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Symmetrical Scission of the Coordinated Tetraborane in $[(Cp^*ReH_2)_2B_4H_4]$ on CO Addition and Reassociation of the Coordinated Diboranes on H_2 Loss[**]

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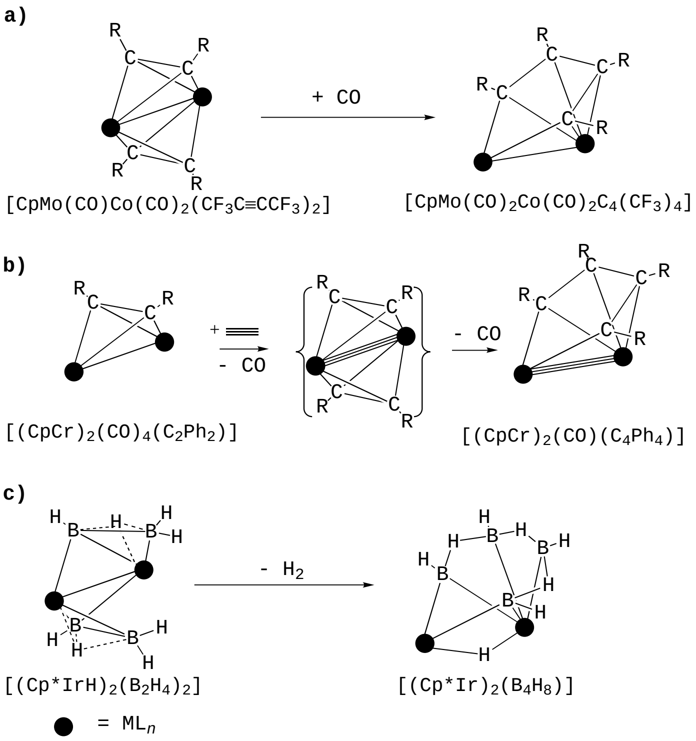
The formation and scission of C–H and C–C bonds within the coordination sphere of a metal lie at the heart of organometallic chemistry.[1] For example, the cleavage of alkynes coordinated to multinuclear metal sites into separated coordinated alkylidyne fragments[2] exhibits more than one mode of scission: dissociation of a dimetal ethyne complex (dimetallatetrahedrane) into two methylidyne complexes[3] or ligand loss from a *nido*-trimetallaalkyne cluster to yield a *closo*-trimetalladialkylidyne cluster.[4] The linking of alkynes at dimetal sites has been documented and, pertinent to this work, are the two systems outlined in Scheme 1 a and b. In the first, a 46 cluster valence electron (cve) bitetrahedral complex is converted into a 48 cve pentagonal-pyramidal complex containing a C_4 fragment.[5] In the other, a μ-alkyne complex is converted into a 44 cve pentagonal-pyramidal complex with a localized Cr≡Cr bond via a postulated 46 cve bitetrahedral intermediate.[6] Both generate a C_4 fragment from two C_2 fragments.

In principle, the incorporation of transition metals into the chemistry of p-block elements other than carbon permits similar manipulation of homonuclear bonding.[7] The literature contains numerous examples for boron,[8–11] but other elements illustrate the possibilities as well.[12] In our own work, the elimination of H_2 from 50 cve $[(Cp^*IrH)_2(B_2H_4)_2]$ leads to the 48 cve complex $[(Cp^*Ir)_2(B_4H_8)]$ in which a B_4 fragment is generated from the fusion of two B_2 fragments (Scheme 1 c).[13] The structure of the latter is analogous to that of the product in Scheme 1 although one reaction (C–C bond formation) is driven by ligand addition and the other (B–B bond formation) by ligand loss. Here we describe a related dirhenium system in which both B–B bond formation on ligand loss and B–B bond breaking on ligand addition are demonstrated.



Scheme 1. Examples of C–C bond formation promoted by a) CO addition to a Mo,Co complex, b) CO loss from (and C_2Ph_2 addition to) a Cr_2 complex, and c) B–B bond formation promoted by H_2 loss from an Ir_2 complex.

The direct synthesis of **1**, from $[Cp^*ReCl_4]$ and $LiBH_4$, permits an examination of the chemistry of its derivatives.[14] Thus, the chemistry of compounds of molecular formula

$[(Cp^*ReH_2)_2(B_4H_4)]$ **1**

$[(Cp^*M)_2B_4H_8]$ as M varies from Cr[15] to Re[16] (and Ru[17] to Ir[13]) unambiguously reveals the role of the transition metal. We have reported that the reaction of 42 cve $[(Cp^*Cr)_2(B_4H_8)]$ with CO leads to 44 cve $[\{Cp^*Cr(CO)\}_2(B_4H_6)]$ in good yield (Scheme 2).[15] Now, the same reaction with the rhenium analogue has been explored.

