Metallaboranes

Synthesis and Characterization of [*exo*-$BH_2(Cp^*M)_2B_9H_{14}$] (M = Ru, Re), and the Conversion of the Ruthenaborane into [$(Cp^*Ru)_2B_{10}H_{16}$] with an Open Cluster Framework Based on a Capped Truncated Tetrahedron**

*Sundargopal Ghosh, Bruce C. Noll, and Thomas P. Fehlner**

The evolution of main-group and transition-metal cluster structural chemistry since the development of the electron-counting rules in the 1970s is an important achievement of modern inorganic chemistry.[1,2] The useful connection between cluster geometry and electronic structure defined by the electron counting rules provides a solid foundation for the rational approach to larger clusters and nanoparticle systems that lie between small clusters and bulk crystalline materials with extended structures.[3]

Given the firm connection between the cluster-electron count and the cluster geometry for subicosahedral main-group clusters, it could be assumed that the structures of clusters based on supraicosahedral frameworks will provide similar unambiguous information. Not so. For example, 14 skeletal electron pair (sep), 12-fragment heteroatomic clusters with carbon or carbon plus a transition metal exhibit at least five different open cluster shapes depending on heteroatom content.[4–6] Even the structure of the 13-vertex closed carborane cluster, $1,2\text{-}\mu\text{-}C_6H_4(CH_2)_2\text{-}3\text{-}Ph\text{-}1,2\text{-}C_2B_{11}H_{10}$, is a variant of the docosahedral structure found by calculations most stable for the 13-vertex homonuclear borane (Scheme 1).[7] In this case, the additional stabilization achieved by generating vertices of connectivity four for the carbon centers more than compensates for that lost in converting a diamond into a rhombus arrangement. Thus for supraicosahedral clusters, the energy differences between possible geometries are much smaller than for subicosahedral clusters and the stabilization achieved by accommodating the properties of hetero atoms determines the observed cluster shape.

Herein novel boron-rich metallaboranes with geometries based on supraicosahedral frameworks provide a carbon-free comparison and demonstrate further structural types. These observations do not define the basic supraicosahedral framework structures for homonuclear boranes even though more of the structures accessible can be mapped out empirically. In addition, provided barriers for interconversion are large relative to room-temperature, intermediates in the cluster-building process are also likely to be isolated. As shown below, this characteristic of supraicosahedral cluster frameworks has allowed us to isolate and characterize a metallaborane with an unusual structure and to demonstrate that it is an intermediate in the boron cluster framework expansion reaction.

In terms of systematic cluster expansion, the most versatile metal is rhenium where known Re_2B_n frameworks run from $n = 4$ to 10.[8] Ruthenium offers fewer compounds[9,10] but revisiting both systems utilizing large BH_3 excess and forcing conditions permits the isolation of three different compounds with the molecular formula [$Cp^*_2M_2B_{10}H_{16}$], M = Ru or Re, $Cp^* = C_5Me_5$. With formal electron counts of 14 and 13 sep they offer an interesting case study for electron counting/supraicosahedral cluster relationships.

The structure of [$Cp^*_2Ru_2B_{10}H_{16}$] (**1**) is shown in Figure 1.[11] The presence of an exopolyhedral boron atom (B11) is clear from the structure solution and the assigned positions of the associated hydrogen atoms (not all found) are completed by two dimensional ^1H–^{11}B NMR spectroscopy experiments. The principal cluster framework of **1** contains one vertex of connectivity six occupied by a ruthenium atom; hence, it can be derived from a 13-vertex docosahedron that is missing two vertices of connectivity five and six. This is the geometry adopted by many 14 sep, 12 fragment metallacarboranes (one vertex of connectivity six unoccupied); however, the formal electron count of **1** is only 13 sep (the

---

[*] S. Ghosh, B. C. Noll, Prof. T. P. Fehlner
Department of Chemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 504-631-7234
E-mail: fehlner.1@nd.edu

[**] This work was supported by the National Science Foundation (CHE-0304008); $Cp^* = \eta^5\text{-}C_5Me_5$.

