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# Cluster Chemistry Driven by Ligand Bulk. Significance of the Synthesis of *nido*-1-($\eta^5$-$C_5Me_5$)Co-2-($\eta^4$-$C_5Me_5H$)$CoB_3H_8$ and Its Dehydrogenation to *nido*-2,4-{($\eta^5$-$C_5Me_5$)Co}$_2B_3H_7$

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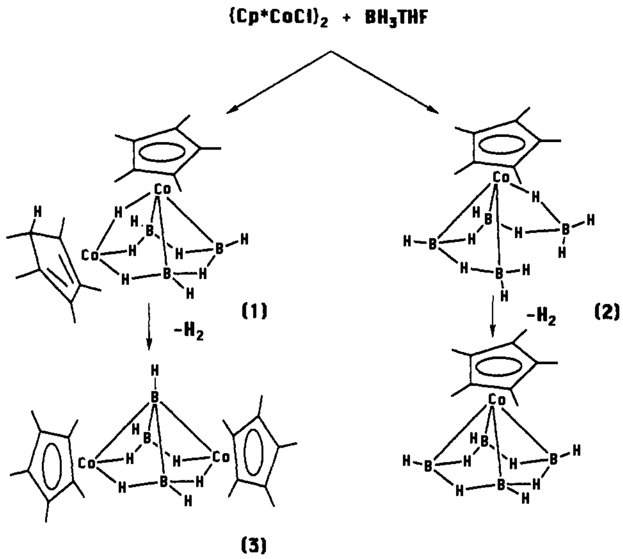
The electron-counting rules for clusters together with the idea of isolobal fragments permit the theoretical design of a large number of compounds containing both boron atoms and transition metals in the cluster cores.[1-3] In fact, a significant number of such metallaboranes have been synthesized, thereby demonstrating the power of these two concepts; e.g., consider the metallapentaborane series $\{M(CO)_3\}_nB_{5-n}H_{9-n}$ of which examples are known for $n = 0$–3.[4-7]

Although there are many similarities, borane and transition metal clusters exhibit significant differences in cluster bonding characteristics.[8] In the mixed systems these competing tendencies can generate structural behavior not seen in the parent clusters. One source of competition originates in the steric demands of the ligands external to the cluster bonding network. In the case of a BH fragment, steric demands are small, whereas the ligands on a metal fragment have substantial bulk. These steric requirements have been defined with the concept of a cluster fragment cone angle.[9] As metal–metal interactions in metal clusters are substantially weaker than the metal–ligand interactions,[10] the possibility of structural perturbations caused by steric factors is increased.

There are metal clusters in which the steric requirements of the metal ligands play a role in cluster structure,[11] but in an isolated example it is difficult to separate electronic and steric effects and assess the importance of each. Grimes and co-workers have extensively studied metallaboranes containing CpCo (Cp = $\eta^5$-$C_5H_5$) fragments[12-14] and have addressed this issue in a comparison of cobaltaboranes containing Cp and $\eta^5$-$C_5Me_5$ (Cp*) ligands on the metal atom.[15,16] These workers expressed surprise at the fact that vicinal Cp*Co fragments were found in closo clusters albeit with significant distortions in the Cp* ligand.[16]

In this work, a comparison of clusters possessing the same electronic requirements, but differing numbers of main group and transition metal atoms, permits a relative evaluation of the importance of the competing demands of the transition metal and main group fragments. We illustrate this point with a cobaltapentaborane system in which the steric demands of the external ligands on the metal fragment compete effectively with the electronic requirements of the cluster core, giving rise to an unusual structural result.

Chart I



Recently we reported that the reaction of $[Cp^*CoCl]_2$ with $[BH_4]^-$ leads ultimately to *closo*-2,3,4-$(Cp^*Co)_3B_2H_4$.[17] As $BH_3{\cdot}L$ forms during the reaction, we have now investigated the reaction of $[Cp^*CoCl]_2$ with $BH_3{\cdot}L$. The reaction[18] proceeds smoothly to yield two cobaltaboranes identified mass spectrometrically as $(Cp^*Co)_2B_3H_9$, **1**, the primary product and $(Cp^*Co)B_4H_{10}$, **2**, a minor product. The spectroscopic data[19] permit the identification of **2** as *arachno*-1-$Cp^*CoB_4H_{10}$, a new metallapentaborane(11) but of a type characterized previously by Shore et al. (Chart I).[20] The molecular formula of **1** suggests that this compound is the analogous dimetallapentaborane(11). However, the spectroscopic data[21] are not consistent with such a formulation. The $^1H$ NMR data are particularly informative and show the presence of a $\eta^4$-$C_5Me_5H$ cyclopentadiene ligand as well as five bridging hydrogens on the cluster framework.

