Designer clusters: synthesis and characterization of $Cp^*_2Rh_2Co_3(CO)_8B_3HCl$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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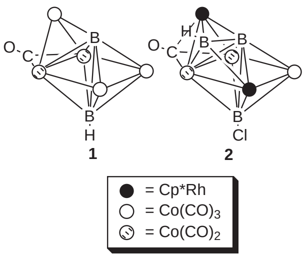
Sigma bond metathesis of B–H in $Cp^*_2Rh_2B_3H_6Cl$ with Co–Co in $Co_2(CO)_8$ leads directly to the title compound.

Both B–H[1,2] and Si–H[3] bonds undergo σ-bond metathesis with the Co–Co bond in $Co_2(CO)_8$ as illustrated in eqns. (1a) and (1b).

$$2\ R_3SiH + Co_2(CO)_8 \rightarrow 2\ (CO)_4CoSiR_3 + H_2 \quad (1a)$$

$$2\ BH_3{\cdot}thf + Co_2(CO)_8 \rightarrow 2\ (CO)_4CoBH_2{\cdot}thf + H_2 \quad (1b)$$

For this reason, the formation of the unusual cluster, $Co_5(CO)_{14}B_2H$ **1**, from the reaction of $BH_3{\cdot}SMe_2$ and $Co_2(CO)_8$ was rationalized using σ-bond metathesis of the B–H bond as an essential feature of the cluster building reaction. [4,5] However, this metallaborane, and an intermediate compound, $Co_2(CO)_6B_2H_4$, were only isolated in low yields partly due to efficient competitive formation of $Co_4(CO)_{12}$. Hence, without confirmation this mechanism remains speculative. For this reason, we have sought support for such a cluster building route in alternative systems. Here, we report the rational synthesis of an analog of **1** formed in good yield from $(Cp^*Rh)_2B_3H_6Cl$ ($Cp^* = \eta^5\text{-}C_5Me_5$), which, in turn, is readily accessible from the reaction of $Cp^*_2Rh_2Cl_4$ and $BH_3{\cdot}thf$. [6,7] The postulated cluster building reaction is corroborated and the structure exhibited by **1** is verified as the preferred core geometry for the cluster electron count.



The reaction of $Cp^*_2Rh_2B_3H_6Cl$ and $Co_2(CO)_8$ under mild conditions gives $(Cp^*Rh)_2Co_3(CO)_8B_3HCl$ **2**, in 30% isolated yield.† The spectroscopic data are consistent with the molecular structure shown in Fig. 1 and derived from a solid state structure determination.‡ Comparison of **2** with **1** reveals the close structural relationship of these two clusters. Compound **1** was shown to be an unanticipated isomeric analog of a trigonal prismatic, boron centered M_6 90 cluster valence electron (cve) cluster.[5,8] Converting one M vertex of the M_6 cluster to BH leads to the observed 80 cve and the M *vs* B size mismatch leads to the isomeric structure observed. As shown in Scheme 1, **2** can be derived from a rectangular face-capped trigonal prismatic, boron centered M_7 102 cve cluster, *e.g.* $[HFe_7(CO)_{20}B]^{2-}$.[9] Just as with **1**, conversion of two M vertices to BH and BCl followed by rearrangement leads to the observed geometry. The predicted cve count is 82 as observed. The difference between the radial properties (size) of main group and transition metal fragments with similar frontier angular orbital properties and populations (isolobal) forces the unexpected isomeric structure observed for **1** and **2**.[10]

The origin of **2** from $Cp^*_2Rh_2B_3H_6Cl$ can be described with a small set of reasonable assumptions that allow the stoichiometric and geometric pathway to **2** *via* **3** to be traced out. We assume the B_3 fragment remains intact; the BH cluster bonds react with the cobalt reagent by σ-bond metathesis; CO loss from the cluster bound $Co(CO)_4$ fragment leads to insertion and consequent cluster expansion; and ML_x fragment rearrangement is facile.[11] The result is shown in Scheme 2. Reaction with $Co_2(CO)_8$ at room temperature leads to the formation of $Cp^*_2Rh_2Co(CO)_3B_3H_3Cl$ **3** (80%, Scheme 2) which has been fully characterized. [7] By itself **3** is stable at 60 °C; however, in the presence of $Co_2(CO)_8$ it is rapidly converted to **2**. Three repetitions of σ-bond methathesis plus insertion lead from reactant to product **2**. Of course the detailed nature of the insertion and rearrangement processes remains unclear, but the overall process is straightforward.

