via* loss of the low-connectivity  $\{BH(NH_2R')\}$  vertex<sup>7</sup>, clusters that contain seven boron atoms. However, apart from the reaction of  $[(EtNH_2)B_8H_{11}NHet]$  (**1a**) with  $[RhCl_2(\eta^5-C_5Me_5)]_2$  (ref.<sup>8</sup>), which demonstrates entry into seven-boron cluster systems, further chemistry is essentially uninvestigated. Here we now report the reaction of compounds of the series  $[(R'NH_2)B_8H_{11}NHR]$  with *cis*- $[PtCl_2(PMe_2Ph)_2]$  and NaH to yield a family of new seven-boron cluster compounds  $[3,3-(PMe_2Ph)_2-3-PtB_7H_{10-\mu}-5,6-(NHR)]$ , with structures based on a contiguous  $\{PtB_7N\}$  unit. Previously reported seven-boron metallaboranes were until recently limited to a monoferraborane<sup>9,10</sup>, a monotungstaborane<sup>11</sup> and an azadirhodaborane (cluster schematics **II** to **IV**, respectively)<sup>7</sup>. More recently, while this communication was under refinement, a seven-boron diplatinaborane (schematic **V**)<sup>12</sup> and seven-boron dimetallaboranes of tungsten and rhenium (both schematic **VI**)<sup>13</sup> have been identified, all obtained by non-specific *Aufbau* processes. Previously, azametallaboranes have been reported in which the nitrogen atom is connected to the rest of the cluster with cluster connectivities of five<sup>14</sup>, four<sup>15-17</sup>, and three<sup>18,19</sup>. The  $\{PtB_7N\}$  clusters reported here exhibit a nitrogen cluster connectivity of two. Preliminary aspects of this work have been mentioned<sup>20</sup>.

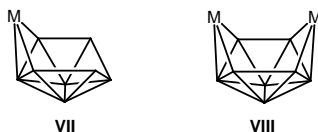


## RESULTS AND DISCUSSION

Addition of  $[(EtNH_2)B_8H_{11}NHet]$  (**1a**) to NaH and *cis*- $[PtCl_2(PMe_2Ph)_2]$  in  $CH_2Cl_2$  gives no apparent initial reaction. However, the colour changes immediately from colourless to dark brown on exposure to air. Chromatography then yields very pale yellow  $[3,3-(PMe_2Ph)_2-3-PtB_7H_{10-\mu}-5,6-(NHet)]$  (**2a**) (44%) (formal nomenclature:  $\mu$ -5,6-(alkylamido)-3,3-bis(dimethylphenylphosphine)-*hypo*-3-platinaoctaborane(10), eight-vertex *nido/arachno*

numbering system). This is characterised as such by single-crystal X-ray diffraction analysis and NMR spectroscopy. The air-induced one-boron vertex-dismantling process may be compared to the air-induced formation of  $[(\text{CO})_3\text{WB}_7\text{H}_{12}]^-$  (schematic **III**) from the  $[\text{B}_9\text{H}_{14}]^-$  anion<sup>11</sup>.

Compound **2a** was reasonably air-stable in the solid state under low humidity, but not very stable in solution. Use of  $[(i\text{-PrH}_2)\text{NB}_8\text{H}_{11}\text{NHi-Pr}]$  (**1b**) or  $[(i\text{-PrNH}_2)\text{B}_8\text{H}_{11}\text{NH}t\text{-Bu}]$  (**1c**), instead of compound **1a**, similarly gave  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}(\text{NHi-Pr})]$  (**2b**) (36%) or  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}(\text{NH}t\text{-Bu})]$  (**2c**) (33%), respectively. The formation of **2c** shows that it is the bridging {NHR} group of compounds **1** that is retained, and that the pendant {NH<sub>2</sub>R'} group, presumably with its corresponding B(3) vertex, is lost. A triphenylphosphine analogue,  $[3,3\text{-}(\text{PPh}_3)_2\text{-}3\text{-PtB}_7\text{H}_{10}\text{-}\mu\text{-}5,6\text{-}(\text{NH}Et)]$  (**3**) (30%), reasonably identified by NMR spectroscopy, similarly results from *cis*- $[\text{PtCl}_2(\text{PPh}_3)]$  with  $[(\text{EtNH}_2)\text{B}_8\text{H}_{11}\text{NH}Et]$  (**1a**) and NaH. Compound **2a** (87%) also results from  $[4,4\text{-}(\text{PMe}_2\text{Ph})_2\text{-}arachno\text{-}4\text{-PtB}_8\text{H}_{12}]$  (cluster schematic **VII**) with NH<sub>2</sub>Et, which also gives  $[6,6,9,9\text{-}(\text{PMe}_2\text{Ph})_4\text{-}arachno\text{-}6,9\text{-Pt}_2\text{B}_8\text{H}_{10}]$  (**4**) (10%) (cluster schematic **VIII**), previously known to result from  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$  and base<sup>21</sup>. An *N,N*-dimethyl analogue,  $[3,3\text{-}(\text{PMe}_2\text{Ph})_2\text{-}3\text{-PtB}_7\text{H}_{10}\text{-}\mu\text{-}5,6\text{-}(\text{NMe}_2)]$  (**5**) (31%) was tentatively identified from the reac-



