Organotransition-Metal Metallacarboranes. 42. Synthesis and Cluster Fusion of Iron-Centered Tetradecker Sandwiches[1,2]

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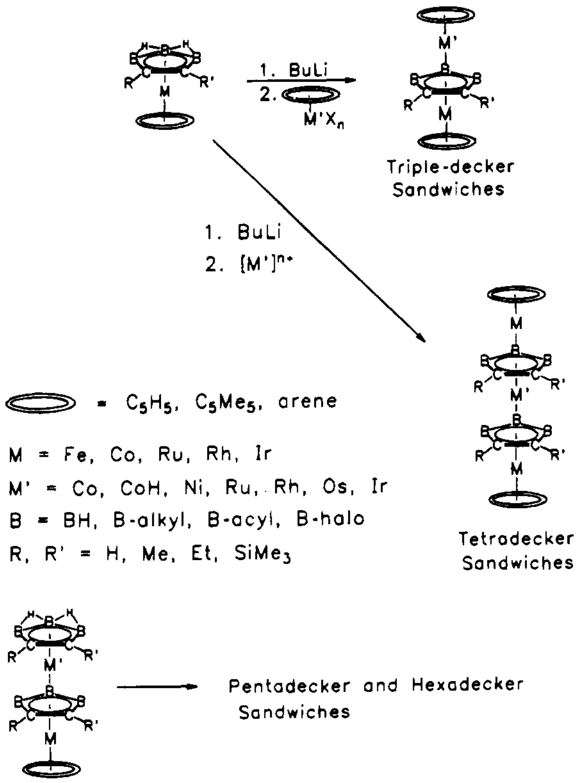
Recent work in our laboratory has shown that metal-stacking reactions of $Cp^*Co(Et_2C_2B_3H_3X)^-$ anions (X = alkyl, acyl, halogen) with metal halides generate air-stable tetradecker sandwiches of the type $[Cp^*Co(Et_2C_2B_3H_2X)]_2M$ in which M is Co, CoH, Ni, Ru, Rh, or Ir. However, attempts to prepare analogous Co−Fe−Co tetradeckers via reactions with $FeCl_2$ have given only $Co_2C_4B_6$ fused clusters or uncharacterizable products. It has been assumed that Fe-centered tetradeckers are formed in such reactions but undergo oxidative fusion during the usual workup on silica in air. We have confirmed this hypothesis via the synthesis and isolation of iron-centered $[Cp^*Co(Et_2C_2B_3H_2X)]_2FeH$ sandwiches (**1**, X = Cl; **2**, X = Me) while avoiding contact with silica in air and demonstrating that both species undergo air oxidation to form respectively the fused products $Cp^*_2Co_2(Et_4C_4B_6H_4X_2)$ (**5**, X = Cl; **6**, X = Me). Different cage structures are exhibited by **5**, a previously prepared and structurally characterized compound, and **6**, whose geometry was established in this work by X-ray crystallography. The structural relationships between these cages and those of other known $Co_2C_4B_6$ clusters are examined from mechanistic and skeletal electron-counting viewpoints. Crystal data for **6**: space group $P2_1/c$; $a = 15.737(5)$ Å, $b = 13.575(4)$ Å, $c = 17.212(5)$ Å, $\beta = 111.13(2)°$; $Z = 4$; $R = 0.058$ for 3340 independent reflections having $I > 3\sigma(I)$.

Introduction

Scheme 1



Stacking reactions involving transition metal ions and small carborane or metallacarborane anions furnish a controlled route to multidecker metal sandwich complexes (Scheme 1).[3] In recent work we have utilized reactions of this type to prepare several families of derivatized tetradecker complexes whose structures, reactivities, and electronic properties have been elucidated in some detail.[1c,4] This building-block approach is remarkably versatile, and in combination with methods for regiospecific substitution,[5] it has allowed us to prepare a wide range of air-stable, isolable complexes in which the metals, the nature and location of substituents on the carborane ring, and the end ligands are systematically varied. For example, in characterized $(L)M(RR'C_2B_3XYZ)M'(RR'C_2B_3XYZ)M(L)$ tetradeckers, L is Cp, Cp* (C_5Me_5), an arene, or a carborane ligand; M is Co, Ru, Rh, or Ir; M′ is Co, CoH, Ni, Ru, Rh, or Ir; R and/or R′ are H or alkyl; and X, Y, and Z are H, alkyl, acyl, and/or halogen. However, conspicuously absent from this group are species having iron as the central metal M′. As we have reported elsewhere,[6] attempts to isolate iron-centered tetradeckers by this approach have been unsuccessful. Typically, the products that are isolated from reactions with the Fe^{2+} ion,