Reaction of **1** with 1 atm of CO and mild heating leads (via an intermediate **2** see below) to the 44 cve complex **3**, which has been characterized spectroscopically and crystallographically (Figure 1).[18] The core structure deduced from the data

$[(Cp^*ReH_2)\{Cp^*Re(CO)\}(B_4H_4)]$ **3**

based on the electron counting rules[19, 20] is consistent with the solid-state structure. The close analogy with the behavior of the unsaturated complex $[(Cp^*Cr)_2B_4H_8]$ is evident—each loses H_2 and adds an appropriate number of CO ligands to the

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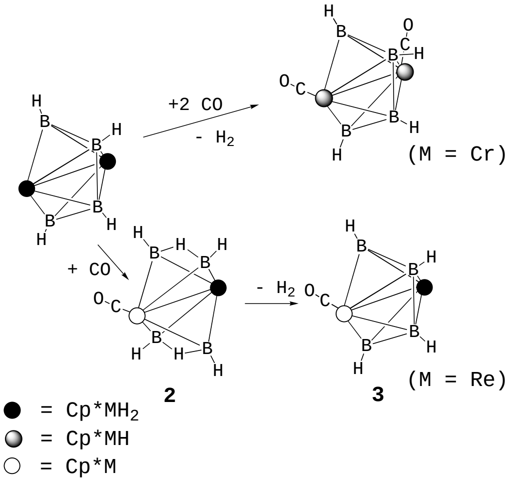


Scheme 2. A comparison of the consequences of the addition of CO to $[(Cp^*Cr)_2B_4H_8]$ and to **1**.

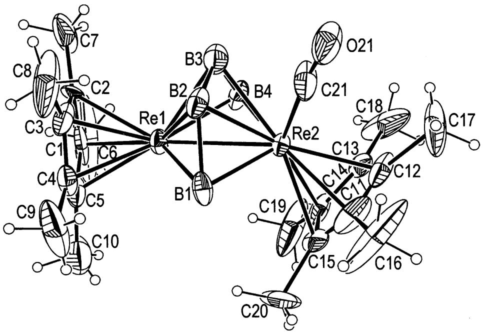


Figure 1. Molecular structure of **3**. Selected bond lengths [Å]: Re1-B1 2.11(2), Re1-B2 2.17(2), Re1-B4 2.26(2), Re1-B3 2.28(2), Re1-Re2 2.7819(8), Re2-B1 2.12(2), Re2-B4 2.17(2), Re2-B2 2.29(2), Re2-B3 2.39(2), B3-B4 1.67(3), B2-B3 1.70(3), B1-B2 1.85(3).

metal centers to achieve the 44 cve count required for a saturated bicapped tetrahedral cluster.

Investigation of the reaction by NMR spectroscopy at room temperature revealed the formation of a metastable intermediate which, when heated, converted cleanly into **3**. Full spectroscopic characterization of this intermediate presented us with a structural puzzle. Either there were two species present or the compound was much more complex than was reasonable to expect. An unambiguous explanation eluded us until an X-ray structure study revealed that there were two molecules of **2**, which differed in geometry, in the crystallographic asymmetric unit (Figure 2).[18] There is precedence for such a situation, for example $[(Cp^*RuCl_2)_2]$[21] and $[Cp_2WOs(CO)_7\{C_2(C_6H_4Me)_2\}]$.[22] The assumption of an approximately 1:1 ratio of these two isomers in solution permits the mass spectrometric, infrared, and ^1H, ^{11}B, and ^{13}C NMR data to be satisfactorily rationalized. The spectra are nearly temperature independent (room temperature and

$[(Cp^*ReH_2)\{Cp^*Re(CO)\}B_4H_6]$ **2**

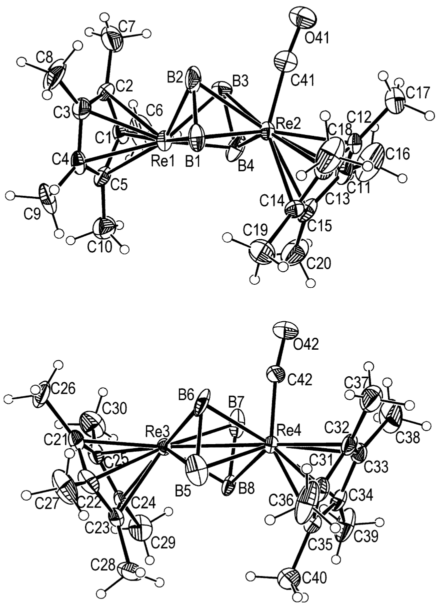
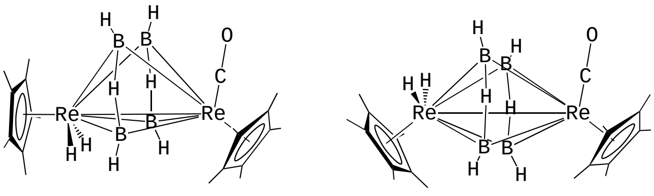


