Synthesis and Structure of $\{\eta^5\text{-}C_5H_5Cr\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$. An Unusual 24-Electron Triple-Decker Sandwich Complex Containing a Metal-Stabilized, Planar Tetraborabenzene

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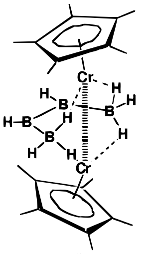
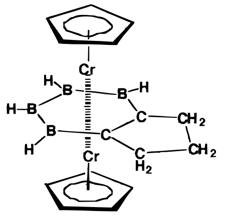
Received October 10, 1997

Recently we demonstrated that Cp*MCl$_n$ complexes,[1] Cp* = η^5-C$_5$Me$_5$, are useful metal synthons for metallaboranes containing Co,[2,3] Cr,[4,5] Mo,[6] and Ta[7] metals. One of these, Cp*$_2$Cr$_2$B$_4$H$_8$, **1**, is selective in its reactions partners.[8,9] We wondered whether this is due to restricted access to the metal sites caused by the bulkiness of the Cp* ligand. Thus, we have explored the synthesis of the η^5-C$_5$H$_5$ (Cp) analogue of **1**. In doing so, we have isolated a byproduct which is a novel member of the family of known triple-decker complexes.[10]



(1)



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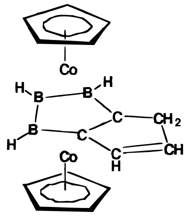

(3)

In attempts to produce the Cp analogue of **1**, a new compound was isolated in low yield.[11] Mass spectrometric data yield the composition C$_{15}$H$_{20}$B$_4$Cr$_2$, which suggests the unexpected formulation Cp$_3$Cr$_2$B$_4$H$_5$.[12] Although the ^{11}B NMR shows two pairs of equivalent boron atoms reminiscent of **1**, the ^{1}H NMR suggests the presence of a −CH$_2$−CH$_2$−CH$_2$− fragment with two equivalent CH$_2$ groups. In addition, there is no sign of B−H−Cr bridging hydrogens. Although related to **1**, the compound was only defined by a structure determination.[13]

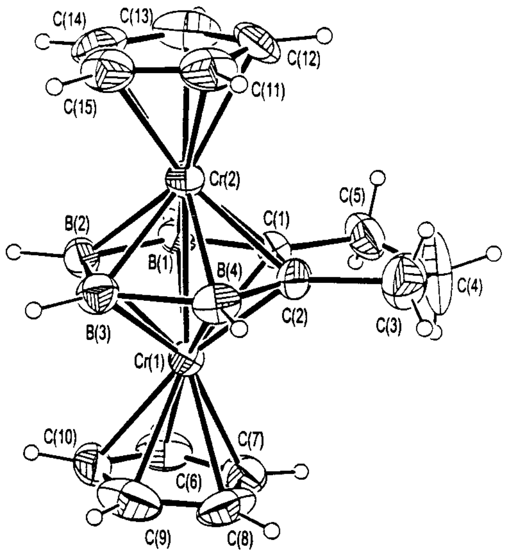

Figure 1. Molecular structure of $\{\eta^5\text{-}C_5H_5Cr\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$, **2**. Selected distances (Å): Cr(1)−Cr(2), 2.6626(11); Cr(1)−C(1,2), 2.075(4), 2.062(5); Cr(1)−B(1,2,3,4), 2.137(5), 2.108(5), 2.087(5), 2.115(6); Cr(2)−C(1,2), 2.085(4), 2.067(5); Cr(2)−B(1,2,3,4), 2.131(5), 2.089(5), 2.100(6), 2.120(5); C(1)−C(2), 1.464(6); C(1)−B(1), 1.561(6); C(2)−B(4), 1.553(7); B(1)−B(2), 1.713(7); B(2)−B(3), 1.734(8); B(3)−B(4), 1.706(8) Å.

The structure of **2** (Figure 1) contains a Cp$_2$Cr$_2$B$_4$H$_4$ fragment qualitatively similar to that in **1** with the four B−H−Cr hydrogen atoms of **1** replaced by two carbyne carbons of the C$_5$ ring derived from the third Cp. Precedent for the incorporation of a Cp fragment comes from the formation of $\{\eta^5\text{-}C_5H_5Co\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(\mu\text{-}1,2\text{-}C_3H_4\text{-}1,2\text{-}C_2B_3H_3)\}$, **3**, in the reaction of [B$_5$H$_8$]$^-$ with NaCp and CoCl$_2$.[14] This molecule contains a planar C$_2$B$_3$ ring sandwiched between two CpCo fragments and has an unsaturated −CH═CHCH$_2$− fragment bridging the carbon atoms of the C$_2$B$_3$ ring.[15] The Co−Co distance in **3** is considerably longer than the Cr−Cr distance in **2** (3.135(1) vs 2.663(1) Å).

