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Organotransition-Metal Metallacarboranes. 44. Construction of Pentadecker and Hexadecker Sandwiches from Triple-Decker Building Blocks[1,2]

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Abstract: Directed syntheses of multidecker sandwich complexes of the title classes, incorporating C$_2$B$_3$ bridging rings and C$_5$Me$_5$ end rings, have been achieved based on the tailored triple-decker synthon Cp*Co(Et$_2$C$_2$B$_3$H$_2$Me)Co(Et$_2$C$_2$B$_3$H$_3$)$^{2-}$ ($\mathbf{1}^{2-}$), the neutral (diprotonated) form of which is described in the preceding paper. Three-way reactions of $\mathbf{1}^{2-}$, the double-decker anions Cp*Co(Et$_2$C$_2$B$_3$H$_2$-5-A)$^{2-}$ (A = H or Me), and Co^{2+} ion in cold THF, with workup of the products in air, afforded the Co$_4$ pentadecker sandwiches Cp*Co(Et$_2$C$_2$B$_3$H$_2$A)M(Et$_2$C$_2$B$_3$H$_3$)CoH(Et$_2$C$_2$B$_3$H$_2$Me)CoCp* (**3**, M = Co, A = H; **4**, M = CoH, A = Me; **5**, M = Co, A = Me). A similar reaction employing Ni^{2+} gave the heterometallic Co$_3$Ni pentadecker [Cp*Co(Et$_2$C$_2$B$_3$H$_2$Me)]$_2$NiCoH(Et$_2$C$_2$B$_3$H$_3$) (**6**). Hexadecker sandwiches were obtained via treatment of $\mathbf{1}^{2-}$ or $\mathbf{1}^{-}$ with Co^{2+} or Pt^{2+} ions, generating respectively the Co$_5$ species [Cp*Co(Et$_2$C$_2$B$_3$H$_2$Me)Co(Et$_2$C$_2$B$_3$H$_3$)]$_2$H$_x$Co (**7**, $x = 1$; **8**, $x = 2$) and the Co$_4$Pt complex [Cp*Co(Et$_2$C$_2$B$_3$H$_2$Me)Co(Et$_2$C$_2$B$_3$H$_3$)]$_2$Pt (**9**). The pentadecker and hexadecker products were obtained as black, moderately air-stable solids in 5−20% individual isolated yields and characterized from their ESR or NMR, UV−visible, and mass spectra, elemental analysis, and an X-ray crystal structure determination on **8**. Except for diamagnetic **4**, all of these complexes are paramagnetic as shown by ESR spectroscopy. In several species the unpaired electrons appear to be extensively delocalized, while in others they are restricted to the region of the interior metal atoms. ESR and electronic spectra are consistent with assignments of the pentadeckers **3**, **4**, and **5** as 53, 54, and 53 valence electron (ve) systems, respectively, with each of the 53 ve species having one unpaired electron. Compound **6**, though a 54 ve system isoelectronic with **4**, is nevertheless paramagnetic. ESR data on the hexadecker sandwiches **7** and **9** are consistent with 64 ve systems having two unpaired electrons, and strong spin−spin interaction is indicated between neighboring Co(IV) centers in **7**. Complex **8**, with two CoH protons, is formulated as a 65 ve species with one unpaired electron and is the largest multidecker sandwich to be confirmed by X-ray crystallography. The stack is somewhat bowed, with Co−Co−Co angles that deviate by 10−12° from linearity. One of the two cobalt-bound protons was located and refined, and was revealed to be an η^1-H ligand on Co, with no apparent bonding interaction with other cluster atoms. Crystal data for **8**: space group $P\bar{1}$; $a = 13.434(2)$ Å, $b = 17.418(3)$ Å, $c = 13.430(2)$ Å, $\alpha = 100.82(1)°$, $\beta = 97.11(1)°$, $\gamma = 102.65(1)°$; $Z = 2$; $R = 0.069$ for 4690 independent reflections having $I > 3\sigma(I)$.

Introduction

Molecular model sandwich complexes having three or more decks represent a conceptual extension of metallocene ("double-decker") chemistry, and the development of systematic, controlled routes to such molecules presents an interesting synthetic challenge. In addition to their potential in the engineering of new materials,[3] multidecker metal sandwiches are excellent candidates for detailed study of metal−metal interactions in organometallic molecular systems. Following the preparation of the original triple-decker species [Cp$_3$Ni$_2$$^+$] in 1972,[4] and the isolation of the first stable (and the first neutral) triple-deckers [Cp$_2$Co$_2$(RR′C$_2$B$_3$H$_3$) isomers] shortly thereafter,[5] multidecker transition-metal sandwich chemistry has expanded greatly with the synthesis of triple-decked complexes having carborane (C$_2$B$_3$),[6] organoboron (C$_3$B$_2$, C$_4$B, C$_4$B$_2$),[7] P$_n$,[8] As$_n$,[8a,b] hydrocarbon,[9] or other rings bridging the two metals. Systems larger than triple-deckers, however, present quite a different picture. There are a few reports of staggered (slipped) transition-metal sandwich structures containing bicyclic or polycyclic bridging ligands such as naphthalene or pentalene whose

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[1] (a) Part 43: Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12218−12226. (b) Part 42: Wang, X.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* In press. (c) Part 41: Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668.

[2] Based in part on the Ph.D. dissertation of Xiaotai Wang, University of Virginia, 1995.

[3] Selected references: (a) Bush, B.; Lagowski, J. J. In *Organic Superconductivity*; Kresin, V. Z., Little, W. A., Eds.; Plenum, New York, 1990; pp 347−358. (b) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (c) Oelckers, B.; Chavez, I.; Manriquez, J. M.; Roman, E. *Organometallics* **1993**, *12*, 3396. (d) Amato, I. *Science* **1993**, *260*, 753. (e) Nicoud, J.-F. *Science* **1994**, *263*, 636. (f) Service, R. F. *Science* **1994**, *265*, 316. (g) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857. (h) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (i) Marks, T. J. *Science* **1985**, *227*, 881. (j) Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805.

[4] Werner, H.; Salzer, A. *Synth. React. Inorg. Met. Org. Chem.* **1972**, *2*, 239.

[5] (a) Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046. (b) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

[6] Recent reviews: (a) Grimes, R. N. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry, Letchworth, 1994; p 269. (b) Hosmane, N. S.; Maguire, J. A. *J. Cluster Sci.* **1993**, *4*, 297. (c) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.

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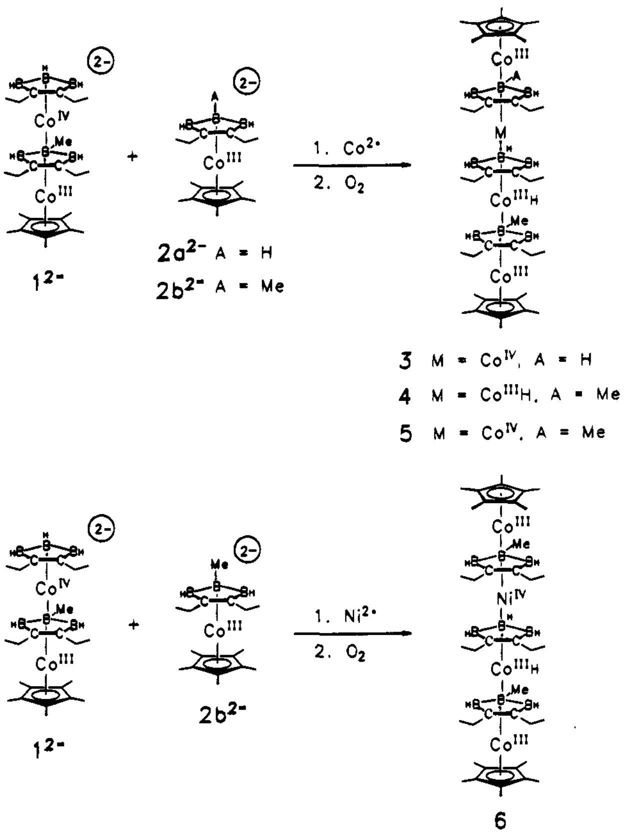
individual rings are facially coordinated to only one metal atom.[3c,10] At present, true (nonstaggered) molecular sandwiches having four or more decks are confined to complexes of C_2B_3 (carborane), C_3B_2 (diborole), or C_2B_2S (thiadiborole) ring ligands. The latter two ligand types have been extensively utilized by Siebert, Wadepohl, and co-workers[7a,b,11] in an elegant series of studies that generated numerous structurally established triple-decker and tetradecker[11] complexes and a pentadecker[12] sandwich, as well as a hexadecker[13] that was characterized from NMR and mass spectroscopic evidence.

