A Novel Coordinated Inorganic Benzene: Synthesis and Characterization of $\{\eta^5\text{-}C_5Me_5Re\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_4H_4Co_2(CO)_5\}$

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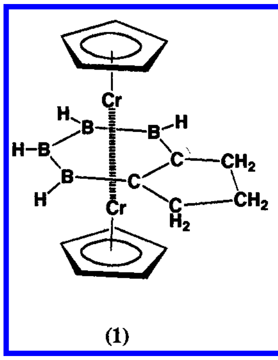
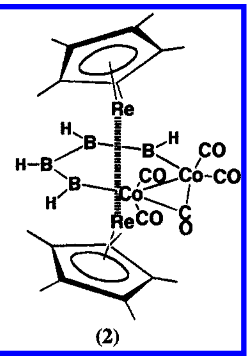
Since the time of Kekule's dream, chemists have been fascinated with the structures of systems possessing the property called aromaticity both in two[1] and three dimensions.[2,3] These include heterobenzenes, e.g., C_5H_5As, in which other p-block elements particpate in the 6 π electron aromatic system[4] and metallabenzenes, e.g., 1-Ir$(PEt_3)_3$-3,5-Me_2-C_5H_3, which has been characterized as a free species[5] as well as when coordinated to another metal fragment, e.g., $(CO)_3Mo\{\eta^6\text{-}[1\text{-}Ir(PEt_3)_3\text{-}3,5\text{-}Me_2\text{-}C_5H_3]\}$.[6] Even the purely inorganic analogue, $H_3B_3N_3H_3$, and coordinated forms, e.g., $(CO)_3Cr\{\eta^6\text{-}H_3B_3N_3H_3\}$, have received considerable attention.[7]

Metal-coordinated benzenes and heterobenzenes are found to possess ring structural parameters nearly identical to those of the free species even for triple-decker complexes.[6,8−10] This means that unusual benzene analogues, too reactive to be isolated as free species, may be sought as metal-stabilized adducts. In this vein, we reported a coordinated tetraborabenzene $(CpCr)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_4H_4C_2R_2\}$, **1**, Cp = η^5-C_5H_5.[11] Consistent with past observations, the ring geometry of free $[C_2B_4H_6]^{4-}$, derived from accurate calculations, is the same as that of the coordinated ring derived from the solid-state structure determination of **1**. Now we report the directed synthesis of $(Cp^*Re)_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}B_4H_4Co_2(CO)_5\}$, **2**, Cp* = η^5-C_5Me_5, an isolobal analogue of **1**, which contains a novel inorganic benzene.


(1)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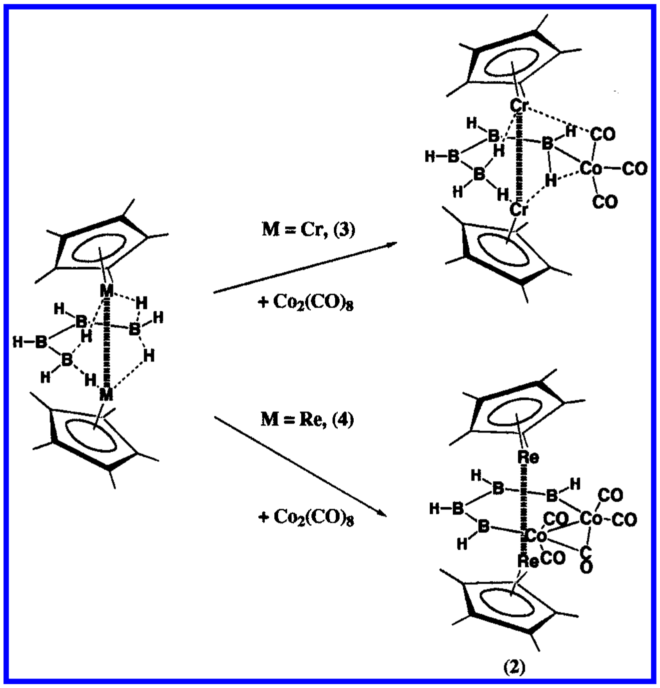
After developing a good route to unsaturated 42 cluster valence electrons[12] (cve) $Cp^*_2Cr_2B_4H_8$, **3**,[13] and a related compound,[14] we attempted to close the central open ring by reaction with main group and transition element fragments. However, with the exception of one successful closure in which a nonplanar B_4S_2C ring was formed by reaction of **3** with CS_2,[15] only ring expansion has been observed until now, e.g., Chart 1.[16−18] Extension of our synthetic method to Re has resulted in the isolation of $Cp^*_2Re_2B_4H_8$, **4**, the saturated 44 cve analogue of **3**. Curiously, the solid-state structure of **4** shows that it possesses the same cluster geometry as **3**; however, the endo hydrogen atoms, which are mainly interacting with boron in **3**, are now found to be principally interacting with the metal (^{1}H chemical shift and coupling constant: δ −3.9, J_{BH} = 70 Hz for **3** and δ −11.5, $J_{BH} \approx$ 15 Hz for **4**). Similar derivative reactions have been surveyed for **4**, and reaction with $Co_2(CO)_8$ results in the replacement of the four endo hydrogen atoms with a 4 electron $Co_2(CO)_5$ fragment and in clean closure of the open face to generate **2**.[19]

