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Inorganica Chimica Acta 227 (1994) 163–166

Inorganica Chimica Acta

Note

Ten-vertex polyhedral azametallaborane chemistry. An *arachno*-6,9-azaplatinadecaborane and a *nido*-6,8-azaruthenadecaborane☆

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Received 11 March 1994; revised 20 May 1994

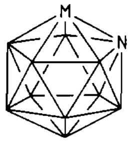
Abstract

$[(PMe_2Ph)_2PtB_8H_{10}NH]$ (**1a**, 63% from $[PtCl_2(PMe_2Ph)_2]$, *arachno*-4-NB_8H_{13} and base) has a ten-vertex {*arachno*-9,6-$PtNB_8$} cluster, whereas $[(\eta^6\text{-}C_6Me_6)RuB_8H_{10}NH]$ (**2a**, 19% from $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ and *nido*-6-NB_9H_{12}) and $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuB_8H_{10}NH]$ (**2b**, 46% from $[(\eta^6\text{-}MeC_6H_4{}^iPr)RuCl_2]_2$ and $[NMe_4]^+[$*arachno*-4-$NB_9H_{13}]^-$) have ten-vertex {*nido*-8,6-$RuNB_8$} clusters.

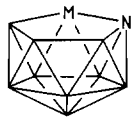
Keywords: Crystal structures; Azaplatinadecaborane complexes; Azaruthenadecaborane complexes

Although carbametallaboranes, particularly the dicarbametallaboranes, are very well recognised [1], heterometallaboranes in which the heteroatom is a first-row element other than carbon are surprisingly rare. Only three oxametallaboranes are known [2–4], and only four azametallaborane types [5–9]. There is now a strong developing interest in azaborane [10–24] and azametallaborane [6–9,22,25] chemistry. Recently in azametallaborane chemistry *closo* twelve-vertex (schematic structure I), [9], *nido* eleven-vertex (schematic structure II) [8] and *closo*-type eleven-vertex (schematic structure III) species [6,7] have been structurally established. In type I the nitrogen centre has a cluster connectivity of five, and in types II and III a cluster connectivity of four.

In view of the vast amount of carbametallaborane chemistry [1], there is now interest also in extending azametallaborane chemistry to other cluster types, and to include other nitrogen-to-cluster connectivity numbers. Here therefore we give a preliminary account of work resulting in two ten-vertex azametallaborane cluster types: *arachno*-6,9-azaplatinadecaborane (schematic configuration IV) and *nido*-6,8-azaruthenadecaborane (schematic configuration V), of which each has a nitrogen-to-cluster connectivity of three. In contrast to the previously reported compounds of structure types I–III these two new ten-vertex species do not have direct cluster metal-to-nitrogen connectivities.



I



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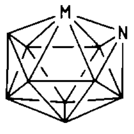

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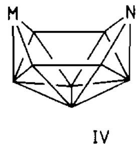

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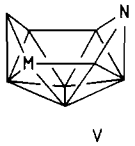

V

Reaction among *arachno*-4-NB_8H_{13} [12,14,15], *N,N,N′,N′*-tetramethylnaphthalenediamine (tmed, 'proton sponge') and the platinum(II) complex [*cis*-$PtCl_2(PMe_2Ph)_2$] (CH_2Cl_2; ~294 K), followed by TLC separation (silica gel G; 8:20 CH_2Cl_2/hexane), gives pale yellow air-stable crystals of $[9,9\text{-}(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}]$ (compound **1a**) (63%). Com-

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☆Contribution No. 45 from the Řež–Leeds Anglo–Czech Polyhedral Collaboration (A.C.P.C.).

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0020-1693/94/$07.00
SSDI 0020-1693(94)04140-Q

pound **1** is characterised by NMR spectroscopy[2] and a single-crystal X-ray diffraction analysis (Fig. 1)[3]. The reaction stoicheiometry is straightforward:

$$\mathrm{HNB_8H_{12} + [PtCl_2(PMe_2Ph)_2] + tmed \longrightarrow [(PMe_2Ph)_2PtB_8H_{10}NH] + 2tmedH^+Cl^-} \quad (1)$$

1a

A previous *arachno*-6,9-azaplatinadecaborane example (compound **1b**) (interpreted at the time as a '*nido*' species) derives via an alternative, redox, route from the platinum(0) complex $[Pt(PPh_3)_4]$ and the *arachno*-4-NB_8H_{13} substrate [5]:

$$\mathrm{HNB_8H_{12} + [Pt(PPh_3)_4] \longrightarrow [(PPh_3)_2PtB_8H_{10}NH] + H_2 + 2PPh_3} \quad (2)$$

1b

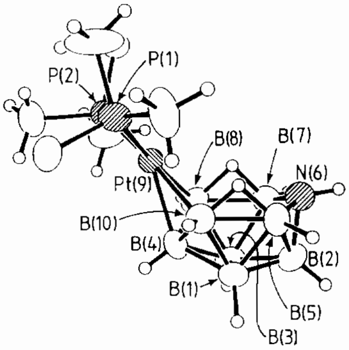

Fig. 1. Drawing of the crystallographically determined molecular structure of [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$] (compound **1a**), with P-phenyl atoms (apart from the *ipso* carbon ones) omitted for clarity. Selected interatomic distances (in pm) are: from Pt(9) to B(4) 222.6(14), B(8) 220.9(14), B(10) 221.7(13), P(1) 230.4(5), P(2) 230.8(5); B(5)–B(10) 188.4(19), B(7)–B(8) 183.2(19), N(6)–B(2) 158.9(17), N(6)–B(5) 153.6(16), N(6)–B(7) 154.2(18) pm; angle P(1)–Pt(9)–P(2) is 96.1(2)°.

