Communications

Synthesis and Characterization of $(Cp^*Co)_3(\mu_3\text{-}HBH)_2$, an Inorganometallic Analog of a Biscarbyne Complex

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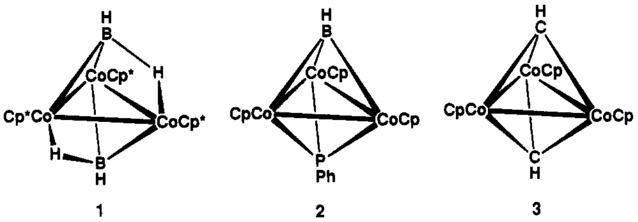
Received April 15, 1993

The comparison of isoelectronic species is an old, but powerful, method of identifying similarities between the electronic structures of compounds of different atomic compositions.[1] The differences are important as well and emphasize the real possibilities of the utilization of element variation in the rational control of chemical properties.[2] Our work has focused on the differences between metallaboranes and their isoelectronic organometallic partners, and we have, for example, been able to use such comparisons to obtain insight into the factors that govern the spatial distribution of bridging hydrogens on main group–transition element clusters.[3] The preparation of these metallaboranes has often been somewhat arcane, but herein we report a straightforward route to a new metallaborane cluster that has an isoelectronic organometallic partner.

In our experience, metallaboranes tend to decompose into separate metal and boron compounds. Hence, the key to their synthesis is the utilization of boron and metal precursors that can combine in a reaction with a barrier smaller than the relatively low barriers associated with decomposition pathways.[4] As $BH_3{\cdot}L$ complexes are readily available, it is the metal precursor that constitutes the problem. For metallaboranes containing the CpCo fragment we have shown that a simple compound like $CpCo(PPh_3)_2$ when reacted with $BH_3{\cdot}THF$ produces a number of interesting metallaboranes.[5–7] However, the yields are small and the large amounts of $BH_3{\cdot}PPh_3$ produced as a byproduct makes product isolation a painfully slow process. Therefore we have sought related routes in which cluster products are more easily isolated.

The paramagnetic $(Cp^*CoCl)_2$ dimer has been described,[8,9] and it occurred to us that reaction with borohydride salts might lead to cobaltaboranes and a simple salt. Ostensibly the reaction is similar to that of $(Cp^*TaCl_2)_2$ with $[BH_4]^-$.[10] Further, it combines in two reagents the three components employed by Grimes and co-workers in the synthesis of a wide variety of cobaltaboranes.[11] In the event, stirring 0.35 g (0.8 mmol) of $(Cp^*CoCl)_2$ in 15 mL of THF with 1.5 mmol of $LiBH_4$ (0.8 mL of a 2 M solution in THF) at room temperature for 16 h resulted in a brown solution and the formation of a precipitate. Removal of THF followed by extraction with hexanes and filtration through Celite gave a red-brown solution containing $(Cp^*Co)_3(\mu_3\text{-}HBH)_2$ (**1**) (see Chart I) as the major boron-containing component in ≈30% yield based on NMR. Fractional crystallization yielded higher purity material; however, only a combination of low-temperature chromatography (silica gel at −20 °C) and recrystallization gave a product free from paramagnetic impurities. The spectroscopic data[12] are consistent with the formulation of the new compound as $(Cp^*Co)_3(\mu_3\text{-}HBH)_2$. In particular note the ^{11}B chemical shift that suggests boron atoms in a highly metallic environment and the low-field ^1H chemical shift of the terminal proton and high BH coupling constant which are consistent with a closo structure. The high-field ^1H resonance suggests the presence of two equivalent protons associated with the cobalt atoms. However, any reasonable structure would require fluxional behavior and the actual framework geometry was only firmly established by a solid-state structure determination.

Chart I



Crystals suitable for the X-ray diffraction study were grown by slow cooling.[13] The ortep diagram is shown in Figure 1 where it can be seen that **1** has a *closo*-trigonal bypyramidal cluster geometry with trans BH fragments. The Co–Co and Co–B distances are within the range expected for either H-bridged or unbridged edges. The bridging hydrogens were not located and would necessarily be disordered because the molecule lies on a site of 3-fold symmetry.

