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Search for a General Route to Metallaboranes via the Reaction of Monocyclopentadienyl Metal Chlorides with Monoborane. Synthesis and Reactivity of the Rhodaborane *nido*-1-Cl-2,3-{(η^5-C_5Me_5)Rh}$_2$$B_3H_6$

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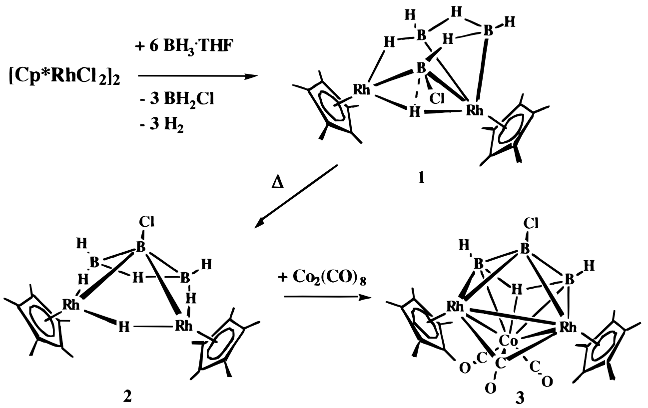
The full potential of metallaborane chemistry, an inorganic mimic of organometallic chemistry,[1] will not be realized unless high-yield syntheses from readily accessible starting materials are developed. Although good routes to selected metallaboranes are known, especially for monometallic compounds, a large fraction of the known compounds have resulted from complex reaction systems producing mixtures of products in low yields.[2−4] For some time we have pursued the use of monoboranes in the synthesis of multinuclear metallaboranes, choosing to assemble the borane fragment on the metal moiety in order to avoid the large barriers associated with activating a main group cage.[5] Recently we have explored monocyclopentadienylmetal chloride dimers as a potentially general source of metallaboranes and have found the halogen to be an excellent leaving group.[6] In most cases, BH_3·THF acts in a dual role, carrying off the chlorine as BH_2Cl and condensing on the dimer framework to form B−B and B−M bonds. Depending on the metal the borane can act in a third role in reducing a higher valent complex to the metallaborane precursor, which eliminates one step in the synthesis.[7] In all cases, kinetic control has been demonstrated, leading to good yields of single metallaboranes on usable scales.

This approach has given new metallaboranes of Co,[6] Cr,[8] Mo,[9] and Ta[10] and has allowed the development of some of their derivative chemistry.[11−13] Although the chemistry of rhodacarboranes is very interesting[4,14,15] and a number of mononuclear rhodaboranes are known,[16,17] dinuclear rhodaboranes are virtually unstudied.[18] Thus, we now report an extension of the synthetic method to rhodium. Once again kinetic control of the reaction leads to a single, seven skeletal electron pair (7 sep), *nido*-dimetallapentaborane, 3-Cl-1,2-(Cp*Rh)$_2$$B_3H_6$ (**1**, Cp* = η^5-C_5Me_5). On warming, **1** undergoes a skeletal rearrangement to form a more stable isomer, 1-Cl-2,3-(Cp*Rh)$_2$$B_3H_6$ (**2**). A high isolated yield allows the reactivity of **2** to be examined, and one example leading to a *closo*-trimetallahexaborane is given.

Chart 1



Reaction of [Cp*RhCl$_2$]$_2$ with BH_3·THF in THF at room temperature results in a change in color from an orange suspension to the characteristic blue of [Cp*RhCl]$_2$.[19] This is accompanied by the formation of BH_2Cl (NMR) and a gas, presumably H_2. On continued reaction, the blue color changes to red-orange, additional BH_2Cl is formed, and a single metallaborane is isolated from the now homogeneous solution in 82% yield. Characterization of the product as a 7 sep *nido*-3-Cl-1,2-(Cp*Rh)$_2$$B_3H_6$ (**1**, Chart 1) results from a comparison of the spectroscopic data[20] with those of its crystallographically characterized structural isomer 1-Cl-2,3-(Cp*Rh)$_2$$B_3H_6$ (**2**) described below. Although each of the metals explored by this synthetic method behave similarly in a general sense, each also expresses some characteristic quirks. Here, one of the metal-bound chlorides of the rhodium dimer is retained in **1**. Also one of the four cluster bridging hydrogens bridges the apical and basal Rh atoms rather than an edge of the open square face as found in B_5H_9 itself and all other known *nido*-metallapentaboranes. However, the distinctly broadened line width of the triplet associated with this proton shows it to be associated with, if not bonded to, B(3); hence, it is placed in a triply bridging position.