tion of dimethylamine with  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$  in ethanol, but appeared less stable than the various monoalkylamido analogues **2a**, **2b**, **2c** and **3**, inhibiting its unequivocal characterisation; another product here was,

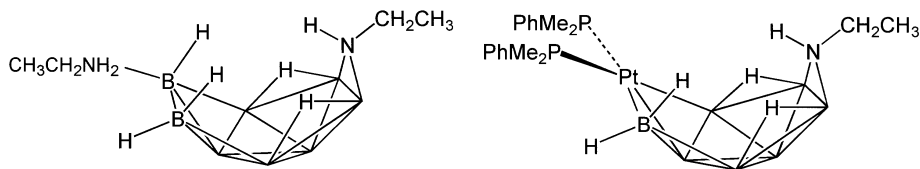


FIG. 1

Schematic representations to illustrate the parallels between the molecular structures of (left)  $[(\text{EtH}_2\text{N})\text{B}_8\text{H}_{11}\text{NH}Et]$  (**1**) (for structural work see refs<sup>4,5</sup>) and (right)  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NH}Et]$  (**2a**). Unlabelled vertices are BH(*exo*) units. The numbering scheme for both is as for compound **2a** in Fig. 2

again,  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_8\text{H}_{10}]$  (**4**) (4%), but now also with its ethoxy derivative  $[6,6,9,9-(\text{PMe}_2\text{Ph})_4\text{-}arachno\text{-}6,9\text{-Pt}_2\text{B}_8\text{H}_9\text{-}5(\text{OEt})]$  (**6**) (7%) which was reasonably suggested as such by NMR spectroscopy.

The crystallographically determined cluster structure of compound **2a** (Fig. 2 and schematic I; see also Fig. 1) has an open eight-vertex shape, resembling the mutually similar gross geometries of the  $\text{B}_8\text{H}_{14}$  and  $\text{B}_8\text{H}_{12}$  *arachno* and *nido* types (both of schematic cluster shape IX) with one open-face B-B edge bridged by {NHet}, and with one of the less contiguous open-face cluster vertices occupied by {Pt(PMe<sub>2</sub>Ph)<sub>2</sub>} rather than a boron unit. It can be seen from Fig. 1 that the cluster structure is very similar to that of  $[(\text{EtNH}_2)_8\text{B}_8\text{H}_{11}\text{NHet}]$  (**1a**), except that the {BH(NH<sub>2</sub>Et)} vertex in the 3 position of **1a** is replaced by {Pt(PMe<sub>2</sub>Ph)<sub>2</sub>}. This is a straightforward isolobal replacement<sup>22,24</sup>, although it should be noted that there is current interest as to whether such a replacement constitutes a “rule-breaking” phenomenon or not<sup>12,24,25</sup>. This equivalence of {BHL} and {Pt(PMe<sub>2</sub>Ph)<sub>2</sub>} centres<sup>22,24</sup> puts the two species **1a** and **2a** in the same general *hypho* eight-vertex structural class<sup>5,6</sup>, although there are also some similarities here to the  $[(\text{CO})_3\text{WB}_7\text{H}_{12}]^-$  anion which has been described as *arachno*-type<sup>11</sup>.

It is pertinent to note here that the eight-vertex shape IX is the one formally expected both for *arachno* eight-vertex, by the removal of two adjacent vertices from a *closo*- $[\text{B}_{10}\text{H}_{10}]^{2-}$ -type of ten-vertex polyhedron, and also for *hypho* eight-vertex, by the removal of three adjacent vertices from a *closo*- $[\text{B}_{11}\text{H}_{11}]^{2-}$ -type of eleven-vertex polyhedron. It is of interest that, an-

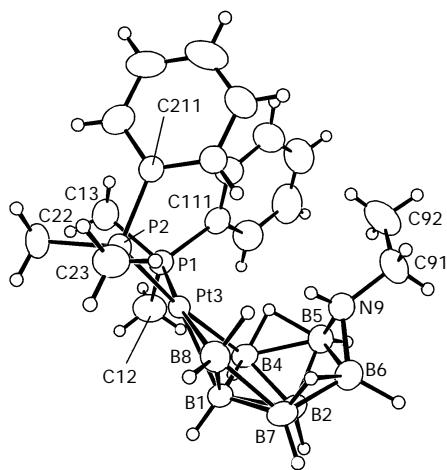


FIG. 2  
ORTEP (ref.<sup>49</sup>) representation of the crystallographically determined molecular structure of  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**2a**) (this work). Ellipses are shown at the 50% probability level. In the interests of clarity hydrogen atoms are drawn as circles with an arbitrary small radius

omalous, it is also the geometry found for *nido* eight-vertex species such as  $B_8H_{12}$ .