Our interest in multidecker sandwiches has centered on the idea of controlled, stepwise construction of specified target molecules from small building-block units, a concept familiar to organic chemists but less commonly employed in inorganic synthesis. In recent years our group has applied this approach to the preparation of carborane-bridged triple-decker and tetradecker molecular sandwiches incorporating a variety of first-, second-, and third-row transition metals.[1,3b,5,6a,14] These studies employed stacking reactions involving double-decker anions of the types $LM(Et_2C_2B_3H_3)^{2-}$ and $LM(Et_2C_2B_3H_4)^-$, where LM is a ligand−metal unit such as CpCo, Cp*Co, Cp*Ir, (arene)Fe, or (arene)Ru (Cp* = η^5-C_5Me_5) as summarized in Scheme 1 of the preceding paper.[1a] In this article we address the extension of this building-block approach to larger systems via "designer" triple-decker synthon complexes that have open C_2B_3 carborane end ligands capable of η^5 binding to metal ions. In the preceding report[1a] we detailed the preparation and modification of these synthons; here we describe their use in the construction of a series of pentadecker and hexadecker sandwiches.

Scheme 1



Results and Discussion

Synthesis of Pentadecker Sandwich Complexes. Mixed-ligand reactions of double-decker and triple-decker cobaltacarborane dianions with divalent metal ions were employed to generate pentadeckers as shown in Scheme 1. Since tetradecker and hexadecker side products were anticipated, a 1:1:1 ratio of reactants was employed in each case in an effort to optimize formation of the desired pentadecker species. Also, given the earlier finding[14a] that the formation of stable tetradecker sandwiches from $LM(Et_2C_2B_3H_3$-5-$A)^-$ monoanions or $LM(Et_2C_2B_3H_2$-5-$A)^{2-}$ dianions is most favored when the substituent A is electron-withdrawing (e.g., halogen, acyl, methyl,[15]) rather than H, the B-methylated dianion[1a] $2b^{2-}$ was expected to give better results than the unsubstituted dianion $2a^{2-}$; this was indeed the case. The reaction of the triple-decker substrate $Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)^{2-}$ (1^{2-}, obtained by deprotonation of the neutral complex **5** in the preceding paper[1a]) with $2a^{2-}$ and cobaltous ion in cold THF followed by workup in air gave the pentadecker complex $Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_3)Co(Et_2C_2B_3H_3)CoCp^*$ (**3**) in 5% yield (Scheme 1), accompanied by the known[16] "fused cluster" $Cp^*_2Co_2(Et_4C_4B_6H_6)$ and unidentified products. The corresponding reaction employing $2b^{2-}$ was more productive, affording the pentadeckers $[Cp^*Co(Et_2C_2B_3H_2Me)]_2(CoH)_2(Et_2C_2B_3H_3)$ (**4**) and $[Cp^*Co(Et_2C_2B_3H_2Me)]_2Co_2H(Et_2C_2B_3H_3)$ (**5**) in a combined yield of 32% together with the known tetradecker complex[14a] $[Cp^*Co(Et_2C_2B_3H_2$-5-$Me)]_2Co$. No hexadecker products were detected in either reaction, suggesting that the complexation of the triple-decker substrate 1^{2-} with

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(7) (a) Siebert, W. *Adv. Organomet. Chem.* **1993**, *35*, 187. (b) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943. (c) Herberich, G. E.; Carstensen, T.; Koeffer, D. P. J.; Klaff, N.; Boese, R.; Hyla-Krypsin, I.; Gleiter, R.; Stephan, M.; Meth, H.; Zenneck, U. *Organometallics* **1994**, *13*, 619 and references therein. (d) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Chapter 5.3.

(8) (a) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104 and references therein. (b) Rink, B.; Scherer, O. J.; Heckmann, G.; Wolmershäuser, G. *Chem. Ber.* **1992**, *125*, 1011. (c) Reddy, A. C.; Jemmis, E. D.; Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. *Organometallics* **1992**, *11*, 3894. (d) Hughes, A. K.; Murphy, V. J.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1994**, 163. (e) Heberhold, M.; Frohmader, G.; Milius, W. *Phosphorus, Sulfur, Silicon* **1994**, *93–94*, 205.

(9) (a) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krueger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479. (b) Lamanna, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 2096. (c) Kudinov, A. R.; Rybinskaya, M. I.; Struchkov, Yu T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187. (d) Lumme, P. O.; Turpeinen, U.; Kudinov, A. R.; Rybinskaya, M. I. *Acta Crystallogr.* **1990**, *C46*, 1410. (e) Schneider, J. J.; Goddard, R.; Werner, S.; Krüger, C. *Angew. Chem, Int. Ed. Engl.* **1991**, *30*, 1124. (f) Cotton, F. A.; Kibala, P. A.; Wojtczak, J. *J. Am. Chem. Soc.* **1991**, *113*, 1462. (g) Herberich, G. E.; Englert, U.; Marken, F.; Hofmann, P. *Organometallics* **1993**, *12*, 4039.

(10) (a) Bush, B. F.; Lagowski, J. J. *Organometallics* **1988**, *7*, 1945. (b) Bochkarev, M. N.; Fedushkin, I. L.; Schumann, H.; Loebel, J. *J. Organomet. Chem.* **1991**, *410*, 321. (c) Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237. (d) Bochkarev, M. N.; Fedushkin, I. L.; Cherkasov, V. K.; Nevodchikov, V. I.; Schumann, H.; Görlitz, F. H. *Inorg. Chim. Acta* **1992**, *201*, 69.

(11) Wadepohl, H. Dissertation, University of Marburg, Germany, 1982.

(12) Whiteley, M. W.; Pritzkow, H.; Zenneck, U.; Seibert, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 453.

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

(14) The earlier work is summarized in ref 3b. Recent papers dealing with multidecker metallacarborane synthesis include: (a) Piepgrass, K. W.; Meng, X.; Hölscher, M.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 5202. (b) Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 3897. (c) Benvenuto, M. A.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 3904. (d) Meng, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 6143. (e) Stephan, M.; Müller, P.; Zenneck, U.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *Inorg. Chem.* **1995**, *34*, 2058. (f) Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014 and references cited therein. (g) Greiwe, P.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 3683.

(15) Recent evidence[14g] suggests that the apparent electron-withdrawing character manifested by B-methylated dianions such as $2b^{2-}$ in these reactions arises from their partial conversion, in THF solution, to a B−CH_2 tautomer via migration of a methyl proton to a BHB bridge location; the electron-withdrawing character of the CH_2 substituent is then responsible for the observed reactivity of these anions in metal sandwich binding.