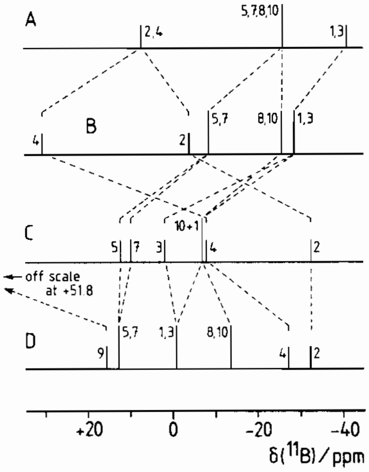

Fig. 2. Stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of (from top to bottom) *arachno*-6,9-$N_2B_8H_{12}$ (A, data from Ref. [17]), [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$] (B, compound **1a**, this work), [8-(η^6-C_6Me_6)-*nido*-8,6-$RuNB_8H_{11}$] (C, compound **2a**, this work), and *nido*-6-NB_9H_{12} (D, assignments by [^{11}B–^{11}B]-COSY experiments from this work; these differ from those in Ref. [15]). Hatched lines link resonances for the equivalent cluster positions in the four compounds. Note the effective inversion in the $\delta(^{11}B)$ sequencing (particularly for $\delta[^{11}B(2)]$ and $\delta[^{11}B(4)]$ in the *nido*–*arachno* comparison, which is diagnostic of a ten-vertex *nido*–*arachno* difference [28–30]. Additionally, the markedly lower ^{11}B shieldings associated with the 4-position (the *arachno* system) [31] and 9-position (*nido* system) [32] are typical for the respective cluster types.

Compound **1b** was also structurally identified [5], but no details of the X-ray work have been reported, nor any NMR characterisation. Interestingly, the electronic structure is now better traced to *arachno* ten-vertex non-metalla analogues such as *arachno*-6,9-$N_2B_8H_{12}$ [7] by ^{11}B NMR shielding behaviour similarities (Fig. 2, upper part of diagram), and by the diagnostic disposition of the two bridging hydrogen atoms; these two factors support an *arachno* character and the *arachno* descriptor, whereas an uncritical electron-counting [5,33] can confusingly suggest a '*nido*' formulation. An incompatibility between (a) formal cluster electron count, and (b) observed geometric structure and implied electronic structure, is often an interesting feature of metallaborane clusters when the metal site is a sixteen-electron transition-element centre [34].

By contrast, the constitution of the more novel species [8-(η^6-Ar)-*nido*-8,6-$RuNB_8H_{11}$] (compounds **2a** and **2b**) (schematic structure VI, M = {$Ru(C_6Me_6)$} (**2a**) or {$Ru(MeC_6H_4$-p-$^iPr)$} (**2b**), unlettered vertices are

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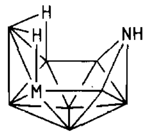
[2] NMR data for [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$] (compound **1**) ($CDCl_3$ solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (rel. F_3BOEt_2) (ppm) [$\delta(^1H)$ in square brackets]): BH(1,3) −28.6 [+1.24], BH(2) −3.9 [+3.64], BH(4) +30.6 [+5.21], BH(5,7) −8.3 [+2.84], BH(8,10) −25.6 [+0.75]; additional $\delta(^1H)$ data: NH(6) +3.85, μH(7,8; 5,10) −1.88, PMe +1.69 and +1.77 (both doublets, $N(^{31}P$–$^1H)$ 9 Hz, with $^3J(^{195}Pt$–$^1H)$ 26 and 28 Hz, respectively); $\delta(^{31}P)$ (rel. 85% H_3PO_4) −3.5 ppm and $^1J(^{195}Pt$–$^{31}P)$ 2866 Hz at 233 K.

