

A Novel Coordinated Inorganic Benzene: Synthesis and Characterization of $\{\eta^5\text{-C}_5\text{Me}_5\text{Re}\}_2\{\mu\text{-}\eta^6\text{-}\eta^6\text{-B}_4\text{H}_4\text{Co}_2(\text{CO})_5\}$

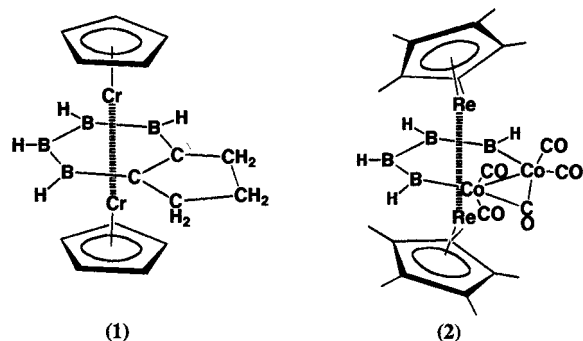
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Since the time of Kekule's dream, chemists have been fascinated with the structures of systems possessing the property called aromaticity both in two¹ and three dimensions.^{2,3} These include heterobenzenes, e.g., $\text{C}_5\text{H}_5\text{As}$, in which other p-block elements participate in the 6 π electron aromatic system⁴ and metallabenzenes, e.g., 1-Ir(PEt₃)₃-3,5-Me₂-C₅H₃, which has been characterized as a free species⁵ as well as when coordinated to another metal fragment, e.g., $(\text{CO})_3\text{Mo}\{\eta^6\text{-}[1\text{-Ir(PEt}_3\text{)}_3\text{-3,5-Me}_2\text{-C}_5\text{H}_3]\}$.⁶ Even the purely inorganic analogue, $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$, and coordinated forms, e.g., $(\text{CO})_3\text{Cr}\{\eta^6\text{-H}_3\text{B}_3\text{N}_3\text{H}_3\}$, have received considerable attention.⁷

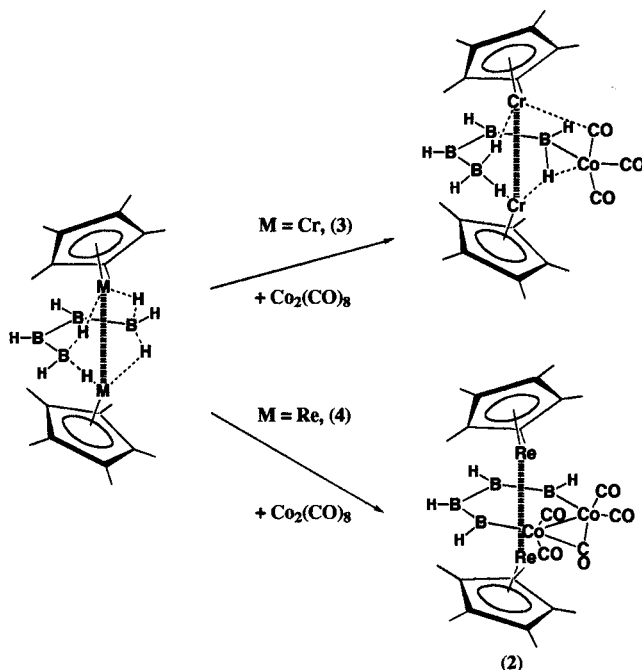
Metal-coordinated benzenes and heterobenzenes are found to possess ring structural parameters nearly identical to those of the free species even for triple-decker complexes.^{6,8–10} This means that unusual benzene analogues, too reactive to be isolated as free species, may be sought as metal-stabilized adducts. In this vein, we reported a coordinated tetraborabenzene $(\text{CpCr})_2\{\mu\text{-}\eta^6\text{-}\eta^6\text{-B}_4\text{H}_4\text{C}_2\text{R}_2\}$, **1**, Cp = $\eta^5\text{-C}_5\text{H}_5$.¹¹ Consistent with past observations, the ring geometry of free $[\text{C}_2\text{B}_4\text{H}_6]^{4-}$, 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 $(\text{Cp}^*\text{Re})_2\{\mu\text{-}\eta^6\text{-}\eta^6\text{-B}_4\text{H}_4\text{Co}_2(\text{CO})_5\}$, **2**, Cp* = $\eta^5\text{-C}_5\text{Me}_5$, an isolobal analogue of **1**, which contains a novel inorganic benzene.