© 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/ange.200500343

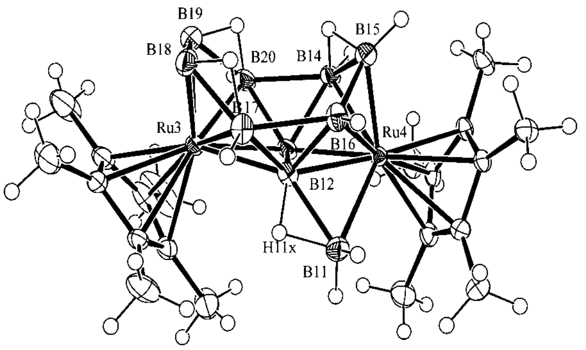


Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°]: Ru3-B18 2.121(7), Ru4-B15 2.103(7), B14-B20 1.948(9), B16-B17 1.976(9), B12-B16 1.811(9); B18-Ru3-B19 49.4(3), B15-Ru4-B14 51.5(3), B11-Ru4-B12 48.2(2), Ru3-B12-B11 142.0(4), B19-B20-B14 120.5(5).

bridging BH_2 unit adds one electron). Some ways by which transition metals can stabilize framework geometries with vertices of high connectivity have been discussed and the susceptibility of these large clusters to secondary factors, such as heteroatom effects, has been pointed out above.[8]

The external BH_2 fragment of **1** bridges a B–Ru edge and is bonded to the boron atom B12 by a B-H-B bridge, that is, the boron atom B12 has no terminal hydrogen atom. On heating, **1** slowly converts exclusively into $[Cp^*{}_2Ru_2B_{10}H_{16}]$ (**2**). The ^{11}B NMR spectrum of **2** exhibits three rather than 10 resonance signals (found for **1**) and none of these signals corresponds to an exopolyhedral borane. Reinsertion of the borane and formation of a cluster framework with higher symmetry is implied and the solid-state structure in Figure 2

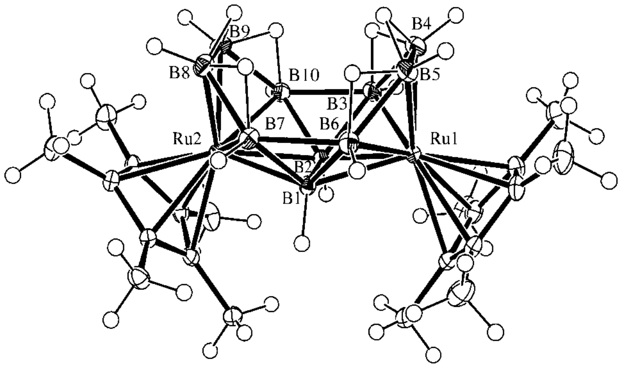
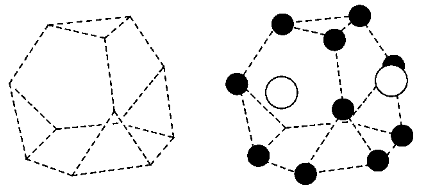


Figure 2. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Ru1-B4 2.129(2), Ru1-B6 2.193(2), B1-B7 1.751(3), B1-B2 1.772(3), B3-B10 1.966(3), B6-B7 1.978(3); B5-Ru1-B3 91.81(8), B3-Ru1-B6 107.82(8), B4-Ru1-B2 89.77(8), B9-Ru2-B10 49.09(8), B8-Ru2-B10 90.69(8), B7-B1-B2 119.03(14).

shows a 12-atom open framework for **2** of C_{2v} symmetry with 6 B-H-B bridges on the open face.[11] The framework can be derived from a capped truncated tetrahedron of a type observed for naked tin clusters in the solid state.[12] As shown in Scheme 1, the two metal atoms occupy two of the four hexagonal faces; the other two hexagonal faces plus the two adjacent three-connect vertices are unoccupied. Like the tetrahedron, this cluster shape requires $n+4$ sep; hence, **2** requires 18 sep whereas formally only 14 sep are available.



Scheme 1. Left: a truncated tetrahedron. Right: representation of a 12-vertex $[Cp^*{}_2Ru_2B_{10}H_{16}]$ framework where two ruthenium atoms cap two of the four hexagonal faces of a truncated tetrahedron and two adjacent 3-connect vertices are missing; ● B, ○ Ru.

