

## METALLABORANE REACTION CHEMISTRY. PART 7.<sup>+</sup> B-FRAME SUPPORTED BIMETALLICS: LIGAND-TO- $\beta$ -METAL ORGANOMETALLIC INTERACTION IN DIMETALLABORANES AND AN INTERESTING LIGAND DISPLACEMENT CASCADE

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*It is a pleasure for the authors to express their best wishes to Dr Stanislav Heřmánek on the occasion of his 70th birthday, both from the point of view of personal friendly acquaintance, and in recognition of his many imaginative insights and considerable contributions to the field of polyhedral boron-containing cluster chemistry over the past four decades.*

Reaction of  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  with  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{10}\text{H}_{12}]$  generates  $[(\text{PMe}_2\text{Ph})_2-\mu-\eta^1(\text{Pt})-\eta^1-(\text{Pt}')-\{\text{PMe}_2(\text{C}_6\text{H}_4)\}-\text{closo-Pt}_2\text{B}_{10}\text{H}_9(\text{PMe}_2\text{Ph})]$  in which the phenyl group of a phosphine ligand on one platinum atom exhibits *ortho*-cyclometallation to the second metal atom, whereas reaction of  $\text{PPh}_3$  with  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_9\text{H}_9\text{Ru}(\text{pcym})]$  generates  $[(\text{PMe}_2\text{Ph})_2-\mu-\eta^6(\text{Ru})-\eta^1(\text{Pt})-(\text{C}_6\text{H}_5\text{PPh}_2)-\text{closo-PtRuB}_9\text{H}_9]$  in which the phenyl group of a phosphine ligand on the platinum atom exhibits tridentate  $\eta^6$  coordination to the second metal atom.

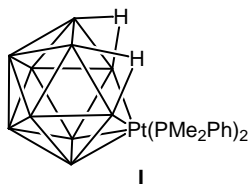
**Key words:** Metallaboranes; Boranes; Cluster bridging ligands; Borane clusters; NMR spectroscopy, <sup>1</sup>H, <sup>11</sup>B, <sup>31</sup>P; X-Ray diffraction.

A carbon atom has one more valence electron than a boron atom, and a metal atom is generally regarded as more electron-deficient than boron. Borane structures and organometallic structures therefore often mimic one another, and boranes and metallaboranes can offer patterns for organometallic behaviour that are not yet recognised, and *vice versa*. Boron-containing clusters are redox-flexible among the *closo*, *nido*, *arachno*, etc. sequence. Metallaboranes that also incorporate redox-flexible transition-

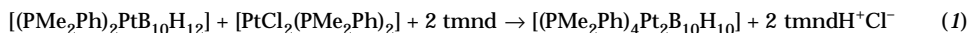
+ For Part 6 see ref.<sup>14</sup>.

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element centres thence offer scope for extensive reaction chemistries, and both earlier<sup>1,2</sup> and more recent results<sup>3-14</sup> suggest that such reaction chemistries can be developed. In the context of the development of metallaborane reaction chemistry, the positioning of two metal centres, rather than just one, on the electronically flexible "B-frame" matrix offers further scope. One target here is to discover how the two metal centres might interact, either (i) through the borane B-frame matrix if the metal centres are positioned remotely, or (ii), if the metal centres are held in adjacent positions in the B-frame matrix, how their more direct interaction might differ from that encountered in more conventional matrices such as the well-examined "A-frame" configuration that is engendered by bidentate phosphines and related electron-rich systems. One potentially interesting and useful aspect of this behaviour of adjacent centres is any unusual organometallic interaction of ligands across the two metal centres. Here we report preliminary observations on two interesting dimetallaborane systems, one twelve-vertex and one eleven-vertex, that demonstrate  $\sigma$ - and  $\pi$ - carbon-to-metal interactions that are unusual in metallaboranes. Each of these two interactions is between a metal centre and the phenyl group of an organophosphine ligand that is P-bound to a second,  $\beta$ -positioned, metal atom.