In the platinum compound **2a**, the open-face B(7)–B(8) vector appears longer, at 193.7(14) pm (Table I), than the equivalent distances of 190.0(4)–191.3(2) pm in the  $[(R'H_2N)B_8H_{11}NHR]$  starting compounds **1a**, **1b** and **1c** (refs<sup>4,5</sup>). These are all long for cluster interboron distances, and longer than the corresponding distance of 184.0(2) pm in the  $[(CO)_3WB_7H_{12}]^-$  anion<sup>11</sup>. These longer distances may be a *hypho* eight-vertex characteristic. Note that for both the series **1** and **2** inclusion of the bridging nitrogen atom also as a vertex in cluster considerations gives nine-vertex *arachno* structures of the rare  $n-B_9H_{15}$  geometry (cluster schematic **X**)<sup>26</sup>, previously observed in metallaborane chemistry only for  $[2-(\eta^6-C_6Me_6)RuB_8H_{14}]$  (cluster schematic **XI**)<sup>27</sup> and, very recently, for  $[(dppe)_2Pt_2B_7H_{11}]$  (cluster schematic **V**)<sup>12</sup>.



The  $\{NHEt\}$ -bridged B(5)–B(6) distance in compound **2a** at 192(2) pm appears shorter than those in the  $[(R'H_2N)B_8H_{11}NHR]$  species **1a**, **1b**, and **1c** (196.2(4)–198.9(9) pm). Main-group bridging elements often induce an interboron lengthening compared to a hydrogen bridge. In  $\{PPh_2\}$ -bridged  $[B_{10}H_{13}-\mu-(PPh_2)]$  (ref.<sup>28</sup>) and  $\{(\eta^5-C_5H_5)(CO)_2Fe\}-B_5H_7-\mu-(PPh_2)\}$  (ref.<sup>29</sup>) the  $\{PPh_2\}$ -bridged interboron distances of 269(2) and 268.3(5) pm, respectively, are non-bonding, suggesting two two-electron two-centre boron–phosphorus bonds<sup>28,30,31</sup>. On the other hand, anionic carbon-bridged  $[PhCB_{10}H_{10}-\mu-(CHPh)]^-$  and  $[MeCB_{10}H_{10}-\mu-(CHMe)]^-$  have  $\{CHR\}$ -bridged interboron distances of 186(2) and 184.7(2) pm, respectively<sup>32,33</sup>. These last two normal deltahedral bonding distances suggest three-centre two-electron boron–carbon–boron bonding<sup>34</sup>. Including data for compound **2a**, the reported  $\{NH_2\}$ -,  $\{NHR\}$ - and  $\{NR_2\}$ -bridged interboron connectivities, which range from 192(2) to 221.1(5) pm (refs<sup>5,35,36</sup>), are intermediate. Thus they may represent a range of intermediacies between the extremes of (i) two-electron three-centre  $\{BBN\}$  bonding and (ii) a four-electron  $\{B-N-B\}$  bridge involving two two-electron two-centre boron–nitrogen bonds. In the two series **1** and **2**, type (i) behaviour would confer eight-vertex *arachno* character on the cluster<sup>4</sup>, and type (ii) behav-

four would confer eight-vertex *hypho* character<sup>6</sup>. Irrespective of these two eight-vertex descriptions, however, both forms would be variations within nine-vertex *arachno* character, consistent with a geometrical description as an analogue of n-B<sub>9</sub>H<sub>15</sub> as mentioned above. The marked variation in bridged interboron distance from 192 to 221 pm could arise from a significant variation of cluster bonding participation by the nitrogen-based lone-pair of the {NHR} group. A related variable participation of the

TABLE I

Selected interatomic distances (pm) and angles (°) for [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>NHET] (**2a**) with estimated standard deviations in parentheses