The structure of **1** was fully revealed by a single-crystal X-ray diffraction study in which all of the hydrogen atoms were located.[22] The structure, Figure 1, shows that the $Co_2B_3$ cluster core exhibits a nido square pyramidal structure with dimensions similar to

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(18) The reaction of 0.84 g of $[Cp^*CoCl]_2$ with 4 equiv of $BH_3{\cdot}THF$ in hexane for 8 h at room temperature yielded after chromatography (silica gel, −18 °C) 0.46 g (60%) of **1** (dark red plates from hexane) and 0.02 g (2%) of **2** (pale yellow microcrystals from sublimation at 29 °C).

(19) Spectroscopic data for **2**: MS (EI), $P^+ = 248$, 4 boron atoms, calcd for $^{12}C_{10}{}^1H_{25}{}^{11}B_4{}^{59}Co$ 248.1660, obsd 248.1630. NMR ($^{11}B$, hexanes, 22 °C): $\delta$ 5.1 d, $J_{BH} = 141$ Hz, {$^1H$}, s, FWHM = 50 Hz, 2B; −5.7 t, $J_{BH} = 121$ Hz, {$^1H$}, s, FWHM = 60 Hz, 2B. NMR ($^1H$, $C_6D_6$, 18 °C): $\delta$ 2.8 q, $J_{BH} = 135$ Hz, BH; 1.43 s, Cp*; −3.9 s FWHM = 155 Hz, 3BHB; −13.6 s, FWHM = 94 Hz, 1BHCo. NMR ($^{13}C$, $C_6D_6$, 18 °C): $\delta$ 97.1, *C*CH$_3$; 9.2, C*C*H$_3$. IR (KBr, cm$^{-1}$): 2521 w, 2486 sh, 2438 w, 2402 sh, BH.

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(21) Spectroscopic data for **1**: MS (FAB), $P^+ = 430$, 3 boron atoms, calcd for $^{12}C_{20}{}^1H_{39}{}^{11}B_3{}^{59}Co_2$ 430.1995, obsd 430.2006. NMR ($^{11}B$, hexanes, 22 °C): $\delta$ 6.4 m, FWHM = 270 Hz, {$^1H$}, s, FWHM = 96 Hz, 1B; −4.6 m, FWHM = 270 Hz, {$^1H$}, s, FWHM = 120 Hz, 2B. NMR ($^1H$, $CD_2Cl_2$, −15 °C): $\delta$ 3.3 br q, BH; 2.50 q, $J_{HH} = 6.1$ Hz, 1H, $C_4(CH_3)_4C(CH_3)\mathit{H}$; 2.26 s, 6H, $C_4(C\mathit{H}_3)_4C(CH_3)H$; 1.92 s, 15H, Cp*; 0.63 s, 6H, $C_4(C\mathit{H}_3)_4C(CH_3)H$; 0.29 d, $J_{HH} = 6.2$ Hz, 3H, $C_4(CH_3)_4C(C\mathit{H}_3)H$; −5.6 br s, FWHM = 59 Hz, CoHCo; −6.0 br s, FWHM = 130 Hz, BHB; −15.7 br d, FWHM = 230 Hz, CoHB. NMR ($^{13}C$, $C_6D_6$, 18 °C): $\delta$ 98.8 s, *C*CH$_3$; 95.0 s, *C*CH$_3$; 60.7 s, *C*CH$_3$; 58.0 d, $J_{CH} = 143$ Hz, *C*(CH$_3$)H; 21.0 q, $J_{CH} = 125$ Hz, C*C*H$_3$; 14.0 q, $J_{CH} = 126$ Hz, C*C*H$_3$; 13.5 q, $J_{CH} = 127$ Hz, C*C*H$_3$; 11.2 q, $J_{CH} = 126$ Hz, C*C*H$_3$. IR (KBr, cm$^{-1}$): 2518 w, 2445 w, BH.