$[Cp^*{}_2Re_2B_{10}H_{16}]$ (**3**) was isolated from a reaction mixture that also contains the closed series of compounds $[Cp^*{}_2Re_2B_nH_n]$, the structure of **3** is shown in Figure 3. The heavy-atom framework corresponds to $[exo\text{-}BH_2\text{-}(Cp^*Re)_2B_9H_{14}]$, and is the same as **1** despite the fact that two rhenium atoms provide two fewer valence electrons than two ruthenium atoms![11] The X-ray structure did not provide the positions of any hydrogen atoms but the NMR spectroscopy results suggest, in contrast to **1**, that the boron atom (B6) of the borane bridged B–Re edge forms a B-H-Re bridge to the other rhenium center rather than a B-H-B bridge to the B atom of the exo-BH_2 fragment. Heating **3** under the same conditions as **1** results in the degradation of **3** but no evidence for either rearrangement to a single cage or hydrogen loss to produce $[Cp^*{}_2Re_2B_{10}H_{10}]$ was forthcoming.

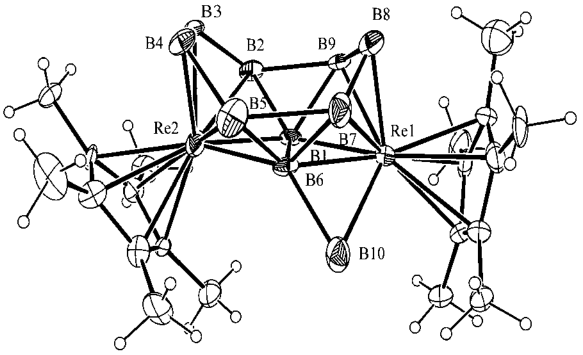


Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Re1-B1 2.15(3), Re1-B7 2.20(4), Re2-B5 2.11(4), B1-B6 1.71(4), B5-B7 2.13(6), B6-B10 1.91(5), B2-B9 1.96(5); B1-Re1-B8 79.9(13), B8-Re1-B6 81.0(15), B8-Re1-B9 48.5(17), B9-B1-Re2 129.7(19), B9-B1-Re1 69.9(14), B6-B5-B4 118(3).

First observed in metallacarborane chemistry,[13] the exopolyhedral BH_2 group now found in both **1** and **3** is likely to be of mechanistic importance in boron fragment growth of metallaboranes. A smaller ruthenacarborane cluster containing a exopolyhedral BH_2 group was shown earlier to be a versatile intermediate. Depending on substituents and conditions, it can undergo reinsertion of the BH_2 bridge, loss of the bridge, or participation of the bridge in external cluster hydroboration to give unusual organoborane cage substituents.[14,15] In principle, then, the same possibilities exist for **1** and **3**. Reversible metal-cluster fragment extrusion is known in metallacarborane chemistry[16] and this mechanistic feature is now shown to apply to main-group-cluster fragments as well. Evidence for its role in other cluster systems can now be sought.