[3] X-ray data for [9,9-$(PMe_2Ph)_2$-*arachno*-9,6-$PtNB_8H_{11}$] (compound **1**). All crystallographic measurements were carried out at ambient temperature on a Nicolet P3/F diffractometer operating in the ω–2θ mode using graphite-monochromated Mo Kα radiation ($\lambda = 71.069$ pm). The data set was corrected for absorption once the structure had been solved [26]. The structure was determined using standard heavy-atom techniques and was refined by full-matrix least-squares using SHELX-76 [27]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl and phenyl hydrogen atoms were placed in calculated positions (C–H = 96 pm) and refined with an overall isotropic displacement parameter, cage-associated hydrogen atoms were located on a Fourier difference map and were freely refined. The weighting scheme $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1/2}$ was used. *Crystal data*. $C_{16}H_{33}BN_8P_2Pt$, 0.8 × 0.6 × 0.2 mm, $M_r = 582.96$, monoclinic, $a = 1940.8(3)$, $b = 1318.5(2)$, $c = 2017.7(3)$ pm, $\beta = 110.42(1)°$, $U = 4.8384(11)$ nm^3, space group $C2/c$, $Z = 8$, $D_x = 1.60$ g cm^{-3}, $\mu = 5.69$ mm^{-1}, $F(000) = 2272$. 4662 unique data were collected in the range $3.0 < 2\theta < 50°$ of which 3409 with $F > 4.0\sigma(F)$ were considered observed and used in refinement. Refinement converged with $R(R_w) = 0.0446(0.0446)$.

{BH(*exo*)} units) is traced, via ^{11}B shielding patterns[4], to the *nido* non-metalla parent *nido*-6-NB_9H_{12} [14,15] (Fig. 2, lower part of diagram). Fig. 2 also demonstrates the typical [28] ten-vertex *arachno–nido* inversion in ^{11}B NMR shielding between the {*arachno*-9,6-$PtNB_8$} and {*nido*-8,6-$RuNB_8$} clusters.



VI

Compound **2a** (yellow solid; air-stable; 19%) was isolated by TLC (silica gel G; 70:30 CH_2Cl_2/hexane) from the reaction between $[Ru(C_6Me_6)Cl_2]_2$ and *nido*-6-NB_9H_{12} in CH_2Cl_2 (30 h at ~294 K), and compound **2b** (46%) similarly (silica gel G; 100% C_6H_6) from the reaction between $[Ru(MeC_6H_4$-*p*-$^iPr)Cl_2]_2$ and $[NMe_4]^+$[*arachno*-6-$NB_9H_{13}]^-$ in CH_2Cl_2 (24 h at ~294 K). We have not yet obtained crystals of **2a** or **2b** suitable for single-crystal X-ray work (there is some solution instability), but the formulations reasonably derive from mass spectrometry, and from NMR spectroscopy based on *nido* ten-vertex {6-NB_9} and {5-MB_9} [32] shielding characters. Other products from these ruthenium reactions include some of eleven-vertex *nido* configuration, for example the two species [8-(η^6-Ar)-*nido*-8,7-$RuNB_9H_{12}$] (of schematic structure II), identified by comparison with their azairidaborane analogues such as [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNB_9H_{11}$] [8], and we hope to describe these more definitively in the near future.

Acknowledgements

We thank the SERC (United Kingdom) and the Academy of Sciences of the Czech Republic (Grant No. 43204), together with Borax Research Ltd. and the Royal Society, for support, Professor N.N. Greenwood, Dr R.A. Walker and Dr D.M. Wagnerová for helpful cooperation, Mr D. Singh for mass spectrometry, and Dr X.L.R. Fontaine for NMR spectroscopy in the early stages of the work.

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[4] NMR and MS data for [8-(η^6-C_6Me_6)-*nido*-8,6-$RuNB_8H_{11}$] (compound **2a**) ($CDCl_3$ solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ in square brackets]): BH(1) ~ −7.1 [+1.15], BH(2) −32.5 [+1.00], BH(3) +1.6 [+2.16], BH(4) −7.8 [+1.96], BH(5) +12.5 [+3.65], NH(6) −[+5.00], BH(7) +10.0 [+3.99], BH(9) +51.8 [+5.42], BH(10) ~ −7.1 [+2.96]; additional $\delta(^1H)$ data: C_6Me_6 +2.20, μH(8,9) −17.15 (compare Ref. [35]), and μH(9,10) −3.09 ppm. MS: m/z_{max} 378; $^{12}C_{12}{}^1H_{29}{}^{11}B_8{}^{14}N_1{}^{103}Ru_1$ requires 378.

NMR and MS data for [8-(η^6-MeC_6H_4-*para*-^iPr)-*nido*-8,6-$RuNB_8H_{11}$] (compound **2b**) (CD_2Cl_2 solution at 294–303 K) (ordered as: assignment $\delta(^{11}B)$ (ppm) [$\delta(^1H)$ in square brackets]): BH(1) −8.4 [+1.82], BH(2) −32.3 [+0.93], BH(3) −1.5 [+2.60], BH(4) −9.68 [+1.42], BH(5) +13.1 [+3.64], NH(6) −[+5.21], BH(7) +6.8 [+4.43], BH(9) +49.7 [+5.72], BH(10) ~ −5.7 [+2.95]; additional $\delta(^1H)$ data: $MeC_6H_4{}^iPr$ +1.26 (apparent triplet, 6H, at 400 MHz), +2.21 (singlet, 3H), +2.75 (apparent septet, 1H, at 400 MHz), +5.95 to +5.63 (multiplet, 4H); μH(8,9) −16.67, μH(9,10) −3.09 ppm. MS: m/z_{max} 350; $^{12}C_{10}{}^1H_{25}{}^{11}B_8{}^{14}N_1{}^{103}Ru_1$ requires 350.

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