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Preliminary Communication

Ten-vertex polyhedral mixed diheteromonometallaborane chemistry. Directed synthesis of *arachno*-9,6,8-platinathiacarbadecaboranes*

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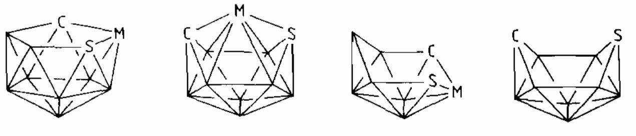
Abstract

[*arachno*-4,6-CSB_7H_{11}], [*cis*-$PtCl_2(PMe_2Ph)_2$] and base yield [9,9-$(PMe_2Ph)_2$-*arachno*-9,6,8-$PtCSB_7H_9$] (**1**, 41%), identified by similarities to [9,9-$(PMe_2Ph)_2$-*arachno*-9,6,8-$PtC_2B_7H_{11}$] (**2**, 52% from [*arachno*-4,6-$C_2B_7H_{13}$], [*cis*-$PtCl_2(PMe_2Ph)_2$] and base). Thermolysis of **1** results in P-phenyl *ortho*-cycloboronation to give [9,9-$(PMe_2Ph)(Me_2P$-*ortho*-$C_6H_4)$-*arachno*-9,6,8-$PtCSB_7H_8$-10] (**3**, 51%), rather than a cluster condensation of the {*arachno*-9,6,8-$PtCSB_7$} unit.

Key words: Borane complexes; Platinaborane complexes; Cluster complexes

Metalladiheteroborane cluster chemistry in which the two heteroatoms are both carbon constitutes one of the best recognised and most investigated areas of polyhedral boron chemistry [1, 2]. By contrast, metalladiheteroboranes in which the two heteroatoms are of different main-group elements are very sparsely represented, and there is consequently interest in developing this area. Recently we reported preliminary results on the directed systematic syntheses of *nido*- and *closo*-structured eleven-vertex metallathiacarbaboranes of configurations I and II, respectively [3], and of nine-vertex *arachno*-structured species of configuration III [4]. Salient features of these syntheses derived from the use of the recently reported [5] ten-vertex substrate [*arachno*-6,9-CSB_8H_{12}] (configuration IV), via systematic addition, condensation and degradation approaches.

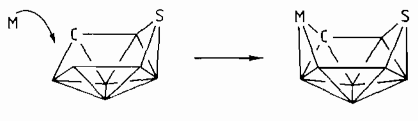


I II III IV

There is much interest in developing systematic synthetic principles for metalladiheteroborane systems with other numbers of vertices, and here we now report preliminary results of the new ten-vertex platinathiacarbaboranes of *arachno* configuration VI. These derive from the site-specific addition of a platinum metal centre to the nine-vertex substrate [*arachno*-4,6-CSB_7H_{11}] configuration V (Scheme 1). In contrast to ten-vertex [*arachno*-6,9-CSB_8H_{12}] [5], nine-vertex [*arachno*-4,6-CSB_7H_{11}] has been known for some years [6]. Surprisingly, however, its use as a useful substrate for metallaheteroborane cluster synthesis has not previously been investigated.

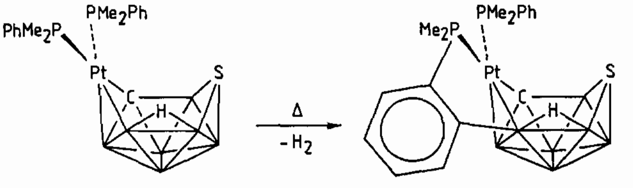
Reaction of [*arachno*-4,6-CSB_7H_{11}] with [*cis*-$PtCl_2(PMe_2Ph)_2$] and the non-nucleophilic base *N*,*N*,*N*′,*N*′-tetramethylnaphthalenediamine (tmed) for 3 h in dichloromethane solution at room temperature, followed by chromatographic separation, yielded [9,9-$(PMe_2Ph)_2$-*arachno*-9,6,8-$PtCSB_7H_9$] (compound **1**, schematic structure VII, Scheme 2) as a pale yellow, air-stable, crystalline solid in 41% yield (unoptimised).

$$[PtCl_2(PMe_2Ph)_2] + [CSB_7H_{11}] + \text{base} \longrightarrow [(PMe_2Ph)_2PtCSB_7H_9] + 2\ \text{baseH}^+Cl^- \quad (1)$$



V VI

Scheme 1.



VII IX

Scheme 2.

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*Contribution No. 42 from the Řež–Leeds Anglo-Czech Polyhedral Collaboration (A.C.P.C.).