After developing a good route to unsaturated 42 cluster valence electrons¹² (cve) $\text{Cp}^*_2\text{Cr}_2\text{B}_4\text{H}_8$, **3**,¹³ and a related compound,¹⁴

- (1) Binsch, G. *Naturwissenschaften* **1973**, *60*, 369.
- (2) Michel, H.; Steiner, D.; Wacadlo, S.; Allwohn, J.; Stamatis, N.; Massa, W.; Berndt, A. *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 607.
- (3) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454.
- (4) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153.
- (5) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606.
- (6) Bleeke, J. R.; Bass, L. A.; Xie, Y.-F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213.
- (7) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1995; p 241.
- (8) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: New York, 1989.
- (9) Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583.
- (10) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.
- (11) Kawamura, K.; Shang, M.; Wiest, O.; Fehlner, T. P. *Inorg. Chem.* **1998**, *37*, 608.

Chart 1



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 $\text{B}_4\text{S}_2\text{C}$ 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 $\text{Cp}^*_2\text{-Re}_2\text{B}_4\text{H}_8$, **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 (¹H chemical shift and coupling constant: $\delta -3.9$, $J_{\text{BH}} = 70$ Hz for **3** and $\delta -11.5$, $J_{\text{BH}} \approx 15$ Hz for **4**). Similar derivative reactions have been surveyed for **4**, and reaction with $\text{Co}_2(\text{CO})_8$ results in the replacement of the four endo hydrogen atoms with a 4 electron $\text{Co}_2(\text{CO})_5$ fragment and in clean closure of the open face to generate **2**.¹⁹

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 $\text{Co}(\text{CO})_2(\text{CO})_{\text{br}}$ 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 $[\text{C}_2\text{B}_4\text{H}_6]^{4-}$ 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

- (12) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.
- (13) Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.
- (14) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1994**, *13*, 4510.
- (15) Hashimoto, H.; Shang, M.; Fehlner, T. P. *Organometallics* **1996**, *15*, 1963.
- (16) Hashimoto, H.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1996**, *118*, 8164.
- (17) Aldridge, S.; Fehlner, T. P.; Shang, M. *J. Am. Chem. Soc.* **1997**, *119*, 2339.
- (18) Aldridge, S.; Hashimoto, H.; Kawamura, K.; Shang, M.; Fehlner, T. P. *Inorg. Chem.* **1998**, *37*, 928.

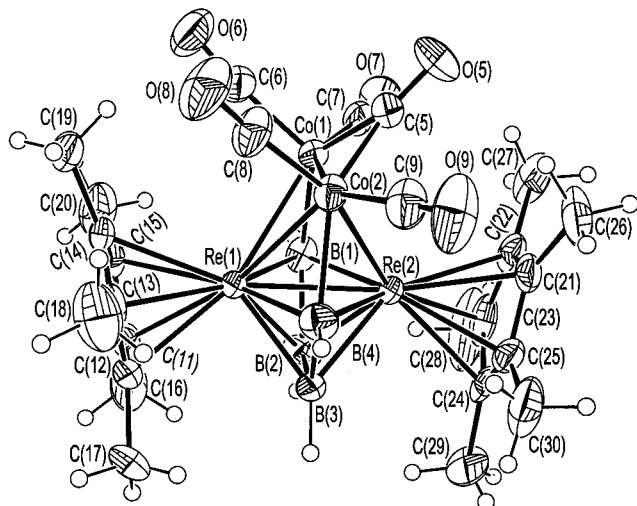


Figure 1. Molecular structure of $\{\eta^5\text{-C}_5\text{Me}_5\text{Re}\}_2[\mu\text{-}\eta^6\text{:}\eta^6\text{-B}_4\text{H}_4\text{Co}_2\text{(CO)}_5\text{]}_2$, **2**. Selected bond distances (Å) and angles (deg): Re1–Re2 2.6393(5), Re1–Co1 2.6478(12), Re1–Co2 2.6854(13), Re2–Co2 2.6157(12), Re2–Co1 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 $(\text{CO})_2(\eta^1\text{-dppm})\text{Co}(\mu\text{-dppm})\text{-BH}_2$, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, 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 isobal **1**.