There are three logical positions for the two endo-hydrogens: Co–Co edge bridging, Co–B edge bridging, or Co_2B face bridging. Three spectroscopic observations narrow the possibilities. First, the high-field ^1H resonance narrows and then broadens with decreasing temperature suggesting thermal ^{11}B–^1H decoupling followed by broadening due to more rapid quadrupolar relaxation. The presence of ^{11}B–^1H coupling rules out Co–H–Co bridging

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(1) Albright, T. A.; Burdett, J. K.; Whango, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(2) Aradi, A. A.; Fehlner, T. P. *Adv. Organomet. Chem.* **1990**, *30*, 189.

(3) Fehlner, T. P. *Polyhedron* **1990**, *9*, 1955.

(4) Meng, X.; Bandyopadhyay, A. K.; Fehlner, T. P.; Grevels, F.-W. *J. Organomet.* **1990**, *394*, 15.

(5) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 1860.

(6) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *J. Organomet. Chem.* **1988**, *348*, C22.

(7) Feilong, J.; Fehlner, T. P.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 424.

(8) Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131.

(9) Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem. Suppl.* **1982**, 230.

(10) Ting, C. Messerle, L. *J. Am. Chem. Soc.* **1989**, *111*, 3449.

(11) Grimes, R. N. *Pure Appl. Chem.* **1982**, *54*, 43.

(12) MS (EI): $P^+ = 608$, 2 boron atoms, calcd for $^{12}C_{30}{}^1H_{49}{}^{11}B_2{}^{59}Co_3$, *m/e* 608.2016, obsd, *m/e* 608.2034. NMR: ^{11}B, hexanes, 22 °C, δ 104 d, $J_{BH} = 165$ Hz, fwhm = 316 Hz $\{^1H\}$, s, fwhm = 183; ^1H, $C_6D_5CD_3$, 19 °C, δ 9.6 partially collapsed q, fwhm = 390 Hz, BH_t; 1.79 s, fwhm = 2 Hz, Cp*; −20.8 s, fwhm = 26 Hz, BHCo; −60 °C, δ 9.6 s, fwhm = 95 Hz; 1.84 s, fwhm = 3 Hz; −20.7 s, fwhm = 14 Hz; ^{13}C, $C_6D_5CD_3$, 19 °C, δ 12.0, (CCH_3); 92.2, (CCH_3). IR (hexanes, cm^{-1}): 2451 w and 2413 w, BH.

(13) Crystallographic data for **1**: $C_{30}H_{49}B_2Co_3$, rhombohedral, $R\bar{3}$, $a = 17.994(1)$ Å, $c = 15.986(1)$ Å, $V = 4477.3(7)$ Å^3, $Z = 6$, $D_x = 1.347$ g cm^{-3}. Of 1965 reflections collected (Siemens P4 diffractometer, Mo Kα, 295 K), 1786 were independent and 1263 were observed ($5\sigma(F_o)$). With all non-hydrogen atoms anisotropically refined and all methyl-group hydrogen atoms idealized (the axial B–H atoms were found but not the bridging ones): $R(F) = 4.28\%$, $R_w(F) = 5.66\%$.

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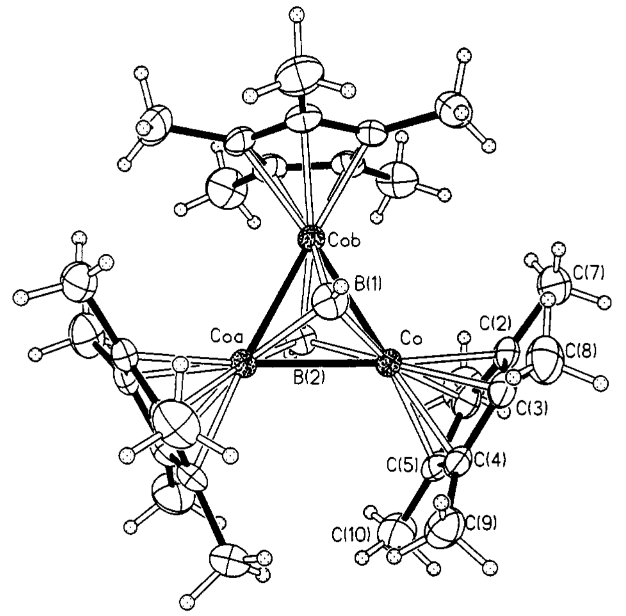