Figure 2. Molecular structure of (top) *trans*-**2** and (bottom) *cis*-**2**. Selected bond lengths [Å]: *trans*-**2**: Re1-B3 2.178(15), Re1-B4 2.205(16), Re1-B2 2.213(17), Re1-B1 2.376(19), Re1-Re2 2.7730(7), Re2-B4 2.194(15), Re2-B1 2.235(15), Re2-B3 2.264(17), Re2-B2 2.355(16), B3-B4 1.63(2), B1-B2 1.72(3), B2-B3 2.32, B1-B4 3.51; *cis*-**2**: Re3-B8 2.125(18), Re3-B5 2.158(14), Re3-B7 2.336(18), Re3-B6 2.417(15), Re3-Re4 2.8274(7), Re4-B5 2.219(16), Re4-B6 2.29(2), Re4-B8 2.298(16), Re4-B7 2.314(14), B7-B8 1.70(3), B5-B6 1.72(3), B5-B8 2.94, B6-B7 3.34.

below) this requires a slow interconversion of the isomeric forms and suggests that the isomers arise from kinetic control of the addition of CO to **1** (likely) or that they have identical free energies (possible but less likely).

As shown in Figure 2 and Scheme 3, the essential difference between the structures of the two isomers of **2** is the disposition of the ancillary ligands relative to the Re–Re axis. This disposition is cisoid (angles Re-Re-Cp*(c) = 149, 154°; Cp*(c) = centroid of Cp* ring) in one case and transoid (angles Re-Re-Cp*(c) = 167, 134°) in the other. Thus, the two Re hydride units seen in the ^1H NMR spectra are likewise cis and trans, respectively, to the CO ligand. Hence, *cis*-**2** probably arises from CO attack cis to the "butterfly" face of **1** while *trans*-**2** arises from *trans* attack. Secondary differences are the positioning of the B_2 ligands relative to the Re–Re axis (the B···B distance corresponding to the bond broken in going from **1** to **2** is 2.94 Å in the *cis* isomer and 2.32 Å in the *trans* isomer) and the Re–Re distances (2.8274(7) Å in the *cis*



trans-**2** *cis*-**2**

Scheme 3. A comparison of the structures of the isomers of **2**.

isomer and 2.7730(7) in the *trans* isomer). Like *trans*-**2**, the Cp* ligands in **3** are *trans* (angles Re-Re-Cp*(c) = 167, 132°; Re–Re = 2.7819(8) Å)

The characterization of **2** as an intermediate in the conversion of **1** into **3** reveals a complexity hidden in the analogous chromium system. As shown in Scheme 2, the addition of CO to **1** precedes H_2 loss. The extra pair of cve causes B–B bond breakage and migration of 2H that leads to two B_2H_3 ligands and a 46 cve bitetrahedral cluster geometry. Elimination of H_2 results in B–B bond reformation and a 44 cve bicapped tetrahedral geometry as found in **1**. Presumably a similar pathway exists for the chromium analogue; however, addition of CO to the metal center is much less facile and at the temperature required for reasonable reaction times any intermediates are rapidly converted into the 44 cve product. With the same ancillary ligands one expects an associative reaction to be more facile for Re than Cr; hence, the lower entrance barrier to intermediate **2**, relative to the exit barrier to **3**, permits its isolation.

In this boron chemistry the relationship to C–C bond cleavage and formation in coordinated alkynes is clear; however, the distinctive character of boron is shown in the analogous processes involving B–B bonds. For example, the ready formation of B-H-B bridge bonds accommodates the addition of CO to **1** and is an essential part of the pathway for the substitution of H_2 by CO.