Pt(3)–P(1)	230.8(2)	Pt(3)–P(2)	230.4(2)
Pt(3)–B(1)	219.0(9)	Pt(3)–B(4)	223.7(9)
Pt(3)–B(8)	225(1)	N(9)–C(91)	148(1)
N(9)–B(5)	153.7(13)	N(9)–B(6)	155(1)
B(1)–B(2)	181(1)	B(2)–B(5)	178(2)
B(1)–B(4)	180.2(13)	B(2)–B(6)	180(2)
B(1)–B(7)	175(2)	B(2)–B(7)	175(2)
B(1)–B(8)	178(2)		
B(4)–B(5)	184.1(14)	B(5)–B(6)	192(2)
B(6)–B(7)	178(2)	B(7)–B(8)	193.7(14)
P(1)–Pt(3)–B(1)	128.9(3)	P(1)–Pt(3)–B(4)	85.9(3)
P(1)–Pt(3)–B(8)	171.1(3)	P(1)–Pt(3)–P(2)	99.74(8)
P(2)–Pt(3)–B(1)	129.5(3)	P(2)–Pt(3)–B(4)	169.7(3)
P(2)–Pt(3)–B(8)	86.4(3)		
B(5)–N(9)–B(6)	76.9(7)		
B(1)–Pt(3)–B(4)	48.0(4)	B(1)–Pt(3)–B(8)	47.2(4)
B(4)–Pt(3)–B(8)	87.1(4)	N(9)–B(5)–B(2)	103.8(7)
Pt(3)–B(4)–B(5)	117.0(6)	N(9)–B(5)–B(4)	118.0(7)
B(4)–B(5)–B(6)	107.0(7)	N(9)–B(5)–B(6)	51.8(5)
B(5)–B(6)–B(7)	105.0(7)	N(9)–B(6)–B(2)	102.4(7)
B(7)–B(8)–Pt(3)	112.7(6)	N(9)–B(6)–B(5)	51.3(5)
B(2)–B(6)–B(5)	57.0(6)	N(9)–B(6)–B(7)	117.1(7)

{NH*t*-Bu} unit in the *arachno* ↔ *nido* behaviour of the [6-(4-ClC<sub>6</sub>H<sub>4</sub>)-*arachno/nido*-6-NB<sub>9</sub>H<sub>10</sub>-9-(NH*t*-Bu)] system can be noted here<sup>37,38</sup>, as can the involvement in cluster bonding of the lone-pair of the {NEt<sub>2</sub>} group in [1-(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)-*isocloso*-1-RhB<sub>10</sub>H<sub>9</sub>-4-(NEt<sub>2</sub>)], of which the cluster thereby exhibits partial *isonido* character<sup>39</sup>.

The close structural similarities among types **1**, **2**, **3** and **5** are reflected in NMR similarities (Table II and Fig. 3). Thus the basic <sup>11</sup>B and <sup>1</sup>H cluster shielding pattern exhibited by the representative non-metallated species [(NH<sub>2</sub>Et)B<sub>8</sub>H<sub>11</sub>NHEt] (**1a**) readily traces through to the platinum compounds of types **2**, **3** and **5**. There is a general <sup>11</sup>B deshielding for the platinaboranes (mean δ(<sup>11</sup>B) for compounds **1a** and **2a** ca -24 and ca -11 ppm, respectively), but the overall sequential shielding pattern is maintained. Compared to compound **1a**, the principal differences for the platinaboranes are deshieldings at the B(1), the B(8) and the "hinge" B(4) positions, all adjacent to platinum, and at the second hinge site, B(7). A nu-

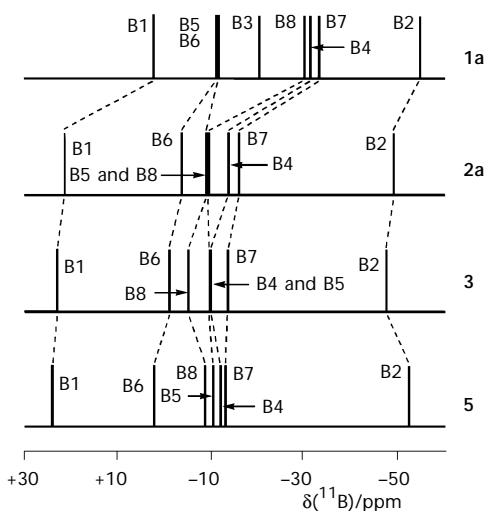


FIG. 3

Stick diagram of the chemical shifts in the <sup>11</sup>B spectra of (from bottom to top) [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>NMe<sub>2</sub>] (**5**), [(PPh<sub>3</sub>)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>NHEt] (**3**), [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>NHEt] (**2a**) and [(EtNH<sub>2</sub>)B<sub>8</sub>H<sub>11</sub>NHEt] (**1a**). Hatched lines join resonances from equivalent positions in the four compounds. The overall sequential shielding pattern of compound **1a** is maintained in the platinaboranes, with <sup>11</sup>B(1) and <sup>11</sup>B(2) resonating to extreme high and low field, respectively, and with the other resonances grouped, in the same sequence in each case, in the centre of the spectrum