Chart 1



(2)

Compound **2** contains a planar (0.032 Å rms deviation, sum of internal angles 719.6°), six-membered B_4Co_2 ring sandwiched between two Cp*Re fragments (Figure 1).[20] However, the necessity of packing the five CO ligands of the Co_2 fragment between the Cp* ligands of Re causes the Cp* ligands to tilt and produces a conrotatory twist of the two $Co(CO)_2(CO)_{br}$ fragments around their pseudo C_3 axes such that the bridging CO lies out of the plane of the B_4Co_2 ring. Within the ring the two types of BB distances are equal to those in the $[C_2B_4H_6]^{4-}$ aromatic ring mentioned above (av 1.719(15) vs av 1.718(8) Å); the BCo distances are within the range found for cobaltaborane clusters

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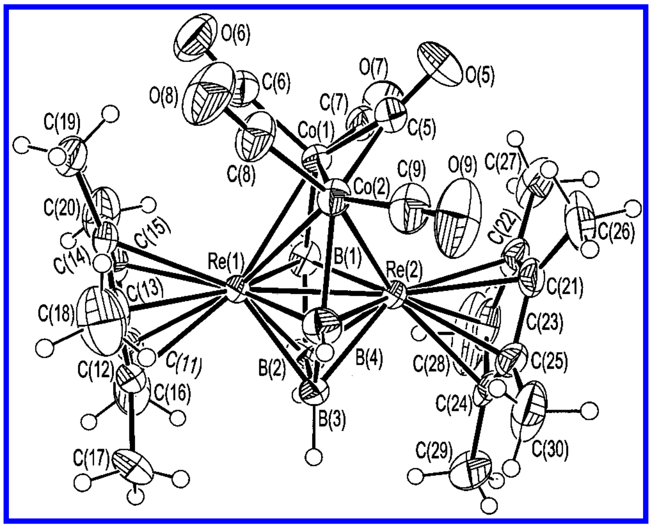

Figure 1. Molecular structure of $\{\eta^5\text{-}C_5Me_5Re\}_2\{\mu\text{-}\eta^6\text{:}\eta^6\text{-}B_4H_4Co_2(CO)_5\}$, **2**. Selected bond distances (Å) and angles (deg): Re1−Re2 2.6393(5), Re1−Co1 2.6478(12), Re1−Co2 2.6854(13), Re2−Co2 2.6157(12), Re2−Co1 2.6460(12), Re1−B3 2.130(10), Re1−B2 2.150(11), Re1−B1 2.189(10), Re1−B4 2.194(11), Re2−B3 2.142(10), Re2−B2 2.161(10), Re2−B1 2.237(10), Re2−B4 2.255(11), Co1−Co2 2.4192(17), Co1−B1 2.010(11), Co2−B4 2.036(11), B1−B2 1.712(15), B2−B3 1.770(15), B3−B4 1.712(15), B1−B2−B3 120.4(7), B4−B3−B2 122.9(8), B3−B4−Co2 130.6(7), B2−B1−Co1 132.8(7), B4−Co2−Co1 106.4(3), B1−Co1−Co2 106.5(3).

but distinctly shorter than that in $(CO)_2(\eta^1\text{-dppm})Co(\mu\text{-dppm})BH_2$, dppm = $Ph_2PCH_2PPh_2$, which contains a CoB single bond (av 2.023(11) vs 2.227(6) Å);[21] and the CoCo distance is significantly shorter than that accepted for a CoCo single bond (2.4192(17) vs 2.49−2.52 Å).[22,23] Thus, the planarity of the ring and its edge lengths are consistent with considering **2** an analogue of a coordinated benzene just like isolobal **1**.