Experimental Section

2: Standard air sensitive techniques were used. Compound **1** (0.12 g, 0.17 mmol) in hexane (10 ml) saturated with CO at 1 atm was stirred for 15 min at room temperature. The solvent was removed in vacuo, the residue extracted with hexane, and filtered through celite. The filtrate was concentrated and crystallization at –40 °C produced air sensitive, light yellow needles of **2** (0.09 g, 75 %) contaminated with $[Cp^*ReH_6]$ (5–15 %). X-ray quality crystals were grown by vapor diffusion—hexane solution of **2** in inner tube, toluene in outer tube at 7 °C. Selected data for *cis*-**2** and *trans*-**2** in solution. MS (EI): *m*/*z*: 722, isotopic pattern for 2Re, 4B, 21C, 1O atoms; calcd for weighted average of isotopomers lying within the instrument resolution: 724.2410; observed: 724.2398; IR (KBr): $\tilde{\nu}$ = 2510w, 2472w (B-H), 1923s, 1889s (Re-CO) cm^{-1}; ^{11}B NMR (C_6D_6, 22 °C): $\delta = 13.6$ (d, $J(B,H) = 163$ Hz, 1B), –1.9 (d, $J(B,H) = 151$ Hz, 1B), –7.7 (d, $J(B,H) = 153$ Hz, 1B), –20.1 (d, $J(B,H) = 161$ Hz, 1B); ^1H NMR (C_6D_6, 22 °C): $\delta = 2.83$ (partially collapsed quartet (pcq), 2BH*t* (*t* = terminal), 2.55 (pcq, 2BH*t*), 1.88 (s, 15H; Cp*), 1.85 (s, 15H; Cp*), 1.84 (s, 15H; Cp*), 1.82 (s, 15H; Cp*), –0.15 (pcq, 2BHt), –0.18 (pcq, 2BH*t*), –2.01 (br s, 4H; 4B-H-B), –12.55 (br s, 2H; 2B-H-Re), –14.42 (s, 2H; 2Re-H); ^{13}C NMR (C_6D_6, 22 °C): $\delta = 206.7$, 204.1 (Re-CO), 95.9, 94.5, 92.4, 89.2 ($C_5(CH_3)_5$), 13.1, 13.04, 12.3, 11.7 ($C_5(CH_3)_5$).

3: Thermolysis of a light yellow solution of **2** (0.05 g, 0.07 mmol) in benzene (12 ml) at 75 °C generated a red solution with complete conversion into a single product (^{11}B NMR ≈78 % yield) after 5 h. Workup as for **2** gave crystalline **3**. MS (EI): *m*/*z*: 720, isotopic pattern for 2Re, 4B, 21C, 1O atoms; calcd for weighted average of isotopomers lying within the instrument resolution: 722.2254; observed: 722.2239; IR (KBr): $\tilde{\nu} = 2504$w (B–H), 1926s (Re–CO) cm^{-1}; ^{11}B NMR (C_6D_6, 22 °C): $\delta = 87.2$ (d, $J(B,H) = 147$ Hz, 2B), –11.7 (d, $J(B,H) = 121$ Hz, 2B); ^1H NMR (C_6D_6, 22 °C): $\delta = 9.96$ (pcq, 2BH*t*), 1.92 (s, 15H; Cp*), 1.77 (s, 15H; Cp*), –0.43 (pcq, 2BH*t*), –13.12 (s, 2H; 2Re-H); ^{13}C NMR (C_6D_6, 22 °C): $\delta = 217.6$ (Re-CO), 97.9, 95.6 ($C_5(CH_3)_5$), 13.1, 10.6 ($C_5(CH_3)_5$); elemental analysis calcd (%) for $C_{21}H_{36}Re_2B_4O$: C 34.26, H 4.92; found: C 34.49, H 5.01.

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[18] Crystal structure data. Data were collected with $Mo_{K\alpha}$ radiation on a Bruker SMART CCD diffractometer at 294 K. Structure solutions were proceeded by direct methods, and subsequent refinements were carried out using SHELXTL. The hydrogen atoms of the Cp* groups were refined isotropically with an idealized riding model while the hydrogen atoms of B–H and Re–H were not found and not included in the final refinement. Structure of **2**: $M_r = 722.15$, monoclinic, space group $P2_1/c$, $a = 16.1604(10)$, $b = 14.9037(10)$, $c = 20.2280(13)$ Å, $\beta = 98.1780(10)°$, $V = 4822.4(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.989$ $Mg\,m^{-3}$. The refinement converged to final values of $R1 = 0.0470$, $wR2 = 0.0985$ for 8398 observed unique reflections ($I > 2\sigma(I)$). Structure of **3**: $M_r = 720.14$, monoclinic, space group $P2_1/c$, $a = 8.1687(9)$, $b = 14.575(2)$, $c = 20.674(2)$ Å, $\beta = 100.770(2)°$, $V = 2418.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.978$ $Mg\,m^{-3}$. The refinement converged to final values of $R1 = 0.0500$, $wR2 = 0.1042$ for 4186 observed unique reflections ($I > 2\sigma(I)$). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140717 (**2**) and -140718 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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