At 60 °C, **1** cleanly isomerizes to **2** formulated as 1-Cl-2,3-(Cp*Rh)$_2$$B_3H_6$ (Chart 1) on the basis of its spectroscopic properties[21] and crystal structure[22] (Figure 1). Alternatively **2** can be prepared directly in 91% isolated yield (140 mg) by carrying out the synthesis at 60 °C. The structure of **2** is closely related to that of 2-(Cp*Os)-3-{(PPh$_3$)$_2$(CO)Rh}B_3H_7.[23] Comparison with the established structures of 1,2-{Fe(CO)$_3$}$_2$$B_3H_7$[24] and 2,4-(Cp*Co)$_2$$B_3H_7$[25] suggests that the metal and its ligands

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[20] Spectroscopic data for **1**: MS (EI), $P^+ = 550$, 3 B, 1 Cl, 2 Rh; calcd for $^{12}C_{20}{}^{1}H_{36}{}^{11}B_3{}^{103}Rh_2{}^{35}Cl$ 550.0907, obsd 550.0896. NMR: ^{11}B (hexane, 22 °C), δ 48.0 br s, 1B; 4.0 d, $J_{B-H} = 150$ Hz, 1B; −5.3 d, $J_{B-H} = 122$ Hz, 1B; ^1H (C_6D_6, 22 °C), δ 3.78 pcq (partially collapsed quartet), 2H, BH; 1.93 s, 15H, Cp*; 1.73 s, 15H, Cp*; −4.01 br, 1H, B−H−B; −14.00 br, 1H, Rh−H−B; −14.83 br t, $J_{Rh-H} = 25$ Hz, 1H, Rh−H−Rh.

[21] Spectroscopic data for **2**: MS (EI), $P^+ = 550$, 3 B, 1 Cl, 2 Rh; calcd for $^{12}C_{20}{}^{1}H_{36}{}^{11}B_3{}^{103}Rh_2{}^{35}Cl$ 550.0907, obsd 550.0896. NMR: ^{11}B (hexane, 22 °C), δ 45.5 br s, 1B; 11.5 d, $J_{B-H} = 120$ Hz, 2B; ^1H (C_6D_6, 22 °C), δ 4.62 pcq, 2H, BH; 1.74 s, 30H, Cp*; −2.48 br, 1H, B−H−B; −11.63 br, 2H, Rh−H−B; −15.57 t, $J_{Rh-H} = 25$ Hz, 1H, Rh−H−Rh. IR (hexane, cm^{-1}): 2510 w (B−H_t). Anal. Calcd for $C_{20}H_{36}B_3Rh_2Cl$: C, 43.66; H, 6.60. Found: C, 44.92; H, 6.59.

S0002-7863(97)04268-6 CCC: $15.00

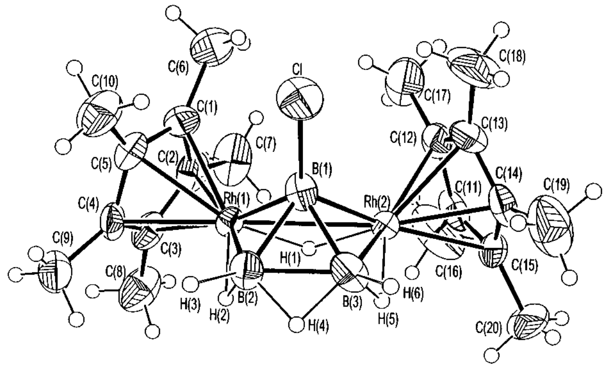

Figure 1. Molecular structure of 1-Cl-2,3-(Cp*Rh)$_2$B$_3$H$_6$ (**2**). Selected bond distances (Å) and angles (deg): Rh(1)−Rh(2) 2.8478(11), Rh(1)−B(1) 2.065(10), Rh(1)−B(2) 2.204(11), Rh(2)−B(1) 2.087(10), Rh(2)−B(3) 2.203(11), B(1)−Cl 1.847(11), B(1)−B(3) 1.74(2), B(1)−B(2) 1.741(14), B(2)−B(3) 1.78(2), B(1)−Rh(1)−B(2) 48.0(4), B(3)−Rh(2)−Rh(1) 75.8(3), B(3)−B(1)−B(2) 61.6(6), B(3)−B(1)−Rh(1) 111.0(7), Rh(1)−B(1)−Rh(2) 86.6(4), B(1)−B(2)−B(3) 59.2(6), B(1)−B(2)−Rh(1) 61.8(5), B(3)−B(2)−Rh(1) 103.6(6).

are important in determining metal positional stability in a nido five-atom cluster. The mechanistic implications of the differences between the Co and Rh cluster structures and the retention of one Cl in **1** but not in 2,4-(Cp*Co)$_2$B$_3$H$_7$ are presently under investigation.