Reaction of  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{10}\text{H}_{12}]$  (compound **1**, schematic cluster constitution **I**)<sup>15-17</sup> with  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  in  $\text{CH}_2\text{Cl}_2$  solution in the presence of the non-nucleophilic base tetramethylnaphthalene-1,8-diamine (tmnda), followed by chromatographic separation on silica, results in the isolation of very dark purple  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_{10}\text{H}_{10}]$  (compound **2**, Fig. 1, schematic cluster constitution **II**) [ca 3% (unoptimised), reaction scale 150  $\mu\text{mol}$ ]. The almost black crystals of compound **2** are surprisingly insoluble when pure. A stoichiometric equation as in Eq. (1) can be written down.

**1****2**

However, the reaction may be more complex than this implies, because there are several other highly-coloured by-products in similar yields, which we believe are mostly other diplatinadodecaboranes. Some of these are also obtained from the reaction of compound **1** with  $\text{PMe}_2\text{Ph}$  (ref.<sup>18</sup>). We have identified one of these as magenta  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{10}\text{H}_9\text{Pt}\{\text{PMe}_2(\text{C}_6\text{H}_4)\}(\text{PMe}_2\text{Ph})]$  (compound **3**) (ca 2%, Fig. 2 and schematic III). Compounds **2** and **3** were characterised by single-crystal X-ray diffraction analysis<sup>19</sup> and NMR spectroscopy<sup>20</sup>. Compounds **2** and **3** both have a metals-adjacent twelve-vertex closed 1,2-diplatinadodecaborane configuration. This is as previously observed for bright orange  $[(\text{PMe}_2\text{Ph})_3\text{ClPt}_2\text{B}_{10}\text{H}_9(\text{PMe}_2\text{Ph})]$  (**4**)<sup>18</sup>, but in compound **3** a phenyl group of the phosphine that is P-bound to the metal atom Pt(1) has now undergone *ortho*-metallation. This generates a carbon-to-metal  $\sigma$  link to the second metal atom Pt(2), resulting in a pentagonal  $\{\text{PtPtPCC}\}$  ring. Although *ortho* phenylation to a boron atom  $\beta$  to the phosphine donor site is well-recognised in metallaborane chemistry<sup>21–25</sup>, such an interaction to a  $\beta$ -positioned metal atom supported by the B-frame matrix is previously unreported. A simple stoichiometry relating compounds **2** and **3** can be written down (Eq. (2)), but, again, this may belie a more complex process.

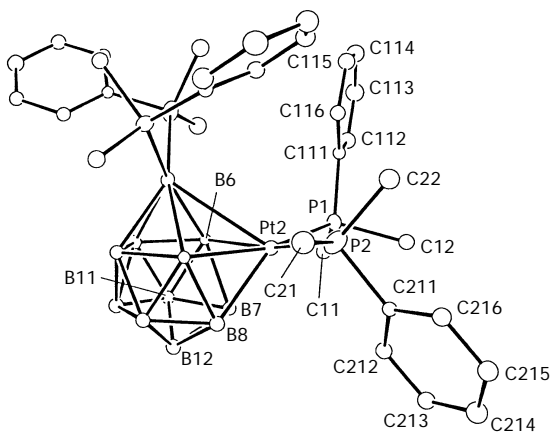
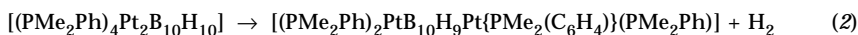


FIG. 1

Representation of the crystallographically determined molecular structure of purple  $[(\text{PMe}_2\text{Ph})_4\text{Pt}_2\text{B}_{10}\text{H}_{10}]$  (compound **2**), with hydrogen atoms omitted. There is crystallographically imposed two-fold symmetry, so that  $\text{Pt}(1) \equiv \text{Pt}(2)$ ,  $\text{B}(7) \equiv \text{B}(4)$ ,  $\text{B}(8) \equiv \text{B}(5)$ ,  $\text{B}(12) \equiv \text{B}(10)$  and  $\text{B}(11) \equiv \text{B}(9)$ . Selected interatomic distances (in pm) are: from Pt(2) to Pt(1) 296.5(1), to P(1) 233.6(2), to P(2) 234.3(3), to B(6) 229.9(11), to B(7) 219.9(13), and to B(8) 223.8(12). Interboron distances are in the range 175(2)–186(2) pm



2

3

The interplatinum distance of 279.9(1) pm in compound **3** is significantly shorter than the 296.5(1) pm of the non-cyclised model compound **2**, but longer than the 262.8(1) pm in the symmetrical doubly-*ortho*- $\beta$ -cyclometallated non-boron-containing bimetallic complex<sup>26</sup>  $[\text{Pt}-\mu\{-\text{ortho}-\text{C}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{PPh}_2\}]_2$ .