There is additional circumstantial evidence supporting the view of **2** as a coordinated 6 π electron $[B_4H_4Co_2(CO)_5]^{6-}$ ring. Compound **2** can be considered a cluster; however, the geometry expected for an 8 vertex closo cluster is a dodecahedron rather than a hexagonal bipyramid.[24,25] Further 9 skeletal electron pairs (sep) are expected although **2** possesses only 6.[26] Alternatively, as **2** contains a ReRe bond (2.6393(5) Å), the compound can be related to the hypoelectronic clusters of tungsten described earlier,[27] but the structural patterns of these new clusters remain to be fully defined. Thus, there is no established cluster structure principle that requires the observed geometry of **2**.

On the other hand, **2** is easily seen to be a 24 valence electron triple-decker complex[28] analogous to **1** with a 6 π electron $[B_4H_4Co_2(CO)_5]^{6-}$ central ring. That is, adding 4 electrons to closo-$C_2R_2B_4H_6$ gives planar, arachno $[C_2R_2B_4H_6]^{4-}$, whereas adding 4 electrons to closo-$[B_4H_4Co_2(CO)_5]^{2-}$, equivalent to known closo-$H_2B_4H_4Co_2Cp_2$,[29,30] yields the planar arachno cobaltaborane ring found in **2**. Like **1**, and 24 valence electron CpTi(μ-η^3:η^3-P_6)TiCp,[31] **2** contains a metal−metal bond. Again like **1**, but unlike CpTi(μ-η^3:η^3-P_6)TiCp, the central ring is planar. With the $C_2R_2B_4H_6$ and $B_4H_4Co_2(CO)_5$ rings, but not with the P_6 ring, there is a good match between the energies of the Cp*M fragment orbitals and the out of plane orbitals of the central ring leading to a good HOMO−LUMO gap without the necessity of ring distortion.[11,32] Further examination of the electronic structure of planar $[B_4H_4Co_2(CO)_5]^{6-}$ as found in **2** is in progress.

$Cp^*_2Re_2B_4H_8$ appears to be a versatile starting material. For example, reaction of **4** with an excess of BH_3THF leads to the formation of $Cp^*_2Re_2B_7H_7$, a hypoelectronic metallaborane described earlier.[33] Additional reaction chemistry of **4**, including a detailed comparison of its geometric and electronic structure with that of **3**, will be reported in the full paper.

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Supporting Information Available: Description of the synthesis and characterization of **4** and X-ray structural information on **2** (PDF). An X-ray crystallographic file for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] A 2-fold excess of $Co_2(CO)_8$ was added to 0.07 g (0.1 mmol) of **4** in 10 mL of hexane in a 100-mL Schlenk tube and stirred at room temperature. After 15 min the solvent was removed under vacuum, and the residue was extracted in hexane, concentrated, and kept at −40 °C to remove $Co_4(CO)_{12}$ by fractional crystallization. The mother liquor was filtered quickly through silica gel to give a yellowish brown solution which generated two types of crystals at −40 °C—white, $Cp^*Re(CO)_3$ (resulting from a Cp^*ReH_6 impurity in **4**) and brown **2** (75% yield by NMR). X-ray quality crystals were obtained by recrystallizing selected brown crystals overnight at −4 °C. MS (EI), $P^+ = 949$, isotope pattern for 2Re, 2Co, and 4B atoms; calcd for weighted average of isotopomers lying within instrument resolution, 950.0558, obsd, 950.0586. ^{11}B NMR (C_6D_6, 22 °C) δ 87.8 d, $J_{B-H} = 172$ Hz, 2B; δ 86.7 d, $J_{B-H} = 162$ Hz, 2B. ^1H NMR (C_6D_6, 22 °C) δ 9.31 partially collapsed quartet (pcq), 2BHt; δ 4.38 (pcq), 2BHt; δ 1.67 s, 30H, 2Cp*; IR (KBr, cm^{-1}): 2536 w, 2453 w (B−H*t*), 2022 s (Co−*CO*), 1997 vs (Co−*CO*), 1972 s (Co−*CO*), 1820 w (Co−(μ-*CO*)).

[20] Crystallographic data: orthorhombic *Pbca*, $a = 23.282(2)$ Å, $b = 16.787(2)$ Å, $c = 15.0481(14)$ Å, $V = 5881.3(10)$ Å^3, $Z = 8$, 20 °C, CAD4 diffractometer, 5186 unique data, θ up to 25°, empirical psi-scan absorption correction, direct methods (Shelxs-86), Shelxl-97, H atoms found from difference Fourier map, refined with riding models, R. ($I \geq 2\sigma(I)$) = 0.0368, $R_w = 0.0757$.

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