Compound **2** displays interesting reaction chemistry with metal carbonyl fragment sources, particularly when compared to that of 2,4-(Cp*Co)$_2$B$_3$H$_7$. For example, reaction of **2** with Co$_2$(CO)$_8$ at room temperature results in the formation of a single product in 80% isolated yield. Both spectroscopic characterization in solution[26] and a solid-state structure determination[27] define the cluster product as the 7 sep *closo*-1-Cl-6-{Co(CO)$_3$}-2,3-(Cp*Rh)$_2$B$_3$H$_3$ (**3,** Figure 2 and Chart 1). The product is an example of the rarely observed M$_3$B$_3$ octahedral cluster structure and the first example of a directed synthesis of such a species.[28−31]

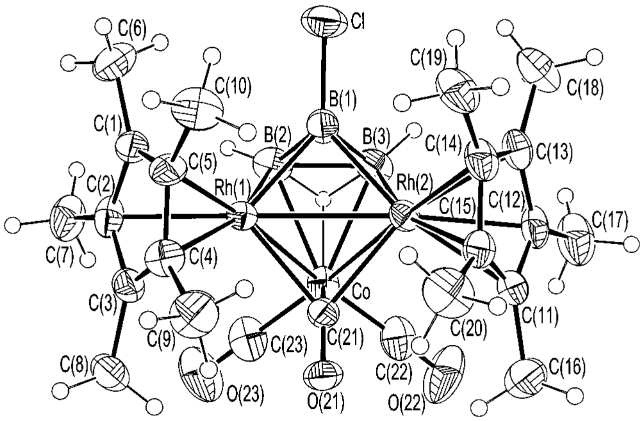

Figure 2. Molecular structure of 1-Cl-6-{Co(CO)$_3$}-2,3-(Cp*Rh)$_2$B$_3$H$_3$ (**3**). Selected bond distances (Å) and angles (deg): Rh(1)−Co 2.5450(12), Rh(2)−Co 2.5465(11), Rh(1)−Rh(2) 2.7070(8), Rh(1)−B(1) 2.114(10), Rh(1)−B(2) 2.170(10), Rh(2)−B(1) 2.125(9), Rh(2)−B(3) 2.152(9), Co−B(2) 2.240(11), Co−B(3) 2.225(12), B(1)−Cl 1.805(11), B(1)−B(2) 1.70(2), B(1)−B(3) 1.71(2), B(2)−B(3) 1.77(2), Co−Rh(1)−Rh(2) 57.91(3), B(1)−Rh(2)−B(3) 47.2(4), B(1)−Rh(2)−Rh(1) 50.1(3), Co−Rh(2)−Rh(1) 57.85(3), B(1)−B(2)−B(3) 59.2(6), B(2)−B(1)−B(3) 62.4(7), B(2)−B(1)−Rh(1) 68.4(5), B(3)−B(1)−Rh(1) 106.3(6), Rh(1)−B(1)−Rh(2) 79.4(3), B(1)−B(2)−Co 95.7(6).

In distinct contrast to the Rh chemistry, reaction of 2,4-(Cp*Co)$_2$B$_3$H$_7$ under similar conditions gives Cp*Co(CO)B$_3$H$_7$ and Cp*Co(CO)$_2$.[32] These observations, as well as additional derivative reactions, will be treated in future publications.

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Supporting Information Available: 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 **2** and **3** (37 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(22) Crystallographic data for **2**: monoclinic, *P*2$_1$/*c*, $a = 15.574(4)$ Å, $b = 8.740(2)$ Å, $c = 18.038(5)$ Å, $\beta = 104.76(2)°$, $V = 2374.2(10)$ Å^3, $Z = 4$, FW = 550.19, $D_c = 1.539$ Mg/m^3. Data (Mo Kα) were collected on an Enraf-Nonius CAD4 diffractometer at 293 K. Structure solution and refinement were performed on a PC by using the SHELXTL package. The refinement converged to a final value of $R_1 = 0.0538$ and $wR_2 = 0.1191$ for 2922 observed unique reflections ($I > 2\sigma(I)$) and $R_1 = 0.0895$ and $wR_2 = 0.1482$ for all 4172 unique reflections including those with negative intensities.

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(26) Spectroscopic data for **3**: MS (EI), P$^+$ = 690, 3 B, 1 Cl, 2 Rh, sequential loss 3 CO. Calcd for $^{12}C_{23}{}^{1}H_{33}{}^{16}O_3{}^{11}B_3{}^{59}Co{}^{103}Rh_2{}^{35}Cl$ 689.9853, obsd 689.9866. NMR: ^{11}B (hexane, 22 °C), δ 62.8 br s, 1B; 37.4 d, $J_{B-H} = 150$ Hz, 2B. ^{1}H (C$_6$D$_6$, 22 °C), δ 5.50 pcq, 2H, BH; 1.67 s, 30H, Cp*; −7.07 br s, 1H, B−H−B. IR (hexane, cm^{-1}): 2513 w (B−H), 2028 s, 1986 m, 1724 w (CO).

(27) Crystallographic data for **3**: orthorhombic, *Pna*2$_1$, $a = 20.167(5)$ Å, $b = 9.120(3)$ Å, $c = 14.547(4)$ Å, $V = 2675.4(13)$ Å^3, $Z = 4$, FW = 690.12, $D_c = 1.713$ Mg/m^3. Data (Mo Kα) were collected on an Enraf-Nonius CAD4 diffractometer at 293K. Structure solution and refinement were performed on a PC by using the SHELXTL package. The refinement converged to a final value of $R_1 = 0.0378$ and $wR_2 = 0.0803$ for 4117 observed unique reflections ($I > 2\sigma(I)$) and $R_1 = 0.0503$ and $wR_2 = 0.0902$ for all 4702 unique reflections including those with negative intensities.

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