The hexagonal bipyramidal geometry of **2** is unknown in metallacarborane chemistry and is not one of the polyhedra

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(1) Poli, R. *Chem. Rev.* **1991**, *91*, 509.

(2) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1993**, *115*, 12224.

(3) Nishihara, Y.; Deck, K. J.; Shang, M.; Fehlner, T. P.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1994**, *13*, 4510.

(4) Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1994**, *116*, 8408.

(5) Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.

(6) Aldridge, S.; Fehlner, T. P.; Shang, M. *J. Am. Chem. Soc.* **1997**, *119*, 2339.

(7) Aldridge, S.; Hashimoto, H.; Shang, M.; Fehlner, T. P. *Chem. Commun.* **1998**, 207.

(8) Hashimoto, H.; Shang, M.; Fehlner, T. P. *Organometallics* **1996**, *15*, 1963.

(9) Hashimoto, H.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1996**, *118*, 8164.

(10) See: Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Abel, E., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 1; see also references therein.

(11) The preparative reaction of **1** was carried out as described previously for Cp* but using NaCp.[5] As only paramagnetic products were observed, THF was removed, toluene added, and the mixture heated at 80 °C for 15 h. A small amount of a brown crystalline material was isolated from the reaction mixture by fractional crystallization.

(12) Spectroscopic data: MS(EI): P$^+$ m/e = 348, $^{12}C_{15}{}^{1}H_{20}{}^{11}B_4{}^{52}Cr_2$; distribution of isotopes consistent with 4B and 2Cr; calculated exact mass 348.0765 (average of $^{11}B^{52}Cr$ and $^{10}B^{53}Cr$ isotopomers), observed 348.0785. ^{11}B NMR (δ; THF, 20 °C): 111.1 d, J_{BH} = 137 Hz, {^{1}H} s; 69.0 d, J_{BH} = 145 Hz, {^{1}H} s. ^{1}H NMR (δ; C$_6$D$_6$, 20 °C): 5.17 s, 10H, C$_5$*H*$_5$; 2.76 t, J_{HH} = 6.7 Hz, 4H, C*H*$_2$CH$_2$C*H*$_2$; 1.98 quint, J_{HH} = 6.7 Hz, 2H, CH$_2$C*H*$_2$CH$_2$.

(13) Crystal data for $\{\eta^5\text{-}C_5H_5Cr\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$, **2**: C$_{15}H_{20}B_4Cr_2$, monoclinic $P2_1/c$ (No. 14), a = 11.820(3) Å, b = 9.836(2) Å, c = 14.471(4) Å, β = 109.46(2)°, V = 1586.4(7) Å^3, Z = 4, D_{calc} = 1.455 g cm^{-3}, 293 K. Data were collected on a crystal of dimensions 0.30 × 0.08 × 0.08 mm in the $\omega/2\theta$ scan mode on a CAD4 diffractometer to a maximum 2θ of 50.0°. Structure solution and refinement were by SHELXTL. All non-hydrogens were refined anisotropically, and the hydrogen atoms were refined isotropically with selected restraints. Using all reflections (including negative intensities), the refinement converged to R_1 = 0.0779, wR_2 = 0.1220 (R_1 = 0.0464, wR_2 = 0.0984 if calculated only for reflections with $I > 2\sigma(I)$).

(14) Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

(15) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10.

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normally associated with eight-vertex closed clusters.[16] Further, the available cluster bonding electrons are insufficient to meet the requirements of a single eight-vertex closo cage. Thus, **2** is better described as a 24-valence-electron (ve) triple-decker complex, $\{\eta^5\text{-}C_5H_5Cr\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}(\mu\text{-}1,2\text{-}C_3H_6\text{-}1,2\text{-}C_2B_4H_4)\}$. This electron count lies considerably below the 30/34-ve rule proposed by Hoffmann et al.[17] and matches that observed for $\{\eta^5\text{-}C_5H_5\text{-}Ti\}_2\{\mu\text{-}\eta^3{:}\eta^3\text{-}P_6\}$ with a puckered central ring.[18,19]

The observed structure is consistent with the description of **2** as a triple-decker complex. The atoms of the C_2B_4 ring plus C(3) and C(5) lie in a well-defined plane (rms deviation 0.010 Å). The two Cr atoms are nearly equidistant from the six atoms of the C_2B_4 ring. The C−C, B−C, and B−B distances within the central ring are comparable to the same parameters in **3**, and the C−C distance is close to the average found in the central C_6 ring of $\{\eta^5\text{-}C_5H_5V\}_2\{\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6\}$ of 1.443(5) Å.[20] The C_5 rings are modestly tilted relative to the C_2B_4 ring.