Experimental Section

1: Colorless **1** was isolated by silica gel thin layer chromatography (TLC) with hexane in 12% yield (20 mg) from the products of the reaction of $[(\mathrm{Cp^*Ru})_2\mathrm{B_4H_8}]$ (0.15 g, 0.28 mmol) in toluene (30 mL) with $\mathrm{BH_3{\cdot}THF}$ (10 equiv) at 105 °C for 28 h. MS (FAB) $\mathrm{P^+}$(max) 597 (isotopic pattern for 2 Ru and 10 B atoms), $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{46}{}^{11}\mathrm{B}_{10}{}^{101}\mathrm{Ru}_2$ calcd: 600.2617; obsd: 600.2642. ^{11}B NMR ($\mathrm{C_6D_6}$, 128 MHz, 22 °C): $\delta = 24.9$ (s, br, $J_{\text{B-H}} = 50$ Hz, 1 B-H-B), 18.1 (d, $J_{\text{B-H}} = 126$ Hz, 1 B), 14.7 (br, 1 B), 14.9 (br, 1 B), 11.5 (d, $J_{\text{B-H}} = 140$ Hz, 1 B), 6.5 (d, $J_{\text{B-H}} = 144$ Hz, 1 B), 4.6 (d, $J_{\text{B-H}} = 142$ Hz, 1 B), −0.8 (d, $J_{\text{B-H}} = 128$ Hz, 1 B), −4.9 (br, 1 $\mathrm{BH_2}$), −6.1 ppm (d, $J_{\text{B-H}} = 152$ Hz, 1 B), ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 22 °C): $\delta = 4.18$ (partially collapsed quartet (pcq), 1 $\mathrm{BH_t}$ ($\mathrm{H_t}$ = terminal)), 3.24 (pcq, 1 $\mathrm{BH_t}$), 3.18 (pcq, 2 $\mathrm{BH_t}$), 2.79 (pcq, 1 $\mathrm{BH_t}$), 2.73 (pcq, 1 $\mathrm{BH_t}$), 2.59 (pcq, 1 H of $\mathrm{BH_2}$), 2.44 (pcq, 2 $\mathrm{BH_t}$ and 1 H of $\mathrm{BH_2}$), 1.76 (s, 15 H, 1 Cp*), 1.52 (s, 15 H, 1 Cp*), −0.81 (br, 1 B-H-B); −2.34 (br, 1 B-H-B); −2.97 (br, 1 B-H-B); −3.28 (br, 1 B-H-B); −5.10 (br, 1 B-H-B); −5.24 ppm (br, 1 B-H-B); IR (hexane): $\tilde{\nu} = 2498$w, 2464w $\mathrm{cm^{-1}}$ (B-$\mathrm{H_t}$). Elemental analysis (%) calcd for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{46}{}^{11}\mathrm{B}_{10}{}^{101}\mathrm{Ru}_2$: C 40.25, H 7.77; found: C40.50, H 7.69.

2: Compound **1** (0.05 g, 0.08 mmol) in $[\mathrm{D_6}]$benzene (0.7 mL) heated for 12 days at 80 °C gave colorless **2** (20 mg, 40%) after TLC hexane. MS (FAB) $\mathrm{P^+}$(max) 597 (isotopic pattern for 2 Ru and 10 B atoms), $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{46}{}^{11}\mathrm{B}_{10}{}^{101}\mathrm{Ru}_2$ calcd: 600.2617; obsd: 600.2616. ^{11}B NMR ($\mathrm{C_6D_6}$, 128 MHz, 22 °C): $\delta = 24.8$ (d, $J_{\text{B-H}} = 120$ Hz, 2 B), 14.2 (d, $J_{\text{B-H}} = 122$ Hz, 4 B), 11.2 ppm (d, $J_{\text{B-H}} = 115$ Hz, 4 B); ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 22 °C): $\delta = 3.96$ (pcq, 2 $\mathrm{BH_t}$), 3.49 (pcq, 4 $\mathrm{BH_t}$), 2.88 (pcq, 4 $\mathrm{BH_t}$), 1.62 (s, 30 H, 2 Cp*), −2.77 (br, 4 B-H-B); −3.53 ppm (br, 2 B-H-B); IR (hexane): $\tilde{\nu} = 2504$w, 2476w $\mathrm{cm^{-1}}$ (B-$\mathrm{H_t}$).

