Metallaboranes

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Borane Mimics of Classic Organometallic Compounds: $[(Cp^*Ru)B_8H_{14}(RuCp^*)]^{0,+}$, Isoelectronic Analogues of Dinuclear Pentalene Complexes[**]

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

Like carbon, the element boron in combination with hydrogen displays rich catenation chemistry.[1] In contrast to carbon, its structural chemistry must reflect a more complex electronic structure which is associated with having to satisfy the same number of valence functions as carbon with one less electron per atom.[2] Hence, one fascinating aspect of metal-

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

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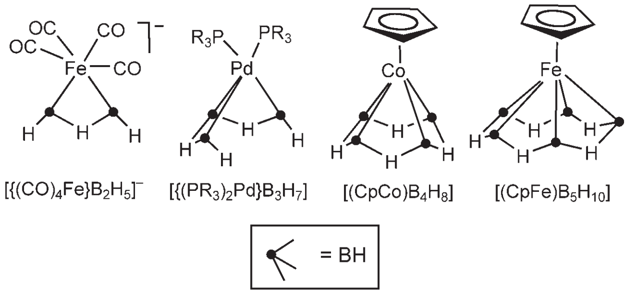
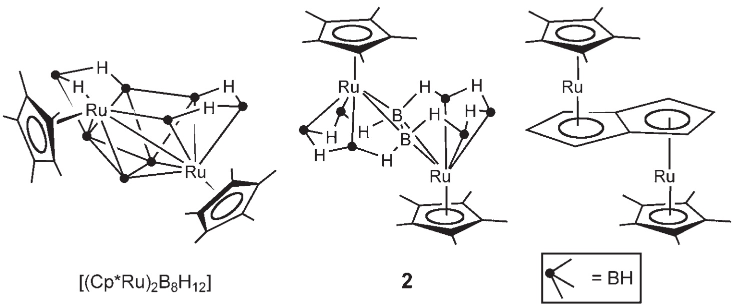
laborane chemistry is that several classic organometallic complexes that defined fundamental structural and bonding paradigms for the field are mimicked by isoelectronic metallaborane analogues.[3] In most cases, the geometric structures can be generated by simply replacing C with B plus B-H-B bridging hydrogen atoms and/or net charge to match the valence electron count. Thus, for analogues of polyhapto π complexes[4] there are: $[(CO)_4Fe(\eta^2\text{-}C_2H_4)]$ versus $[\{(CO)_4Fe\}B_2H_5]^-$;[5] $[(PR_3)ClPd(\eta^3\text{-}C_3H_5)]$ versus $[\{(PR_3)_2Pd\}B_3H_7]$;[6] $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4H_4)]$ versus $[\{(\eta^5\text{-}C_5H_5)Co\}B_4H_8]$;[7] and $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_5)]$ versus $[\{(\eta^5\text{-}C_5H_5)Fe\}B_5H_{10}]$[8] (Scheme 1).



Scheme 1. A selection of metallaboranes with borane fragments that are analogous to π ligands in organometallic complexes. $Cp = \eta^5\text{-}C_5H_5$.

Related are polyhapto organic ligands capable of binding two metal centers. In these complexes the metal–metal interactions are of significant interest particularly when mixed-valence organometallic complexes may be formed.[9] In particular, the chemistry of dinuclear metal complexes of pentalene, C_8H_6, (Scheme 2) has been developed extensively because the strength of the electronic coupling between the two metal centers can be larger than that found in cationic Werner complexes such as the Creutz–Taube ion.[10–12] Herein, we present the synthesis and characterization of borane analogues of $[Cp^*Ru(pentalene)RuCp^*]^{0,+}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) where the monocation is a mixed-valence complex.



Scheme 2. Schematic drawings of the structures of polyhedral $[(Cp^*Ru)_2B_8H_{12}]$, pentalene analogue **2**, and $[Cp^*Ru(pentalene)RuCp^*]$.

Recently we have shown that the reaction of $[(Cp^*Ru)_2B_3H_9]$ with $BH_3{\cdot}THF$ leads to metallaboranes containing six, eight, and ten boron atoms.[13,14] The ten boron atom cluster has two colorless isomeric forms, one with an exo-cluster borane atom on a Ru_2B_9 cluster framework. This species was shown to be an intermediate on the path to the second isomer which has a Ru_2B_{10} cluster framework. Given the importance of this isomer pair in defining the broad mechanistic outlines of the cluster-building process, we have investigated this system more extensively for the presence of additional colorless products that may be intermediates in the cluster-building process. This approach has led to the isolation of $[(1\text{-}Cp^*Ru)B_5H_{10}]$ (**1**; in which the Cp*Ru fragment occupies the 1-position of the BH cage) and $[(Cp^*Ru)B_8H_{14}(RuCp^*)]$ (**2**). Metallabarane **2** converts into the isomer pair $[(Cp^*Ru)_2B_{10}H_{16}]$[14] on heating in the presence of $BH_3{\cdot}THF$ showing that it is indeed another intermediate in the cluster-building process.

