Metallaboranes

Transition-Metal Variation as a Probe of the Origins of Hypoelectronic Metallaboranes: Eight- and Ten-Vertex Open Ruthenaboranes**

*Sundargopal Ghosh, Alicia M. Beatty, and Thomas P. Fehlner**

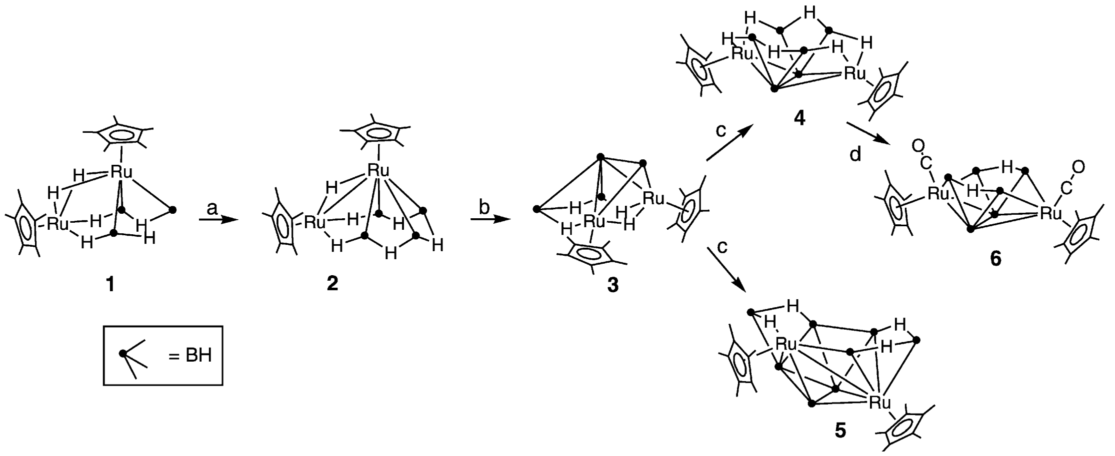
Recently we described a homologous series of closo-rhenaboranes, $[(Cp^*Re)_2B_nH_n]$, $n = 6$–10 ($Cp^* = \eta^5$-C_5Me_5), of unusual shape and skeletal electron count.[1,2] Although related to a larger set of "disobedient" clusters,[3] these compounds are particularly significant as they demonstrate systematic and large deviations from the cluster shape/electron count principle, which has proven satisfactory for understanding the structures of a majority of borane and transition-metal clusters.[4,5] An analysis of this rhenaborane series relative to existing models of electronic structure has appeared.[6] Herein we show that an ability to vary metal identity at near constant stoichiometry provides insight into the role of the metal fragments in the electronic structure of main-group/transition-element clusters.

The thermodynamic control implied by the reaction conditions in the hypoelectronic rhena- and tungstaborane systems,[7] suggests other metallaboranes containing extra hydrogen atoms should be susceptible to condensation. The {Cp*Ru} fragment drew our renewed attention as it has one more electron than the {Cp*Re} fragment and one less electron than the ideal two-electron {Cp*M} fragment, M = Group 9 metal. Loss of the two "extra" metal hydride units from $[(Cp^*RuH)_2B_3H_7]$ (**1**),[8,9] hydrides which are required to make up the seven skeletal electron pairs (sep) associated with the square-pyramidal geometry, might yield compounds with structures bridging the behavior patterns of the Group 7 and Group 9 compounds.

The reactions in Scheme 1 in which **1** is converted into $[(Cp^*Ru)_2B_4H_{10}]$, (**2**) and then $[(Cp^*Ru)_2B_4H_8]$ (**3**), have been discussed earlier.[8] Vigorous heating of **3** with BH_3·THF leads to good yields of two new, stable diruthenaborane clusters. Single-crystal X-ray structure determinations define the cluster geometries which are in full accord with the solution spectroscopic data. The structures of $[(Cp^*RuH_2)_2B_6H_8]$ (**4**) and $[(Cp^*Ru)_2B_8H_{12}]$ (**5**), are shown in Figure 1 and 2.[10] We have been unable to convert **4** into **5** by the addition of borane.