The use of $Co_2(CO)_8$ as a metal fragment source is well illustrated in cluster chemistry.[12] Evidence for a radical pathway was found for reactions of $Co_2(CO)_8$ with organome-

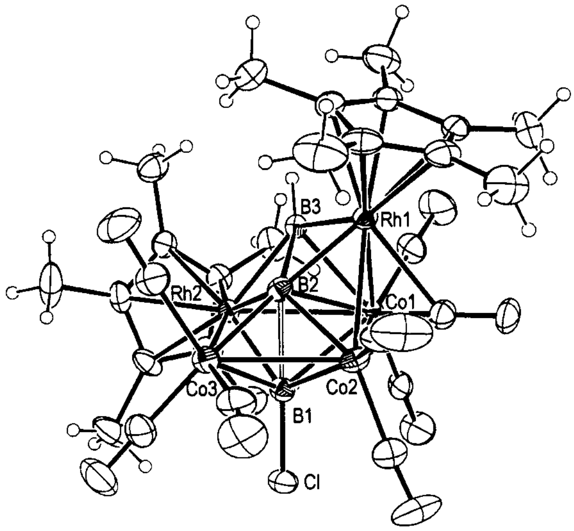
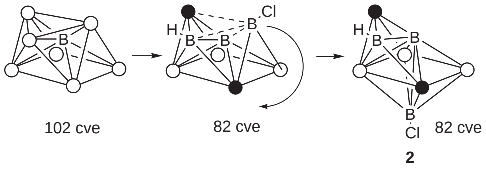
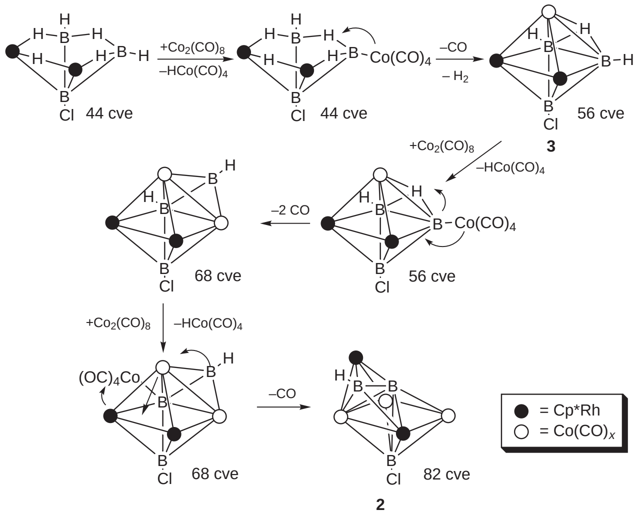


Fig. 1. Molecular structure of $Cp^*_2Rh_2Co_3(CO)_8B_3HCl$ **2**. Selected bond distances (Å) and angles (°): Rh1–Co1 2.5960(7), Rh1-Co2 2.5981(8), Rh2-Co3 2.7111(9), Rh2-Co1 2.7207(8), Co1-Co2 2.5157(10), Co2-Co3 2.6434(10), Rh1-B2 2.077(5), Rh1-B3 2.138(5), Rh1-C23, 2.297(5), Rh2-B2 2.056(5), Rh2-B1 2.066(5), Rh2-B3 2.103(5), Co1-C23 1.892(5), Co1-B3 2.161(5), Co1-B2 2.231(5), Co1-B1 2.299(5), Co2-C23 2.007(5), Co2-B2 2.082(5) Co2-B1 2.194(5), Co3-B2 1.984(5), Co3-B1 2.071(5), B1-B2 1.973(7), B2-B3 1.680(7), Cl-B1 1.831(5), B2-Rh1-B3 46.9(2), B3-Rh1-Co2 91.80(14), Co1-Rh1-Co2 57.94(2), B2-Rh2-B1 57.2(2), B2-Rh2-B3 47.6(2), B1-Rh2-B3 94.9(2), B2-Rh2-Co3 46.7(2), B3-Co1-B1 87.0(2), B2-Co1-B1 51.6(2), B3-Co1-Co2 93.54(14), B1-Co1-Rh1 97.94(13), Co2-Co1-Rh2 89.48(3), Rh1-Co1-Rh2 91.71(2), Co1-Co2-Co3 94.74(3), Rh1-Co2-Co3 93.69(3), Co2-Co3-Rh2 87.08(3).