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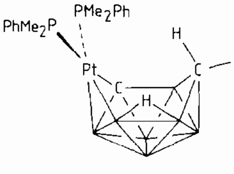
Compound **1** was characterised by mass spectrometry and NMR spectroscopy*. In particular there were many similarities to the metalladicarbaborane analogue [9,9-(PMe$_2$Ph)$_2$-*arachno*-9,6,8-PtC$_2$B$_7$H$_{11}$] (compound **2**, structure VIII)**, which we made for comparison by use of the reaction of [*arachno*-4,6-C$_2$B$_7$H$_{13}$] [7] with [*cis*-PtCl$_2$(PMe$_2$Ph)$_2$] and tmed in refluxing dichloromethane for 2.5 h (52% yield). Compound **2**, also a pale yellow, air-stable, crystalline solid, is itself previously unreported, although other examples of the ten-vertex {*arachno*-9,6,8-PtC$_2$B$_7$} structural motif have been recognised for some time [1, 2, 8]. The NMR similarities are apparent from Fig. 1, which also demonstrates that the ten-vertex *arachno* ^{11}B shielding patterns are readily traced back to fundamental simple analogues exemplified by [*arachno*-6,9-C$_2$B$_8$H$_{14}$] [9].



VIII

The eleven-vertex metallathiacarbaboranes of configuration I can be induced under very mild conditions to undergo cluster condensation [3, 4]. By choice of metal centre, this can be directed to occur either by dihydrogen loss [3] or by cluster-vertex loss [4] to give compounds of cluster configurations II or III, respectively. By contrast, our preliminary results on compound **1** show (i) that much more forcing conditions are required for condensation, and (ii) that a different condensation process occurs.

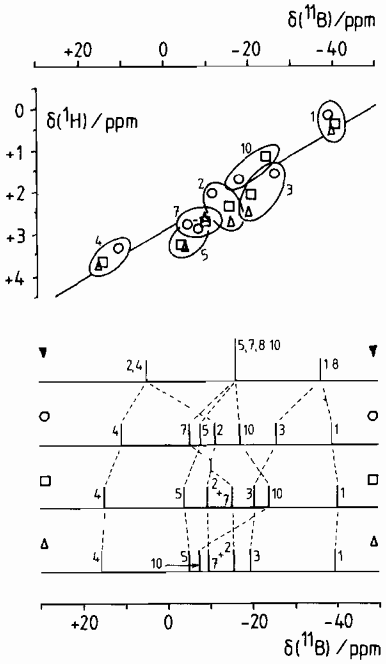


Fig. 1. NMR data for [9,9-(PMe$_2$Ph)$_2$-*arachno*-9,6,8-PtCSB$_7$H$_9$] (□, **1**) and [9,9-(PMe$_2$Ph)(Me$_2$P-*ortho*-$\overline{C_6H_4}$)-*arachno*-9,6,8-PtCSB$_7$H$_8$-$\overline{10}$] (△, **3**), together with those for [9,9-(PMe$_2$Ph)$_2$-*arachno*-9,6,8-PtC$_2$B$_7$H$_{11}$] (○, **2**) and [*arachno*-6,9-C$_2$B$_8$H$_{14}$] (▼, data from ref. 9) for comparison. The bottom diagrams are stick representations of the ^{11}B NMR spectra, with hatched lines linking resonances for the equivalent cluster positions in the four compounds. The top diagram is a plot of $\delta(^1H)$ vs $\delta(^{11}B)$ for the BH(*exo*) units of the metallaheteroboranes **1**, **2** and **3**. The line drawn has slope $\delta(^1H)$ $\delta(^{11}B)$ 1.17, intercept +2.95 in $\delta(^1H)$.

The heating of compound **1** *in vacuo* at *c*. 480 K for 2 h resulted in dihydrogen loss to give [9,9-(PMe$_2$Ph)(Me$_2$P-*ortho*-$\overline{C_6H_4}$)-*arachno*-9,6,8-PtCSB$_7$H$_8$-$\overline{10}$] (compound **3**, structure IX, Scheme 2), again as a pale yellow solid (51% after purification). Compound **3** was readily identified by its NMR properties† relative to those of compound **1**, in particular by the loss of the ^{1}H(10) resonance and by the shift of the ^{11}B(10) resonance to low field, a characteristic of organyl-for-hydrogen substitution (Fig. 1).

It is of interest that, in contrast to the eleven-vertex compounds of configuration I, the condensation of compound **1** does not result in cluster change. Instead, the {*arachno*-9,6,8-PtCSB$_7$} cluster constitution is re-

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*NMR data for [9,9-(PMe$_2$Ph)$_2$-*arachno*-9,6,8-PtCSB$_7$H$_9$] (1) (CDCl$_3$ solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (in ppm rel F$_3$BOEt$_2$) [$\delta(^1H)$ in square brackets]): BH(1) −40.3 [+0.34], BH(2) and BH(7) −9.6 [+2.66] and −15.3 [+2.34], BH(3) −20.6 [+2.10], BH(4) +14.7 [+3.66], BH(5) −4.0 [+3.27], CH(8) [+2.03], BH(10) −24.1 [+1.24]. Additional $\delta(^1H)$ data: μH(5,10) −0.63; PCH$_3$ +1.80, +1.79, +1.70, +1.67 ppm, all with $^2J(^{31}P-^1H)$ in range 9.0–10.5 Hz and $^3J(^{195}Pt-^1H)$ in range 25–35 Hz. $\delta(^{31}P)$ (213 K; in ppm rel. 85% H$_3$PO$_4$) −8.8 [broader, $^1J(^{195}Pt-^{31}Pt)$ 2929 Hz] and −10.7 [sharper, $^1J(^{195}Pt-^{31}P)$ 3377 Hz]