In contrast to most of the dirhenaboranes,[11] **4** and **5** retain bridging hydrogen atoms in the product frameworks and the structures are reminiscent of those of 10 sep B_8H_{12} and 12 sep $B_{10}H_{14}$, respectively.[12] Considering a {Cp*Ru} fragment as a three-orbital, one-electron fragment, the formal electron counts are 10 sep for **4** and 11 sep for **5**: the structure of the former follows the borane analogy whereas the latter is formally one pair short. Note that like **1**, complex **4** contains one "extra" H per {Cp*Ru} fragment relative to the analogous borane whereas **5** does not.

The view of **4** as an "obedient" metallaborane can be tested. For example, we have previously shown that the addition of CO to unsaturated five sep compound $[(Cp^*Cr)_2B_4H_8]$ leads to saturated six sep compound $[(Cp^*CrCO)_2B_4H_6]$[13] whereas addition of CO to saturated six sep $[(Cp^*ReH_2)_2B_4H_4]$ leads to saturated six sep compound $[(Cp^*ReCO)(Cp^*ReH_2)B_4H_4]$].[14] If **4** is indeed a 10 sep saturated cluster, addition of two CO units should lead to $[(Cp^*RuCO)_2B_6H_8]$, which is analogous to $C_2B_6H_{10}$, that is, a {Cp*RuCO} fragment is generated that functions as a three-orbital, three-electron fragment ("into the t_{2g} set").[15] As



Scheme 1. Stepwise conversion of **1** into $[(Cp^*RuH_2)_2B_6H_8]$ (**4**), $[(Cp^*Ru)_2B_8H_{12}]$ (**5**), and $[(Cp^*RuCO)_2B_6H_8]$ (**6**). Conditions: a) 60°, BH_3·THF; b) 90°; c) 95°, BH_3·THF; d) 55°, $[Co_2(CO)_8]$. The structures shown are schematic representations, —H— indicates an H-bridged bond.

---

[*] Prof. Dr. T. P. Fehlner, Dr. S. Ghosh, Dr. A. M. Beatty
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 574-631-6652
E-mail: fehlner.1@nd.edu

[**] The support of the National Science Foundation (CHE99-86880) is gratefully acknowledged. We thank Prof. Bruce King for helpful discussions.

DOI: 10.1002/ange.200352101

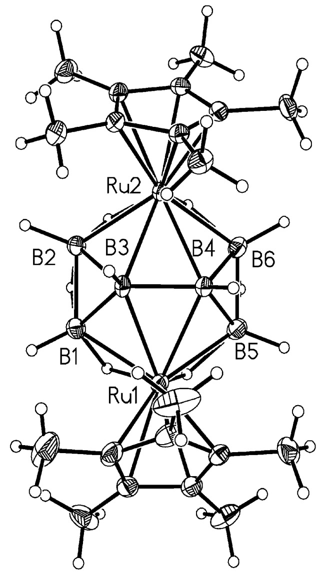


Figure 1. Molecular structure of **4**. Selected bond lengths [Å]: Ru1-B5 2.208(5), B1-B2 1.734(6), Ru2-B2 2.200(4).

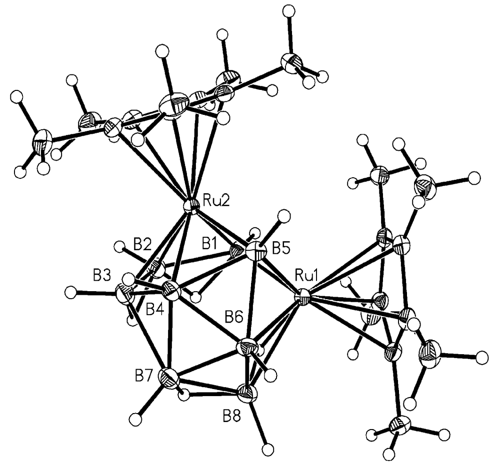


Figure 2. Molecular structure of **5**. Selected bond lengths [Å]: Ru1-B1 2.158(2), Ru1-B8 2.207(2), Ru1-B6 2.288(2), Ru1-Ru2 2.8897(2), B3-B4 1.758(3), B3-B7 2.014(3).

shown in Scheme 1, addition of CO to **4** does lead to $[Cp^*RuCO)_2B_6H_8]$ (**6**; Figure 3) corroborating the assignment of the {Cp*Ru} fragment in **4** as a three-orbital, one-electron fragment.