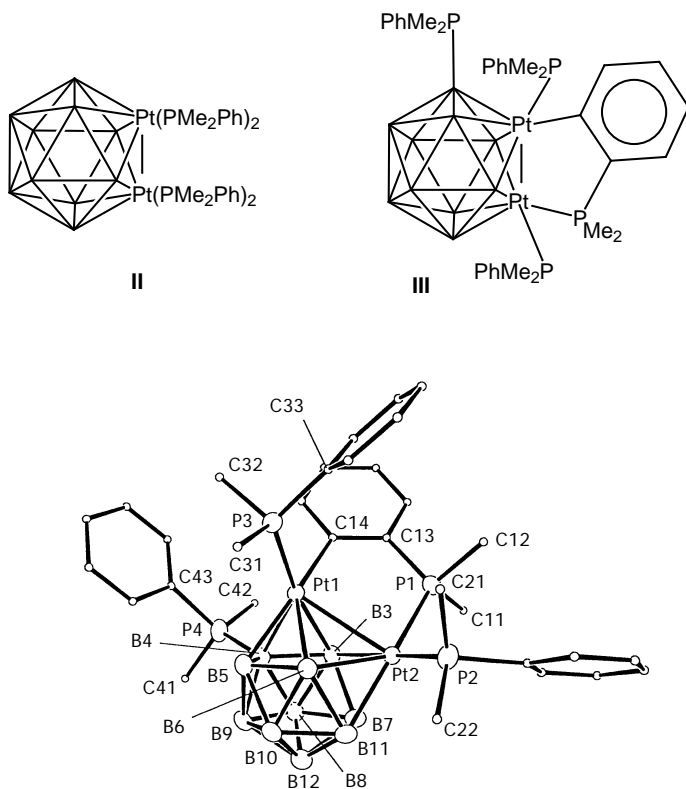


FIG. 2

Representation of the crystallographically determined molecular structure of  $[(\text{PMe}_2\text{Ph})_2\{\text{PMe}_2(\text{C}_6\text{H}_4)\}\text{Pt}_2\text{B}_{10}\text{H}_9(\text{PMe}_2\text{Ph})]$  (compound **3**), with hydrogen atoms omitted. Selected interatomic distances (in pm) are: from Pt(1) to Pt(2) 279.86(6), to P(3) 230.7(2), to C(14) 205.9(8), to B(3) 232.9(9), to B(4) 217.5(10), to B(5) 225.1(9), and to B(6) 2.346(11); from Pt(2) to P(1) 231.7(2), to P(2) 230.7(2), to B(3) 231.0(9), to B(6) 232.6(9), to B(7) 223.9(11), and to B(11) 221.4(11). B(4)–P(4) is 190.4(11), and interboron distances are in the range 174.5(16)–182.3(14), except for B(3)–B(4) at 188.1(13) and B(6)–B(11) at 193.6(16)



tates (ii) an entropically favoured replacement of pcym on ruthenium by a phenyl group of the incoming  $\text{PPh}_3$  moiety. The platinum–ruthenium distance of 269.3(1) pm in *closo* compound **6** is at the lower end of reported platinum–ruthenium bonding distances, which range from *ca* 265 pm upwards, with the bulk of the range being 270–290 pm<sup>28,29</sup>, and thereby significantly shorter than that of 296.4(1) pm in the (unrearranged) *isonido* starting substrate **5**.