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(1) (a) Part 41: Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668. (b) Part 40: Stockman, K. E.; Garrett, D. L.; Grimes, R. N. *Organometallics* **1995**, *14*, 4661. (c) Part 39: Greiwe, P.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 3683. (d) Part 38: Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014.

(2) Based in part on the Ph.D. dissertation of X.W., University of Virginia, 1995. Presented in part at the Fourth Boron U.S.A. Workshop, Syracuse University, Syracuse, NY, July 1994; Abstract 69.

(3) Recent reviews: (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Grimes, R. N. In *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: London, 1994; p 269. (c) Pentadecker sandwiches: Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.*, in press. (d) Hexadecker sandwiches: Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 2687; *J. Am. Chem. Soc.*, in press.

(4) (a) Piepgrass, K. W.; Meng, X.; Hölscher, M.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1992**, *31*, 5202. (b) Meng, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 6143. (c) Pipal, J. R.; Grimes, R. N. *Organometallics* **1993**, *12*, 4452. (d) Pipal, J. R.; Grimes, R. N. *Organometallics* **1993**, *12*, 4459. (e) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 2687. (f) Rh and Ir tetradeckers: Franz, D. A.; Müller, P.; Grimes, R. N. To be submitted for publication.

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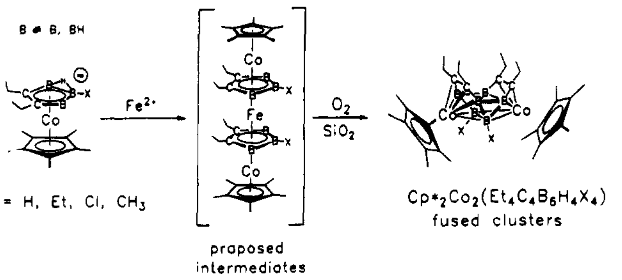
Scheme 2



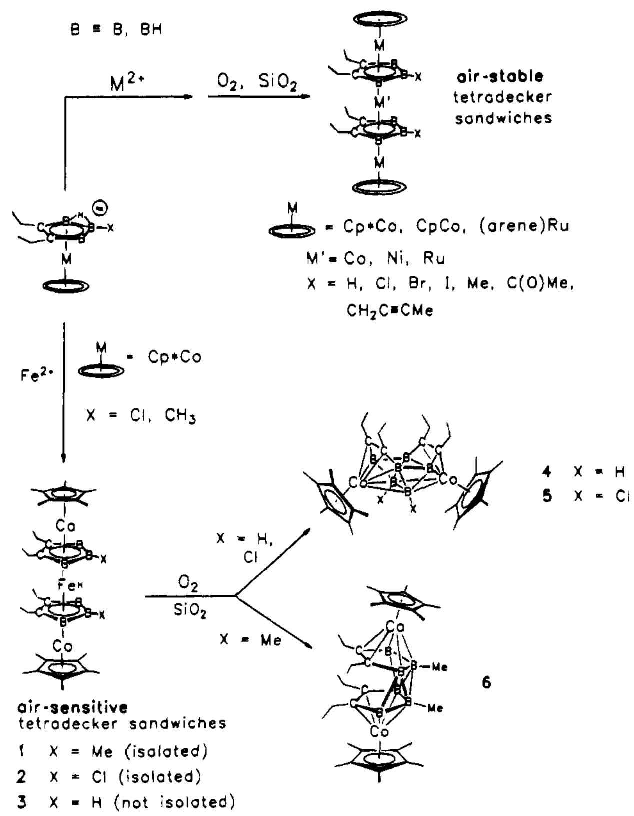
following workup on silica chromatographic columns, are fused clusters such as those depicted in Scheme 2.

