Another "Rule-Breaker". Characterization of the Unusual Cobalt Carbonyl Borane $Co_5(CO)_{13}(\mu\text{-}CO)B_2H$

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The "rule-breakers" [1] gave rise to the electron counting rules[2,3] which express the relationship between the geometric and electronic structures of cluster compounds. Addition of the idea of isolobal main-group and transition-metal fragments[4] permits mixed main-group transition-element clusters to be related to the parent clusters with homonuclear cores. These ideals have led to an improved understanding of cluster compounds. However, the counting rules veil the differing electronic[5] and steric demands[6] of fragments in clusters with heteronuclear cores. The particularly diverse demands of main-group and transition-element fragments give rise to unexpected structures. Examples that have been analyzed in detail previously include octahedral $Fe_4(CO)_{12}(\mu_4\text{-}PR)_2$[7,8] and dodecahedral $Cp_4M_4B_4H_4$, M = Co, Ni.[9–13] The new compound reported herein shows that such differences need not be subtle ones. The remarkable geometry observed for this cobaltacarbonyl borane cluster vividly demonstrates that the rules governing mixed main-group transition-element cluster structure remain to be fully defined.

There are only a few known examples of metallaboranes and carboranes incorporating the $Co(CO)_3$ fragment.[14–17] We have demonstrated previously that the reaction of $BH_3{\cdot}THF$ with $Co_2(CO)_8$ leads to $(CO)_4CoBH_2{\cdot}THF$ in high yield.[18] Although this metal-substituted borane was not crystallographically characterized, the structure of a phosphine derivative $(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2$, since published, provides geometric parameters for the structure postulated in our work.[19] Because of facile reaction with THF above 0 °C, all attempts to use $(CO)_4CoBH_2{\cdot}THF$ as a cluster building unit failed. Further efforts have now demonstrated that the substitution of $BH_3{\cdot}SMe_2$ for the borane source and higher reaction temperatures lead to the production of metal-rich cobaltaboranes containing $Co(CO)_x$ fragments.

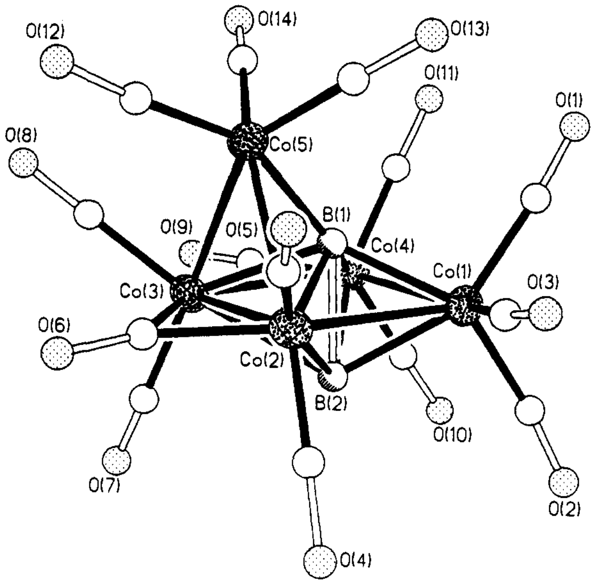

Figure 1. Molecular structure of $Co_5(CO)_{13}(\mu\text{-}CO)B_2H$. Selected bond distances (Å): Co(1)–Co(2) = 2.700(5), Co(1)–Co(4) = 2.668(4), Co(3)–Co(2) = 2.484(4), Co(3)–Co(4) = 2.714(5), Co(3)–Co(5) = 2.553(6), Co(2)–Co(5) = 2.553(6), Co(1)–B(1) = 1.95(3), Co(1)–B(2) = 2.09(2), Co(2)–B(1) = 2.06(2), Co(2)–B(2) = 2.26(3), Co(3)–B(1) = 2.08(2), Co(3)–B(2) = 2.25(3), Co(4)–B(1) = 1.99(3), Co(4)–B(2) = 2.08(3), Co(5)–B(1) = 1.99(3), B(1)–B(2) = 1.85(4).

The reaction of $BH_3{\cdot}SMe_2$ with $Co_2(CO)_8$ in toluene at 75 °C for 15 min results in a dark solution. After removal of the volatile products in vacuo and the copious quantities of $Co_4(CO)_{12}$ formed in the reaction by fraction crystallization, the isolation in less than 1% yield of a very dark red-brown solid (**1**) by column chromatography (silica gel, −20 °C, second band, R_f = 0.45) with hexane is possible. The material is highly air sensitive but thermally stable. The spectroscopic data are consistent with the molecular formula $Co_5(CO)_{13}B_2H$ (MS-FAB, hexane/NBA, p^+ = 681.58 obsd, 681.63 calcd, 2 borons) and the molecule contains terminal and bridging carbonyls (2070 s, 2061 vs, 2044 s, 2034 m, 2026 sh, 1975 w, 1861 w, cm^{-1}, hexane), a boron with a BH terminal bond, and a boron atom with no hydrogen ligand ($\delta(^{11}B)$ 74, d, J_{BH} = 144 Hz; 150, s; hexane, 20 °C).

