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Synthesis and Characterization of $Cp^*_3Ru_3B_3H_8$, $Cp^* = \eta^5\text{-}C_5Me_5$, Exhibiting a Capped Nido Geometry. Cluster Geometry Driven by Hydrogen Bridging

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In the cluster electron counting paradigms,[1,2] bridging hydrogen atoms as well as interstitial atoms simply provide their valence electrons to cluster bonding and have no explicit role in determining the polyhedral shape observed. However, when there is more than one geometric isomer possible for a given number of skeletal electron pairs (sep), the steric and electronic demands of bridging hydrogens contribute substantially to the energetics and may determine the isomeric form observed. At the time the electron counting rules were being developed, the distinctive role of bridging and "extra" skeletal hydrogens in cage bonding gave rise to rules for their placement.[3] Later, molecular orbital calculations justified these empirical rules.[4] The situation for metal clusters is defined by the classic example of isomerization accompanying protonation of $[Os_6(CO)_{18}]^{2-}$.[5,6] This dianion exhibits an octahedral structure in accord with its 7 sep whereas $H_2Os_6(CO)_{18}$ displays a capped square pyramidal structure also consonant with 7 sep. The ability of the proton to stabilize structures with asymmetric charge distributions as well as the greater localization of charge in a hydrogen bridge bond have been suggested as important factors driving isomerizations such as this one.[7]

There are no unambiguous examples of similar behavior in metallaborane chemistry although the skeletal hydrogens clearly play a role in the observed structure of a borane-capped *nido*-diferraborane.[8] In principle a mixed cluster system offers the advantages of a borane framework more robust than that of an all metal system and, at the same time, metal fragments with frontier orbital populations that can be adjusted by variation in metal and/or ancillary ligands. Reduction of the metal fragment contribution to cluster bonding below two electrons per metal creates a driving force for the framework to pick up extra hydrogen atoms to meet the required sep. If observed, such a response would permit the effects of these extra hydrogens on structure to be measured.

Recently we have begun to explore the synthesis of metallaboranes containing the Cp*Ru, $Cp^* = \eta^5\text{-}C_5Me_5$, moiety which is a formal three-orbital, one-electron fragment. The route constitutes one example of a general synthetic method by which dinuclear metallaboranes containing Cp*M (M = Co,[9] Rh,[10] Cr,[11] Mo[12]) have been prepared from $[Cp^*MX_n]_2$ and monoboranes. In several cases, minor products containing one or three metal atoms have been isolated. Thus, in the ruthenium system we isolated the trinuclear ruthenaborane described below. It demonstrates that bridging hydrogens can determine relative isomer stabilities for a given sep even though more are required to tilt the energetics than is found in the case of an all metal cluster such as $H_2Os_6(CO)_{18}$.

The trinuclear ruthenaborane was isolated from the reaction of $[Cp^*RuCl_2]_n$ with $[BH_4]^-$.[13] Spectroscopic characterization suggested the formulation $Cp^*_3Ru_3B_3H_8$, **1**,[14] with sep = 7. With six cluster fragments, a closo octahedral cluster analogous to that known for $Cp_3Co_3B_3H_5$,[15,16] $Cp^*_3Co_3B_3H_5$, **2**,[9] and $Cp^*_2Rh_2Co(CO)_3B_3H_4$[10] comes to mind (Chart 1). However, the large chemical shift range spanned by the boron resonances and the positioning of the five skeletal hydrogens are hard to accommodate with a closo structure.

A solid-state structure determination of **1** yields the molecular geometry shown in Figure 1 and schematically represented in Chart 1.[17] It consists of a 1,2,3-$\{Cp^*Ru\}_3B_2H_2$ square pyramid with the triruthenium face capped by the third BH fragment. Four

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(13) $LiBH_4$ (5 equiv) was added $[Cp^*RuCl_2]_n$ (0.40 g, 1.28 mmol) in 30 mL of THF at −40 °C. The red slurry turned into a red solution with gas formation on warming to room temperature. After 1 h, the THF was removed and the residue extracted with hexane and chromatographed. After removal of the diruthenium compounds, elution with ether gives a red orange **1** (40 mg, 12% based on the Ru).