This analysis of **4** serves as a basis for understanding **5**. The framework geometry of **5** resembles that of $B_{10}H_{14}$ except that the diamond in the cluster framework containing the two ruthenium atoms has undergone a diamond-square-diamond (dsd) rearrangement thereby increases the connectivity of the ruthenium sites to five and six and decreases the connectivities of the two boron sites correspondingly (Figure 4).[16] Based on our previous analysis of $[(Cp^*Cr)_2B_4H_8]$,[17,18] we suggest that a pair of occupied “t_{2g}” ruthenium orbitals of bonding symmetry interact to form a lower-energy filled bonding and higher-energy unfilled antibonding orbital with-

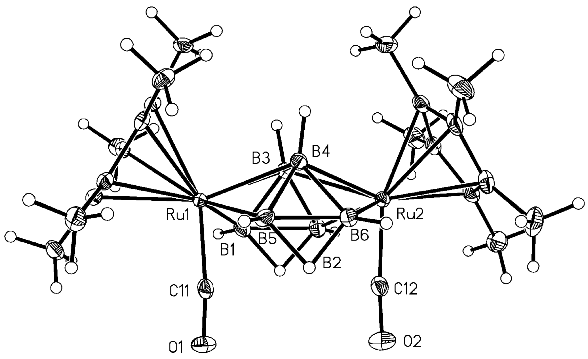


Figure 3. Molecular structure of **6**. Selected bond lengths [Å]: Ru1-B1 2.174(3), Ru1-B4 2.277(3), B2-B3 1.726(4), B5-B6 1.693(4). The torsion angle between Ru1-C11 and Ru2-C12 is −0.8°

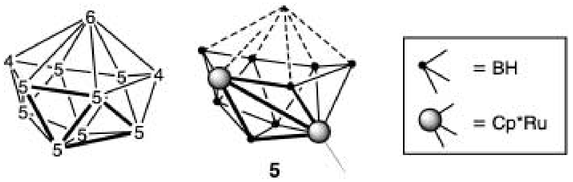


Figure 4. The observed geometry of **5** is generated by removing the connectivity-six vertex from an octadecahedron and by performing one dsd rearrangement.

out strongly perturbing the energies of orbitals of high boron content. It is the dsd rearrangement that makes possible the utilization of a pair of metal “t_{2g}” orbitals.

Earlier analyses of metallaboranes with low sep and geometries related by dsd rearrangements to geometries of analogous boranes has led to competing descriptions which differ in the manner in which the valence electron density is partitioned. One, with the designation iso- (closo, nido, or arachno), requires the normal cluster-electron count to be met.[3,19,20] To do so, the metal fragment utilizes one of its nonbonding sets; something that is seen to occur in organometallic compounds.[15,21] The second description, with the designation hyper-closo, requires the metals to be restricted to a three-orbital contribution to cluster bonding.[22] In this case it is the change in shape that adjusts the number of cluster bonding orbitals or, more precisely, the number of unfilled antibonding orbitals.[23,24] The analysis of **5** can be equally well described as the generation of another unavailable orbital (the M–M antibonding orbital) or as the generation of another pair of electrons for the cluster bonding network from the “t_{2g}” set albeit involving both metals (the M–M bonding orbital). The approaches are the same and can both be described by the term hypoelectronic.[16,25]

Diruthenaborane **5** possesses two {Cp*Ru} fragments which must be counted differently if the electron-counting rules are to be satisfied. This flaw originates in partitioning electrons between cluster bonding and all other filled orbitals by using a main-group-atom model. Transition-metal fragments will not be constrained to the monolithic behavior of main-group fragments.