We have postulated[6] that iron-centered sandwiches are, in fact, initially formed in such reactions but undergo oxidative fusion[7] with loss of Fe to generate the observed $Co_2C_4B_6$ clusters (Scheme 2). In much earlier work,[8] the observed formation of several isomeric, but structurally dissimilar, $Cp_2Co_2Me_4C_4B_6H_6$ complexes was proposed to occur via fusion of a cobalt-centered $(CoC_2B_3)_2Co$ tetradecker intermediate. While these suggestions seemed reasonable, the direct synthesis of fused clusters from tetradecker sandwiches had not been experimentally demonstrated. The present study was undertaken in an effort to isolate and characterize iron-centered tetradeckers and to establish that they do indeed undergo oxidative cage fusion as proposed.

Results and Discussion

Synthesis and Characterization of $[Cp^*Co(Et_2C_2B_3H_2X)]_2FeH$ Complexes. On the assumption that the key to isolating the target species is to avoid prolonged contact with air or silica, the workup procedure was altered accordingly from that employed in previous tetradecker syntheses.[4] Following deprotonation of *nido*-$Cp^*Co(Et_2C_2B_3H_4$-5-X) (X = Me or Cl) with *n*-butyllithium in THF, the anion was treated with anhydrous $FeCl_2$ at room temperature, and the nearly black solid product was flash-chromatographed through 2 in. of alumina to afford pure **1** (X = Cl) or **2** (X = Me), as shown in Scheme 3, bottom. For reasons as yet unexplained, the isolated yield of **2** was much higher than that of **1** (83 vs 17% based on starting complex consumed). Complexes **1** and **2** are black crystalline solids that survive brief exposure to air but are reactive toward O_2 in solution (vide infra). These products were characterized from UV–visible, ESR, and mass spectra and elemental analysis, and are paramagnetic, consistent with their proposed 41-valence-electron structures. The ESR signals at 115 K in CH_2Cl_2 are closely similar, that of **2** having a slightly broader line width. Both species exhibit a **g** tensor or axial symmetry, with nearly identical values of $g_{\parallel}$ (2.34) and $g_{\perp}$ (2.05), and no ^{59}Co hyperfine splitting is seen. These spectra strikingly resemble those observed in related C_2B_3-bridged sandwich complexes, e.g., $Cp^*Fe^{III}(Et_2C_2B_3H_2R)Co^{III}Cp^*$ (R = H, Cl, Br),[9] as well as several diborolyl–carboranyl "hybrid" complexes containing Fe(III),[10] and support the designation of a formal +3 oxidation state on the iron atom in **1** and **2**. This assignment also is consistent with the presence in both structures of a single hydrogen ligand (formally H^+) on Fe, as implied by the mass

Scheme 3



spectroscopic data (parent *m/z* = 749 and 709 for **1** and **2**, respectively). Thus, the alternative possibility that these are Fe(IV)-centered sandwiches can be discounted, although such species may form initially on oxidation of **1** and **2** (vide infra).

As previous work[6] has demonstrated, attempts to prepare the parent tetradecker **3** via the corresponding treatment of the unsubstituted complex *nido*-$Cp^*Co(Et_2C_2B_3H_5)$ led directly to the fused cluster $Cp^*_2Co_2(Et_4C_4B_6H_6)$ (**4**, Scheme 3); **3** itself, the presumed intermediate, could not be isolated. These observations further underline the crucial role played by the X substituents in metal-promoted fusion and stacking reactions.

Synthesis of $Co_2C_4B_6$ Clusters from Tetradecker Sandwich Complexes. Exposure of a solution of **1** in CH_2Cl_2 to air for several days gave a single isolable product, obtained in 71% yield as a brown solid and characterized as $Cp^*_2Co_2(Et_4C_4B_6H_4Cl_2)$ (**5**) from its ^1H and ^{11}B NMR, UV–visible, and mass spectra and elemental analysis. The cage geometry of **4** and **5**, shown in Scheme 3, has been established by X-ray crystallography[6] and is, as far as we are aware, unique to these compounds; the relation of this cage system to the present study is discussed below. In this work, compound **2** was shown to undergo rapid oxidative fusion in CH_2Cl_2–hexane solution on a silica plate, forming purple $Cp^*_2Co_2(Et_4C_4B_6H_4Me_2)$ (**6**) in 87% yield. Unlike their paramagnetic tetradecker precursors **1** and **2**, the cluster compounds **5** and **6** are diamagnetic, and their NMR data strongly suggest dissimilar cage structures, the more complex spectra of **6** implying a geometry of symmetry lower than that of **5**.