(14) Spectroscopic data for **1**: MS (FAB), $P^+ = 753$, 3 B, 3 Ru atoms, calcd for weighted average of isotopomers lying within the instrument resolution, 753.1635, obsd, 753.1617. NMR: ^{11}B (hexane, 22 °C), δ 128.3 (br, $J_{B-H} = 140$ Hz, $\{^1H\}$, s, 1B), 14.4 (br, $J_{B-H} = 130$ Hz, $\{^1H\}$, s, 2B); ^1H (toluene-d_8, −80 °C), 9.11 (br, 1H, B-H_t), 4.56 (br, 1H, B-H_t), 2.40 (br, 1H, B-H_t), 2.07 (s, 15H, C_5Me_5), 1.86 (s, 15H, C_5Me_5), 1.72 (s, 15H, C_5Me_5), −3.52 (s, 1H, B-*H*-B), −13.16 (s, 1H, Ru-*H*-Ru), −15.55 (br, 1H, B-*H*-Ru), −15.80 (br, 1H, B-*H*-Ru), −16.59 (s, 1H, Ru-*H*-Ru); $^{13}C\{^1H\}$ (toluene-d_8, 22 °C), 95.49 (C_5Me_5), 90.30 (C_5Me_5), 12.08 (C_5Me_5), 11.91 (C_5Me_5). IR (hexane, cm^{-1}): 2608 m, sh, 2601 m, sh, 2597 m (B-H_t). Anal. Calcd for $C_{30}H_{53}B_3Ru_3$: C, 48.08; H, 7.13. Found: C, 48.31; H, 7.11.

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(17) Crystallographic data for **1**: triclinic, $P\bar{1}$, $a = 8.4142(7)$ Å, $b = 11.0943(16)$ Å, $c = 18.1697(19)$ Å, $\alpha = 90.023(8)°$, $\beta = 95.992(8)°$, $\gamma = 107.529(9)°$, $V = 1607.6(3)$ Å^3, $Z = 2$, fw = 749.36, $D_c = 1.548$ g/cm^3. Structure solution and refinement were performed on a PC by using the SHELXTL package (Sheldrick, G. M. Siemens Industrial Automation Inc.: Madison, WI, 1994). It was found that one of the Cp* groups was disordered over two sites with occupancy coefficients 0.5. In the final refinement hydrogen atoms for the two sets of disordered pentamethylcyclopentadienyl groups were refined with an idealized riding model. After all nonhydrogen atoms were refined anisotropically and hydrogen atoms of Cp* groups refined isotrpically, difference Fourier synthesis located the rest of the hydrogen atoms including the two disordered Ru−H−Ru bridging hydrogen atoms which were refined isotropically with bond length restraints. The refinement converged to a final value of R1 = 0.0386, wR2 = 0.1083 for 5077 observed unique reflections ($I > 2\sigma(I)$).

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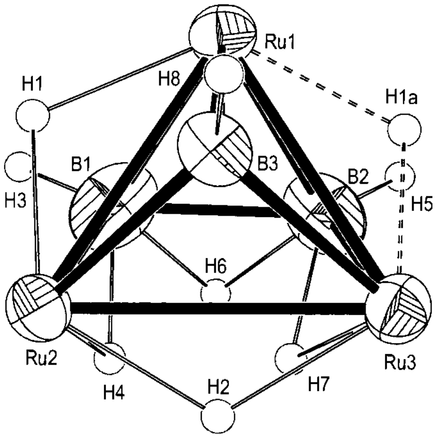
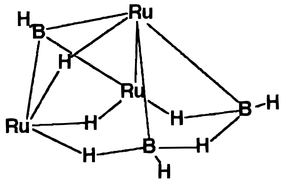