(19) A 2-fold excess of $\text{Co}_2(\text{CO})_8$ 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 $\text{Co}_4(\text{CO})_{12}$ 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, $\text{Cp}^*\text{Re}(\text{CO})_5$ (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), $\text{P}^+ = 949$, isotope pattern for 2Re, 2Co, and 4B atoms; calcd for weighted average of isotopomers lying within instrument resolution, 950.0558, obsd, 950.0586. ¹¹B NMR (C_6D_6 , 22°C) δ 87.8 d, $J_{\text{B-H}} = 172$ Hz, 2B; δ 86.7 d, $J_{\text{B-H}} = 162$ 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–Hr), 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, $V = 5881.3(10)$ Å³, $Z = 8$, 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, $R(I) \geq 2\sigma(I) = 0.0368$, $R_w = 0.0757$.

(21) Elliot, D. J.; Levy, C. J.; Puddephatt, R. J.; Holah, D. G.; Hughes, A. N.; Magnuson, V. R.; Moser, I. M. *Inorg. Chem.* **1990**, *29*, 5014.

(22) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

There is additional circumstantial evidence supporting the view of **2** as a coordinated 6 π electron $[\text{B}_4\text{H}_4\text{Co}_2(\text{CO})_5]^{6-}$ 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 complex²⁸ analogous to **1** with a 6 π electron $[\text{B}_4\text{H}_4\text{Co}_2(\text{CO})_5]^{6-}$ central ring. That is, adding 4 electrons to closo- $\text{C}_2\text{R}_2\text{B}_4\text{H}_6$ gives planar, arachno $[\text{C}_2\text{R}_2\text{B}_4\text{H}_6]^{4-}$, whereas adding 4 electrons to closo- $[\text{B}_4\text{H}_4\text{Co}_2(\text{CO})_5]^{2-}$, equivalent to known closo- $\text{H}_2\text{B}_4\text{H}_4\text{Co}_2\text{Cp}_2$,^{29,30} yields the planar arachno cobaltaborane ring found in **2**. Like **1**, and 24 valence electron $\text{Cp}^*\text{Ti}(\mu\text{-}\eta^3\text{:}\eta^3\text{-P}_6)\text{TiCp}$,³¹ **2** contains a metal–metal bond. Again like **1**, but unlike $\text{Cp}^*\text{Ti}(\mu\text{-}\eta^3\text{:}\eta^3\text{-P}_6)\text{TiCp}$, the central ring is planar. With the $\text{C}_2\text{R}_2\text{B}_4\text{H}_6$ and $\text{B}_4\text{H}_4\text{Co}_2(\text{CO})_5$ 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 $[\text{B}_4\text{H}_4\text{Co}_2(\text{CO})_5]^{6-}$ as found in **2** is in progress.

$\text{Cp}^*\text{Re}_2\text{B}_4\text{H}_8$ appears to be a versatile starting material. For example, reaction of **4** with an excess of BH_3THF leads to the formation of $\text{Cp}^*\text{Re}_2\text{B}_7\text{H}_7$, 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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(23) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990.

(24) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210.

(25) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.

(26) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(27) Weller, A. S.; Shang, M.; Fehlner, T. P. *Organometallics* **1999**, *18*, 853.

(28) Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 1, p 197.

(29) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 252.

(30) Weiss, R.; Bowser, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1522.

(31) Scherer, O. J.; Swarowsky, H.; Wolmershäuser, G.; Kaim, W.; Kohlmann, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1153.

(32) Reddy, A. C.; Jemmis, E. D.; Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. *Organometallics* **1992**, *11*, 3894.

(33) Weller, A. S.; Shang, M.; Fehlner, T. P. *Chem. Commun.* **1998**, 1787.