The structure of **6** was determined crystallographically and is presented in Figure 1, with data collection parameters listed in Table 1 and bond distances and angles in Table 2.

The cage geometry in **6** lacks even idealized symmetry and can be described as two CoC_2B_3 units that are partially fused, with bonding connections between their respective B–B edges. The C–C edges on the two units are far apart (ca. 2.8 Å) and clearly nonbonding, as are C(2)–B(11) and C(8)–B(4). While

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

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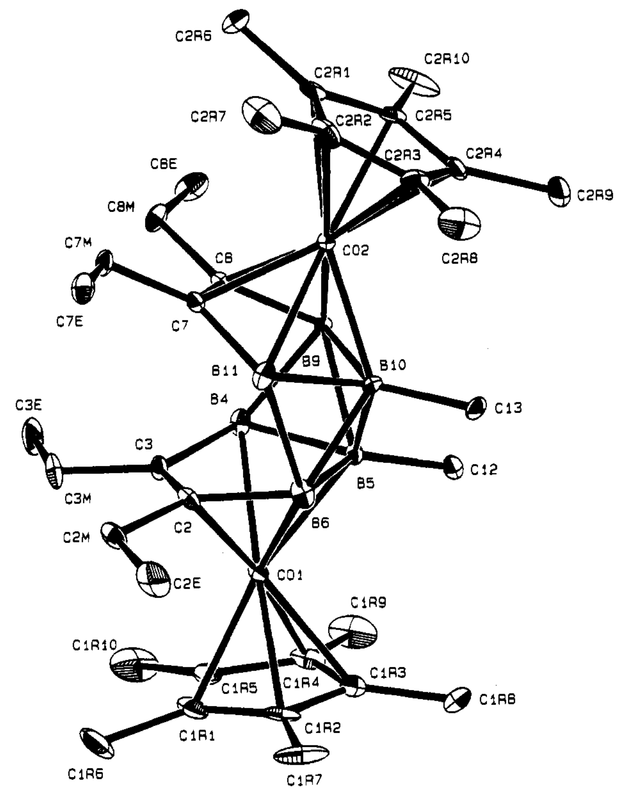

Figure 1. ORTEP view of **6**.

Table 1. Experimental X-ray Diffraction Parameters and Crystal Data for **6**

empirical formula	$Co_2C_{34}B_6H_{60}$
fw	651.6
crystal color, habit	black block
crystal dimens, mm	0.46 × 0.42 × 0.38
space group	$P2_1/c$
a, Å	15.737(5)
b, Å	13.575(4)
c, Å	17.212(5)
β, deg	111.13(2)
V, Å^3	3430
Z	4
μ, cm^{-1} (Mo Kα)	9.87
transmission factors	0.86–1.00
D(calcd), g cm^{-3}	1.262
$2\theta_{max}$, deg	46.0
no. of reflns measd	5219
no. of reflns obsd [$I > 3\sigma(I)$]	3340
R	0.058
R_w	0.077
largest peak in final diff map, e/Å^3	0.77