Recrystallization from hexane by slow cooling yielded single crystals suitable for a structure determination.[20] The solid-state structure, Figure 1, shows that the molecular formula of cluster **1** is actually $Co_5(CO)_{14}B_2H$ and that its structure is an unusual one. There is a plane of symmetry (not crystallographically imposed) containing Co(5), B(1), B(2), and the one bridging CO. The single hydrogen atom was not located. Most likely it is bound to B2 in a terminal fashion ($\delta(^1H)$ 9.5, partially collapsed quartet, ν_{BH} = 2511 vw, cm^{-1}) as, if it were associated with B(1), it would almost certainly be bridging and appear at higher field. Curiously, the Co–Co and Co–B distances, although they all fall within ranges that can be associated with bonding, can be divided into sets of short and long distances. That is, all of the metal interactions with B(1) plus those between Co(1) and Co(4) with B(2) are similar, d(CoB(av)) = 2.03(3) Å. The two other metal interactions with B(2) are longer, d(CoB(av)) = 2.26(3) Å. The three Co–Co distances in the triangle made up by Co(2), Co(3), and Co(5) are short, d(CoCo(av)) = 2.53(1) Å, whereas the

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(20) Cluster **1** crystallizes in the orthorhombic space group *Pna*2, with a = 24.886(4) Å, b = 9.846(5) Å, c = 9.248(3) Å, V = 2266.3(9) Å^3, z = 4. Of 1588 data collected ($2\Theta_{max}$ = 45°, Siemens P4, 239 K), 1103 were observed at $4\sigma F_o$. Although **1** possesses an approximate mirror plane defined by B(1), B(2), and Co(5), it does not coincide with the crystallographic c axis; thus the noncentrosymmetric space group is required. The data were corrected for absorption. Limitations in data restricted anisotropic refinement to the Co atoms. $R(F)$ = 5.94%, $R(wF)$ = 5.89%. A Rogers test was used to determine the preference for the hand reported.

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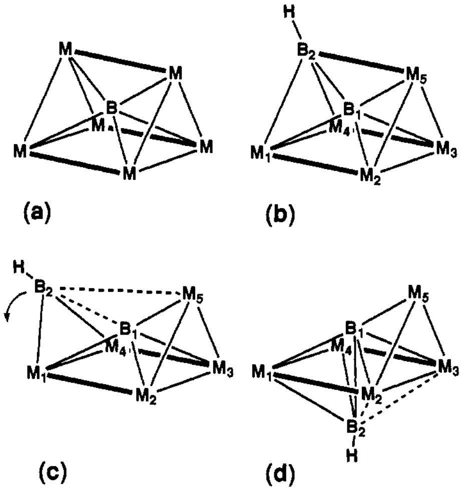
other three Co–Co edges (Co(1)–Co(2), Co(1)–Co(4), Co(3)–Co(4)) are long (d(CoCo(av)) = 2.69(1) Å). The B–B distance is 1.85(4) Å, which is within the range observed for polyhedral boranes with B–B bonding.[2] How can this unusual structure and the bimodal distribution of atom–atom distances be understood?

Beginning with the observed geometry is not fruitful. A metal face-capped M_6 octahedron requires a pec of 98 (pec, polyhedral electron count),[3] so the same structure with two main-group and five metal fragments would require 78. **1** has a pec of 80. Viewing **1** as an analog of square pyramidal $CFe_5(CO)_{15}$ with a face-capping metal fragment (pec 86) leads to a predicted pec of 76.

Beginning with the observed spectroscopic parameters is more profitable. The ^{11}B chemical shifts are consistent with the presence of boride boron atom[19] and a B–H vertex. If **1** were analogous to a $M_6(B)$ boride cluster in which one metal vertex has been replaced by an isolobal BH fragment, **1** would have a pec of 90 − 10 = 80. An example of such a boride has recently been reported,[21] and as expected, the M–M distances on the unbridged edges of the triangular faces are $\approx$0.1 Å shorter than the axial M–M distances as indicated in structure a by the bold lines (Chart I). Thus **1**, is expected to have structure b, which it obviously does not. The observed structure can be generated by breaking the B(2)–Co(5) and B(2)–B(1) interactions and bending the B(2) atom out, around, and underneath a rectangular face, structure c, to re-form the B(2)–B(1) interaction and two long B(2)–Co(2) and B(2)–Co(3) interactions. With the exception of the Co(1)–Co(4) distance, this model predicts the observed bimodal distribution of M–B and M–M distances, and as expected for a trigonal prism, the Co(4)–Co(3)–Co(5) angle is nearly a right angle (88.3(2)°).

Chart I



The formation of this unexpected isomeric form appears to be driven by the geometric bonding constraints of Co vs B. Using average Co–B (2.0 Å) and B–B (1.6 Å) distances would force a very long B(2)–Co(5) interaction (2.8 Å) in structure b whereas structure d permits reasonable B–B *and* Co–B interactions. The electron counting rules suggest that there should be a tendency for **1** to lose two electrons in order to achieve a pec appropriate for a capped octahedron. The fact that the FAB mass spectrum of **1** shows no parent ion at all suggests that the loss of one CO is indeed very facile.

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Supplementary Material Available: Tables of crystal, data collection, and refinement parameters, atomic positional and equivalent isotropic displacement parameters, selected bond distances and bond angles, and anisotropic displacement parameters for **1** (7 pages); listing of observed and calculated structure factors for **1** (4 pages). Ordering information is given on any current masthead page.

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