Although separated initially from the other reaction products as a mixture, both **1** and **2** are insensitive to air and moisture and can be separated by careful thin-layer chromatography on the laboratory bench by using UV light for detection. Mass spectrometric data for **1** yield the composition $C_{10}H_{25}RuB_5$ which suggests a molecular formulation of $Cp^*RuB_5H_{10}$. In addition to 15 Cp* protons, the ^1H NMR spectrum of **1** shows one resonance at $\delta = 2.71$ ppm arising from five terminal hydrogen atoms and one resonance at $\delta = -4.05$ ppm for five bridging hydrogen atoms. In the ^{11}B NMR spectrum of **1**, the high symmetry is confirmed by the observation of a single doublet at $\delta = -0.6$ ppm which collapses to a sharp singlet upon proton decoupling. No suitable crystals for structure determination were obtained but, given the similarity of the spectroscopic data to those of $[(CpFe)B_5H_{10}]$ (Scheme 1),[8] **1** is proposed to be 1-ruthenahexaborane, a borane analogue of ruthenacene.

The mass spectroscopic data for **2** showed a molecular formula two mass units higher than that of red $[(Cp^*Ru)_2B_8H_{12}]$, a compound which has structure based on a $B_{10}H_{14}$ skeleton which has undergone one diamond-square-diamond (dsd) rearrangement associated with its low formal skeletal electron pair (sep) count of 12 (Scheme 2).[13] With 13 sep does **2** have the structure of $[(Cp^*Ru)_2B_8H_{14}]$ but without the dsd rearrangement? In fact, the three resonances in the intensity ratio 2:2:4 found in the ^{11}B NMR spectrum would be consistent with such a structure if the metals occupied the 2,4-positions. However, the six terminal and eight B-H-B bridging hydrogen atoms suggested by the ^1H NMR spectrum are not consistent with this cluster shape and heating **2** in the absence of $BH_3{\cdot}THF$ did not produce $[(Cp^*Ru)_2B_8H_{14}]$.

A solid-state structure determination of **2** (Scheme 2 and Figure 1)[15] revealed an unexpected geometry. It could be viewed as two ruthenaborane cages of **1**, fused in a transoid fashion with two common boron atoms, to give a planar B_8 fragment, and eight B-H-B bridges on the eight available edges. It is, in fact, a structure analogous to those of isoelectronic dinuclear pentalene complexes $[Cp^*M(C_8H_6)MCp^*]$, M = Fe, Ru (Scheme 2).[10,16] In **2** the ruthenium atoms are bonded symmetrically to the Cp* ligands (Ru–C 2.04 Å av) but the binding to the five-membered boron rings is not quite symmetric (Ru–B 2.15 Å av versus Ru–BH 2.10 Å av). This asymmetry is also found in structures of dinuclear pentalene complexes.[10]

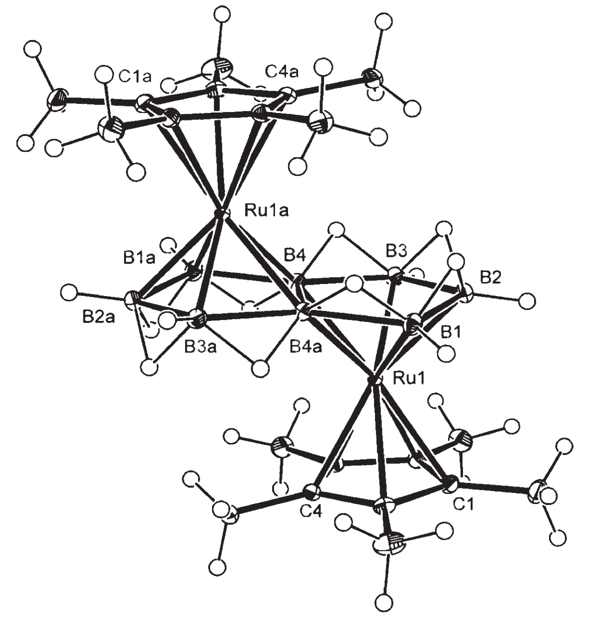
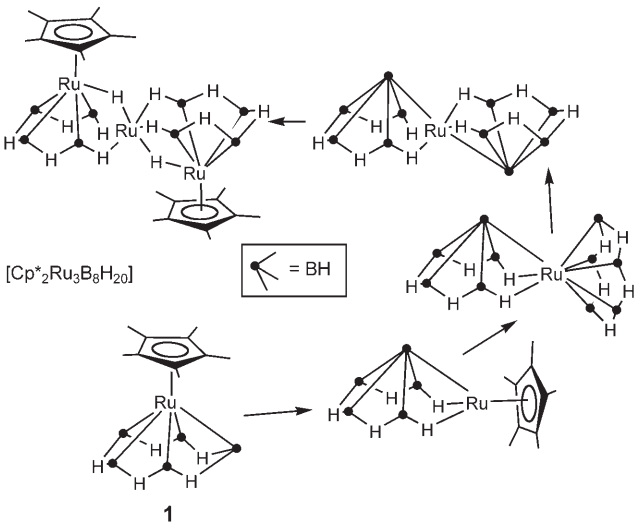


