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Communications

11-Vertex Polyhedral Rhodathiacarbaborane Chemistry.[1] Synthesis and Characterization of Nido-Structured [8,8-$(PPh_3)_2$-8-H-8,7,9-$RhCSB_8H_{10}$] and Closo-Structured [1,1-$(PPh_3)_2$-1,2,3-$RhCSB_8H_9$]

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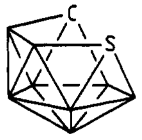
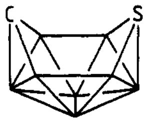
The systematic investigation of polyheteroborane derivative chemistry has previously been inhibited by the lack of systematic routes to suitable polyheteroborane starting substrates. Recently we reported the designed syntheses of the 10-vertex mixed diheteroborane species [*arachno*-6,9-CSB_8H_{12}] (compound **1**, schematic cluster structure I) and its nitrogen congener [*arachno*-6,9-CNB_8H_{11}] and suggested that these species might be useful as starting materials to develop metalladiheteroborane chemistry.[2] We have started to explore this latter possibility, and here we are now able to report preliminary results on compounds derived from the reaction of [*arachno*-6,9-CSB_8H_{12}] (compound **1**) with [$RhCl(PPh_3)_3$]. The two products described can be obtained in very high yield and constitute rare examples in the as yet sparsely represented but potentially vast class of polyhedral metalladiheteroboranes that have disparate types of heteroatoms.



IA



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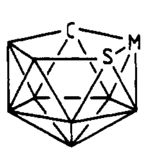

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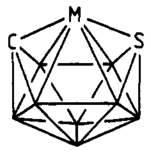

III

Reaction of [*arachno*-6,9-CSB_8H_{12}] (compound **1**)[3] with [$RhCl(PPh_3)_3$] in ethanol solution at room temperature in the presence of base for 5 h yielded [8,8-$(PPh_3)_2$-8-H-8,7,9-$RhCSB_8H_{10}$] (compound **2**) as a yellow crystalline air-stable solid in high yield.[3] The stoichiometry is straightforward (eq 1).

$$[RhCl(PPh_3)_3] + \underset{\mathbf{1}}{[CSB_8H_{12}]} + \text{base} \rightarrow \underset{\mathbf{2}}{[(PPh_3)_2HRhCSB_8H_{10}]} + PPh_3 + \text{baseH}^+Cl^- \quad (1)$$

Single-crystal X-ray diffraction analysis (on the dichloromethane monosolvate)[4] revealed it to be a species with an open nido-shaped[5] 11-vertex {$RhCSB_8$} cluster (Figure 1), as may perhaps be expected from its formal Wadian[6] $2n + 4$ cluster-electron count. In this last regard, it offers an interesting contrast to the recently reported 11-vertex non-carbon rhodathiaborane [8,8-$(PPh_3)_2$-8,7-

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(1) Contribution No. 21 from the Leeds-Řež Anglo-Czech Polyhedral Collaboration (ACPC).

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

(3) A solution of [$RhCl(PPh_3)_3$] (200 mg, 216 μmol), [6,9-CSB_8H_{12}] (31 mg, 217 μmol), and tetramethylnaphthalenediamine (47 mg, 219 μmol) in dry EtOH (ca. 30 cm^3) was stirred for 5 h under N_2. Compound **2** was formed as a yellow precipitate, which was filtered off, washed with EtOH (3 × ca. 5 cm^3), and dried in vacuo to give 162 mg (211 μmol, 98%) of compound **2**. NMR results for compound **2** (CD_2Cl_2 solution) [δ in ppm, $\delta(^{11}B)$ relative to $F_3B{\cdot}OEt_2$, $\delta(^{31}P)$ relative to 85% H_3PO_4]: cluster ^{11}B and ^1H data {given as $\delta(^{11}B)$ [$\delta(^1H)$ of directly bound H in square brackets]} +17.1 [+3.44], +2.7 [+2.22], +2.7 [+5.17], −3.7 [+3.11], −11.5 [+2.22], −18.9 [+0.41], −20.2 [+1.56], −27.4 [+1.31]; other $\delta(^1H)$ values CH(cluster) +3.39, BHB −3.35, RhH −11.85 [$^1J(^{103}Rh{-}^1H) = 34$ Hz, $^2J(^{103}Rh{-}^{31}P)$(mean) = ca. 16 Hz]; $\delta(^{31}P)$ (−50 °C) +44.0 [$^1J(^{103}Rh{-}^{31}P) = 123$ Hz], +39.1 [$^1J(^{103}Rh{-}^{31}P)$ 121 Hz], $^2J(^{31}P{-}^{31}P) = 15$ Hz.