Table 2. Bond Distances and Selected Bond Angles for **6**

Bond Distances, Å

Co(1)−C(2)	2.008(6)	C(8M)−C(8E)	1.528(9)
Co(1)−C(3)	2.008(6)	C(1R1)−C(1R2)	1.40(1)
Co(1)−C(1R1)	2.105(6)	C(1R1)−C(1R5)	1.40(1)
Co(1)−C(1R2)	2.082(6)	C(1R1)−C(1R6)	1.51(1)
Co(1)−C(1R3)	2.106(7)	C(1R2)−C(1R3)	1.42(1)
Co(1)−C(1R4)	2.083(7)	C(1R2)−C(1R7)	1.49(1)
Co(1)−C(1R5)	2.091(7)	C(12)−B(5)	1.604(9)
Co(1)−B(4)	2.206(7)	C(1R3)−C(1R4)	1.41(1)
Co(1)−B(5)	2.119(7)	C(1R3)−C(1R8)	1.50(1)
Co(1)−B(6)	2.128(7)	C(13)−B(10)	1.605(9)
Co(2)−C(7)	2.023(6)	C(1R4)−C(1R5)	1.43(1)
Co(2)−C(8)	2.037(6)	C(1R4)−C(1R9)	1.50(1)
Co(2)−C(2R1)	2.111(6)	C(1R5)−C(1R10)	1.50(1)
Co(2)−C(2R2)	2.090(7)	C(2R1)−C(2R2)	1.42(1)
Co(2)−C(2R3)	2.094(6)	C(2R1)−C(2R5)	1.414(9)
Co(2)−C(2R4)	2.104(6)	C(2R1)−C(2R6)	1.50(1)
Co(2)−C(2R5)	2.095(6)	C(2R2)−C(2R3)	1.42(1)
Co(2)−B(9)	2.116(7)	C(2R2)−C(2R7)	1.51(1)
Co(2)−B(10)	2.111(7)	C(2R3)−C(2R4)	1.417(9)
Co(2)−B(11)	2.192(8)	C(2R3)−C(2R8)	1.50(1)
C(2)−C(2M)	1.533(8)	C(2R4)−C(2R5)	1.42(1)
C(2)−C(3)	1.408(8)	C(2R4)−C(2R9)	1.526(9)
C(2)−B(6)	1.62(1)	C(2R5)−C(2R10)	1.48(1)
C(2M)−C(2E)	1.54(1)	B(4)−B(5)	1.82(1)
C(3)−C(3M)	1.529(8)	B(4)−B(9)	1.93(1)
C(3)−B(4)	1.551(8)	B(5)−B(6)	1.89(1)
C(3M)−C(3E)	1.52(1)	B(5)−B(9)	1.849(9)
C(7)−C(7M)	1.504(8)	B(5)−B(10)	1.82(1)
C(7)−C(8)	1.426(8)	B(6)−B(10)	1.80(1)
C(7)−B(11)	1.56(1)	B(6)−B(11)	1.91(1)
C(7M)−C(7E)	1.521(9)	B(9)−B(10)	1.89(1)
C(8)−C(8M)	1.513(8)	B(10)−B(11)	1.80(1)
C(8)−B(9)	1.619(9)		

Selected Bond Angles, deg

Co(1)−C(2)−C(2M)	128.3(4)	C(3)−B(4)−B(5)	108.3(5)
C(2M)−C(2)−C(3)	119.4(5)	C(12)−B(5)−B(4)	126.0(5)
C(2M)−C(2)−B(6)	124.7(5)	C(12)−B(5)−B(6)	136.1(5)
C(3)−C(2)−B(6)	115.9(5)	C(12)−B(5)−B(9)	108.1(5)
C(2)−C(2M)−C(2E)	116.0(5)	C(12)−B(5)−B(10)	110.0(5)
Co(1)−C(3)−C(3M)	128.7(5)	B(4)−B(5)−B(6)	95.8(4)
C(2)−C(3)−C(3M)	120.9(5)	Co(1)−B(5)−C(12)	116.5(4)
C(2)−C(3)−B(4)	113.9(5)	C(2)−B(6)−B(5)	103.4(5)
C(3M)−C(3)−B(4)	124.8(5)	C(2)−B(6)−B(10)	123.7(6)
C(3)−C(3M)−C(3E)	115.2(5)	C(2)−B(6)−B(11)	80.5(4)
Co(2)−C(7)−C(7M)	128.5(4)	C(8)−B(9)−B(10)	104.2(4)
C(7M)−C(7)−C(8)	120.3(5)	C(8)−B(9)−B(5)	124.4(5)
C(7M)−C(7)−B(11)	126.4(5)	C(8)−B(9)−B(4)	81.1(4)
C(8)−C(7)−B(11)	113.0(5)	Co(2)−B(10)−C(13)	115.7(4)
C(7)−C(7M)−C(7E)	116.6(5)	B(9)−B(10)−B(11)	95.4(4)
Co(2)−C(8)−C(8M)	127.9(4)	C(13)−B(10)−B(5)	109.1(5)
C(7)−C(8)−C(8M)	119.0(5)	C(13)−B(10)−B(6)	107.0(5)
C(7)−C(8)−B(9)	115.2(5)	C(13)−B(10)−B(9)	136.4(5)
C(8M)−C(8)−B(9)	125.7(5)	C(13)−B(10)−B(11)	125.7(5)
C(8)−C(8M)−C(8E)	117.9(5)	C(7)−B(11)−B(6)	123.1(5)
C(3)−B(4)−B(9)	121.2(5)	C(7)−B(11)−B(10)	109.5(5)