TABLE II  
Selected  $^{11}\text{B}$  and  $^1\text{H}$  NMR parameters for [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>(NHet)] (**2a**), [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>(NH*i*-Pr)] (**2b**), [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>(NH*t*-Bu)] (**2c**), [(PPH<sub>3</sub>)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>(NHet)] (**3**) and [(PPhMe<sub>2</sub>)<sub>2</sub>PtB<sub>7</sub>H<sub>10</sub>(NMe<sub>2</sub>)] (**5**), in CDCl<sub>3</sub> at 294–297 K

Position	<b>2a</b> <sup>a</sup> δ( <sup>11</sup> B) [δ( <sup>1</sup> H)]	<b>2b</b> <sup>b</sup> δ( <sup>11</sup> B) [δ( <sup>1</sup> H)]	<b>2c</b> <sup>c</sup> δ( <sup>11</sup> B) [δ( <sup>1</sup> H)]	<b>3</b> <sup>d</sup> δ( <sup>11</sup> B) [δ( <sup>1</sup> H)]	<b>5</b> <sup>e</sup> δ( <sup>11</sup> B) [δ( <sup>1</sup> H)]
(1)	+21.9 <sup>f</sup> [+4.03] <sup>h</sup>	+22.0 <sup>g</sup> [+4.03] <sup>i</sup>	+21.6 <sup>h</sup> [+4.5] <sup>m</sup>	+22.8 <sup>i</sup> [+4.47] <sup>n</sup>	+24.6 <sup>j</sup> [+4.24] <sup>o</sup>
(2)	-49.6 [-0.62] <sup>p</sup>	-49.8 [-0.62] <sup>q</sup>	-50.8 [-0.66] <sup>r</sup>	-48.8 [-0.64] <sup>s</sup>	-52.2 [-0.53] <sup>t</sup>
(4)	-13.6 [+1.76]	-13.1 [+1.79]	-13.5 [+1.82]	-9.7 [+1.59]	-11.1 [+1.80]
(5)	<i>ca</i> -9.3 [+2.44]	-9.4 [+2.44]	-11.5 [+2.62]	-9.7 [+1.88]	-10.1 [+3.14]
(6)	-2.3 [+3.17]	-2.7 [+3.19]	-4.6 [+3.32]	-0.9 [3.05]	+2.7 [+3.46]
(7)	-15.6 [+2.34]	-14.9 [+2.48]	-15.2 [+2.45]	-13.5 [+2.36]	-12.0 [+1.80]
(8)	<i>ca</i> -9.3 [+2.33] [+0.79] <sup>v</sup>	-9.4 [+2.26] [+0.48] <sup>w</sup>	-11.5 [+2.25] [+0.88] <sup>x</sup>	-5.0 [+2.00] [+0.70] <sup>y</sup>	-8.8 [+2.35] [+1.65] <sup>z</sup>
(6,7)	[-0.93]	[-0.95]	[-1.12]	[-0.87]	[-1.38]
(4,5)	[-1.62] <sup>aa</sup>	[-1.65] <sup>ab</sup>	[-1.86] <sup>ac</sup>	[-1.79] <sup>ad</sup>	[-2.18]
(5,6) NH	[-0.02]	[-0.19]	[+0.013]	[+0.22]	-