A comparison with triple-decker complexes that contain a central P_6 moiety is instructive. In the 28-ve $\{\eta^5\text{-}C_5Me_5Mo\}_2\text{-}\{\mu\text{-}\eta^6{:}\eta^6\text{-}P_6\}$, a planar and symmetric 6π P_6 species is found "trapped" by two CpMo fragments.[21] However, for $CpMP_6MCp$ complexes with 26- and 24-ve, variations in the geometries of the central P_6 have been correlated with the orbital interactions of the metals with the ring.[19,22] That is, in contrast to the 28-ve complex, both known 26-ve complexes (M = V, Nb) have in-plane distortions of the central ring and the 24-ve complex (M = Ti) has a puckered ring. This behavior has been traced to two MO's: a metal-ring antibonding orbital (e_2' symmetry, 4d* in Figure 3, ref 22) and a metal−metal bonding orbital (a_1' and the SHOMO in Figure 3, ref 22). The former is fully occupied, and the HOMO for 28-ve is but half-occupied for 26-ve leading to in-plane distortions that remove the degeneracy. It is empty for 24-ve and although a planar ring is not ruled out, puckering of the ring permits an increase in the HOMO−LUMO gap.

Fenske−Hall calculations[23,24] for **2** generate a similar MO diagram in which the HOMO is a Cr−Cr bonding orbital and the LUMO is a nearly degenerate pair of orbitals corresponding to the ring−metal antibonding orbitals described above. The difference in **2** compared to $CpTiP_6TiCp$ arises from the lower energies of the Cr d functions relative to Ti and the higher energies of the C_2B_4 ring orbitals relative to P_6. This yields a substantial HOMO−LUMO gap without the necessity of ring distortion. In addition, as the empty metal−ring antibonding MO's (4d* in Figure 3, ref 22) are largely metal based and derived from two occupied metal fragment orbitals, electrons are transferred away from the two Cr centers in forming **2**. Simultaneously, a pair of C_2B_4-based, occupied MO's of **2** are derived mainly from the empty, nearly degenerate set of out-of-plane π-bonding orbitals of the C_2B_4 ring and electrons are transferred to the ring on forming **2**. These two orbital interactions suggest that **2** can be viewed as a 6π $[C_2B_4H_4R_2]^{4-}$ ring bridging a $[CpCr^{III}-Cr^{III}Cp]^{4+}$ ion.

For this reason we have explored a planar structure of $[C_2B_4H_6]^{2n-}$, $n = 0-2$, with ab initio techniques.[25] Neither $C_2B_4H_6$ nor $[C_2B_4H_6]^{2-}$ was found to have a stable planar form (three out-of-plane and two in-plane imaginary frequencies, respectively), but planar $[C_2B_4H_6]^{4-}$ is a true minimum on the potential energy surface.[26] The calculated bond distances (C−C = 1.464, C−B = 1.548, and B−B = 1.716 and 1.706 Å) are equal within experimental error to those of **2**. As the distortions observed for P_6 triple-deckers are clearly related to changes in ring orbital populations on coordination, the excellent correspondence between the parameters in the free ligand structure and related parameters in **2** gives added validity to the model suggested.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Text describing the structure determination and tables providing further crystallographic details, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen atom coordinates and least-squares planes, as well as energies, imaginary frequencies, and coordinates of $[C_2B_4H_6]^{2n-}$, $n = 0-2$ (31 pages). An X-ray crystallographic file, in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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[16] Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.

[17] Hoffmann, R.; Lauher, J. W.; Elian, M.; Somerville, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

[18] Scherer, O. J.; Swarowsky, H.; Wolmershäuser, G.; Kaim, W.; Kohlmann, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1153.

[19] Reddy, A. C.; Jemmis, E. D.; Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. *Organometallics* **1992**, *11*, 3894.

[20] Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.

[21] Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351.

[22] Jemmis, E. D.; Reddy, A. C. *Organometallics* **1988**, *7*, 1561.

[23] Fenske, R. F. *Pure Appl. Chem.* **1988**, *27*, 61.

[24] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

[25] McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317.

[26] All calculations were performed using the G94 series of programs and the Becke3LYP hybrid functional with a 6-31G* basis set: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; E. S. Replogle, Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.