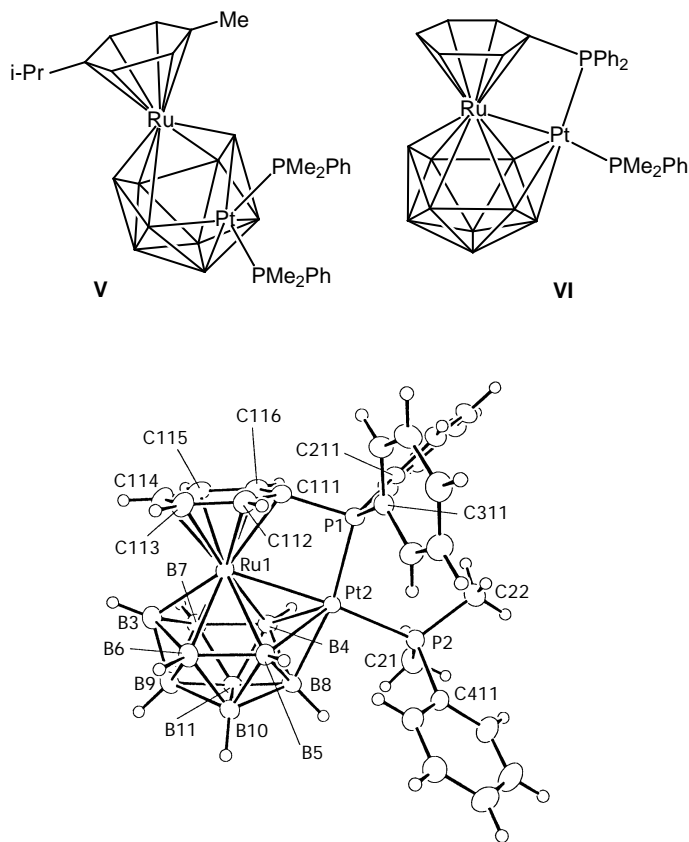


FIG. 4

Representation of the crystallographically determined molecular structure of compound **6**. Selected interatomic distances (in pm) are: from Ru(1) to Pt(2) 269.4(1), to B(3) 211.7(5), to B(4) 237.2(5), to B(7) 231.2(5), to B(6) 232.8(5), and to B(5) 238.3(4); from Pt(2) to P(1) and P(2) both 226.4(1), to B(4) 225.1(4), to B(5) 222.6(4), and to B(8) 222.6(4). Interboron distances are in the range 169.8(7)–185.3(6), and Ru–C distances are in the range 225.1(4)–228.7(4)

These extreme examples of (i)  $\eta^1$  monodentate and (ii)  $\eta^6$  tridentate arene-to-metal ligand  $\beta$ -interactions suggest that intermediate interesting types of organometallic interaction will be observable, and that other interesting organometallic chemistry will emerge from the reaction chemistry of these and other related B-frame-supported bimetallics. We are currently examining for some of these possibilities.

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19. Crystals of compounds **2** (black), **3** (red) and **6** (yellow) were obtained by diffusion of hexane into solutions of the compounds in dichloromethane at ambient temperature.

Crystallographic data for the structures of [(PMe<sub>2</sub>Ph)<sub>4</sub>Pt<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] **2** [(PMe<sub>2</sub>Ph)<sub>2</sub>(PMe<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>))Pt<sub>2</sub>B<sub>10</sub>H<sub>9</sub>(PMe<sub>2</sub>Ph)] **3** and [(PMe<sub>2</sub>Ph)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>PPH<sub>2</sub>)PtRuB<sub>9</sub>H<sub>9</sub>] **6** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos CCDC 115796, 115797 and 115798, respectively. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

Compound **2**: [(PMe<sub>2</sub>Ph)<sub>4</sub>Pt<sub>2</sub>B<sub>10</sub>H<sub>10</sub>], C<sub>32</sub>H<sub>54</sub>B<sub>10</sub>P<sub>4</sub>Pt<sub>2</sub>, *M* = 1 060.91; monoclinic, space group *I2/a* [Non standard setting of *C2/c*, No. 15], *a* = 17.310(4), *b* = 11.473(3), *c* = 20.222(5) Å, β = 102.78(2)°, *U* = 3 916.5(2) Å<sup>3</sup>, *Z* = 4; λ = 0.71073 Å (MoKα), μ = 7.324 mm<sup>-1</sup>, *T* = 293 K; *R*1 = 0.0623 for 3 169 reflections with *F*<sup>2</sup> > 2.0σ(*F*<sup>2</sup>), and *wR*2 = 0.1857 for all 3 302 unique reflections.