Figure 1. X-ray structure of **2**. Selected interatomic distances [Å] and angles [°]: Ru1-B1 2.1115(10), Ru1-B2 2.1076(10), Ru1-B3 2.1067(10), Ru1-B4 2.1491(9), B1-B2 1.8204(15), B2-B3 1.8233(15), B3-B4 1.8274(14), B1a-B4 1.8232(14), B1-B4a 1.8232(14), B4-B4a 1.8198(18); B2-Ru1-B1 51.12(4), B2-Ru1-B4 85.39(4), B3-Ru1-B4a 88.55(4), B2-B1-B4a 104.84(7), Ru1-B4-Ru1a 129.94(4), B3-B4-Ru1a 136.54(6), B4a-B4-B3 109.22(8), B1a-B4-B3 141.75(7).

There is another known ruthenaborane related to both **1** and **2**. It has the formula $Cp^*_2Ru_3B_8H_{20}$ and a structure corresponding to *commo*-[{1-(Cp^*Ru)(μ-H)B_4H_9}$_2$Ru] as shown in Scheme 3.[17] Viewed as a pair of fused pentagonal pyramidal clusters with one common atom, it is a structural variation on **2**. But a relationship to **1** follows from the retro isolobal synthesis shown in Scheme 3 based on the following connections: {Cp^*Ru}+H is equivalent to BH; {1-(Cp^*Ru)B_5H_{10}} is an analogue of ruthenacene; and {2-(Cp^*Ru)B_5H_{10}} is an accessible isomer of {1-(Cp^*Ru)B_5H_{10}}. Hence, although the production of the pentalene analogue **2** from a ruthenaborane cluster and its conversion into a larger ruthenaborane cluster may seem bizarre, the analysis in Scheme 3 is a reminder that forms analogous to organometallic complexes are just one structural guise available to chameleonic metallaboranes.



Scheme 3. A retro-isolobal analysis showing the relationship between ruthenacene analogue **1**, and the *commo*-cluster [$Cp^*_2Ru_3B_8H_{20}$].

In addition to conceptual connections to pentalene dinuclear complexes, there are real chemical connections to **2**. In its cyclic voltammogram, [$Cp^*Ru(C_8H_6)RuCp^*$] exhibits one reversible oxidation wave and an irreversible wave at 0.29 V higher potential.[10] The irreversible behavior is attributed to the oxidation reaction of the Cp* ligand and is analogous to the behavior of [Cp^*_2Ru] on oxidation.[18] Likewise **2** exhibits two successive one-electron oxidations separated by approximately 0.8 V. The first redox event $\mathbf{2}^0/\mathbf{2}^+$ is quasireversible, but the second oxidation $\mathbf{2}^+/\mathbf{2}^{2+}$ is not reversible as shown by the lack of a return wave. The larger ΔE observed for **2** compared to the pentalene analogue may result from a stronger interaction between the metal centers as well as more extensive delocalization in the mixed-valence $\mathbf{2}^+$ form.[19] If so, the greater delocalization found for the borane analogue of [$Cp^*Ru(C_8H_6)RuCp^*$]$^+$ is consistent with a better match of frontier-orbital energies of the borane and ruthenium fragment energies than of the pentalene and ruthenium fragment energies.

The B_8H_{14} fragment of **2** is a true analogue of the η^5-η^5-pentalene ligand. However, comparison with two related ruthenaboranes both containing eight boron atoms, [$(Cp^*Ru)_2B_8H_{14}$] and *commo*-[{1-(Cp^*Ru)(μ-H)B_4H_9}$_2$Ru], reveals once more the versatility of the boron/hydrogen element combination in accommodating the electronic requirements of a set of metal fragments.