(16) Piepgrass, K. W.; Curtis, M. A.; Wang, X.; Meng, X.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1993**, *32*, 2156.

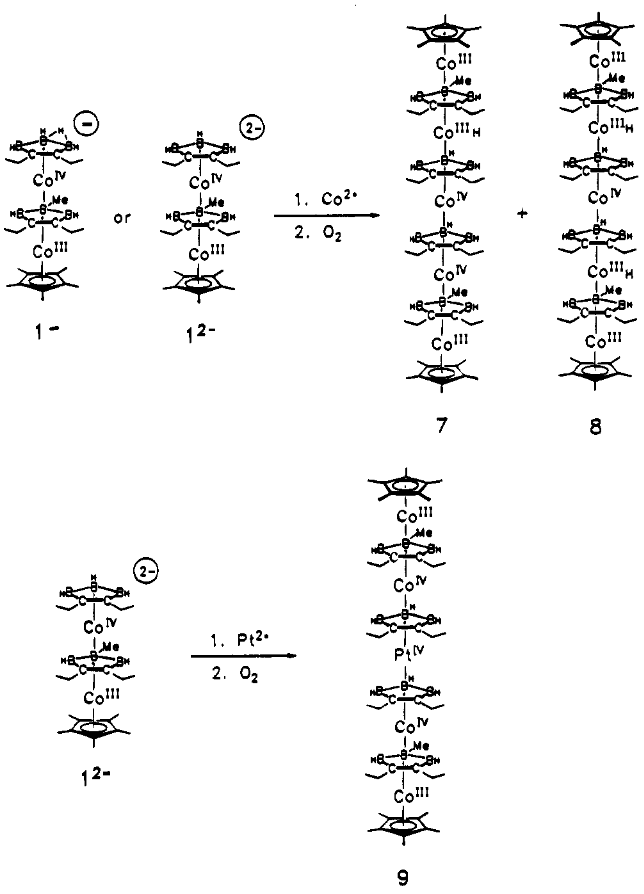
cobaltous ion is slow compared to that of the double-decker species **2a**$^{2-}$ and **2b**$^{2-}$.

Paramagnetic **3**, diamagnetic **4**, and paramagnetic **5** were isolated as black, moderately air-stable solids and characterized via UV–visible, ESR or NMR, and FAB negative-ion mass spectra. The formal oxidation states shown in Scheme 1 are assigned from spectroscopic data, to be discussed, facilitated by comparison with earlier studies; however, these are *formal* assignments and certainly do not preclude electron delocalization between the metal centers, which is likely to be present to a degree. The locations of the "extra" protons associated with some of the cobalt centers are not certain, and the assignments shown are guided largely by precedent (for example, crystallographically defined CoH protons in multidecker systems are found in "interior" locations (as in complex **4** in ref 1a) rather than on end CoCp* groups. Given that the formal $Et_2C_2B_3H_2A^{4-}$ ring ligands (isoelectronic with $C_5Me_5^-$) are 6-electron donors, complexes **3**, **4**, and **5** are respectively 53, 54, and 53 ve (valence electron) systems (the "extra" protons associated with some cobalt centers do not affect the electron count).[17] The X-band ESR spectrum of **3** at 115 K in CH_2Cl_2 contains one band that indicates axial **g**-tensor symmetry with $g_\perp = 2.07$, consistent with the presence of one unpaired electron and supporting the assignment of a formal Co(IV) d^5 metal center.

The 54 ve sandwich **4** is a diamagnetic species, exhibiting normal ^1H and ^{11}B NMR spectra (see Experimental Section) in accord with the proposed structure containing four Co(III) d^6 metal atoms. The single Cp* and $B-CH_3$ resonances in the proton NMR spectrum support the symmetric geometry having equivalent CoCp* end units, as do the ethyl CH_3 and CH_2 signals. The large downfield shift of the $B-CH_3$ resonance at δ 2.17, relative to the corresponding values of δ 0.34 in neutral **2b** and δ 1.28 in the tetradecker $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)]_2Ni$,[14a] reveals significant differences in electronic structure in these diamagnetic species. The deshielding of the B-methyl groups in **4** suggests a larger donation of electron density from the central C_2B_3 rings to their coordinated metal atoms than is the case in the double-decker and tetradecker sandwiches. This conclusion is buttressed by the ^{11}B NMR spectrum of **4**, whose signals appear in the range δ 101 to 34, well downfield of the patterns exhibited by comparable tetradecker sandwich species.[14a] The CoH proton resonance appears at δ 0.34 as a partially resolved multiplet, suggesting $^{59}Co-^1H$ coupling. As in complex **4** in ref 1a, the CoH hydrogens may in fact be associated with their respective Co–B–B triangular faces.

The X-band ESR spectrum of **5** is similar to that of **3**, with $g_\perp = 2.08$, $g_\parallel$ unresolved, and no observable hyperfine splitting, but it is more overlapped and broadened in the parallel region. Although **5** is clearly paramagnetic, its ^1H NMR spectrum is largely interpretable via comparison with that of diamagnetic **4**. Thus, while the ethyl CH_3 resonances in **5** are broadened and a very broad peak appears near δ 0, possibly arising from the $B-CH_3$ protons, there is essentially no change in the Cp* resonance in **5** compared to **4**. These observations suggest that the unpaired electron density in **5** resides mainly on one or both of the interior cobalt atoms, while the outer (end) cobalts are diamagnetic d^6 Co(III) centers as suggested in Scheme 1. Very likely, the ability of C_2B_3 rings to accommodate delocalized electron density and the relatively lesser capacity of the Cp* ligands to do so promotes delocalization in the region of the central cobalt atoms. In this view, the single unpaired electron in **5** occupies a frontier singly occupied molecular orbital (SUMO) arising primarily from interaction between the interior cobalts and the three adjacent C_2B_3 ligands.

Scheme 2



A heterometallic pentadecker complex was obtained via a similar route. The reaction of $NiBr_2$ with $\mathbf{1}^{2-}$ and $\mathbf{2b}^{2-}$ and workup in air afforded black, paramagnetic $[Cp^*Co(Et_2C_2B_3H_2\text{-}Me)]_2NiCoH(Et_2C_2B_3H_3)$ (**6**) in about 10% isolated yield (Scheme 1). Despite its 54 valence electrons, corresponding to the "magic number" for a filled-shell pentadecker sandwich comprised of five 6-electron rings and four d^6 metal centers, **6** is a paramagnetic compound. Its X-band ESR spectrum is similar to those of **3** and **5** discussed above, with $g_\perp = 2.07$ and no resolved $g_\parallel$ or hyperfine structure. The proton NMR spectrum has paramagnetic characteristics such as broad peaks, but some of its features are interpretable. There are two distinct, nearly superimposed Cp* resonances separated by only 0.009 ppm, indicating that the end CoCp* units are slightly inequivalent as expected. The broad signal at δ −10.49, assigned to an M–H proton, is consistent with association of that hydrogen with cobalt, nickel, or both metals. The paramagnetism of **6** suggests the presence of partially occupied degenerate (or closely spaced nondegenerate) frontier orbitals, but a more detailed picture must await further investigation.