Experimental Section

Synthesis of **4** and **5**: [$(Cp^*Ru)_2B_4H_8$] (**3**; 0.15 g, 0.28 mmol) in toluene (15 mL) was heated with sixfold excess of $BH_3{\cdot}THF$ (1.73 mL, 1.73 mmol) at 95 °C for 16 h. After filtration, the residue was subjected to thin layer chromatography (TLC) on silica gel plates. Elution with hexane:CH_2Cl_2 (75:25 v/v) yielded two well-separated bands: yellow **4** (0.08 g, 52 %); red **5** (0.05 g, 36 %).

Selected data for **4**: MS (FAB) P^+(max) 547 (isotopic pattern for 2 Ru and 6 B atoms), $^{12}C_{20}{}^{1}H_{42}{}^{11}B_6{}^{101}Ru_2$, calcd: 550.1775; obsd: 550.1797 (exact mass calculated for [M^+-2]); ^{11}B NMR (C_6D_6, 400 MHz, 22 °C): $\delta = 37.87$ (d, $J_{B\text{-}H} = 110$ Hz, 4 B), 1.19 ppm (d, $J_{B\text{-}H} = 116$ Hz, 2 B); ^{1}H NMR (C_6D_6, 400 MHz, 22 °C): $\delta = 6.39$ (partially collapsed quartet (pcq), 4 BH_t (t = terminal)), 2.33 (pcq, 2 BH_t), 1.67 (s, 30 H, 2 Cp*), −0.67 (s, br, 2 B-H-B), −13.55 ppm (s, br, 4 Ru-H-B); IR (hexane): $\tilde{\nu} = 2529$ w, 2449 cm^{-1} w (B-H_t).

Selected data for **5**: MS (FAB) P^+(max) 567 (isotopic pattern for 2 Ru and 8 B atoms), $^{12}C_{20}{}^{1}H_{42}{}^{11}B_8{}^{101}Ru_2$, calcd: 571.1805; obsd: 571.1851 (exact mass calculated for [M^+-4]); ^{11}B NMR (C_6D_6, 400 MHz, 22 °C): $\delta = 109.17$ (d, $J_{B\text{-}H} = 145$ Hz, 1 B), 63.11 (d, $J_{B\text{-}H} =$ 125 Hz, 1 B), 33.66 (d, $J_{B\text{-}H} = 123$ Hz, 1 B), 16.22 (d, $J_{B\text{-}H} = 114$ Hz, 1 B), 13.51 (d, $J_{B\text{-}H} = 125$ Hz, 1 B), 9.13 (d, $J_{B\text{-}H} = 128$ Hz, 1 B), 2.16 (d, $J_{B\text{-}H} = 137$ Hz, 1 B), −27.24 ppm (d, $J_{B\text{-}H} = 136$ Hz, 1 B); ^{1}H NMR (C_6D_6, 400 MHz, 22 °C): $\delta = 9.86$ (pcq, 1 BH_t), 6.18 (pcq, 1 BH_t), 5.56 (pcq, 1 BH_t), 5.36 (pcq, 1 BH_t), 3.41 (pcq, 1 BH_t), 3.05 (pcq, 1 BH_t), 2.58 (pcq, 1 BH_t), 1.28 (pcq, 1 BH_t), 1.60 (s, 15 H, 1 Cp*), 1.44 (s, 15 H, 1 Cp*), 0.83 (s, br, 1 B-H-B), −0.41 (s, br, 1 B-H-B), −2.40 (s, br, 1 B-H-B), −17.09 ppm (s, br, 1 Ru-H-B): IR (hexane): 2494 w, 2449 cm^{-1} w (B-H_t).