Experimental Section

1 and **2**: [$(Cp^*Ru)_2B_3H_9$] (0.19 g, 0.369 mmol) in toluene (25 mL) was stirred with 10 equivalent of BH_3·THF (3.7 mL, 3.69 mmol) for 20 h at 100 °C. The solvent was removed in vacuo; the residue was extracted in hexane/CH_2Cl_2, (2:8, v/v) and the filtrate was purified by chromatography on silicagel TLC plates. Elution with pure hexane yielded **1** (0.004 g, 4 %) and **2** (0.05 g, 26 %).

Selected data for **1**: MS (FAB) P^+(max) 293 (isotopic pattern for 1Ru and 5B atoms), exact mass; calcd for [$C_{10}H_{24}B_5Ru$]$^+$ fragment ion as weighted average of isotopomers lying within the instrument resolution 302.1465, obsd 302.1483. ^{11}B NMR (C_6D_6, 22 °C, 128 MHz): $\delta = -0.6$ ppm (d, $J_{B\text{-}H} = 151$ Hz, 5B); ^{1}H NMR (C_6D_6, 22 °C, 400 MHz): $\delta = 2.71$ (partially collapsed quartet (pcq), $5BH_t$), 1.80 (s, 15H, Cp*), −4.05 ppm (br, 5B-H-B); IR (hexane): $\tilde{\nu} = 2502$w, 2428w cm^{-1} (B-H_t). Several attempts to grow X-ray quality crystals of **1** failed. All attempts generated very thin hair-like crystals that gave data sets with no viable solution.

Selected data for **2**: MS (FAB) P^+(max) 567 (isotopic pattern for 2Ru and 8B atoms), exact mass; calcd for [$C_{20}H_{36}B_8Ru_2$]$^+$ fragment ion as weighted average of isotopomers lying within the instrument resolution 569.1727, obsd 569.1702; ^{11}B NMR (C_6D_6, 22 °C, 128 MHz): $\delta = 11.2$ (d, $J_{B\text{-}H} = 147$ Hz, 2B), −0.7 (d, $J_{B\text{-}H} = 143$ Hz, 2B-H*t*), −3.1 ppm (d, $J_{B\text{-}H} = 148$ Hz, 4B-H*t*); ^{1}H NMR (C_6D_6, 22 °C, 400 MHz): $\delta = 3.03$ (pcq, $4BH_t$), 2.41 (pcq, $2BH_t$), 1.68 (s, 30H, 2Cp*), 0.02 (pcq, 4B-H-B); −4.44 ppm (pcq, 4B-H-B); IR (hexane): $\tilde{\nu} = 2508$ w, 2478w cm^{-1} (B-H*t*); elemental analysis calcd (%) for $C_{20}H_{44}B_8Ru_2$, C 41.91, H. 7.74; found: C 40.95, H 7.42.

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The cyclic voltammetry of **2** was carried out in CH_2Cl_2/toluene (8.5:1.5 v/v) as scan rates of 50–100 $mV\,s^{-1}$ using a Pt working electrode, Pt plate counter electrode, and Pt wire pseudo reference electrode, and 0.1M Bu_4NPF_6 as supporting electrolyte. Under these conditions the ferrocene/ferrocenium ion couple appears at 0.46 V. For a scan from −0.8 to 0.6 V at 50 $mV\,s^{-1}$, the $\mathbf{2}^0/\mathbf{2}^+$ couple is found at 0.17 V ($E_{1/2} = 0.258$, 0.085 V) and in a scan from −0.2 to 1.2 V at 50 $mV\,s^{-1}$, the difference in the half wave potentials for $\mathbf{2}^0 \rightarrow \mathbf{2}^+$ and $\mathbf{2}^+ \rightarrow \mathbf{2}^{2+}$ is 0.76 V.

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[15] Crystal structure data for **2** ($C_{20}H_{44}B_8Ru_2$): Crystal size, $0.36 \times 0.27 \times 0.11\ mm^3$, triclinic, space group: $P\bar{1}$. Unit cell dimensions, $a = 8.6697(1)$, $b = 10.9546(1)$, $c = 14.3313(2)$ Å, $\alpha = 110.559(1)$, $\beta = 95.017(1)$, $\gamma = 94.021(1)°$; $Z = 2$, ρ_{calcd} 1.508 $Mg\,m^{-3}$. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0175$, $wR2 = 0.0426$, R indices (all data) $R1 = 0.0208$, $wR2 = 0.0460$. Goodness-of-fit on F^2 1.130. Crystals were examined under light hydrocarbon oil. Cell parameters were determined using reflections harvested from three sets of 20 0.3° ω scans and refined using 9065 reflections with $I \geq 10\sigma(I)$ and $2.37° \leq \theta \leq 36.44°$ from the entire data collection. The asymmetric unit consists of two half-molecules; each is completed by inversion. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. CCDC-275048 (**2**) contains 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.
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