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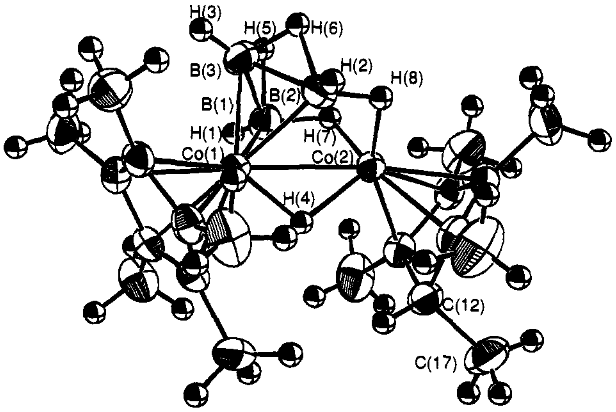

**Figure 1.** ORTEP drawing of *nido*-1-($\eta^5$-$C_5Me_5$)Co-2-($\eta^4$-$C_5Me_5H$)-$CoB_3H_8$ (**1**). Selected distances (Å): Co(1)–H(4) = 1.53(3), Co(2)–H(4) = 1.68(3), Co(1)–B(1) = 2.035(3), Co(1)–B(2) = 2.035(4), Co(1)–B(3) = 1.984(4), av Co(1)–C = 2.079(12), Co(2)–C(11) = 2.038(3), Co(2)–C(13) = 2.032(3), Co(2)–C(14) = 2.006(3), Co(2)–C(15) = 2.005(3).

those of $Fe_2(CO)_6B_3H_7$.[6] In order to accommodate the two additional hydrogen atoms in **1**, the exo-cluster ligand on the cobalt atom in the 2-position has been converted to a four-electron ligand $\eta^4$-$C_5Me_5H$ and the Co–Co edge has been bridged with the other hydrogen atom. Hence, the cluster core contains the 14 cluster bonding electrons (Cp*Co, 2; $\eta^4$-($C_5Me_5H$)Co, 1; 3 BH, 6; 5 $\mu$-H, 5) appropriate for the observed nido structure.

The role of the steric demand of the Cp* ligand becomes evident in comparing the structure of **1** with a hypothetical cluster with two $\eta^5$-Cp* ligands. The distance between the unique H on the cyclopentadiene ligand and the closest lying carbon of the $\eta^5$-Cp* of **1** (2.9 Å) is slightly less than the sum of the van der Waals radii. Keeping the same core dimensions and placing a $\eta^5$-Cp* ligand on the cobalt atom in the 2-position leads to an extremely short interligand C–C distance of 2.3 Å. Thus, the steric demands of the Cp* ligand, combined with the ease of hydrogen transfer, result in a different cluster core structure for the dimetalla derivative relative to the monometalla derivative.

The capped octahedral structure of $Cp^*{}_3Co_3B_4H_4$ exhibits vicinal Cp*Co fragments and has the same cluster geometry as the CpCo derivative.[16] This demonstrates that although intraligand steric repulsions sufficiently large to distort the ligands exist, they do not give rise to either a different cluster geometry or a positional isomer. The five-atom nido cluster geometry, e.g., that of **1**, is considered to be a fragment of an octahedron, but in this case borane fragment addition to the Cp*Co dimer leads to the unusual behavior described above.

The interpretation of the observations on **1** and **2** in terms of external ligand steric effects is corroborated by the thermal dehydrogenation of the two compounds. Pyrolysis of **2** at 70 °C leads to the known *nido*-1-Cp*$CoB_4H_8$ (Chart I).[15] Pyrolysis of **1** under similar conditions leads to *nido*-2,4-$(Cp^*Co)_2B_3H_7$, **3**, with the structure shown in the ORTEP diagram in Figure 2.[23,24] Loss of $H_2$ in the case of **2** leads to an arachno to nido conversion whereas loss of $H_2$ in the case of **1** leads to retention of the nido structure but framework rearrangement yielding nonadjacent metal centers, each of which possesses $\eta^5$-Cp* ligands. As the 1,2-isomer is apparently the most stable one of the three geometric isomers available to a *nido*-$M_2B_3$ core in the absence of large steric effects,[25] the stability of the 2,4-isomeric framework of **3** is clearly driven by the steric bulk of the Cp* ligands.