Compound **3**: [(PMe<sub>2</sub>Ph)<sub>2</sub>(PMe<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>))Pt<sub>2</sub>B<sub>10</sub>H<sub>9</sub>(PMe<sub>2</sub>Ph)], C<sub>32</sub>H<sub>52</sub>B<sub>10</sub>P<sub>4</sub>Pt<sub>2</sub>, *M* = 1 058.90; monoclinic, space group *P2<sub>1</sub>/n*, *a* = 11.456(2), *b* = 15.536(3), *c* = 22.709(4) Å, β = 102.52(2)°, *U* = 3 945.6(12) Å<sup>3</sup>, *Z* = 4; λ = 0.71073 Å (MoKα), μ = 7.270 mm<sup>-1</sup>, *T* = 293(2) K; *R*1 = 0.034 for 4 649 reflections with *F*<sup>2</sup> > 2.0σ(*F*<sup>2</sup>), and *wR*2 = 0.0965 for all 5 181 unique reflections.

Compound **6**: [(PMe<sub>2</sub>Ph)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>PPH<sub>2</sub>) PtRuB<sub>9</sub>H<sub>9</sub>], C<sub>26</sub>H<sub>35</sub>B<sub>9</sub>P<sub>2</sub>PtRu, *M* = 802.93; triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 10.0327(12), *b* = 10.2761(11), *c* = 16.185(3) Å, α = 71.897(12), β = 74.368(12), γ = 85.153(12)°, triclinic, *U* = 1 527.4(4) Å<sup>3</sup>, *Z* = 2; λ = 0.71073 Å (MoKα), μ = 5.191 mm<sup>-1</sup>, *T* = 160 K; *R*1 = 0.0231 for 5 218 reflections with *F* > 4σ(*F*<sub>o</sub>), and *wR*2 = 0.0584 for all 5 373 unique reflections.

20. Selected NMR data for compounds **2**, **3** and **6** [δ(<sup>31</sup>P) relative H<sub>3</sub>PO<sub>4</sub> and δ(<sup>11</sup>B) relative BF<sub>3</sub>(OEt<sub>2</sub>)].

Compound **2**: this species was surprisingly insoluble; only tentative values can be given (CD<sub>2</sub>Cl<sub>2</sub> at 294 K): δ(<sup>31</sup>P) +0.1, <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) *ca* 2 450 Hz, *ca* +27 (1B), +25.8 (2B), *ca* +24.8 (1B), +20.4 (2B), and -25.8 (2B).

Compound **3** (CD<sub>2</sub>Cl<sub>2</sub>): δ(<sup>31</sup>P) (196 K) [unassigned except for P(4)] A +41.6 ppm [<sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) 2 920 Hz], B +18.9 ppm [<sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) 2 785 Hz], C -10.1 ppm [P(4), broad], and D -14.3 ppm [<sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) 3 020 Hz], with <sup>2</sup>*J*(<sup>31</sup>P-<sup>31</sup>P)(AB) *ca* 15 Hz and <sup>2</sup>*J*(<sup>31</sup>P-<sup>31</sup>P)(BD) *ca* 30 Hz. δ(<sup>1</sup>H)(P-methyl) values were as follows (294 K): A +1.72 and +1.74, B +1.81 and +0.27, C +1.61 and +1.01, D +1.63, +0.70 ppm, assignments by <sup>1</sup>H-<sup>31</sup>P to <sup>31</sup>P resonances A, B, C and D as indicated. δ(<sup>11</sup>B) (unassigned, 294 K, all 1B) at +30.3, +21.2, +18.5, +13.5, +13.1, +12.0, +11.4, -2.8, -20.3 and -27.6 ppm.

Compound **6** (CDCl<sub>3</sub>): δ(<sup>31</sup>P) (223 K) +2.3 with <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) 3 714 Hz and +25.1 with <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>31</sup>P) 2 536 Hz, <sup>2</sup>*J*(<sup>31</sup>P-<sup>31</sup>P) 25 Hz. <sup>11</sup>B and <sup>1</sup>H data (294 K) [ordered as assignment δ(<sup>11</sup>B) [δ(<sup>1</sup>H) in square brackets]]: BH(3) +70.7 [+9.30], BH(4,5) +37.3 [+4.53], BH(8) +25.6 [+5.32], BH(6,7) -2.9 [+1.26], BH(p) -11.8 [+3.22] and B(10,11) -15.1 [+0.99]; additionally δ(<sup>1</sup>H) (η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>) +4.38 (2H), +5.42 (2H) and +6.68 (1H), other aromatics *ca* +7.2 to +7.8.

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