this structure differs from that of **5**, it closely resembles that of a previously described cluster,[11] $Cp_2Co_2(Me_4C_4B_6H_6)$. For example, the dihedral angle subtended by the C_2B_3 ring planes, which serves as a measure of the distortion of the cage framework from a closed icosahedron, is 26.3° in the latter compound and 29.4° in **6**. This same open-cage architecture is essentially identical to that found in the isoelectronic 12-vertex monocobalt species[12] $CpCo(Me_4C_4B_7H_6{-}OEt)$ and in the analogous tetracarbon carboranes $R_4C_4B_8H_8$ in which R is ethyl[13] or benzyl.[14] (It is, however, different from the more nearly closed geometry adopted by $Me_4C_4B_8H_8$, which features a C3−C7 bond connecting the two C_2B_4 units.[15])

Considerations of Cage Geometry and Skeletal Bonding. Chart 1 depicts the three distinct $Co_2C_4B_6$ cluster types that have been isolated and structurally defined by X-ray crystallography in this and earlier work[6,11,12] (a fourth cage isomer, not shown, has been spectroscopically characterized and a distorted icosahedral geometry has been proposed[11b]). Of the cage isomers shown here, type I is exhibited by complex **6** in the present study and by the $Cp_2Co_2(Me_4C_4B_6H_6)$ species mentioned above; type II, a novel cage geometry, is represented by **4** and **5** in the current investigation and in recent work;[6] and

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(11) (a) Wong, K.-S.; Bowser, J. R.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 5045. (b) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 1936.

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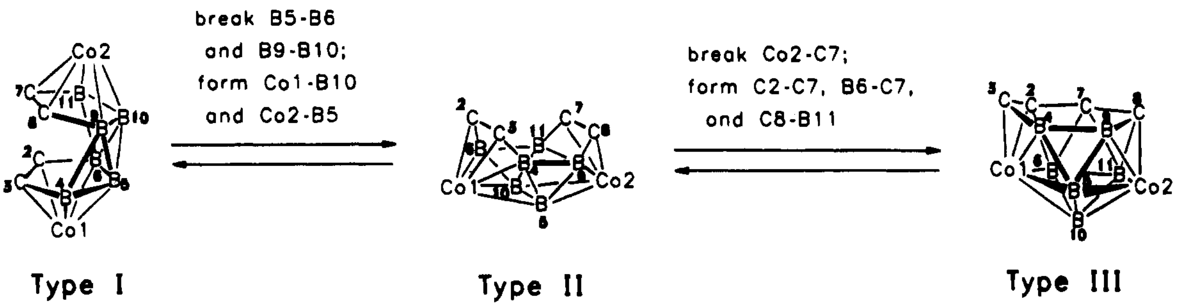
Chart 1



type III is seen in a second $Cp_2Co_2(Me_4C_4B_6H_6)$ product, obtained in the same reaction that generated its type I isomer.[11a] The geometric relationship between these cages was discussed by Pipal and Grimes in a 1979 paper[8] in which type II, unknown at the time, was postulated as an intermediate in the conversion of I to III. As is evident from Chart 1, these interconversions would seem to require only minimal cage rearrangement, and hence it is not surprising that two or more cage isomers have been isolated from the same reaction.[11]

Skeletal-electron-counting (sec) theory[16] predicts that the *most stable* geometry for a 28-electron,[17] 12-vertex $Cp_2Co_2(R_4C_4B_6H_6)$ cluster (a $(2n + 4)$-electron system) will be a nido structure corresponding to a 13-vertex closo polyhedron with one missing vertex. The type III geometry fits this description, but obviously I and II do not; indeed, II is a fragment of a 16-vertex T_d closo cage from which 4 contiguous vertices have been removed,[6] a structure which would require 34 $(2n + 10)$ electrons according to the sec rules. In our view, expressed elsewhere recently,[6] these findings present no "violation" of sec theory as long as one recognizes that the sec approach predicts thermodynamically favored cage geometries and is not applicable to kinetically stabilized structures. Consequently, in syntheses of metallacarboranes and metallaboranes conducted under mild conditions, as is the case with all the species discussed here, it is not unusual to encounter kinetically stabilized "non-Wade" cage structures.