3: Brown **3** (0.004 g, 4%) was isolated by TLC with hexane from the products of the reaction of $[(\mathrm{Cp^*Re})_2\mathrm{B_4H_8}]$ (0.1 g, 0.14 mmol) in toluene (30 mL) with $\mathrm{BH_3{\cdot}THF}$ (10 equiv) at 95 °C for 18 h. MS (FAB) $\mathrm{P^+}$(max) 765.45 (isotopic pattern for 2 Re and 10 B atoms), $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{46}{}^{11}\mathrm{B}_{10}{}^{186}\mathrm{Re}_2$ calcd: 765.3544; obsd: 765.3568 (Exact mass calculated for $[M^+-2]$; ^{11}B NMR ($\mathrm{C_6D_6}$, 128 MHz, 22 °C): $\delta = 68.6$ (br, $J_{\text{B-H}} = 50$ Hz, 1 ReHB), 13.2 (d, $J_{\text{B-H}} = 122$ Hz, 1 B), 4.1 (br, 2 B); 2.9 (br, 1 B), 0.25 (br, $J_{\text{B-H}} = 60$ Hz, 1 B), −5.7 (d, $J_{\text{B-H}} = 140$ Hz, 1 B), −8.9 (d, $J_{\text{B-H}} = 142$ Hz, 1 B), −15.3 (d, $J_{\text{B-H}} = 136$ Hz, 1 B), −19.8 ppm (br, 1 $\mathrm{BH_2}$); ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz, 22 °C): $\delta = 4.88$ (pcq, 1 $\mathrm{BH_t}$), 3.84 (pcq, 1 $\mathrm{BH_t}$), 3.66 (pcq, 1 $\mathrm{BH_t}$), 3.41 (pcq, 1 $\mathrm{BH_t}$), 3.11 (pcq, 1 H of $\mathrm{BH_2}$), 3.00 (pcq, 1 H of $\mathrm{BH_2}$), 2.89 (pcq, 1 $\mathrm{BH_t}$), 2.73 (pcq, 1 $\mathrm{BH_t}$), 1.30 (pcq, 1 $\mathrm{BH_t}$), −0.07 (pcq, 1 $\mathrm{BH_t}$), 1.79 (s, 15 H, 1 Cp*), 1.68 (s, 15 H, 1 Cp*), −1.41 (br, 1 B-H-B), −2.22 (br, 1 B-H-B), −3.67 (br, 1 B-H-B), −5.43 (br, 1 B-H-B), −7.06 (br, 1 B-H-B), −15.09 ppm (br, 1 Re-H-B). IR (hexane): $\tilde{\nu} = 2496$w, 2472w $\mathrm{cm^{-1}}$ (B-$\mathrm{H_t}$).

Received: January 28, 2005
Published online: April 13, 2005

Keywords: boron · metallaboranes · rhenium · ruthenium

---

[1] K. Wade, *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 559.

[2] D. M. P. Mingos, *Nature Phys. Sci.* **1972**, *236*, 99.

[3] D. M. P. Mingos, D. J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, New York, **1990**.

[4] J. R. Pipal, R. N. Grimes, *J. Am. Chem. Soc.* **1978**, *100*, 3083.

[5] J. R. Pipal, R. N. Grimes, *Inorg. Chem.* **1979**, *18*, 1936.

[6] K. J. Donaghy, P. J. Carroll, L. G. Sneddon, *J. Organomet. Chem.* **1998**, *550*, 77.

[7] A. Burke, C. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair, A. J. Welch, *Angew. Chem.* **2003**, *115*, 235; *Angew. Chem. Int. Ed.* **2003**, *42*, 225.

[8] L. Guennic, H. Jiao, S. Kahal, J.-Y. Saillard, J.-F. Halet, S. Ghosh, M. Shang, A. M. Beatty, A. L. Rheingold, T. P. Fehlner, *J. Am. Chem. Soc.* **2004**, *126*, 3203.

[9] X. Lei, M. Shang, T. P. Fehlner, *J. Am. Chem. Soc.* **1999**, *121*, 1275.

[10] S. Ghosh, A. M. Beatty, T. P. Fehlner, *Angew. Chem.* **2003**, *115*, 4826; *Angew. Chem. Int. Ed.* **2003**, *42*, 4678.

[11] CCDC-234012, CCDC-234011, and CCDC-251474 (the structures of **1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] S. Bobev, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 3359.

[13] H. Yan, A. M. Beatty, T. P. Fehlner, *Angew. Chem.* **2002**, *114*, 2690; *Angew. Chem. Int. Ed.* **2002**, *41*, 2578.

[14] H. Yan, A. M. Beatty, T. P. Fehlner, *J. Organomet. Chem.* **2003**, *680*, 66.

[15] H. Yan, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2003**, *125*, 16367.

[16] J. A. Belmont, J. Soto, R. E. King III, A. J. Donaldson, J. D. Hewes, M. F. Hawthorne, *J. Am. Chem. Soc.* **1989**, *111*, 7475.