<sup>a</sup> δ(<sup>31</sup>P) -2.8 and -6.7 ppm at 233 K, <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 16 Hz, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 2 980 and 2 624 Hz, respectively; additionally, δ(<sup>1</sup>H) +2.69, +2.77 ppm (two multiplets, 2 × 1 H, CH<sub>2</sub>CH<sub>3</sub> methylene); +1.05 ppm (triplet, 3 H, CH<sub>2</sub>CH<sub>3</sub> methyl); +1.63, +1.71, +1.73, +1.82 ppm (four doublets, 4 × 3 H, PCH<sub>3</sub>); +7.30 to +7.80 ppm (multiplet, 10 H, 2 × C<sub>6</sub>H<sub>5</sub>). <sup>b</sup> δ(<sup>31</sup>P) -2.1 and -6.3 ppm at 297 K, <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 20 Hz, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 2 930 and 2 680 Hz, respectively; additionally, δ(<sup>1</sup>H) +2.75 ppm (multiplet, 1 H, CH); +1.76, +1.73 ppm (two doublets, 2 × 3 H, CH(CH<sub>3</sub>)<sub>2</sub>); +1.80 to +1.60 ppm (doublets, 4 × 3 H, PCH<sub>3</sub>) not measurable more accurately due to overlap with δ(<sup>1</sup>H(CH(CH<sub>3</sub>)<sub>2</sub>)); +7.29 to +7.80 ppm (multiplet, 10 H, 2 × C<sub>6</sub>H<sub>5</sub>). <sup>c</sup> δ(<sup>31</sup>P) -1.9 and -6.0 ppm at 297 K, <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 16 Hz, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 3 000 and 2 565 Hz, respectively; additionally, δ(<sup>1</sup>H) +1.07 ppm (singlet, 9 H, C(CH<sub>3</sub>)<sub>3</sub>); +1.67 to +1.79 ppm (4 × 3 H, PCH<sub>3</sub>); *ca* +7.28 ppm (multiplet, 10 H, 2 × C<sub>6</sub>H<sub>5</sub>). <sup>d</sup> δ(<sup>31</sup>P) +33.1 and +29.5 ppm at 223 K, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 3 057 and 2 769 Hz, respectively; additionally, δ(<sup>1</sup>H) +1.10 ppm (triplet, 3 H, CH<sub>2</sub>CH<sub>3</sub>); +7.30 to +7.80 ppm (multiplet, 30 H, 6 × C<sub>6</sub>H<sub>5</sub>). <sup>e</sup> δ(<sup>31</sup>P) -2.3 and -7.1 ppm at 223 K, <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) = 21 Hz, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) = 2 974 and 2 510 Hz, respectively; additionally, δ(<sup>1</sup>H) +1.80, +1.50 ppm (two singlets, 2 × 6 H, N(CH<sub>3</sub>)<sub>2</sub>); +1.84, +1.74, +1.70, +1.58 ppm (4 × 3 H, PCH<sub>3</sub>); *ca* +7.28 ppm (multiplet, 10 H, 2 × C<sub>6</sub>H<sub>5</sub>). <sup>f</sup> <sup>1</sup>J(<sup>195</sup>Pt-<sup>11</sup>B) = 340 Hz. <sup>g</sup> <sup>1</sup>J(<sup>195</sup>Pt-<sup>11</sup>B) = 320 Hz. <sup>h</sup> <sup>1</sup>J(<sup>195</sup>P-<sup>11</sup>B) = 320 Hz. <sup>i</sup> <sup>1</sup>J(<sup>195</sup>P-<sup>11</sup>B) = 340 Hz. <sup>j</sup> <sup>1</sup>J(<sup>195</sup>Pt-<sup>11</sup>B) = 341 Hz. <sup>k</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 33 Hz. <sup>l</sup> <sup>2</sup>J(<sup>195</sup>P-<sup>1</sup>H) = 35 Hz. <sup>m</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 40 Hz. <sup>n</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 56 Hz. <sup>o</sup> Not measured due to broadness of resonance. <sup>p</sup> <sup>3</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 46 Hz. <sup>q</sup> <sup>3</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 45 Hz. <sup>r</sup> <sup>3</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 45 Hz. <sup>s</sup> <sup>3</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 40 Hz. <sup>t</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) = 54 Hz. <sup>u</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 50 Hz. <sup>v</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 68 Hz. <sup>w</sup> <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) *ca* 50 Hz. <sup>x</sup> Any J(<sup>195</sup>Pt-<sup>1</sup>H) not resolved.



clear deshielding of adjacent boron sites by a  $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$  vertex is well recognised<sup>21,23</sup>, presumably arising from lower excitation energies associated with the metal centre, and the hinge  $^{11}\text{B}(4)$  and  $^{11}\text{B}(7)$  resonances seem generally prone to large shielding variations within the *arachno/hypho* eight-vertex system<sup>6</sup>. It may be relevant here that the B(7)–B(8) distance is long at *ca* 194 pm. For the  $\{\text{PtB}_7\text{N}\}$  compounds **2**, **3** and **5**, the markedly different values of about 3 000 and 2 500 Hz for the two couplings  $^1J(^{195}\text{Pt}-^{31}\text{P})$  are interesting, because geometrically there is no significant differential platinum–phosphorus bonding (230.4(2) and 230.8(2) pm in compound **2a**). The averages of *ca* 2 750 Hz can be compared to the symmetrical species  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$  (2 724(2) Hz) and  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_8\text{H}_{10}]$  (**4**) (2 757(2) Hz)<sup>21</sup>, both geometrically essentially identical to **2a** in their  $\eta^3$  borane-to-metal bonding<sup>23</sup>.