Synthesis of Hexadecker Sandwich Complexes. Unlike the assembly of pentadeckers, which requires mixed-ligand reactions as just described, hexadecker systems were obtained in comparatively simple two-way interactions of metal ions with suitable triple-decker synthons. The mono- and dianions $\mathbf{1}^-$ and $\mathbf{1}^{2-}$ are each well-suited to this purpose, and the reaction of either of these substrates with cobaltous ion, followed by chromatography in air, afforded the hexadeckers $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2H_xCo$ (**7**, $x = 1$; **8**, $x = 2$) as shown in Scheme 2.[18] The combined isolated yields of **7** and **8** were ca. 20% in each reaction, but only minor amounts of **8** were obtained from the dianion. Both products were isolated

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[17] The same electron counts are, of course, obtained by invoking neutral $Et_2C_2B_3H_2A$ (2 ve), Co (9 ve), Cp* (5 ve), and "extra" H (1 ve) units.

[18] A preliminary account of a portion of this work has appeared; see: Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 2687.

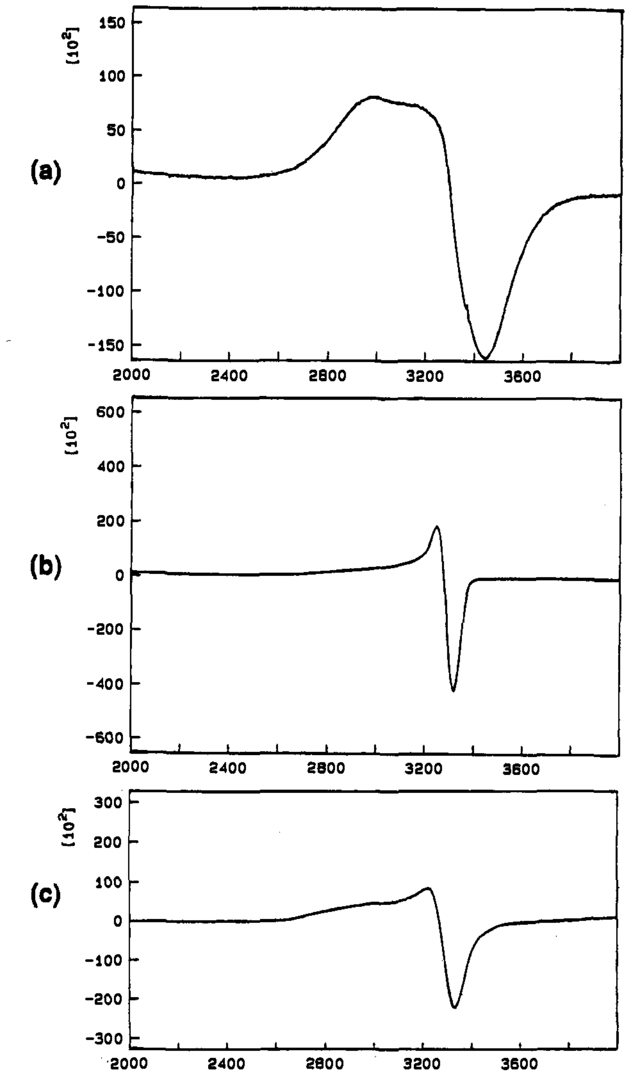

Figure 1. X-band ESR spectra of **7** (a), **8** (b), and **9** (c) in CH_2Cl_2 glass at 115 K, 9.44 GHz.

as black, crystalline, moderately air-stable paramagnetic solids whose NMR spectra consist of extremely broad, uninformative bands. Characterization of these compounds was based on UV−visible, ESR, and FAB negative-ion mass spectra and elemental analysis, supported by an X-ray diffraction study of **8**. Both species incorporate four $Et_2C_2B_3H_2A^{4-}$ and two $C_5Me_5^-$ ligands; electroneutrality therefore requires that if two of the metal centers are Co^{3+}, the other three must be Co^{4+} and/or $Co^{3+}H^+$ units. Compound **7** is formulated as a 64 ve complex having two Co(IV) centers and one Co(III)H, while **8** is formulated as a 65 ve system having two metal-associated hydrogen atoms and only one Co(IV) unit. (No evidence was found for the triprotonated 66 ve complex $[Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_3)]_2CoH$, a presently unknown species, presumably diamagnetic, in which all metals are Co(III) and all bonding orbitals are filled.) Notwithstanding the high molecular weights of **7** and **8** and the difference of only one mass unit between them, the FAB mass spectral data[18] and ESR spectra (Figure 1) support these assignments.

The X-band ESR spectrum of **7** at 115 K in $CHCl_3$, shown in Figure 1a, contains two broad overlapped bands, consistent with the presence of two unpaired electrons having a spin−spin interaction. Since the splitting ΔH produced by dipolar spin−spin interaction is inversely proportional to r^3, where r is the mean separation between the electrons,[19] delocalization of unpaired electron density from the metal centers onto nearby ligands would cause r to vary over a wide range, producing very broad lines. This appears to be the case in **7**, if two unpaired electrons associated with the two formal Co(IV) centers interact via delocalization onto the bridging C_2B_3 ligand. Preliminary electrochemical data[20] on **7** tend to support this model: five reversible waves are observed, consisting of one oxidation and four reductions between −0.16 and −3.09 V vs ferrocene. The oxidation and the first two reductions generate respectively 63, 65, and 66 ve systems from the neutral 64 ve complex, and are well separated, consistent with our hypothesis that they involve bonding electrons delocalized over several metal centers. The last two reductions, which occur very close together near −3.0 V, would then involve occupancy of degenerate (or nearly so) antibonding orbitals which are presumably located on the end cobalts.

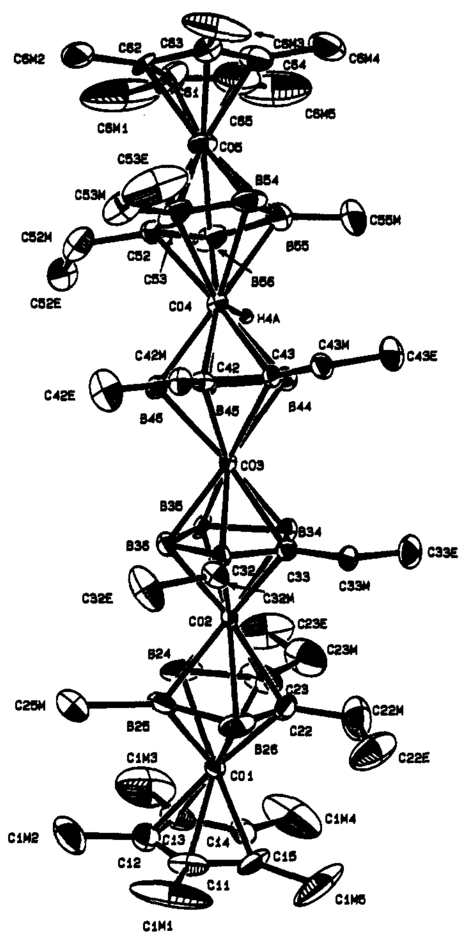

Figure 2. Molecular structure of $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2H_2Co$ (**8**), drawn with 30% thermal ellipsoids.

The ESR spectrum of **8**, shown in Figure 1b, contrasts with that of **7** and closely resembles the spectrum of the pentadecker **3** discussed earlier, exhibiting axial **g**-tensor symmetry with $g_\perp = 2.03$ and no resolved $g_\parallel$, as expected in a system having one unpaired electron. The hexadecker structure of **8** was confirmed by low-temperature X-ray crystallography, making this compound the largest structurally established molecular sandwich. The molecular geometry and unit cell are depicted in Figures 2 and 3, respectively, with data collection parameters listed in Table 1 and bond distances and angles in Table 2. All six ring ligands are planar within experimental error, and the C_2B_3 rings are nearly coplanar with the carbon atoms of their ethyl substituents. All five cobalt atoms are essentially equidistant

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[19] Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1976**, *13*, 136.

