Inorganica Chimica Acta, 214 (1993) 17–19

Inorganica
Chimica Acta
Preliminary Communication

Polyhedral metallacarbathiaborane chemistry. Designed synthetic routes to nine-vertex mixed diheteromonometallaborane cluster compounds*

Karl Nestor and John D. Kennedy**
School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)
Josef Holub and Bohumil Štíbr
Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež (Czech Republic)

(Received June 24, 1993)

Abstract

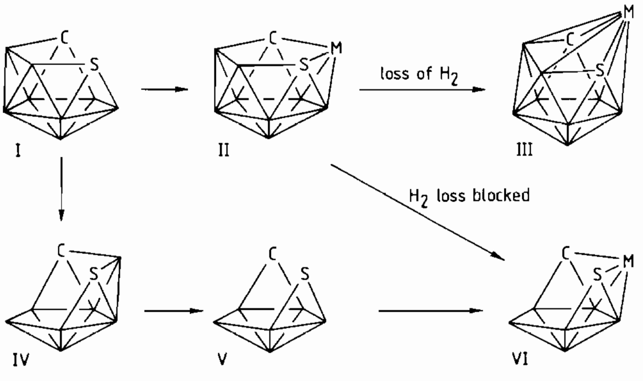
The synthesis of nine-vertex metallacarbathiaboranes [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$MCSB_6H_{10}$], where M = Rh or Ir, can be engineered either from the ten-vertex substrate [*arachno*-6,9-CSB_8H_{12}] by a site-specific addition of the metal centre that is accompanied by the directed elimination of specified boron cluster vertices, or by the directed successive removal of two boron vertices from [*arachno*-6,9-CSB_8H_{12}], or of one vertex from [*arachno*-4,6-CSB_7H_{11}] prior to the site-specific addition of the metal centre.

Although polyhedral dicarbaboranes [1] and metalladicarbaboranes [2] are the best recognized and most studied polyhedral boron-containing cluster compounds, diheteroboranes and metalladiheteroboranes in which the two heteroatoms are different are surprisingly rare. For the development of this interesting area it is important to develop systematic synthetic routes. Recently we reported the systematic synthesis of the useful mixed diheteroborane starting material [*arachno*-6,9-CSB_8H_{12}] (structure I, Scheme 1) [3], and its ready systematic conversion, by reaction with [$RhCl(PPh_3)_3$] in the presence of base, to give the eleven-vertex *nido*-structured rhodathiacarbaborane [$(PPh_3)_2HRhCSB_8H_{10}$] (schematic cluster structure II) [4]. We expected this open eleven-vertex *nido* structural type to be quite reactive, and indeed found that mild thermolysis resulted in dihydrogen loss, quantitatively, to give *closo*-structured [$(PPh_3)_2RhCSB_8H_9$] of schematic cluster structure III [4].

There is merit in designing routes to metalladiheteroboranes with successively fewer vertices. These compounds are of increasing interest as the proportion of boron to the other atoms within the polyhedral clusters is progressively reduced.

In the II → III conversion of Scheme 1, the cluster closure by dihydrogen loss is facilitated by having two labile hydrogen atoms in the open face. If this dihydrogen elimination is not possible, then preferential elimination of the open-face B(10) and B(11) vertices should occur, because these positions are flanked by open-face {CH_2} and {S} units and are therefore very susceptible to elimination [1, 5]. A reaction to give an intermediate of general structure II that does not have even numbers of labile hydrogen atoms available should therefore result in B(10)B(11) loss under reasonably mild conditions to give a nine-vertex {$MCSB_6$} system of schematic cluster structure VI (Scheme 1).

In accord with this, we report preliminary results that show that reaction of [(η^5-C_5Me_5)MCl_2]$_2$ (where M = Rh or Ir) with [*arachno*-6,9-CSB_8H_{12}] in CH_2Cl_2 solution for one hour in the presence of non-nucleophilic base, followed by chromatographic separation of the products, resulted in the isolation of the new nine-vertex metalladiheteroboranes [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$MCSB_6H_{10}$], where M = Rh or Ir, as orange (Rh) or yellow (Ir) crystalline solids in yields of *c.* 10% (as yet unoptimised). Each compound was identified and characterised by mass spectrometry and NMR spec-



Scheme 1

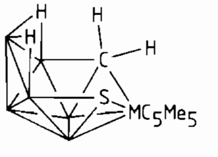
---

*Contribution No. 32 from the Řež–Leeds Anglo–Czech Polyhedral Collaboration (A.C.P.C.)