## EXPERIMENTAL

### General

$[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  (ref.<sup>40</sup>),  $[\text{PtCl}_2(\text{PPh}_3)_2]$  (ref.<sup>40</sup>),  $[(\text{EtNH}_2)_8\text{B}_8\text{H}_{11}\text{NHet}]$  (**1a**)<sup>3</sup>,  $[(i\text{-PrNH}_2)_8\text{B}_8\text{H}_{11}\text{NHi-Pr}]$  (**1b**),  $[(i\text{-PrNH}_2)_8\text{B}_8\text{H}_{11}\text{NH}t\text{-Bu}]$  (**1c**)<sup>5</sup> and  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$  (ref.<sup>21</sup>) were prepared by literature methods. NaH was obtained commercially. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Merck, type GF254) made from water slurries on glass plates of dimensions 20 × 20 cm<sup>2</sup>, followed by drying in air at 80 °C. Criteria of compound identity for the series **2a**, **2b**, **2c**, **3** and **5** were provided by the diffraction analysis for the representative species **2a**, with corroborative single and multiple resonance  $^{31}\text{P}$ ,  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectroscopy.

### Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy was performed at *ca* 5.9 and 9.4 T (fields corresponding to 250 and 400 MHz  $^1\text{H}$  frequencies, respectively) using commercially available instrumentation and using techniques and procedures as described and enunciated elsewhere<sup>41–44</sup>. Assignments were by homonuclear and heteronuclear “one-dimensional” and “two-dimensional” techniques and by the incidence of satellites arising from couplings  $^1J(^{195}\text{Pt}-^{11}\text{B})$ . Chemical shifts  $\delta$  are given in ppm relative to  $\Xi = 100$  MHz for  $\delta(^1\text{H})$  ( $\pm 0.05$  ppm) (nominally TMS),  $\Xi = 40.480$  730 MHz for  $\delta(^{31}\text{P})$  ( $\pm 0.5$  ppm) (nominally 85%  $\text{H}_3\text{PO}_4$ ) and  $\Xi = 32.083$  972 MHz for  $\delta(^{11}\text{B})$  ( $\pm 0.5$  ppm) (nominally  $[\text{F}_3\text{BOEt}_2]$  in  $\text{CDCl}_3$ )<sup>44</sup>,  $\Xi$  being defined as the resonance frequency corresponding to the field strength at which the  $^1\text{H}$  signal from TMS occurs at *exactly* 100 MHz (ref.<sup>45</sup>).

Preparation of  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**2a**),  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHi-Pr}]$  (**2b**),  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NH}t\text{-Bu}]$  (**2c**), and  $[(\text{PPh}_3)_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**3**)

$[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  (200 mg, 370  $\mu\text{mol}$ ) was added to a stirred solution of  $[(\text{EtH}_2\text{N})_8\text{B}_8\text{H}_{11}\text{NHet}]$  (**1a**) (75 mg, 400  $\mu\text{mol}$ ) and NaH (19 mg, 800  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (30 ml) under  $\text{N}_2$ . After 1 h no reaction had occurred. On brief exposure to air, the mixture immediately darkened, be-

coming dark brown. Filtration through silica gel (TLC grade) (with the aid of additional  $\text{CH}_2\text{Cl}_2$  as solvent), followed by TLC separation of the mixture (mobile phase  $\text{CH}_2\text{Cl}_2$ ), gave one main product,  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**2a**) ( $R_F$  0.76, 98 mg, 44%). Similar experimentation using  $[(i\text{-PrNH}_2)_2\text{B}_8\text{H}_{11}\text{NHi-Pr}]$  (**1b**) (86 mg, 400  $\mu\text{mol}$ ) or  $[(i\text{-PrNH}_2)_2\text{B}_8\text{H}_{11}\text{NHt-Bu}]$  (**1c**) (91 mg, 400  $\mu\text{mol}$ ), respectively, gave  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHi-Pr}]$  (**2b**) ( $R_F$  0.65, 88 mg, 36%) or  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHt-Bu}]$  (**2c**) ( $R_F$  0.60, 82 mg, 33%). Repetition with  $[\text{PtCl}_2(\text{PPh}_3)_2]$  (200 mg, 350  $\mu\text{mol}$ ) in place of  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  gave  $[(\text{PPh}_3)_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**3**) ( $R_F$  0.64, 94 mg, 30%). Compounds **2a**, **2b**, **2c** and **3** were very pale yellow solids when pure.

