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Communications

Synthesis and Characterization of $(Cp^*Ru)_3Co(CO)_2(\mu_3\text{-}CO)B_3H_3$ ($Cp^* = \eta^5\text{-}C_5Me_5$): A Metallaborane with Cubane Cluster Structure

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Summary: Addition of a cobalt carbonyl fragment to $(Cp^*Ru)_3(\mu\text{-}H)_2B_3H_6$ leads to hydrogen loss and formation of the highly condensed $(Cp^*Ru)_3Co(CO)_2(\mu_3\text{-}CO)B_3H_3$ cluster. Viewed as a 60-electron tetranuclear metal cluster with six M−M bonds, it completes the series: 64-electron $(CpCo)_4B_4H_4$ with four M−M bonds; 68-electron $(CpNi)_4B_4H_4$ with two M−M bonds.

The cluster electron counting rules[1,2] and the concept of transition-metal fragments isolobal with a B−H fragment[3,4] permit the vast majority of metallaborane structures to be simply related to the composition of the compound.[5−9] However, isolobal does not mean identical, and there are instances in which a given cluster structure is not easily rationalized in such a fashion.[10] Two examples of metallaboranes from Grimes' laboratory are $(CpNi)_4B_4H_4$ (**1**) and $(CpCo)_4B_4H_4$ (**2**).[11,12] Both exhibit a *closo*-dodecahedral cluster geometry (Chart 1) which requires nine skeletal electron pairs (sep). They differ in the sense that the cobalt compound has the metal atoms occupying the four five-coordinate vertexes whereas the nickel compound has the metal atoms occupying the four four-coordinate vertexes. As the former metallaborane possesses eight sep and the latter ten sep, these compounds have been the subject of a number of studies seeking to rationalize the structures with electron counts.[13−15] The recent synthesis and characterization of dodecahedral $(CpFe)_4C_4H_4$ (represented in the paper as $Cp_4Fe_4(HC{\equiv}CH)_4$), which is isoelectronic and isostructural with **2**, show that the problem is not peculiar to boron.[16]

In his review, Kennedy[7] drew a connection between **1** and **2** and the well-studied class of tetranuclear metal complexes M_4X_4 known as cubanes.[17] Two fragment analyses have been productive. In one[18] the focus is on the properties of the complete M_4X_4 core surrounded by

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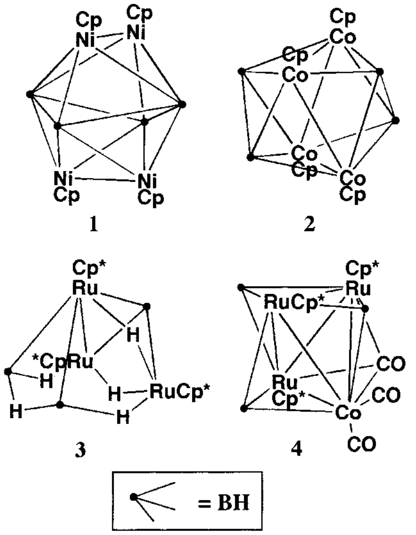
Chart 1



ancillary metal ligands, whereas the other[19] begins with the appropriate ML_n geometry and describes the perturbation of the four mononclear metal complexes on formation of the cubane cluster. Both emphasize the importance of the high-lying metal-based orbitals in relating structure to electron count. Hence, Kennedy described **1** as a 68-electron cluster with two Ni−Ni bonds and **2** as a 64-electron cluster with four Co−Co bonds. Further, he suggested that the putative $(CpFe)_4B_4H_4$ cluster with 60 electrons should exhibit a cubane structure with six Fe−Fe bonds and a fully bonded metal tetrahedron. We now report an example of a 60-electron tetrametal metallaborane that verifies this prediction, thereby demonstrating that it is the population of the metal-centered bonding, antibonding, and nonbonding orbital manifold that constitutes the driving force behind the unusual geometrical structures observed for these metallaboranes.