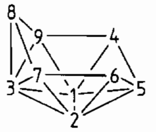
**Author to whom correspondence should be addressed.

0020-1693/93/$6.00

troscopy*, and has the cluster configuration as in structure VII (in which unlettered vertices are BH(*exo*) units). In this NMR characterisation the ^{11}B NMR shielding patterns have a relationship to that** of the [*hypho*-7,8-CSB_6H_{11}]$^-$ anion [6] that is similar to that between the previously reported [7] metalladithiaborane [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$CoS_2B_6H_8$] and the [*hypho*-7,8-$S_2B_6H_9$]$^-$ anion [8] (Fig. 1).



VII



VIII

An alternative systematic approach to the nine-vertex {$MSCB_6$} system from the ten-vertex [*arachno*-6,9-CSB_8H_{12}] starting substrate is via a selective successive manipulation and dismantling of the two vulnerable open-face boron vertices from the diheteroborane *before* addition of the metal centre (Scheme 1, sequence I → IV → V → VI). Thus deprotonation to [*arachno*-6,9-CSB_8H_{11}]$^-$ followed by thermolysis results in cluster comproportionation to give the nine-vertex [*arachno*-4,6-CSB_7H_{10}]$^-$ anion (schematic structure IV) and the eleven-vertex [*nido*-7,9-CSB_9H_{10}]$^-$ anion[†]. The eight-vertex [*hypho*-CSB_6H_{11}]$^-$ anion** of schematic structure V may then be obtained in 65% yield from [*arachno*-4,6-CSB_7H_{10}]$^-$ by heating at reflux in aqueous acetone solution. Treatment of this [7,8-CSB_6H_{11}]$^-$ anion with [(η^5-C_5Me_5)MCl_2]$_2$ in dichloromethane solution, followed by chromatographic separation, then results in the isolation of the two nine-vertex [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$MCSB_6H_{10}$] compounds in yields of *c.* 20% (as yet unoptimised).

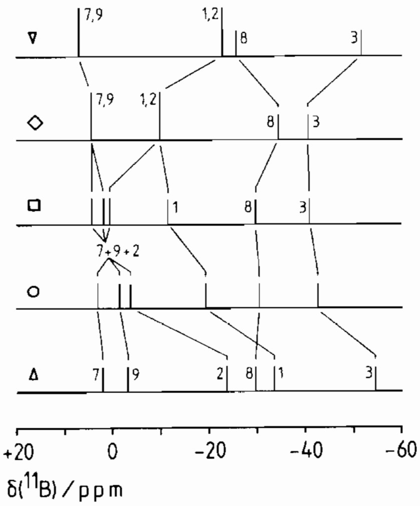


Fig. 1. Stick diagrams of the relative intensities and chemical shifts δ of the resonances in the ^{11}B NMR spectra of (from bottom to top) the [SCB_6H_{11}]$^-$ anion (Δ, data from ref 6), [(C_5Me_5)$IrCSB_6H_{10}$] (○, this work), and [(C_5Me_5)$RhCSB_6H_{10}$] (□, this work), together with [(C_5H_5)$CoS_2B_6H_6$] (◇, data from ref. 8) and the [$S_2B_6H_9$]$^-$ anion (∇, data from ref. 7) for comparison The nine-vertex *arachno* numbering system VIII (with the 5-vertex missing) is used for the [CSB_6H_{11}]$^-$ and [$S_2B_6H_9$]$^-$ anions to facilitate comparison Assignment among the 7, 9 and 2 positions for the {$MCSB_6$} species is at present tentative.

Present work is aimed at the application of this approach to cover other metal centres, and to other cluster substrate types that are prone to selective cluster dismantling approaches.