Figure 1. Molecular structure of $Cp^*_3Ru_3B_3H_8$. The Cp* ligands are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−Ru3, 2.7761(6); Ru1−Ru2, 2.8055(6); Ru2−Ru3, 2.8424(5); Ru1−B1, 2.131(8); Ru1−B2, 2.174(6); Ru1−B3, 2.083(4); Ru2−B1, 2.269(8); Ru2−B3, 2.126(5); Ru3−B2, 2.295(7); Ru3−B3, 2.151(5); B1−B2, 1.874(11); Ru3−Ru1−Ru2, 61.225(15); B1−Ru1−B2, 51.6(3); B3−Ru1−B1, 99.8(2); B3−Ru1−B2, 101.2(2); B3−Ru1−Ru3, 50.11(13); B1−Ru1−Ru3, 81.51(19); B2−Ru1−Ru3, 53.59(19); B3−Ru2−B1, 94.3(2); B3−Ru3−B2, 95.3(2); B3−Ru3−Ru1, 47.98(12); Ru1−B1−Ru2, 79.2(2); Ru1−B2−Ru3, 76.75(19); Ru1−B3−Ru2, 83.60(16); Ru1−B3−Ru3, 81.91(16); Ru2−B3−Ru3, 83.29(16).

Chart 1



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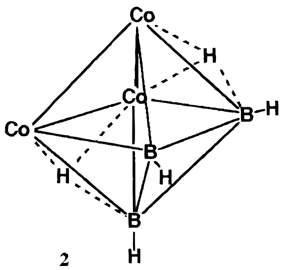

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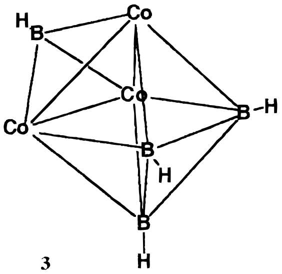

3

of the endo-hydrogens bridge the open distorted square face and the fifth is found bridging one of the other two Ru−Ru edges. This hydrogen is found disordered between these two equivalent Ru−Ru edges in the structure determination and variable temperature ^1H NMR reveals a fluxional process that moves the fifth hydrogen between the two equivalent Ru−Ru edges. However, the positions of the bridging hydrogens resulting from the structure determination are in full accord with the low temperature ^1H NMR data.

Except for a shorter bridged Ru−Ru distance on the open square face (0.17 Å), the structural metrics of the Ru_3B_2 square pyramid of **1** are similar to those of 7 sep *nido*-1,2,3-$\{(CO)_3Ru\}_3B_2H_6$[18] which has been structurally characterized as a monophosphine derivative.[19] The shorter distance is undoubtedly associated with the fact that the Ru_3 face of **1** is capped by a BH fragment. $Cp^*_3Co_3B_4H_4$, **3**,[20,21] (Chart 1) provides a rare earlier example of a metallaborane which displays a BH fragment capping a metal triangle.

The important comparison is between **1** and the isoelectronic 7 sep closo-1,2,3-$\{Cp^*Co\}_3B_3H_5$, **2**,[9] and $Cp_3Co_3B_3H_5$,[15,16] i.e, three of the skeletal protons of **1** are found in the Co nuclei of **2**. Compound **2** exhibits an octahedral cluster geometry which, in contrast to $H_2Os_6(CO)_{18}$, supports two skeletal hydrogen atoms plus adjacent Cp*Co fragments. The greater degree of robust homonuclear B−B bonding in octahedral **2** makes up for the destabilizing effects of two bridging hydrogens. However, in **1** the steric and electronic demands of the three additional skeletal hydrogens make the capped nido structure more favorable presumably because it supplies an open face to accommodate four of the hydrogens.

As demonstrated previously in the characterization of unsaturated[22] and highly condensed metallaborane structures,[23] the ability to tune the metal fragment frontier orbital properties over a significant range of energies and populations permits the manipulation of metallaborane skeletal structures. The result has been to reveal an even richer structural and reaction chemistry than initially expected. It is a chemistry based on the electron counting rules but not fully anticipated by them.

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Supporting Information Available: A file, in CIF format, is available on the Internet only. Information on data collection and reduction and structure solution and refinement, tables of crystallographic parameters, atomic coordinates and equivalent isotropic temperature factors, bond distances and bond angles, and anisotropic temperature factors for **1** are also available (14 pages). Ordering and access instructions are given on any current masthead page.

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