Earlier we reported the isolation of $(Cp^*Ru)_3(\mu\text{-H})_2B_3H_6$ (**3**) as a byproduct of the synthesis of $(Cp^*Ru)_2(\mu\text{-H})_2B_3H_7$ from $[Cp^*RuCl_2]_2$ and $LiBH_4$.[20,21] Although the yield is modest, we have examined the reactivity of **3** relative to metal fragment addition. Reaction with $Fe_2(CO)_9$ led to decomposition, whereas treatment with $Co_2(CO)_8$ gives a single metallaborane product in good yield.[22] The spectroscopic data[23] are consistent with the formulation $(Cp^*Ru)_3Co(CO)_2(\mu_3\text{-CO})B_3H_3$ (**4**), which means that the addition of the three-electron fragment $Co(CO)_3$ to **3** was accompanied by the loss of all five bridging hydrogens. Assuming no fluxional behavior, the ^1H and ^{11}B NMR data show that **4** contains a plane of symmetry. The IR indicates the presence of terminal as well as bridging carbonyl ligands. Compound **4** has six sep, suggesting a structure based on a tetrahedron. With seven cluster fragments to accommodate, this requires a tricapped tetrahedron. Presumably the metal atoms occupy the vertexes of highest connectivity and, thus, BH fragments cap three of the four faces of a metal tetrahedron.

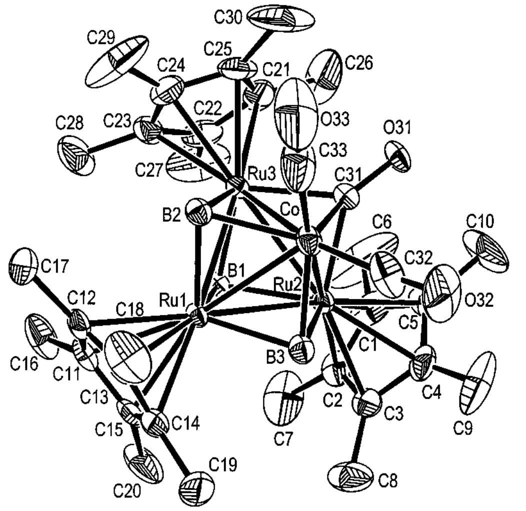


Figure 1. Structure of $\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu_3\text{-CO})Co(CO)_2B_3H_3$ (**4**). Selected bond distances (Å): Ru1−B1 = 2.103(4), Ru1−B3 = 2.107(5), Ru1−Co = 2.5920(7), Ru1−Ru3 = 2.7260(5), Ru2−B2 = 2.052(5), Ru2−B3 = 2.063(4), Ru2−B1 = 2.089(4), Ru2−Co = 2.6229(6), Ru2−Ru3 = 2.7415(5), Ru2−C(31) = 2.063(4), Ru3−B2 = 2.060(5), Ru3−B1 = 2.095(4), Ru3−Co = 2.6151(8), Ru3−C(31) = 2.063(5), Co−C(32) = 1.73(2), Co−C(33) = 1.74(2), Co−B3 = 2.036(5), Co−C31 = 2.053(5), Co−B2 = 2.063(5).

A solid-state structure determination[24] of **4** (Figure 1) reveals a $(Cp^*Ru)_3Co(CO)_2$ tetrahedral core capped by three BH fragments, thereby generating an incomplete, fully M−M bonded cubane structure. The Ru−B bonds fall in the normal range of other known ruthenaboranes, and the Ru−Ru and Ru−Co distances are within the range accepted for M−M bonding.[21] Note that the uncapped face of the metal tetrahedron supports a triply bridging CO ligand. As both CO and BH are 2-electron species and Cp*Ru and $Co(CO)_2$ are 1-electron fragments, the compound can also be viewed as a complete cube equivalent to the hypothetical 60-electron

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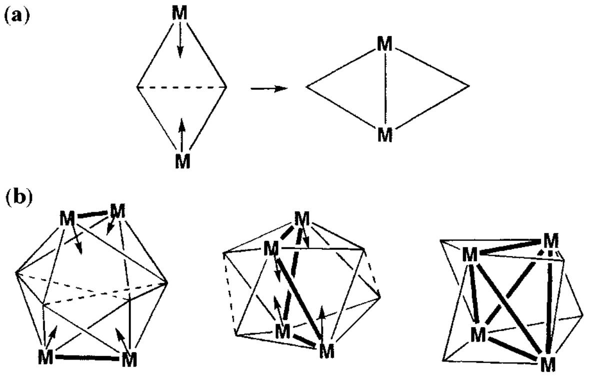
(22) **3** (0.05 g, 0.067 mmol) and $Co_2(CO)_8$ (0.032 g, 0.1 mmol) were loaded in a 50 mL Schlenk tube, and 5 mL of freshly distilled toluene was added by plastic syringe. The resulting dark brown solution was stirred for 1 h at 60 °C. Column chromatography with hexane gave a dark brown band ($Co_4(CO)_{12}$), which was discarded, and then with ether afforded a dark red solution which yielded 0.02 g of black crystals (40% based on Ru).