6: **4** (0.15 g, 0.27 mmol) in hexane (15 mL) was stirred with [$Co_2(CO)_8$] (0.47 g, 1.36 mmol) for 5 h at 55 °C. Extraction in hexane, filtration through silica gel, and TLC (hexane:CH_2Cl_2 7:3) yielded **6** (0.07 g, 44 %). MS (FAB) P^+(max) 600 (isotopic pattern for 2 Ru and 6 B atoms), $^{12}C_{22}{}^{1}H_{38}{}^{11}B_6{}^{101}Ru_2{}^{16}O_2$, calcd: 604.1517, obsd: 604.1534; ^{11}B NMR (C_6D_6, 400 MHz, 22 °C): $\delta = 52.54$ (d, $J_{B\text{-}H} = 135$ Hz, 4 B), 6.68 ppm (d, $J_{B\text{-}H} = 115$ Hz, 2 B); ^{1}H NMR (C_6D_6, 400 MHz, 22 °C): = 7.18 (pcq, 4 BH_t), 1.53 (pcq, 2 BH_t), 1.66 (s, 30 H, 2 Cp*), −0.05 ppm (s, br, 2 B-H-B); ^{13}C NMR (C_6D_6, 300 MHz, 22 °C): $\delta = 201.5$ (Ru-CO), 100.8 ($C_5(CH_3)_5$), 9.6 ppm ($C_5(CH_3)_5$); IR (hexane): $\tilde{\nu} = 2488$ w, 2415 w (B-H_t), 1967.1 s, 1942.9 cm^{-1} w (Ru-CO) with calculated dihedral angle between the CO units = 20°.

Received: June 10, 2003 [Z52101]

Keywords: boranes · cluster compounds · electronic structure · metallaboranes · ruthenium

---

[1] S. Ghosh, M. Shang, Y. Li, T. P. Fehlner, *Angew. Chem.* **2001**, *113*, 1159; *Angew. Chem. Int. Ed.* **2001**, *40*, 1125.

[2] S. Ghosh, A. M. Beatty, T. P. Fehlner, *J. Am. Chem. Soc.* **2001**, *123*, 9188.

[3] J. D. Kennedy in *The Borane, Carborane, Carbocation Continuum* (Ed.: J. Casanova), Wiley, New York, **1998**, p. 85.

[4] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

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

[6] H. Wadepohl, *Angew. Chem.* **2002**, *114*, 4394; *Angew. Chem. Int. Ed.* **2002**, *41*, 4220.

[7] A. S. Weller, M. Shang, T. P. Fehlner, *Organometallics* **1999**, *18*, 853.

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

[9] Y. Kawano, H. Matsumoto, M. Shimoi, *Chem. Lett.* **1999**, 489.

[10] CCDC-211168, CCDC-211169, and CCDC-211884 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] S. Ghosh, A. L. Rheingold, T. P. Fehlner, *Chem. Commun.* **2001**, 895.

[12] R. E. Williams in *The Borane, Carborane, Carbocation Continuum* (Ed.: J. Casanova), Wiley-Interscience, New York, **1997**, p. 3.

[13] J. Ho, K. J. Deck, Y. Nishihara, M. Shang, T. P. Fehlner, *J. Am. Chem. Soc.* **1995**, *117*, 10292.

[14] S. Ghosh, X. Lei, C. L. Cahill, T. P. Fehlner, *Angew. Chem.* **2000**, *112*, 3022; *Angew. Chem. Int. Ed.* **2000**, *39*, 2900.

[15] R. Hoffmann, *Science* **1981**, *211*, 995.

[16] T. P. Fehlner, *Adv. Chem.* **2002**, *822*, 49.

[17] T. P. Fehlner, *J. Organomet. Chem.* **1998**, *550*, 21.

[18] T. P. Fehlner, *J. Chem. Soc. Dalton Trans.* **1998**, 1525.

[19] J. D. Kennedy, *Inorg. Chem.* **1986**, *25*, 111.

[20] R. B. King, I. Silaghi-Dumitrescu, A. Kun, *Inorg. Chem.* **2001**, *40*, 2450.

[21] C. Elschenbroich, A. Salzer, *Organometallics*, VCH, New York, **1989**.

[22] R. T. Baker, *Inorg. Chem.* **1986**, *25*, 109.

[23] R. L. Johnston, D. M. P. Mingos, *Inorg. Chem.* **1986**, *25*, 3321.

[24] R. L. Johnston, D. M. P. Mingos, P. Sherwood, *New J. Chem.* **1991**, *15*, 831.

[25] J. D. Corbett, *Struct. Bonding (Berlin)* **1997**, *87*, 157.