[20] Lovelace, S.; Geiger, W. E. Private communication. We thank Professor Geiger for permission to quote these data and for suggestions on their interpretation.

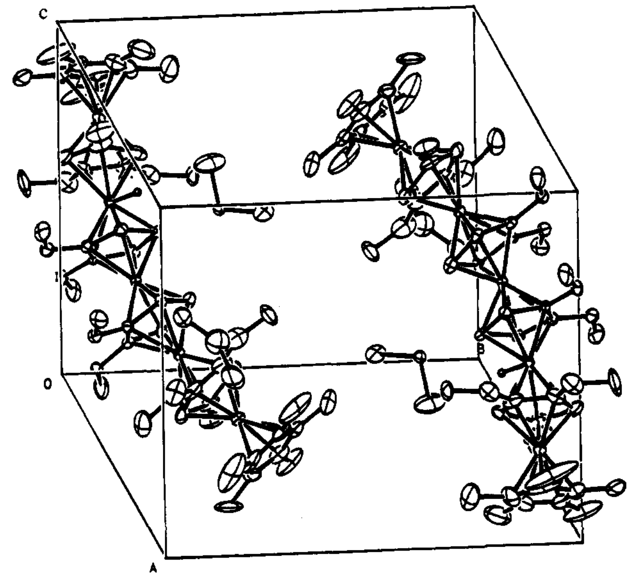

Figure 3. Unit cell packing diagram for **8**.

Table 1. Experimental X-ray Diffraction Parameters and Crystal Data for **8**

empirical formula	$Co_5C_{46}B_{12}H_{88}{\cdot}CH_2Cl_2$
formula weight	1150.52
crystal color, habit	black plate
crystal dimens, mm	0.48 × 0.26 × 0.16
space group	$P\bar{1}$
a, Å	13.434(2)
b, Å	17.418(3)
c, Å	13.430(2)
α, deg	100.82(1)
β, deg	97.11(1)
γ, deg	102.65(1)
V, Å^3	2967
Z	2
μ, cm^{-1} (Mo Kα)	14.88
transmission factors	0.75−1.00
D(calcd), g cm^{-3}	1.281
$2\theta_{max}$, deg	46.0
no. of reflectns measd	8673
no. of reflectns obsd [$I > 3\sigma(I)$]	4690
R	0.069
R_w	0.090
largest peak in final diff map, e/Å^3	2.28

from their bound B and C atoms and are located over the centroids of their coordinated ligands, with no significant horizontal slippage of the metals. A conspicuous feature of the structure is the bending of the five-cobalt chain, as measured by the deviation of the Co(1)−Co(2)−Co(3)−Co(4)−Co(5) array from linearity [Co(1)−Co(2)−Co(3), 169.5°; Co(2)−Co(3)−Co(4), 167.7°; Co(3)−Co(4)−Co(5), 168.5°] and by the dihedral angles subtended by the rings: ring 2 vs 3, 12.3°; 3 vs 4, 16.4°; 4 vs 5, 12.3°, where the rings shown in Figure 2 are numbered 1−6 from bottom to top. This nonlinearity is interpreted as primarily electronic in origin, since the structures of several C_2B_3-bridged tetradecker sandwiches having Cl or acetyl substituents on the middle boron atoms are less severely bent (Co−M′−Co ca. 171°, M′ = Co or Ni).[14a] A possible contributing factor in **8** may be the depletion of electron density at the central metal [Co(3)], as has been suggested in the case of a severely bowed Co−Ru−Co tetradecker which deviates by 15° from linearity.[14a] Binding between a highly electron-deficient metal center and its neighboring carborane ligand could induce such distortion as a way of increasing metal−boron orbital overlap and thereby strengthening the covalent interaction.

Of the two cobalt-bound hydrogen atoms, the X-ray data permitted location and refinement of the one near Co(4) [H(4A)]; the other, near Co(2), was not successfully refined. Interestingly, H(4A) is much closer to Co(4) [1.40(14) Å] than to its nearest-neighbor borons (ca. 1.6−1.7 Å), and thus merits description as an η^1-H ligand on Co rather than as a bridging or face-capping atom. This stands in rather sharp contrast to the metal-associated hydrogens in other metalloboron clusters,[21] which tend toward B−B edge-bridging or M−B−B face-capping roles as discussed in ref 1a.

The rotational twist angles of the four C_2B_3 rings show an interesting pattern. The twist between two nearest-neighbor rings, defined[14a,g] as the dihedral angle subtended by their Co−B(5)−Co planes where B(5) is the unique "middle" boron, provides a measure of the extent to which the rings are rotated away from an eclipsed conformation in which their corresponding atoms are directly aligned. In **8**, the twist angle between rings 2 and 3 [those coordinated to Co(2)] is 93°, and that between rings 4 and 5 [coordinated to Co(4)] is 86°, but the middle rings (3 and 4) show a twist of only 10°. thus, the two innermost rings are nearly eclipsed, but are rotated by ca. 90° with respect to the outer C_2B_3 ligands. This pattern is reminiscent of those seen in some tetradecker structures discussed elsewhere,[14a,g] but defies simple explanation at this point. It does seem likely, however, that these twists are primarily of electronic origin, and are probably related to differences in the overlap of cobalt valence orbitals with those of the boron vs carbon atoms in the carborane rings. Additional multidecker structures will of course contribute to a better understanding of these trends as they become available.

The reaction of the dianion $\mathbf{1}^{2-}$ with $PtBr_2$ gave a single isolable product, $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2Pt$ (**9**, Scheme 2), obtained in low yield as a black paramagnetic solid and characterized as a 64 ve hexadecker sandwich analogous to **7**. The negative-ion FAB mass spectrum shows a clear, strong parent envelope (base peak at m/z 1199) whose intensities are consistent with the calculated pattern based on natural isotope abundances. Although **9** is proposed to contain two Co(IV) centers and two unpaired electrons, its X-band ESR spectrum (Figure 1c) differs from that of **7**, exhibiting a resolvable $g_\perp$ value of 2.07 with only a slight indication of a second broad signal. The difference between these isoelectronic species may lie in the fact that in **9**, unlike **7**, the Co(IV) centers are well separated with a diamagnetic Pt(IV) and two carborane ligands between them, and thus are expected to interact only weakly.

Electronic Absorption Spectra. The UV−visible spectra of each of the pentadecker and hexadecker species reported here exhibit one major and one or more smaller bands, with the dominant band having maximum absorbance between 390 and 410 nm. This falls within the range of maxima in the spectra of closely related C_2B_3-bridged tetradecker complexes (350 to 440 nm),[14a] but with a tendency toward higher wavelengths than those of comparable triple-deckers (330−380 nm).[1a] The pentadecker and hexadecker sandwiches therefore appear to be electronically similar to their smaller tetradecker counterparts and, at least in these compounds, do not continue the trend toward lower-energy transitions with increasing stack size that is seen in going from double- to triple-decker systems.[1a] This is what one expects if the large stacks experience only limited delocalization of unpaired electron density, i.e., extending over just two or three metal centers rather than the entire system, and is in accord with the ESR data discussed above. Continuing studies in this area, including electrochemical investigations, should help to place these findings in sharper perspective.

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(21) We have enountered one other example in metallacarborane sandwich chemistry, of a metal-bound hydrogen that binds as an η^1-H on the metal, in $Cp^*RuH(Et_2C_2B_4H_4)$: Houser, E. J.; Sabat, M.; Grimes, R. N. To be submitted for publication.