Figure 1. Solid-state structure of $(Cp^*Co)_3(\mu_3\text{-}HBH)_2$ (**1**). Bridging hydrogens were not found and are not shown. Selected bond distances (Å): Co–CoA = 2.507(1), B(1)–Co = 2.013(8), B(2)–Co = 1.985(6), Co–C(1) = 2.101(4), Co–C(2) = 2.094(4), Co–C(3) = 2.095(4), Co–C(4) = 2.096(5), Co–C(5) = 2.095(5), C(1)–C(2) = 1.419(8), C(2)–C(3) = 1.416(8), C(3)–C(4) = 1.402(8), C(4)–C(5) = 1.446(7), C(1)–C(5) = 1.413(9).

hydrogens. Second, typical chemical shifts for spectroscopically and crystallographically characterized bridging hydrogens are δ −15.6 for H triply bridging a Co_3 face,[5] −12.6 for H triply bridging a Co_2B,[14] and −21.2 for H bridging a CoB edge.[6] However, there is a considerable chemical shift range for Co–H–B bridges (δ −14 to −21),[15] and although the observed shift of δ −20.8 favors edge bridging, we cannot rule out a face bridging hydrogen on this basis. Third, we have demonstrated empirically for metal-rich ferraboranes that the addition of a B–H–Fe proton shifts the boron resonance 34 ppm to higher field.[16] In **1** the ^{11}B chemical shift of the boron atoms is ≈46 ppm to higher field than that observed for an analogous compound, $(CpCo)_3(\mu_3\text{-}BH)(\mu_3\text{-}PPh)$, **2** (Chart I), with no bridging hydrogens.[7] However the bridging protons are placed they must still be fluxional down to −90 °C as neither the ^1H or ^{13}C NMR spectra show any evidence for either H or Cp* inequivalence at −90 °C. Thus, we represent the structure of **1** with CoB edge bridging hydrogens as shown in Chart I.

Cluster **1** represents the first example of a metallaborane that is isoelectronic with biscarbyne tricobalt clusters, **3** (Chart I),[17,18] which have a significant organmetallic chemistry.[19] All three clusters have a polyhedral electron count (pec) of 52 and the closo-structure expected.[20,21] Recently, there has been a report of another metallaborane cluster with a cluster core structure similar to that of **1**.[22] However, it is formulated as $(Cp^*Ru)_3(BH_3)_2$, which has a pec of 51.

An examination of the reaction progress by ^{11}B NMR shows that **1** is not the initial product. The growth and decay of one predominant species which contains boron is observed. It exhibits the ^1H and ^{11}B NMR signatures of a paramagnetic species and is postulated as an intermediate in the formation of **1**. It is also of interest to note that the reaction of $(Cp^*CoCl)_2$ with $[AlH_4]^-$ leads to two unusual hydrides, $(Cp^*Co)_3(\mu\text{-}H)_3(\mu_3\text{-}H)$ and $(Cp^*Co)_2(\mu\text{-}H)_3$.[23] As metal borohydride complexes are known to serve as precursors to metal hydrides, it is possible that borane cluster **1** and these hydrides originate from analogous intermediates.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, atomic positional and equivalent isotropic displacement parameters, and selected bond distances and bond angles for **1** (6 pages). Ordering information is given on any current masthead page.

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[14] Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

[15] Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982; p 269.

[16] Rath, N. P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 5345.

[17] Pardy, R. B. A.; Smith, G. W.; Vickers, M. E. *J. Organomet. Chem.* **1983**, *252*, 341.

[18] Wadepohl, H.; Pritzkow, H. *Polyhedron* **1989**, *8*, 1939.

[19] Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559.

[20] Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[21] Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29.

[22] Suzuki, H.; Takaya, Y.; Tada, K.; Kakigano, T.; Igarashi, M.; Tanaka, M. In *Symposium on Organometallic Chemistry-Abstracts*; Kinki Chemical Society: Tokyo, 1992; p 154.

[23] Kersten, J. L.; Rheingold, A. L.; Theopold, K. H.; Casey, C. P. Widenhoefer, R. A.; Hop, C. E. C. A. *Angew. Chem.* **1992**, *104*, 1364.