#### Reactions of $[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$ with $\text{NH}_2\text{Et}$ and $\text{NHMe}_2$

$[(\text{PMe}_2\text{Ph})_2\text{PtB}_8\text{H}_{12}]$  (200 mg, 350  $\mu\text{mol}$ ) was added to a refluxing solution (bath +110 °C, condenser -70 °C) of  $\text{NH}_2\text{Et}$  (0.10 ml, 1 400  $\mu\text{mol}$ ) in toluene (25 ml). After 15 min, the mixture was cooled to room temperature, and treated as above, yielding very pale straw-coloured  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHet}]$  (**2a**) ( $R_F$  0.44, 141 mg, 87%) and  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_8\text{H}_{10}]$  (**4**) ( $R_F$  0.24, 18 mg, 10%). Compound **4** was identified by NMR spectroscopy<sup>21</sup>. A similar procedure, but using a solution of  $\text{Me}_2\text{NH}$  (50 mg, 1 100  $\mu\text{mol}$ ) in EtOH (100 mg, 2 170  $\mu\text{mol}$ ), gave  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NMe}_2]$  (**5**) ( $R_F$  0.59, 49 mg, 31%),  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_8\text{H}_{10}]$  (**4**) ( $R_F$  0.25, 6 mg, 4%) and  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_8\text{H}_9\text{-5-(OEt)}]$  (**6**) ( $R_F$  0.10, 10 mg, 7%). NMR data for compound **6** in  $\text{CDCl}_3$  at 294–297 K were as follows (assignment  $\delta(^{11}\text{B})$  [ $\delta^1(\text{H})$ ): BH(1) -19.6 [+1.79]; BH(2) +25.2 [+5.17]; BH(3) -18.3 [+2.06]; BH(4) +23.6 [+4.06]; B(5) +21.8 [ethoxy-substituted]; BH(7) -3.0 [+2.99]; BH(8) and BH(10) both *ca* +0.3 [+3.05 and +2.50];  $\mu\text{-H}(5,10)$  [+0.61];  $\mu\text{-H}(7,8)$  [-1.48]; additionally,  $\delta(^1\text{H})$  +1.47 (quartet) and +1.06 ppm (triplet) for the OEt group, and +1.73 ppm, +1.66 ppm, +1.61, and +1.53 ppm (four doublets, 4  $\times$  3 H, for the four P-methyl groups);  $\delta(^{31}\text{P})$  (233 K) *ca* -8.3, -8.3, -6.0 and -4.2 ppm, with  $^1J(^{195}\text{Pt}\text{-}^{31}\text{P})$  *ca* 2 430, 2 790, 2 840 and 2 930 Hz, respectively.

#### Single-Crystal X-Ray Diffraction Analysis of $[(\text{PMe}_2\text{Ph})_2\text{PtB}_7\text{H}_{10}\text{NHet}]$ (**2a**)

Tan-coloured crystals were obtained from  $\text{CH}_2\text{Cl}_2$ -hexane. Measurements were carried out at 293 K on a Nicolet P3/F diffractometer operating in the  $\omega$ - $2\theta$  scan mode using graphite-monochromated  $\text{MoK}\alpha$  X-radiation ( $\lambda = 71.073$  pm). The intensity data were corrected for absorption using an empirical method<sup>46</sup>, with maximum and minimum transmission factors 0.601 and 0.185, respectively. Structure determination was by direct methods (SHELXS97)<sup>47</sup> and refinement by full-matrix least-squares (based on  $F^2$ ) (SHELXL97)<sup>48</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. Phenyl groups were restrained so that they were of  $C_{2v}$  symmetry and organyl hydrogen atoms constrained to calculated positions. Cluster hydrogen atoms were located using Fourier difference syntheses but their positional parameters were not refined. The weighting scheme used was  $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 15.6157P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . The final Fourier difference synthesis was flat with no features of chemical significance: maximum and minimum residual densities were +1.842 and -1.006  $\text{e}\ \text{\AA}^{-3}$ .

*Crystal data:*  $\text{C}_{18}\text{H}_{38}\text{B}_7\text{NP}_2\text{Pt}$ , 0.45  $\times$  0.25  $\times$  0.10 mm,  $M = 601.19$ , monoclinic, space group  $P2_1/n$ ,  $a = 897.24(12)$ ,  $b = 1\ 500.1(2)$ ,  $c = 1\ 882.6(2)$  pm,  $\beta = 90.261(9)^\circ$ ,  $U = 2.534(3)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.576$  Mg m<sup>-3</sup>,  $\mu = 5.670$  mm<sup>-1</sup>,  $F(000) = 1\ 184$ .

*Data collection:* 4.32  $< 2\theta < 50.10^\circ$ ; scan widths 2.0° +  $\alpha$ -doublet splitting; scan speeds 2.0–29.3° min<sup>-1</sup> (subject to a fast pre-scan). Number of data collected is 4 478, number observed [ $F_o^2 > 2.0 \sigma(F_o^2)$ ] = 4 146,  $T = 295$  K.

**Structure refinement:** Number of parameters is 262;  $R = \{|\Sigma|F_o| - |F_c|/|\Sigma|F_o|\} = 0.0398$ ;  $wR_2 = \{(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}\} = 0.1097$ ; goodness of fit is 1.320 for all unique data and 267 parameters,  $\max \Delta/\sigma = 0.002$ .

**Deposition:** Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-113639. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

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