---

*NMR data for [(C_5Me_5)$MCSB_6H_{10}$] as follows ($CDCl_3$, 294–297 K), ordered as: assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm) in square brackets] For M=Ir: BH(7, 2 or 9) +3.3 [+4.53], BH(9, 7 or 2) −1.6 [+3.93], BH(2, 7 or 9) −3.4 [+2 51], BH(7) −19.1 [+1.02], BH(8) −30.0 [+3 08(*exo*), −0.99(μ), −2.89(μ)], BH(3) −42.6 [+0.20]; $\delta(^1H)[CH_2(4)]$ −0.21 and −1.55, $\delta(^1H)(C_5Me_5)$ +2 02. For M=Rh: BH(7, 2 or 9) +4.4 [+3.66], BH(9, 2 or 7) +1.9 [+2.66], BH(2, 7 or 9) +0.3 [+3 18], BH(7) −11 3 [+1.58], BH(8) −29 2 [+1.95(*exo*), −0.86(μ), −2.64(μ)], BH(3) −40.4 [+0 37]; $\delta(^1H)[CH_2(4)]$ −0 48 and −1 53, $\delta(^1H)(C_5Me_5)$ + 1.93. The mass spectrum of each compound (70 eV, EI) showed a high-mass cut-off corresponding to the highest isotopomer molecular ion.

**NMR data [6] for [*hypho*-CSB_6H_{11}]$^-$ as follows ([PPh_4]$^+$ salt, $CDCl_3$, 294–297 K), ordered as· assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ (ppm) in square brackets] BH(7) +2.0 [+3.45], BH(9) −3.1 [+2.45], BH(2) −23.9 [+1.91], BH(8) −29 4 [+1.41], BH(1) −33 2 [+0.57], BH(3) −54.8 [−0 81]; additional $\delta(^1H)$ data· $CH_2(4)$ −0 16 and −1 74, μH(1,2) −0 67, μH(8,9) −1.27, μH(7,8) −2.51. (Numbering, for convenience of comparison, as in VIII but with the 5-vertex missing)

[†] These two cluster systems are best separated by chromatography, after protonation to give a mixture of the two neutral species [4,6-CSB_7H_{11}] and [7,9-CS_9H_{11}] Deprotonation by base of the separated neutral species then regenerates the pure anions. Here it should however be pointed out that, although this sequence nicely illustrates a synthetic principle, at present in practice the more convenient route to [*arachno*-CSB_7H_{11}] is via the previous literature method [9]

Acknowledgements

We thank the SERC (UK) and the Czech Academy of Sciences (Grant No. 43204), together with Borax Research Ltd. and the Royal Society, for support, Dr D.M. Wagnerová, Dr R.A. Walker and Dr T.S. Griffin for helpful cooperation, and Mr D. Singh for mass spectrometry.

References

1 B. Štíbr, *Chem Rev*, *22* (1992) 225, and refs therein
2 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.

3 J. Holub, T. Jelínek, J. Plešek, B Štíbr, S Heřmánek and J.D. Kennedy, *J. Chem Soc, Chem Commun*, (1991) 1389–1390.

4 K Nestor, J.D. Kennedy, M. Thornton-Pett, J. Holub and B. Štíbr, *Inorg. Chem*, *31* (1992) 3339.

5 B. Štíbr, J. Plešek, J. Jelínek, K. Baše, Z. Janoušek and S Heřmánek, in S. Heřmánek (ed.), *Boron Chemistry (Proc. Sixth Int. Meet. Boron Chemistry IMEBORON VI, Bechyně, Czechoslovakia, June 22–26, 1987)*, World Scientific, Singapore, 1987, pp. 175–206, and refs. therein.

6 J. Holub, J D Kennedy, T. Jelínek and B. Štíbr, *J. Chem. Soc, Dalton Trans*, (1993) submitted for publication.

7 G.J. Zimmerman and L.G Sneddon, *J Am. Chem. Soc.*, *103* (1981) 1102–1111.

8 S.O. Kang and L.G. Sneddon, *J. Am Chem. Soc.*, *111* (1989) 3281–3289.

9 J. Plešek, S. Heřmánek and Z. Janoušek, *Collect. Czech. Chem. Commun*, *38* (1973) 335.