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Synthesis and Structure of a Hexadecker Sandwich[1]

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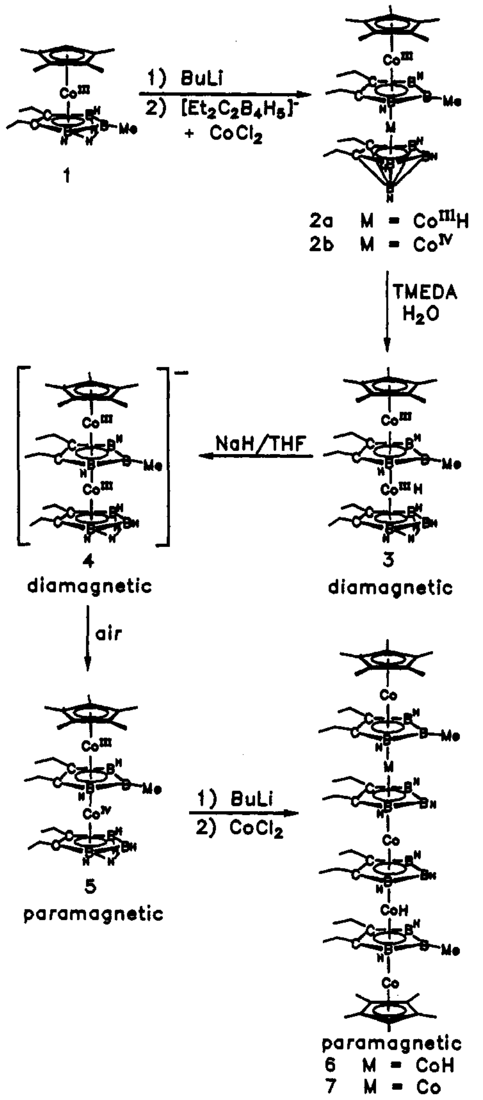
Stacking reactions of small double-decker metallacarborane sandwich anions of the type $[Cp^*Co(Et_2C_2B_3H_3R)]^-$ have been developed in our laboratory as a controlled route to air-stable, neutral triple-decker and tetradecker sandwich complexes.[2] In principle, it appeared possible to extend this approach to the synthesis of larger stacks: *e.g.*, hexadecker sandwiches should be accessible via coordination of two suitably designed triple-decker substrates to a central metal ion. Triple-decker synthons for this purpose must have open C_2B_3 end rings capable of deprotonation and face-bonding to a metal center. We have prepared such a complex via "decapitation" of the mixed-ligand species **2a** and **2b** (Scheme 1) that have pyramidal C_2B_4 end units,[3] affording the desired open-ended sandwich **3**. As shown, the yellow double-decker complex $Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}Me)$ (**1**) was bridge-deprotonated and treated with the *C,C'*-diethylcarborane anion and $CoCl_2$ to generate red-brown diamagnetic $Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)CoH(Et_2C_2B_4H_4)$ (**2a**) and dark brown paramagnetic[4] $Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)Co(Et_2C_2B_4H_4)$ (**2b**). Reaction of either **2a** or **2b** with wet TMEDA gave dark green diamagnetic $Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)CoH(Et_2C_2B_3H_5)$ (**3**) as the major isolable product, purified via chromatography on silica and obtained as air-stable crystals.[5]

Compound **3** has two types of acidic hydrogens, as CoH and B–H–B bridge groups, and this presented a problem: deprotonation in the usual manner removes only the metal-bound proton, forming the anion **4** whose B–H–B hydrogens remain intact, preventing complexation by metal ions. The difficulty was circumvented by oxidation of **4** to neutral, dark brown paramagnetic $Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)Co(Et_2C_2B_3H_5)$ (**5**). Bridge-deprotonation of this species with *n*-butyllithium followed by reaction with $CoCl_2$ gave a nearly black solution that was chromatographed on silica to give two dark brown bands.[6] The negative-ion FAB mass spectra of these products correspond to $[Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_3)]_2Co$ (**6**) and $Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)Co(Et_2C_2B_3H_3)CoH(Et_2C_2B_3H_2\text{-}Me)CoCp^*$ (**7**). The spectrum of **6** is shown in Figure 1. Compounds **6** and **7** survive exposure to air for several hours in solution and for days in the solid state; both exhibit proton NMR spectra typical of paramagnetic species.[4] The hexadecker sandwich geometry of **6** was confirmed via X-ray crystallography, which revealed the structure shown in Figure 2.[7] The four independent C_2B_3 carborane rings are essentially planar and are nearly coplanar with their attached ethyl groups. The Co–B and Co–C distances are closely similar, and the cobalt atoms lie approximately above the centroids of their attached rings; there is no indication of significant slippage of the metals. The molecule is significantly bent, as measured by the deviation of the Co1–Co2–Co3–Co4–Co5 array from linearity (Co1–Co2–Co3 angle, 169.5°; Co2–Co3–Co4, 167.7°; Co3–Co4–Co5, 168.5°) and by the dihedral angles subtended by the six rings (ring 2 vs 3, 12.3°; 3 vs 4, 16.4°; 4 vs 5, 12.3°). Since Co–M–Co (M = Co, Ni)

Scheme 1



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[1] Organotransition-Metal Metallacarboranes. 34. Parts 32 and 33: Pipal, J. R.; Grimes, R. N. *Organometallics* **1993**, *12*, 4452 and 4459.