(4) Crystal data for compound **2**:[18] $C_{37}H_{40}B_8P_2RhS{\cdot}CH_2Cl_2$, $M = 853.06$, monoclinic, $a = 1039.02$ (12) pm, $b = 3104.4$ (4) pm, $c = 1288.00$ (14) pm, $\beta = 103.707$ (10)°, $V = 4.0362$ (8) nm^3, $Z = 4$, space group $P2_1/c$, $D_c = 1.40$ Mg m^{-3}, $\mu = 6.39$ cm^{-1}, $F(000) = 173.99$, $T = 270$ K, R (R_w) = 0.0441 (0.0451) for the refinement of 4982 absorption-corrected reflections with $I > 2.0\sigma(I)$ and $4.0 < 0 < 50.0°$.

(5) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210–214; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67–142.

(6) Wade, K. *Chem. Commun.* **1971**, 792–793; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.

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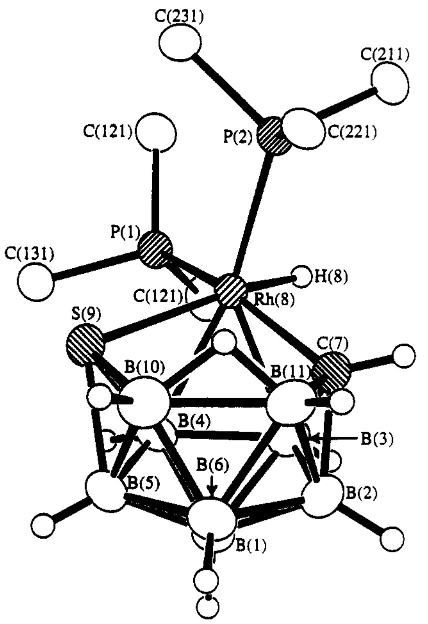

Figure 1. Modified ORTEP drawing of the molecular structure of [8,8-$(PPh_3)_2$-8-H-8,7,9-$RhCSB_8H_{10}$] (compound **2**). Selected interatomic distances (pm): from Rh(8) to P(1) 233.1 (3), to P(2) 233.6 (3), to H(8) 147 (6), to C(7) 217.5 (7), to S(9) 244.7 (3), to B(3) 218.8 (8), and to B(4) 223.7 (8); from C(7) to B(2) 166.1 (10), to B(3) 165.4 (10), and to B(11) 163.4 (11); from S(9) to B(4) 205.4 (9), to B(5) 196.8 (9), and to B(10) 194.1 (10); from B(10) to B(11) 186.3 (12). Other interboron distances are in the range 171.1 (12)–189.9 (12) pm.

$RhSB_9H_{11}$],[7] which has a similar nido cluster geometrical structure but a formal closo count. Compound **2** is in fact more akin to 11-vertex metallathiaboranes such as [8-(η^6-C_6H_5Me)-8,7-$FeSB_9H_{11}$][8] and [8-(η^5-C_5Me_5)-8,7-$IrSB_9H_{11}$],[9] which have both nido structures and formal nido electron counts.

The cluster of compound **2** has the rhodium, carbon, and sulfur atoms in adjacent positions on the open face (schematic structure II), as expected from a straightforward systematic addition of the metal center to the {*arachno*-6,9-CSB_8} unit of compound **1** (schematic structure IA), and it is of interest that the preferred configuration of the exopolyhedral rhodium {$H(PPh_3)_2$} ligation sphere has the hydrogen atom trans to the cluster sulfur atom rather than carbon. Here any indication of any metal-sphere fluxionality[7,10–14] would be of some interest, but so far an investigation for this has been precluded by the thermal instability of the compound.