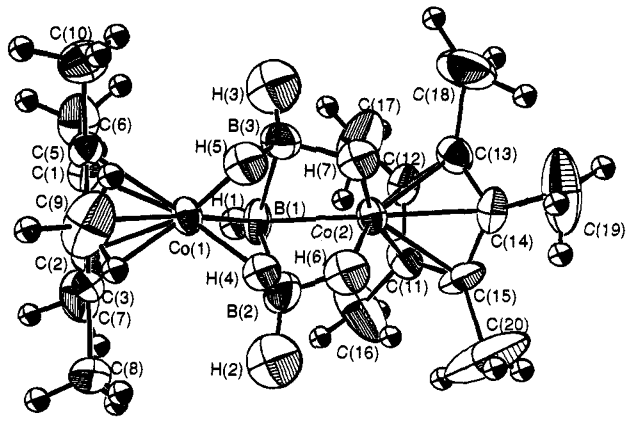

**Figure 2.** ORTEP drawing of *nido*-2,4-{($\eta^5$-$C_5Me_5$)Co}$_2B_3H_7$ (**3**). Selected distances (Å): Co(1)–B(1) = 1.986(5), Co(2)–B(1) = 1.980(5), B(1)–B(2) = 1.674(9), B(1)–B(3) = 1.733(8), av Co(1)–C = 2.042(11), av Co(2)–C = 2.031(19).

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**Supplementary Material Available:** Tables of crystal data, atomic positional and displacement parameters, and distances and bond angles for **1** and **3** (26 pages); listing of observed and calculated structure factors for **1** and **3** (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(22) Crystallographic data for **1**: $C_{20}H_{39}B_3Co_2$, monoclinic, $P2_1/n$, $a$ = 8.076(1) Å, $b$ = 20.359(2) Å, $c$ = 13.880(2) Å, $\beta$ = 91.234(8)°, $V$ = 2281.7(6) Å$^3$, $Z$ = 4, $D_{calcd}$ = 1.251 g cm$^{-3}$. Of 7057 reflections collected (CAD4 diffractometer, Mo K$\alpha$, 293 K), 6593 were independent and 4186 were observed ($3\sigma(F_o{}^2)$). All non-hydrogen atoms were anisotropically refined and all hydrogen atoms found and refined isotropically. $R_1$ = 0.0427, $R_2$ = 0.0537.

(23) Spectroscopic data for **3**: MS (EI), P$^+$ = 428, 3 boron atoms, calcd for $^{12}C_{20}{}^1H_{37}{}^{11}B_3{}^{59}Co_2$ 428.1838, obsd 428.1856. NMR ($^{11}$B, hexanes, 22 °C): $\delta$ 65.8 d, $J_{BH}$ = 116 Hz, {$^1$H}, s, FWHM = 156 Hz, 1B; –18.1 m, FWHM = 270 Hz, {$^1$H}, s, FWHM = 120 Hz, 2B. NMR ($^1$H, $C_6D_6$, 18 °C): $\delta$ 6.28 br d, FWHM = 390 Hz, BH; 1.70 s, Cp*; –12.7 br d, FWHM = 150 Hz, BHCo. NMR ($^{13}$C, $C_6D_6$, 18 °C): $\delta$ 10.3 C$CH_3$; 89.6, $C$CH$_3$. IR (KBr, cm$^{-1}$): 2452 w, 2402 w, BH.

(24) Crystallographic data for **3**: $C_{20}H_{37}B_3Co_2$, tetragonal, $P4_2/n$, $a$ = $b$ = 23.440(4) Å, $c$ = 8.317(2) Å, $V$ = 4570(1) Å$^3$, $Z$ = 8, $D_{calcd}$ = 1.244 g cm$^{-3}$. Of 3360 reflections collected (CAD4 diffractometer, Mo K$\alpha$, 293 K), 3156 were independent and 2076 were observed ($3\sigma(F_o{}^2)$). All non-hydrogen atoms were anisotropically refined and all hydrogen atoms found and either refined isotropically or involved only in the structure factor calculation. $R_1$ = 0.0349, $R_2$ = 0.0423.

(25) Heating of *nido*-1,2-{$Fe(CO)_3$}$_2B_3H_7$ results in conversion to {$Fe(CO)_3$}$_2B_2H_6$ with no sign of isomerization. L. Crascall, private communication.