[2] (a) Piepgrass, K. W.; Meng, X.; Hoelscher, M.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 5202 and references therein. (b) Meng, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 6143.

[3] Compounds of this type have been reported recently: Waterworth, S.; Grimes, R. N. *Abstracts of Papers*, 3rd Boron USA Workshop, Washington State University, Pullman, WA, July 1992; Abstract 51.

[4] Complexes designated herein as diamagnetic show normal proton NMR spectra and are assumed to contain only formal Co(III); those designated as paramagnetic exhibit widely dispersed NMR signals, indicating the presence of one or more formal Co(IV) centers. Paramagnetism was confirmed in **6** and **7** via ESR spectroscopy (vide infra).

[5] Preparative details and analytical and spectroscopic data on **2a**,**b**, **3**, and **5** are included as supplementary material.

[6] Compound **5** (240 mg, 0.48 mmol) in 60 mL of THF was treated with 1 equiv of butyllithium in hexane at −10 °C, the solution was warmed to room temperature, stirred for 30 min, and placed in a dry ice bath, and 0.24 mmol of $CoCl_2$ was added. After the mixture was stirred at room temperature for 10 h, the solvent was removed and the black residue was washed through silica in hexane followed by CH_2Cl_2, giving dark brown solutions. Chromatography of the hexane fraction gave green **3** (16 mg) and dark brown **5** (140 mg). The CH_2Cl_2 fraction was evaporated to dryness and chromatographed in 1.5:1 CH_2Cl_2/hexane, affording two major bands, which were **7** and **6** (10% each), both obtained as black crystals. FAB negative-ion mass spectra: for **6**, cutoff at *m/z* 1067 corresponding to parent ion envelope, base peak *m/z* 1065; for **7**, cutoff at *m/z* 1066, base peak *m/z* 1064. In both compounds, the intensity pattern is consistent with the calculated spectrum on the basis of natural isotope abundances. Anal. Calcd for $Co_5C_{46}B_{12}H_{88}$ (**6**): C, 51.85; H, 8.32. Found: C, 50.74; H, 7.63. Calcd for $Co_5C_{46}B_{12}H_{87}$ (**7**): C, 51.90; H, 8.24. Found: C, 52.72; H, 8.03. UV–visible absorptions (nm): for **6**, 280 (56%), 390 (100%), 612 (15%); for **7**, 291 (57%), 390 (100%), 610 (18%). ESR spectra: data were collected at −115 °C in $CHCl_3$/hexane. The spectrum of **6** exhibits a single band with $g = 2.06$, supporting the assignment of one unpaired electron. The spectrum of **7** contains two broad, overlapping peaks, consistent with two unpaired electrons with intramolecular electron exchange. In neither case was there evidence of resolved hyperfine splitting.

[7] Crystal data: space group $P\bar{1}$; $Z = 2$; $a = 13.434(2)$ Å, $b = 17.418(3)$ Å, $c = 13.430(2)$ Å; $\alpha = 100.82(1)°$, $\beta = 97.11(1)°$, $\gamma = 102.65(1)°$; $V = 2967(2)$ Å^3; crystal size 0.48 × 0.26 × 0.16 mm; μ(Mo Kα) = 14.88 cm^{-1}. Data collection parameters: $2\theta_{max} = 46.0°$; $R = 0.069$ for 4690 reflections having $F_o^2 > 3.0\sigma(F_o^2)$.

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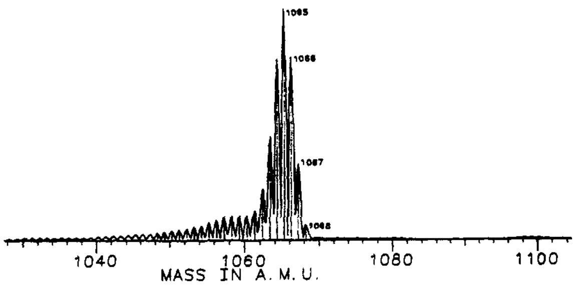

Figure 1. Negative-ion FAB mass spectrum of **6** in a 3-nitrobenzyl alcohol matrix.