(23) Spectroscopic data for **4**: MS (EI) P^+ at *m/z* 890, 3B, 3Ru, 1Co atoms, fragment peaks corresponding to sequential loss of three CO; calcd mass for weighted average of isotopomers lying within the instrument resolution 890.0395, obsd 890.0363. NMR: ^{11}B (hexane, 22 °C) δ 134.5 (b, s, fwhm = 466 Hz, $\{^1H\}$, fwhm = 390 Hz, b, s, 1B), 120.0 (b, s, fwhm = 567 Hz, $\{^1H\}$, fwhm = 573 Hz, b, s, 2B); ^1H (C_6D_6, 22 °C) δ 8.36 (b, H, BH_t), 1.72 (s, 30H, C_5Me_5), 1.66 (s, 15H, C_5Me_5); $^1H\{^{11}B\}$ (tol-d_8, 22 °C) δ 8.51 (s, 1H, BH_t), 8.24 (s, 2H, BH_t), 1.72 (s, 30H, C_5Me_5), 1.67 (s, 15H, C_5Me_5). IR (C_6D_6, cm^{-1}): 2498 w, 2436 w (B−H); 1990 vs, 1948 s, 1677 s (CO). Anal. Calcd for $C_{33}H_{48}Co_3B_3O_3Ru_3$: C, 44.67; H, 5.45. Found: C, 44.67; H, 5.61.

(24) Structure of **4**: Black crystals suitable for X-ray diffraction were obtained by slowly evaporating a saturated toluene solution at room temperature under N_2 for 3 days. One capping BH group and the triply bridging carbonyl were disordered over two sites, causing the two terminal carbonyls to be disordered also. Accordingly, these atoms were refined with occupancy coefficients 0.5. After all non-hydrogen atoms were refined anisotropically and hydrogen atoms of pentamethylcyclopentadienyl groups refined isotropically, difference Fourier synthesis located the rest of the hydrogen atoms, including that on the disordered BH group. The refinement converged to final values of R1 = 0.0320 and wR2 = 0.0866 for 5619 observed unique reflections ($I > 2\sigma(I)$) and R1 = 0.0358 and wR2 = 0.0897 for all 6125 unique reflections, including those with negative intensities.



1 2 4

Figure 2. (a) Diamond–square–diamond (dsd) rearrangement. The arrows the represent direction of bond formation, and the dashed line represents the bond being broken. (b) Interconversion of **1**, **2**, and **4** via two dsd processes each.

$(CpFe)_4B_4H_4$ mentioned above.[25] Thus, in going from **1** to **2** to **4** the population of M–M antibonding orbitals decreases and an increase in M–M bonding occurs (Figure 2). The geometric connection between the three structures is also interesting. Two diamond–square–diamond (dsd) rearrangements convert **1** to **2** (a degenerate rearrangment in that four 4-connect and four 5-connect vertexes are converted into four 5-connect and four 4-connect vertexes). Two additional dsd processes convert **2** to **4** (four 4-connect and four 5-connect vertexes are converted into four 3-connect and four 6-connect vertexes). The same type of geometric connection is found to exist between the so-called *closo* and *isocloso* cluster structures with $n + 1$ and n sep, where n is the number of cluster fragments.[26,27]

Although adequately described as a tricapped tetrahedron, **4** also is closely related to the hypoelectronic clusters[28] $(Cp^*W)_3(\mu\text{-}H)B_8H_8$ and $(Cp^*Re)_2B_7H_7$ described recently.[29] Compound **4** has 6 sep or $n - 1$ sep, as there are 7 cluster fragments. Hence, it is 2 short of the prescribed number of 8 sep. The tungsten and rhenium compounds are $n - 4$ and $n - 2$ systems; 5 and 3 sep short of the prescribed number for a *closo* cluster constructed of n fragments. Although the latter compounds can be viewed as capped systems, in contrast to **4** there is no transparent way of generating the observed structures from smaller polyhedra.[30] It seems clear that there are several types of highly condensed structures accessible to metallaboranes, thereby permitting electron counts considerably less than $n + 1$ sep. This phenomenon depends on, and is controlled by, the metal fragment contained within the metallaborane framework.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic displacement coefficients for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) There is precedent for this. For example, $(CpFe)_4(\mu_3\text{-}CO)_4$ (King, R. B., *Inorg. Chem*. **1966**, *5*, 2227) can be viewed either as a tetrahedral M_4 cluster or a fully M–M bonded cubane cluster; i.e., the μ_3 main-group fragments in the cubane structure are considered to be ligands. Thus, **4** is a mixed-metal, mixed μ_3-ligand cubane.

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