Table 2. Bond Distances and Selected Bond Angles for $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2H_2Co$ (**8**)

Bond Distances, Å							
Co(1)−C(11)	2.04(1)	Co(3)−B(46)	2.08(1)	C(12)−C(13)	1.33(2)	C(52M)−C(52E)	1.53(2)
Co(1)−C(12)	2.04(1)	Co(4)−C(42)	2.10(1)	C(13)−C(1M3)	1.54(3)	C(52)−C(53)	1.53(2)
Co(1)−C(13)	2.07(1)	Co(4)−C(43)	2.08(1)	C(13)−C(14)	1.35(2)	C(52)−B(56)	1.52(2)
Co(1)−C(14)	2.05(1)	Co(4)−C(52)	2.04(1)	C(14)−C(1M4)	1.49(2)	C(53)−C(53M)	1.49(2)
Co(1)−C(15)	2.05(1)	Co(4)−C(53)	2.13(1)	C(14)−C(15)	1.46(2)	C(53)−B(54)	1.52(2)
Co(1)−C(22)	2.04(1)	Co(4)−B(44)	2.07(1)	C(1M5)−C(15)	1.46(2)	C(53M)−C(53E)	1.52(2)
Co(1)−C(23)	2.05(1)	Co(4)−B(45)	2.06(1)	C(22M)−C(22)	1.48(2)	C(55M)−B(55)	1.63(3)
Co(1)−B(24)	2.05(1)	Co(4)−B(46)	2.08(1)	C(22M)−C(22E)	1.61(3)	C(6M1)−C(61)	1.55(3)
Co(1)−B(25)	2.04(1)	Co(4)−B(54)	2.30(1)	C(22)−C(23)	1.41(2)	C(61)−C(62)	1.54(3)
Co(1)−B(26)	2.02(1)	Co(4)−B(55)	2.27(2)	C(22)−B(26)	1.42(2)	C(61)−C(65)	1.32(2)
Co(2)−C(22)	2.15(1)	Co(4)−B(56)	2.04(1)	C(23M)−C(23)	1.45(2)	C(6M2)−C(62)	1.60(3)
Co(2)−C(23)	2.07(1)	Co(5)−C(52)	2.01(1)	C(23M)−C(23E)	1.56(3)	C(62)−C(63)	1.51(3)
Co(2)−C(32)	2.08(1)	Co(5)−C(53)	2.02(1)	C(23)−B(24)	1.62(3)	C(63)−C(6M3)	1.45(2)
Co(2)−C(33)	2.11(1)	Co(5)−C(61)	2.04(2)	C(25M)−B(25)	1.70(2)	C(63)−C(64)	1.38(2)
Co(2)−B(24)	2.05(1)	Co(5)−C(62)	2.01(1)	C(32M)−C(32)	1.51(1)	C(64)−C(6M4)	1.49(2)
Co(2)−B(25)	2.18(1)	Co(5)−C(63)	2.05(1)	C(32M)−C(32E)	1.51(2)	C(64)−C(65)	1.32(2)
Co(2)−B(26)	2.22(2)	Co(5)−C(64)	2.05(1)	C(32)−C(33)	1.43(1)	C(65)−C(6M5)	1.50(3)
Co(2)−B(34)	2.11(1)	Co(5)−C(65)	2.07(2)	C(32)−B(36)	1.52(2)	B(24)−B(25)	1.64(3)
Co(2)−B(35)	2.06(1)	Co(5)−B(54)	2.04(2)	C(33)−C(33M)	1.54(1)	B(25)−B(26)	1.68(3)
Co(2)−B(36)	2.04(1)	Co(5)−B(55)	2.11(2)	C(33)−B(34)	1.55(2)	B(34)−B(35)	1.77(2)
Co(3)−C(32)	2.15(1)	Co(5)−B(56)	2.11(1)	C(33M)−C(33E)	1.45(2)	B(35)−B(36)	1.72(2)
Co(3)−C(33)	2.16(1)	Cl(1)−C(1S)	1.79(2)	C(42)−C(42M)	1.51(1)	B(44)−B(45)	1.77(2)
Co(3)−C(42)	2.17(1)	Cl(2)−C(1s)	1.69(2)	C(42)−C(43)	1.45(1)	B(45)−B(46)	1.74(2)
Co(3)−C(43)	2.17(1)	Cl(3)−C(2S)	1.53(4)	C(42)−B(46)	1.55(2)	B(54)−B(55)	1.77(3)
Co(3)−B(34)	2.05(1)	Cl(4)−C(2S)	1.55(4)	C(42M)−C(42E)	1.53(2)	B(55)−B(56)	1.65(3)
Co(3)−B(35)	2.00(1)	C(1M1)−C(11)	1.51(2)	C(43M)−C(43)	1.53(1)	Co(4)−H(4A)	1.40(14)
Co(3)−B(36)	2.05(1)	C(11)−C(12)	1.38(2)	C(43M)−C(43E)	1.52(2)	B(44)−H(4A)	1.67(15)
Co(3)−B(44)	2.07(1)	C(11)−C(15)	1.44(2)	C(43)−B(44)	1.52(2)	B(45)−H(4A)	1.59(14)
Co(3)−B(45)	2.00(1)	C(1M2)−C(12)	1.55(2)	C(52M)−C(52)	1.54(2)	B(56)−H(4A)	1.72(15)

Selected Bond Angles, deg					
Co(1)−C(22)−C(22M)	131(1)	C(32)−C(32M)−C(32E)	116(1)	C(42)−B(46)−B(45)	106(1)
Co(2)−C(22)−C(22M)	128(1)	C(33)−B(34)−B(35)	105(1)	Co(4)−C(52)−C(52M)	125.2(9)
C(22M)−C(22)−C(23)	121(2)	B(34)−B(35)−B(36)	99(1)	Co(5)−C(52)−C(52M)	128.9(9)
C(22M)−C(22)−B(26)	123(2)	C(32)−B(36)−B(35)	108(1)	C(52M)−C(52)−C(53)	120(1)
C(23)−C(22)−B(26)	116(1)	Co(2)−C(33)−C(33M)	133.0(7)	C(52M)−C(52)−B(56)	129(1)
C(22)−C(22M)−C(22E)	112(2)	Co(3)−C(33)−C(33M)	132.1(7)	C(53)−C(52)−B(56)	111(1)
Co(2)−C(23)−C(23M)	126(1)	C(32)−C(33)−C(33M)	121(1)	C(52)−C(52M)−C(52E)	115(1)
C(22)−C(23)−C(23M)	121(2)	C(32)−C(33)−B(34)	114(1)	Co(5)−C(53)−C(53M)	127(1)
C(22)−C(23)−B(24)	109(1)	C(33M)−C(33)−B(34)	125(1)	C(52)−C(53)−C(53M)	117(1)
Co(1)−C(23)−Co(2)	102.8(6)	C(33)−C(33M)−C(33E)	114(1)	C(52)−C(53)−B(54)	112(1)
Co(1)−C(23)−C(23M)	131(1)	Co(3)−C(42)−C(42M)	132.7(7)	C(53M)−C(53)−B(54)	131(2)
C(23)−C(23M)−C(23E)	110(2)	Co(4)−C(42)−C(42M)	132.4(7)	Co(4)−C(53)−C(53M)	129(1)
C(23)−B(24)−B(25)	105(1)	C(42M)−C(42)−C(43)	121(1)	C(53)−C(53M)−C(53E)	110(2)
B(24)−B(25)−B(26)	101(1)	C(42M)−C(42)−B(46)	125(1)	C(53)−B(54)−B(55)	106(1)
Co(1)−B(25)−C(25M)	131.7(9)	C(43)−C(42)−B(46)	113(1)	Co(5)−B(55)−C(55M)	136(1)
Co(2)−B(25)−C(25M)	127.0(8)	C(42)−C(42M)−C(42E)	115(1)	C(55M)−B(55)−B(54)	132(2)
C(25M)−B(25)−B(26)	138(1)	Co(3)−C(43)−C(43M)	135.8(7)	C(55M)−B(55)−B(56)	126(2)
C(25M)−B(25)−B(24)	121(2)	Co(4)−C(43)−C(43M)	128.7(7)	B(54)−B(55)−B(56)	101(1)
C(22)−B(26)−B(25)	109(1)	C(42)−C(43)−C(43M)	118(1)	Co(4)−B(55)−C(55M)	129(1)
C(32M)−C(32)−C(33)	119(1)	C(42)−C(43)−B(44)	115(1)	C(52)−B(56)−B(55)	109(1)
Co(2)−C(32)−C(32M)	130.0(7)	C(43M)−C(43)−B(44)	127(1)	B(44)−Co(4)−H(4A)	53(6)
Co(3)−C(32)−C(32M)	134.2(7)	C(43)−C(43M)−C(43E)	114(1)	B(45)−Co(4)−H(4A)	51(6)
C(32M)−C(32)−B(36)	127(1)	C(43)−B(44)−B(45)	105(1)	B(56)−Co(4)−H(4A)	57(6)
C(33)−C(32)−B(36)	114(1)	B(44)−B(45)−B(46)	100.4(9)		