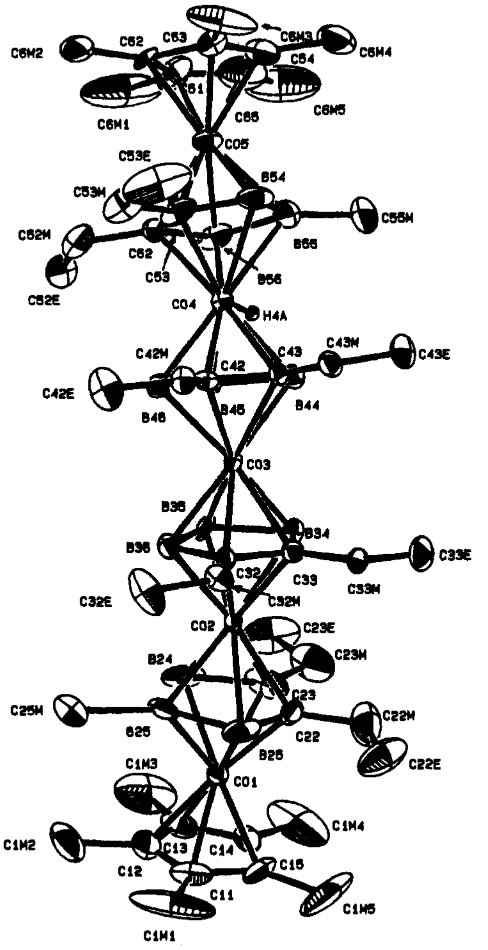

Figure 2. Molecular structure of **6** (30% thermal ellipsoids) with hydrogen atoms omitted except for H4A.

tetradecker sandwiches having $Et_2C_2B_3H_2R$ ring ligands (R = Cl, C(O)Me) are less severely bowed (ca. 171°),[2a,b] the nonlinearity of **6** is apparently an electronic rather than a steric effect; depletion of electron density at the central metal [Co(3)] may be a contributing factor (a similar qualitative argument has been applied[2a] to the case of a Co–Ru–Co tetradecker that is bent by 15°).

One of the two cobalt-bound hydrogen atoms, H4A, was located near Co4 and refined; although there were indications of the presence of the other hydrogen near Co2, this peak did not survive the refinement process. H4A is much closer to Co4 [1.40(14) Å] than to the nearest-neighbor borons (ca. 1.6–1.7 Å), in contrast to the face-capping hydrogens in other metal–boron clusters,[8] in which the reverse is true. Hence, H4A appears to be better described as an η^1-H ligand on Co rather than as a bridging or face-capping atom.

Complexes **6** and **7** are 65-electron and 64-electron systems, respectively; in the as yet unknown neutral 66-electron diamagnetic species $[Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_3)]_2CoH$, all five metals would be Co(III) and all bonding orbitals filled. In **6** and **7**, electrical neutrality requires the presence of one and two formal Co(IV) centers, respectively;[9] however, delocalization of the unpaired electron(s) in these systems is likely, especially in view of the electrochemical and other evidence for delocalization in carborane-bridged triple-decker and tetradecker sandwiches.[1,10] This question is one of many aspects of these hexadecker complexes that merit further study.

Compound **6** is the first crystallographically established hexadecker molecular sandwich, the largest previous example of a structurally characterized multidecker being the diborole-bridged pentadecker $Cp_2Co_2Ni_2(Et_2MeC_3B_2Et)_3$ prepared by Siebert and co-workers.[11] A hexadecker structure has been proposed for a Co_2Ni_3 diborole sandwich that was synthesized by the same group and characterized by NMR and mass spectroscopy.[12] To our knowledge, all known examples of true (nonstaggered) multidecker molecular sandwiches of more than three decks have either diborole (C_3B_2) or carborane (C_2B_3) bridging ligands; most of these compounds are neutral and air-stable.[13] The obvious stabilizing role of boron in stacked metal complexes is a focus of continuing interesting in our laboratory.

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Supplementary Material Available: Details on the synthesis and characterization of **2a,b**, **3**, and **5**, tables of crystal structure data, thermal parameters, atom coordinates, bond distances and angles, and mean planes, and a unit cell diagram for **6** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(8) In $[(Et_2C_2B_4H_4)FeH(C_5Me_4)]_2C_6H_4$, Fe–H = 1.63 Å, B–H = 1.44 and 1.45 Å: Stephan, M.; Davis, J. H., Jr.; Meng, X.; Chase, K. P.; Hauss, J.; Zenneck, U.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, *114*, 5214. In 1,2-$Cp_2Co_2B_4H_6$, Co–H = 1.62 and 1.48 Å, B–H = 1.51 Å: Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 252.

(9) The two $C_5Me_5^-$ and four $Et_2C_2B_3H_2R^{4-}$ ligands are balanced by two Co^{3+} and three Co^{4+} and/or $Co^{3+}H^+$ units. Thus, complex **6**, with two metal-bound protons, requires only one Co^{4+} center.

(10) Merkert, J. M.; Davis, J. H., Jr.; Geiger, W. E.; Grimes, R. N. *J. Am. Chem. Soc.* **1992**, *114*, 9846.

(11) Whitely, M. W.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 453.

(12) Kuhlmann, T.; Siebert, W. *Z. Naturforsch.* **1985**, *40B*, 167.

(13) (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251, and references therein. (b) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943; *Pure Appl. Chem.* **1987**, *59*, 947.