Concluding Remarks

The synthesis of **5** and **6** from **1** and **2** provides strong support for the proposal[8] that tetradecker sandwich intermediates are involved in the fusion of MC_2B_3 units to form $M_2C_4B_6$ clusters. This process is closely analogous to the oxidative fusion of $R_2C_2B_4H_4$ ligands in $(R_2C_2B_4H_4)_2MH_x$ bis(carborane) complexes, where MH_x is CoH, FeH_2, or other metal unit,[7] and presumably involves a similar mechanism[18] wherein the central metal facilitates a bonding interaction between B−B edges of the opposing ligands, followed by further interligand binding (fusion) and expulsion of the metal as the element or as an oxygenated product. However, in the case of the tetradecker systems, the question arises as to why the Fe-centered species are more prone to undergo fusion than their Co- or Ru-centered counterparts, which in most cases are readily isolated in air (Scheme 3, top). As we have speculated,[4a] the relatively electron-poor iron center (which is formally $Fe^{III}H$ but may well be converted to d^4 Fe(IV) on oxidation) may draw its coordinated C_2B_3 rings closer together and thereby facilitate fusion. Some indirect support for this view is provided by an X-ray diffraction study of an analogous Ru(IV)-centered tetradecker,[4a] which, while it is an air-stable compound and does not fuse, is severely bent in such a way as to bring the B−B edges of the two C_2B_3 rings into close proximity. If similar bending occurs in Fe-centered stacks, the smaller metal relative to Ru may well promote B−B binding and thus initiate the fusion process. Consequently, the structural characterization of iron tetradeckers by X-ray crystallography is an objective in our continuing studies in this area.

Experimental Section

Instrumentation and Procedures. ^1H NMR spectra (300 MHz) and ^{11}B NMR spectra (115.8 MHz) were recorded on GE QE-300 and Nicolet NT-360 spectrometers, respectively. Unit resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. In each case, a strong parent envelope was observed and the observed and calculated unit-resolution spectral patterns were in close agreement. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN Analyzer using 2,4-dinitrophenylhydrazone as a standard. X-band ESR spectra were obtained at 115 K in CH_2Cl_2 glass on a Bruker ESP 300 spectrometer at 9.44 GHz. Visible−ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode array with an HP Vectra computer interface.

Materials and Procedures. All reactions were conducted under an inert atmosphere unless otherwise indicated. Workup of products was generally carried out in air using benchtop procedures. Methylene chloride was distilled from CaH_2, and THF was distilled from Na/K alloy−benzophenone immediately prior to use. Column chromatography was performed on silica gel 60 (Merck) or neutral alumina. The starting complexes *nido*-$Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}Me)$[5a] and *nido*-$Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}Cl)$[5c] were prepared by literature procedures.

Synthesis of $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Me)]_2FeH$ (2). A 164 mg (0.50 mmol) sample of *nido*-$Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}Me)$ was placed in a three-neck flask that was fitted with a septum and attached to a vacuum line. $FeCl_2$ (32 mg, 0.25 mmol) was placed in a tip tube subsequently attached to the third neck. THF (30 mL) was condensed into the flask under vacuum while cooled in dry ice−ethanol, giving a yellow-orange solution. To this solution was added via syringe 1 equiv of *tert*-butyllithium in pentane (0.15 mL, 1.7 M), and the solution was warmed to room temperature and stirred for 30 min, during which the color changed from yellow to deep orange-red. The solution was cooled to 0 °C, and the $FeCl_2$ was added from the tip tube, producing an immediate color change to nearly black. After the solution was stirred for 4 h, it was opened to the air and solvent removed by rotary evaporation. The dark brown residue was dissolved in hexane, and the solution was eluted through a 2-in. alumina column in hexane, giving one yellow band which proved to be recovered starting complex (50 mg). The eluent was switched to 1:1 hexane−CH_2Cl_2, producing a green band which was **2**, 100 mg (0.14 mmol, 83% based on starting complex consumed). MS: *m/z* 709 (molecular ion envelope). UV−visible absorptions (nm): 346 (100%), 442 (35%). Anal. Calc for $Co_2FeC_{34}B_6H_{61}$: C, 57.64; H, 8.68. Found: C, 58.07; H, 9.11.