Concluding Remarks

This rationale behind this work, as presented in this and other recent publications, has been twofold: (1) to develop a synthetic methodology for the stepwise construction of specific multidecker sandwich target molecules, and (2) to use these approaches to generate new classes of polynuclear organometallic systems that are stable, soluble, and amenable to detailed study, thereby exploiting the extraordinary stabilizing ability of carborane and organoboron ligands in metal complexes. Extensions of the basic metal-stacking approach employed in this study to larger systems (e.g., octadeckers), to other metals including main-group, lanthanide, and actinide elements, and to other molecular architectures, seem entirely feasible and are open to exploration.

Experimental Section

Instrumentation and Procedures. ESR, NMR, and UV−visible spectra and analyses were obtained as described in ref 1a, and the experimental methods employed were as given previously.[1a] Fast-atom bombardment (FAB) negative-ion mass spectra were acquired in a $CHCl_2$ or 3-nitrobenzyl alcohol matrix. The neutral starting complexes **1**,[1a] **2a**,[22] and **2b**[22] were prepared as reported in earlier publications. The mass spectrum of each new compound exhibits a strong parent envelope (parent + Cl in the case of **3**) whose intensity pattern is consistent with that calculated for the specified composition.

Synthesis of $Cp^*Co(Et_2C_2B_3H_2Me)CoH(Et_2C_2B_3H_3)Co(Et_2C_2B_3H_3)CoCp^*$ (3). A previously described apparatus[23] consisting of a 3-necked flask (B) fitted with a rubber septum and a tip-tube and a second flask (A) having a septum and connected to flask B via a filter frit and a stopcock was charged with 152 mg (0.30 mmol) of **1** in flask A, 94 mg (0.30 mmol) of **2a** in flask B, and 39 mg (0.30 mmol) of dry $CoCl_2$ in the tip tube, and the apparatus was evacuated to high vacuum. THF (40 mL) was condensed into flask B at dry ice temperature

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(22) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171.

(23) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776, Figure 3c.

(−78 °C), giving a yellow-orange solution which was isolated from the remainder of the apparatus by closing the stopcock. Two equivalents of *tert*-butyllithium in pentane (0.35 mL of 1.7 M) was added to flask B at −78 °C via syringe, and the solution was warmed to room temperature and stirred for 30 min, producing a deep orange color. During this time, 30 mL of THF was condensed into flask A, forming a brown solution, to which 2.0 equiv of *tert*-butyllithium in pentane was added at −78 °C via syringe. Flask A was warmed to room temperature and the solution was stirred for 30 min, after which the stopcock connecting flasks A and B was opened and the solution in A was transferred through the filter frit into B. The combined solution was cooled to −78 °C, $CoCl_2$ was added from the tip tube, and the solution was warmed to room temperature, stirred overnight, opened to the air, and the solvent was removed by rotary evaporation. The black sludge obtained was washed through 2 cm of silica gel with hexane followed by CH_2Cl_2. The hexane fraction was chromatographed in hexane on a silica gel column, affording two major bands. The first band was yellow and consisted of unreacted **2a** (7 mg) and the second was brown **1** (40 mg). The CH_2Cl_2 fraction was stripped of solvent and the residue was chromatographed on silica TLC plates in 1:1 CH_2Cl_2−hexane, yielding seven bands of which the third, sixth, and seventh were major. These three bands were extracted with CH_2Cl_2 and the solvent was removed to give the known[16] fused compound $Cp^*_2Co_2(Et_4C_4B_6H_6)$ (6 mg) from the third band, 7 mg of an unidentified compound from the sixth band, and 10 mg of **3** from the third band, corresponding to 5% yield based on **1** consumed. MS base peak for **3** (monochlorinated molecular ion envelope, FAB/CH_2Cl_2), *m/z* 907. Anal. for 3: calcd for $Co_4C_{39}B_9H_{72}$, C 53.59, H 8.30; found C 54.51, H 8.45.

Syntheses of $[Cp^*Co(Et_2C_2B_3H_2Me)]_2(CoH)_2(Et_2C_2B_3H_3)$ (4) and $[Cp^*Co(Et_2C_2B_3H_2Me)]_2Co_2H(Et_2C_2B_3H_3)$ (5). The setup, procedure, and molar quantities of reagents employed were identical with those used in the synthesis of **3**, except that the B-methylated complex **2b** (99 mg, 0.30 mmol) was employed in place of **2a**. From the hexane fraction obtained on workup, 14 mg of **2b** and 45 mg of **1** were recovered. The CH_2Cl_2 fraction was chromatographed on silica TLC plates in 1:1 hexane−CH_2Cl_2, yielding four brown bands. After extraction with CH_2Cl_2 and removal of solvent, the first band afforded 20 mg of the tetradecker complex[14a] $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)]_2Co$. The second band was not identified, but the third band gave 23 mg (0.026 mmol, 12% based on **1** consumed) of black solid **4** and the fourth band afforded 38 mg (0.043 mmol, 20%) of **5**, also a black solid. MS base peaks (molecular ion envelopes, FAB/CH_2Cl_2): for **4**, *m/z* 889; for **5**, *m/z* 888. UV−visible absorptions (nm): for **4**, 232 (34%), 390 (100%), 608 (14%); for **5**, 230 (45%), 386 (100%). ^1H NMR for **4** (δ, $CDCl_3$ solution): 2.44 (CH_2, m), 2.17 ($B-CH_3$, s), 1.65 (C_5Me_5, s), 1.06 (ethyl CH_3, t), 0.90 (ethyl CH_3, t), −0.34 (CoH, m). ^{11}B NMR for **4** (δ vs $BF_3\cdot OEt$, CH_2Cl_2 solution): 101.3 (2B), 84.9 (1B), 46.3 (4B), 34.0 (2B). ^1H NMR for **5** (δ, $CDCl_3$ solution): 2.44 (CH_2, m br), 1.65 (C_5Me_5, s), 1.06 (ethyl CH_3, t br), 0.90 (ethyl CH_3, t br), 0.00, −0.34 (CoH, m). Anal. for **4**: Calcd for $Co_4C_{40}B_9H_{75}$, C 54.04, H 8.50; found C, 53.96, H 8.63. Anal. for **5**: Calcd for $Co_4C_{40}B_9H_{74}$, C 54.10, H 8.40; found C 54.07, H 8.86.