**NMR data for [9,9-(PMe$_2$Ph)$_2$-*arachno*-9,6,8-PtC$_2$B$_7$H$_{11}$] (2) (CDCl$_3$ solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (in ppm rel. F$_3$BOEt$_2$) [$\delta(^1H)$ in square brackets]): BH(1) −40.9 [+0.14], BH(2) −13.3 [+2.01], BH(3) −27.8 [+1.51], BH(4) +8.8 [+3.30], BH(5) −9.8 [+2.82], CH$_2$(6) [−0.09 and −0.17], BH(7) −7.4 [+2.76], CH(8) [+2.58], BH(10) −19.4 [+1.65]. Additional $\delta(^1H)$ data: μH(5, 10) −2.42, PCH$_3$ +1.83 (A), +1.78 (B), +1.74 (C), +1.60 (D) ppm, with $^2J(^{31}P-^1H)$ 9.7 (A), 9.5 (B), 8.9 (C), 8.8 (D) Hz and $^3J(^{195}Pt-^1H)$ 34.7 (A), 32.8 (B), 26.1 (C), 24.3 (D) Hz. $\delta(^{31}P)$ (213 K: in ppm rel. 85% H$_3$PO$_4$) −7.7 [broader, $^1J(^{195}Pt-^{31}P)$ 2825 Hz] and −9.1 [sharper, $^1J(^{195}Pt-^{31}P)$ 3374 Hz].

†NMR data for [9,9-(PMe$_2$Ph)(Me$_2$P-*ortho*-$\overline{C_6H_4}$-*arachno*-9,6,8-PtCSB$_7$H$_8$-$\overline{10}$] (3) (CDCl$_3$ solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (in ppm rel. F$_3$BOEt$_2$) [$\delta(^1H)$ in square brackets]): BH(1) −39.7 [+0.57], BH(2) and BH(7) −9.5 [+2.62] and −15.6 [+2.76], BH(3) −19.4 [+2.52], BH(4) +15.6 [+3.70], BH(5) −5.0 [+3.29], CH(8) [+2.30], B(10) −7.5 [C-substituted]. Additional $\delta(^1H)$ data: μH(5,10) +1.43; PCH$_3$ +2.04, +1.99 [both with $^2J(^{31}P-^1H)$ *c*. 9.0 Hz], +1.56, +1.52 [both with $^2J(^{31}P-^1H)$ *c*. 9.9 Hz], and all with $^3J(^{195}Pt-^1H)$ in range 25–35 Hz. $\delta(^{31}P)$ (−60 °C; in ppm rel. 85% H$_3$PO$_4$) −6.7 [broader, $^1J(^{195}Pt-^{31}P)$ 2978 Hz] and +11.1 [sharper, $^1J(^{195}Pt-^{31}P)$ 3295 Hz].

tained, with dihydrogen loss resulting now in *ortho*-cycloboronation of the P-phenyl group of one of the PMe_2Ph ligands. This phenomenon has been noted before for PPh_3 ligands in ten-vertex *arachno*-platina-heteroboranes [10].

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References

1 R.N. Grimes, in G. Wilkinson, F.G.A. Stone and E. Abel (eds.), *Comprehensive Organometallic Chemistry,* Part I, Pergamon, Oxford, 1982, Ch. 5.5, pp. 459–542, and refs. therein.
2 A K. Saxena and N.S. Hosmane, *Chem. Rev., 93* (1993) 1081, and refs. therein
3 K. Nestor, J.D. Kennedy, M. Thornton-Pett, J. Holub and B. Štíbr, *Inorg Chem, 31* (1992) 3339.
4 K. Nestor, J.D. Kennedy, J. Holub and B. Štíbr, *Inorg. Chim Acta, 214* (1993) 17.
5 J. Holub, T. Jelínek, J Plešek, B. Štíbr, S. Heřmánek and J.D. Kennedy, *J Chem Soc, Chem Commun.,* (1991) 1389.
6 J. Plešek, S. Heřmánek and Z. Janoušek, *Collect. Czech. Chem. Commun., 42* (1977) 785.
7 B. Štíbr, J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun, 38* (1973) 335.
8 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.,* (1975) 2274.
9 K. Nestor, T. Jelínek, X.L.R. Fontaine, J.D. Kennedy, M. Thornton-Pett, K. Baše and B. Štíbr, *J. Chem. Soc, Dalton Trans.,* (1990) 2887.
10 G.A. Kukina, V.S Sergienko, M.A Porai-Koshits, K. Baše and I.A. Zakharova, *Izv. Akad. Nauk S.S S.R, Ser. Khim.,* (1981) 2838.