Synthesis of $[Cp^*Co(Et_2C_2B_3H_2\text{-}5\text{-}Cl)]_2FeH$ (1). A procedure nearly identical to the above was followed using 172 mg (0.5 mmol) of *nido*-$Cp^*Co(Et_2C_2B_3H_4\text{-}5\text{-}Cl)$. However, after the unreacted starting material (26 mg) was removed via chromatography in hexane, a series

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[16] (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990.

[17] CpCo, BH, and CR units contribute 2, 2, and 3 electrons, respectively, to the skeletal bonding molecular orbitals.

[18] Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983.

of mixtures ranging from 10:1 to 4:1 hexane:CH_2Cl_2 was employed to elute a minor green band which was discarded, following which a 1:1 hexane:CH_2Cl_2 mixture was used to give one major green band which was **1**, 27 mg (0.036 mmol, 17% based on starting complex consumed). MS: *m/z* 749 (molecular ion envelope). UV−visible absorptions (nm): 380 (100%), 328 (92%), 232 (57%), 546 (15%). Anal. Calc for $Co_2FeCl_2C_{32}B_6H_{55}$: C, 51.30; H, 7.40. Found: C, 51.27; H, 7.76.

Oxidative Fusion of 1. A solution of 13 mg of **1** in CH_2Cl_2 was exposed to air for 17 d, after which the solvent was removed to give a brown solid which was dissolved in 1:1 hexane−CH_2Cl_2. The solution was transferred via pipet to a flask and the solvent removed to give 8 mg of **5** (identified from its ^{1}H NMR, ^{11}B NMR, and mass spectra[6]) corresponding to a 71% yield based on **1** consumed.

Oxidative Fusion of 2. A 25 mg sample of **2** was dissolved in a minimal amount of 1:1 hexane−CH_2Cl_2, and the solution was placed on silica gel plates which were eluted in 6:1 hexane−CH_2Cl_2 to give a green and a purple band. As they moved on the plate, the green band (**6**) became smaller and the purple band larger; after 1 h, only the purple band remained. This band was extracted with CH_2Cl_2 and the solvent removed to afford 20 mg (87%) of purplish-black solid **6**. MS: *m/z* 652 (molecular ion M), 338 [M− Cp*Co($Et_2C_2B_3H_3$)$^+$]. UV−visible absorptions (nm): 362 (100%), 232 (52%), 524 (30%). Anal. Calc for $Co_2C_{34}B_6H_{60}$: C, 62.67; H, 9.28. Found: C, 62.20; H, 9.94. ^{1}H NMR (δ, $CDCl_3$ solution): 3.00 (CH_2, m, 4H), 2.37 (CH_2, m, 4H), 1.64 (B−CH_3, s, 6H), 1.54 (C_5Me_5, s, 30H), 1.25 (ethyl CH_3, t, 6H), 0.94 (ethyl CH_3, t, 6H). ^{11}B NMR (δ vs BF_3·OEt, CH_2Cl_2 solution): 43.5, −13.6, −8.3 (broad peaks, unresolved and partially overlapped).

X-ray Structure Determination of 6. Diffraction data were collected on a Rigaku AFC6S diffractometer at −120 °C using Mo Kα radiation. Details of the data collections and structure determinations are listed in Table 1. The intensities of three standard reflections were monitored, showing no significant variation. Empirical absorption corrections were applied following ψ scanning of several reflections (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.[19] The structure was solved by direct methods in SIR88,[20] and full-matrix least-squares refinement with anisotropic thermal displacement parameters was carried out for all non-hydrogen atoms, with the results summarized in Table 1. The hydrogen atoms were found from difference Fourier maps and included in calculations without further refinement. The final difference Fourier map was essentially featureless.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and calculated mean planes for **6** (4 pages). Ordering information is given on any current masthead page.

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(19) TEXSAN 5.0: *Single Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX 77381, 1989.

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