Synthesis of $[Cp^*Co(Et_2C_2B_3H_2Me)]_2NiCoH(Et_2C_2B_3H_3)$ (6). The setup and procedure described for the synthesis of **3** were employed, using 0.25 mmol each of **2b**, **1**, and $NiBr_2$. From the hexane fraction, 40 mg of **2b** and 60 mg of **1** were recovered. The CH_2Cl_2 fraction was column-chromatographed with 1:4 CH_2Cl_2−hexane to elute one brown band (7 mg), identified as the known tetradecker[14a] $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)]_2Ni$. The eluent was changed to 1:1 CH_2Cl_2−hexane, which eluted another dark brown band that was black solid **6** (11 mg, 10%). MS base peak (molecular ion envelope, FAB/CH_2Cl_2), *m/z* 889. UV−visible absorptions (nm): 212 (54%), 232 (56%), 288 (58%), 408 (100%). ^1H NMR (δ, $CDCl_3$ solution): 2.50 (m), 2.17 (m), 1.73 (s br), 1.65 (s), 1.48 (t), 1.440 (C_5Me_5, s), 1.431 (C_5Me_5, s), 1.33 (t), 0.58 (s), 0.07 (s), −10.49 (CoH, s). Anal. for **6**: Calcd for $NiCo_3C_{40}B_9H_{74}$, C 54.12, H 8.40; found C 54.05, H 8.51.

Syntheses of $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2HCo$ (7) and $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2H_2Co$ (8). (a) From the 1^- Monoanion. A 215-mg (0.42 mmol) sample of **1** was placed in a 3-neck flask fitted with a septum and attached to a vacuum line. $CoCl_2$ (27 mg, 0.21 mmol) was placed in a tip tube and attached to the flask. The apparatus was evacuated on a vacuum line and 50 mL of dry THF was vacuum-distilled into the flask, which was cooled in dry ice−ethanol. The dark brown solution was warmed to −10 °C and 1 equiv of butyllithium in hexane was added via syringe. The solution was warmed to room temperature, stirred for 30 min, and cooled in dry ice−ethanol, and the $CoCl_2$ was tipped in. The mixture was stirred for 10 h at room temperature, after which the solvent was removed and the black residue was washed through 2 cm of silica gel using hexane followed by CH_2Cl_2, giving brown solutions. Column chromatography of the hexane fraction in hexane gave 109 mg (0.22 mmol) of recovered **1** as the only major band. The CH_2Cl_2 fraction was eluted on silica TLC plates in 3:2 CH_2Cl_2−hexane, affording two major bands which were respectively **7** (15 mg, 0.014 mmol, 13%) and **8** (10 mg, 0.0094 mmol, 9%), both obtained as black solids. FAB negative-ion mass spectra (3-nitrobenzyl alcohol matrix): for **7**, cutoff at *m/z* 1066, base peak *m/z* 1064; for **8**, cutoff at *m/z* 1067 corresponding to parent ion envelope, base peak *m/z* 1065. In both compounds, the intensity pattern is consistent with the calculated spectrum based on natural isotope abundances (the spectrum of **8** is presented in ref 18). Anal. for **7**: Calcd for $Co_5C_{46}B_{12}H_{87}$, C, 51.90; H, 8.24. Found: C, 52.72; H, 8.03. Anal. for **8**: Calcd for $Co_5C_{46}B_{12}H_{88}$ (**8**): C, 51.85; H, 8.32. Found: C, 50.74; H, 7.63. UV-visible absorptions (nm) for **7**: 291 (57%), 390 (100%), 610 (18%); for **8**: 280 (56%), 390 (100%), 612 (15%).

(b) From the 1^{2-} Dianion. The setup and procedures were similar to those employed in the monoanion-based synthesis, except that 2 equiv of *tert*-butyllithium in pentane were employed to generate the dianion. A 200-mg (0.40 mmol) sample of **1** and 0.5 equiv of $CoCl_2$ were used in the reaction. On workup as before, 82 mg (0.17 mmol) of **1** was recovered, while 18 mg (0.017 mmol, 15%) of **7** and 3 mg (0.003 mmol, 3%) of **8** were obtained.

Synthesis of $[Cp^*Co(Et_2C_2B_3H_2Me)Co(Et_2C_2B_3H_3)]_2Pt$ (9). The setup and procedure were similar to those employed in the dianionic approach to **7** and **8**, described above, using 222 mg (0.44 mmol) of **1** and 0.5 equiv of $PtBr_2$. Workup as in the preceding syntheses gave 123 mg (0.24 mmol) of recovered **1**. The CH_2Cl_2 fraction was column-chromatographed in 3:2 CH_2Cl_2−hexane to elute one brown band consisting of **9** (8 mg, 0.067 mmol, 7%). MS base peak (molecular ion envelope, FAB/CH_2Cl_2), *m/z* 1199. UV−visible absorptions (nm): 208 (59%), 230 (51%), 286 (52%), 406 (100%).

X-ray Structure Determination on 8. Diffraction data were collected on a Rigaku AFC6S diffractometer at −120 °C using Mo Kα radiation. Details of the data collection and structure determination are listed in Table 1. Preliminary measurements indicated a triclinic unit cell. The cell reduction routines of the TEXSAN 5.0[24] and SHELXTL PLUS[25] packages did not reveal any unit cell of higher symmetry. The unit cell dimensions were determined by least-squares refinement of the setting angles of 25 high-angle reflections. The intensities of three standard reflections, monitored throughout, showed no significant variation. Empirical absorption corrections were applied following ψ scanning of several reflections having χ angles close to 90° (transmission factors are reported in Table 1). All calculations were performed on a VAX station 3520 computer employing the TEXSAN 5.0 crystallographic software package.[24] The structure was solved by direct methods in SIR88,[26] and full-matrix least-squares refinement with anisotropic thermal displacement parameters was carried out for all non-hydrogen atoms except the carbon atoms of the CH_2Cl_2 solvent molecules, with the results summarized in Table 1. Several methyl and ethyl carbon atoms, especially those in the C_5Me_5 groups, were affected by high thermal vibrations; however, several attempts to resolve this disorder were unsuccessful. High thermal parameters of the two CH_2Cl_2 solvent molecules suggested partial occupancy; consequently, these atoms were refined with population parameters of 0.5. Despite the problems with the thermal vibrations, difference Fourier maps revealed the location of all hydrogen atoms bound to boron. These atoms were included as fixed contributions to the refinement. In the latter stages of the refinement, a difference map clearly showed the location of the hydrogen H(4A) bound to the Co(4) atom. The coordinates and isotropic factor of H(4A) were successfully

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(24) TEXSAN 5.0: Single Crystal Structure Analysis Software; Molecular Structure Corporation: The Woodlands, TX 77381, 1989.

(25) SHELXTL PLUS: Siemens Analytical X-Ray Instruments Inc.: Madison, WI 53719, 1990.

(26) SIR88: Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

refined, but several efforts to locate unequivocally and refine the other CoH hydrogen failed, possibly owing to disorder. All other hydrogen atoms were located from difference Fourier maps. The carborane ring hydrogens were refined with isotropic thermal displacement parameters, and the remaining methyl and methylene hydrogens were included in the calculations without further refinement. The highest peak in the final difference Fourier map was 2.28 e/Å^3 high, located close to C(2S), Cl(3), and Cl(4) in the CH_2Cl_2 molecule.

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Supporting Information Available: Tables of atomic coordinates (including hydrogen atom positions), anisotropic thermal parameters, bond angles, and calculated mean planes for **8** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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