Scheme 1



Scheme 2

tallic clusters resulting in metal fragment substitution or cluster expansion.[13,14] Presumably the cluster metal–metal bonding network is directly involved. The nature of the cluster building pathway observed here appears distinctly different. This is consistent with earlier work which demonstrates that BH bonds can interact directly with transition metal centers.[15–18] For example, the activity of exocluster B–H bonds towards metal addition has been utilized in promoting the addition of unsaturated organic substrates to borane cages.[19] Thus, even though we have no direct evidence for the cluster–$Co(CO)_4$ intermediates proposed in Scheme 2, their existence is reasonable.

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Notes and references

† *Experimental procedure:* a mixture of $Cp^*_2Rh_2B_3H_6Cl$ (0.14 g, 0.26 mmol) and $Co_2(CO)_8$ (0.25 g, 0.60 mmol) in 10 mL of hexane was heated to 60 °C for 1 h. Removal of insoluble black solids by filtration (Celite) was followed by column chromatography. After $Co_4(CO)_{12}$ was removed (hexane), elution with ether afforded a greenish brown solution which gave 0.075 g of **1** (31% based on Rh). MS (EI), P^+ = 946 (3B, 1Cl, 2Rh atoms, loss of 8 CO). Calc. for weighted average of isotopomers lying within the instrument resolution, *m*/*z* 946.8144, obs. 946.8180. NMR: ^{11}B(hexane, 22 °C), δ 90.9 (s, {^1H}, s, 1B), 92.0 (s, {^1H), s, 1B), 87.1 (d, J_{BH} 160 Hz, s, {^1H}, 1B); $^1H(C_6D_6$, 22 °C), δ 10.22 (partially collapsed quartet, 1H, BH_t), 1.68 (s, 15H, C_5Me_5), 1.59 (s, 15H, C_5Me_5), IR(hexane, cm^{-1}): 2513w (B-H); 2058s, 2033s, 2016w, 1999m, 1986s, 1964w, 1880w, 1778w (CO). Anal. calc. for $C_{28}H_{31}O_8B_3Cl_1Co_3Rh_2$: C, 35.53, H, 3.30. Found: C, 35.60; H, 3.41%.

‡ *Crystal data:* **2**: black crystals, $C_{28}H_{31}O_8B_3Cl_1Co_3Rh_2$, triclinic, space group $P\bar{1}$, a = 9.498(2), b = 9.4931(13), c = 21.394(3) Å, α = 88.104(10), β = 77.308(14), γ = 62.825(11)°, V = 1669.1(4) Å^3, Z = 2, M = 946.02, D_c = 1.882 g cm^{-3}, μ = 2.553 mm^{-1}, Mo-Kα radiation, λ = 0.71073 Å, T = 293K, Enraf-Nonius CAD4, crystal size, 0.16 × 0.12 × 0.10 mm, $2\theta_{max}$ = 50°. Structure solution and refinement were performed on a PC by using the SHELXTL package (G. M. Sheldrick, Siemens Industrial Automation Inc. Madison, WI 1994); $R1$ = 0.0348, $wR2$ = 0.0821 for 4737 observed unique reflections [I > 2σ(I)] and $R1$ = 0.0475, $wR2$ = 0.0884 for all 5874 unique reflections including those with negative intensities. The maximum and minimum residual electron densities on the final difference Fourier map were 0.611 and −0.855 e Å^{-3}, respectively. CCDC 182/1230. See http://www.rsc.org/suppdata/cc1999/933/ for crystallographic files in .cif format.

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