Thermolysis of compound **2** in solution in fact readily results in a rapid and quantitative condensation to give the orange/red

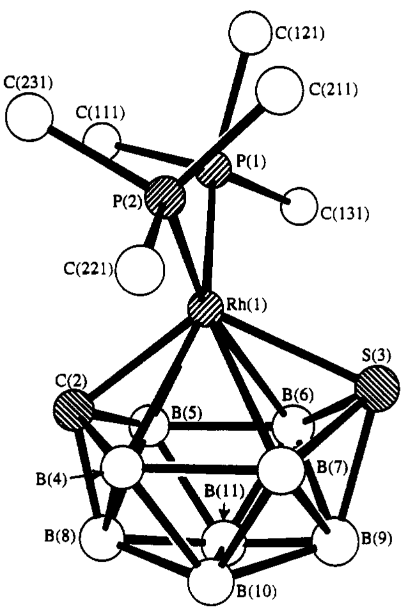

Figure 2. Modified ORTEP drawing of the molecular structure of [1,1-$(PPh_3)_2$-1,1-$RhCSB_8H_9$] (compound **3**). Selected interatomic distances (pm): from Rh(1) to P(1) 235.4 (3), to P(2) 231.5 (3), to C(2) 211.8 (5), to S(3) 234.8 (3), to B(4) 232.1 (5), to B(5) 238.5 (5), to B(6) 246.1 (5), and to B(7) 236.4 (5); from C(2) to B(4) 158.8 (6), to B(5) 158.8 (6), and to B(8) 165.6 (6); from S(3) to B(6) 191.2 (5), to B(7) 192.7 (5), and to B(9) 200.2 (5); from B(4) to B(7) 188.4 (7), and from B(5) to B(6) 187.9 (7). Other interboron distances are in the range 174.4 (7)–189.6 (7) pm.

crystalline species [1,1-$(PPh_3)_2$-1,1-$RhCSB_8H_9$] (compound **3**) (eq 2).[15] This quantitative condensation also occurs spontaneously in a variety of solvents in 3–4 days at room temperature.

$$\underset{\mathbf{2}}{[(PPh_3)_2HRhCSB_8H_{10}]} \rightarrow \underset{\mathbf{3}}{[(PPh_3)_2RhCSB_8H_9]} + H_2 \qquad (2)$$

The results of single-crystal X-ray diffraction analysis on compound **3** (Figure 2)[16] show that it has a closed deltahedral 11-vertex {1,2,3-$RhCSB_8$} cluster structure that adheres to the classical Williamsian[5] closo 11-vertex geometry. It can be regarded as being formed by straightforward closure from the

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(7) Ferguson, G.; Jennings, M. C.; Lough, A. J.; Coughlan, S.; Spalding, T. R.; Kennedy, J. D.; Fontaine, X. L. R.; Štíbr, B. *J. Chem. Soc., Chem. Commun.* **1990**, 891–894.

(8) Kang, S. O.; Carroll, S. P. J.; Sneddon, L. G. *Organometallics* **1988**, *7*, 772–776.

(9) Nestor, K.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2657–2667.

(10) Marder, T. B.; Baker, R. T.; Long, J. A.; Doi, J. A.; Hawthone, M. F. *J. Am. Chem. Soc.* **1981**, *103*, 2988–2994.

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(12) Kennedy, J. D.; Thornton-Pett, M.; Štíbr, B.; Jelínek, T. *Inorg. Chem.* **1991**, *30*, 4481–4484. Kennedy, J. D.; Štíbr, B.; Jelínek, T.; Fontaine, X. L. R.; Thornton-Pett, M. *Collect. Czech. Chem. Commun.*, submitted for publication (additional work on the closo-type {1,2,3-PtC_2B_8} system).

(13) Štíbr, B.; Jelínek, J.; Kennedy, J. D.; Fontaine, X. L. R.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.*, to be submitted for publication (work on the [8,8-$(PMe_2Ph)_2$-*nido*-8,7-$PtCB_9H_{11}$] system).

(14) The quasiisoelectronic anionic nido 11-vertex species [7,7,7-(CO)$(PPh_3)_2$-*nido*-7-$IrB_{10}H_{11}$-1-$(PPh_3)$$]^-$ is fluxional ($\Delta G^{\ddagger}_{320}$ = ca. 65 kJ mol^{-1}) with regard to rotation of the exopolyhedral {(CO)$(PPh_3)_2$} ligand sphere relative to the {η^4-B_{10}} cluster [Crook, J. E. Synthetic and Structural Studies on Some Novel Metallaborane Clusters. Ph.D. Thesis, University of Leeds, Leeds, England, 1982].

(15) A yellow solution/suspension of compound **2** in toluene was heated overnight at reflux and then cooled to give an orange solution and orange/red crystals of compound **3** that were suitable for the X-ray diffraction experiment.[16] NMR analysis of the crystals ($CDCl_3$ solution) and the supernatant liquid showed that conversion to compound **3** was quantitative. BH NMR data for compound **3** {ordered as relative intensity $\delta(^{11}B)(CDCl_3)$ [$\delta(^1H)(CDCl_3)$ in square brackets]}: 1 BH +26.6 [+4.13], 1 BH +4.5 [+3.13], 2 BH −5.2 [+0.52], 2 BH −12.2 [+0.95], 2 BH −26.3 [+0.25]. Other NMR data: $\delta(^1H)$(cluster CH) +6.85, $\delta(^{31}P)(CDCl_3)$ +40.3, $^1J(^{103}Rh–^{31}P)$ = 156 Hz [δ in ppm, $\delta(^{11}B)$ relative to $F_3B{\cdot}OEt_2$, $\delta(^{31}P)$ relative to 85% H_3PO_4].

(16) Crystal data for compound **3**:[18] $C_{37}H_{39}B_8P_2RhS$, M = 767.12, orthorhombic, a = 1714.8 (2) pm, b = 2026.4 (2) pm, c = 2074.0 (2) pm, V = 7.2070 (13) nm^3, Z = 8, space group *Pbca*, D_c = 1.41 Mg m^{-3}, μ = 5.74, $F(000)$ = 3135.97, T = 200 K, R (R_w) = 0.0274 (0.0290) for the refinement of 4947 absorption-corrected reflections with $I > 2.0\sigma(I)$ and $4.0 < 2\theta < 50.0°$.

(17) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446–452.

(18) All crystallographic measurements were made on a Stoe STADI4 diffractometer operating in the ω/θ scan mode using graphite-monochromated molybdenum Kα radiation. The structures of both **2** and **3** were solved using standard heavy-atom methods and were refined by full-matrix least-squares refinement. All non-hydrogen atoms for both complexes were refined with anisotropic thermal parameters, with the exception of the chlorine and carbon atoms of a CH_2Cl_2 solvent molecule in the crystal of **2**, which were refined with isotropic thermal parameters. Phenyl groups were treated as rigid bodies with idealized hexagonal symmetry (C–C = 139.5 pm). The phenyl hydrogen atoms of both compounds were included in calculated positions (C–H = 96 pm) and, in each case, were refined with an overall isotropic thermal parameter. In both cases, the borane cluster hydrogen atoms were located in Fourier difference maps and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$ was used for both compounds.

nido compound **2** in a classical 2-electron loss[17] via dihydrogen elimination. In the overall conversion **1** → **2** → **3** (schematic cluster structures I → II → III), the six-membered open face of the starting unmetalated $\{CSB_8\}$ cluster (schematic structure IB) is effectively capped completely by the metal center (schematic structure III). In this context it is interesting to note that although the closed cluster structure[5] is compatible with its formally closo Wadian[6] $2n + 2$ cluster-electron count, there appears to be a similarity in the cluster ^{11}B shielding pattern with that[2,19] of the 10-vertex arachno starting compound **1**. If these parallels reflect parallels in electronic structure, then this may imply that compound **3** is not in fact a straightforward *closo*-$[B_{11}H_{11}]^{2-}$ analogue, a consideration that is at present adequately dealt with elsewhere using examples from metalladicarbaborane chemistry.[12,20]

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Supplementary Material Available: For compounds **2** and **3**, tables of atomic positional parameters, interatomic distances and angles, thermal parameters, and data collection parameters (18 pages); listings of structure factors (16 pages). Ordering information is given on any current masthead page.

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(19) NMR $\delta(^{11}B)$ values (in ppm relative to $F_3B{\cdot}OEt_2$) for [*arachno*-6,9-CSB_8H_{12}] (compound **1**): B(2) +10.7, B(4) +6.1, B(8,10) −12.6, B(5,7) −21.6, B(1,3) −34.1 ($CDCl_3$ solution, data from ref 2).

(20) Kennedy, J. D.; Nestor, K.; Štíbr, B.; Thornton-Pett, M.; Zammitt, G. S. A. *J. Organomet. Chem.*, in press (Alwyn G. Davies special edition).