Organotransition-Metal Metallacarboranes. 28. Controlled Substitution at Cage Carbon Atoms in CoC_2B_4 Clusters. Linkage of Bis(cobaltacarborane) Sandwich Complexes via Carbon-Bound Bridging Groups[1]

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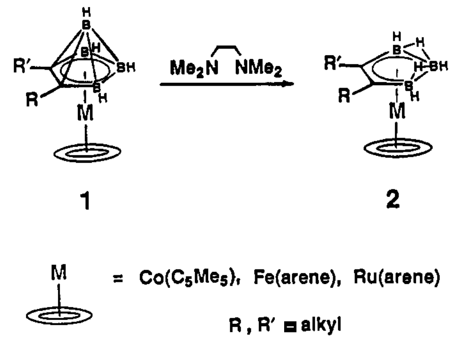
The *closo*-cobaltacarboranes $Cp^*Co[(Me_3Si)_2C_2B_4H_4]$ ($Cp^* = \eta^5$-C_5Me_5) and $(\eta^5$-$C_5Ph_5)Co[(Me_3Si)_2C_2B_4H_4]$ were catalytically desilylated by tetrabutylammonium fluoride in wet THF at room temperature, generating the respective $(C_5R_5)Co(C_2B_4H_6)$ parent complexes (**6a**, R = Me; **6b**, R = Ph). By adjustment of reaction conditions, the monosilyl species $Cp^*Co[(Me_3Si)C_2B_4H_5]$ (**5**) was also prepared. The C–H protons in **6a** are less acidic toward nucleophiles than are those in 1,2- or 1,7-$C_2B_{10}H_{12}$ (*o*- or *m*-carborane); however, reaction of **6a** with butyllithium in THF occurred readily to produce $Li^+Cp^*Co(C_2B_4H_5)^-$, which in turn can be treated with alkyl halides to give mono- or di-C-alkylated derivatives. This was demonstrated by the preparation of the *C*-ethyl and *C*-ethyl-*C′*-benzyl derivatives of **6a** and a *C*-chloro derivative of *nido*-$Cp^*Co(C_2B_3H_7)$. Base-induced removal of the apex BH unit (decapitation) in the closo clusters generated open-faced *nido*-$Cp^*Co(RR'C_2B_3H_5)$ complexes (R, R′ = H, alkyl, arylalkyl). Halogenation of the nido compounds afforded the corresponding B(5)–Cl derivatives, which are projected as precursors to tetradecker sandwich complexes via previously described stacking reactions. The application of this chemistry to the synthesis of multicluster systems linked via framework carbons was explored by reactions of **5** and **6a** with dibromomethane or *o*-, *m*-, or *p*-dibromoxylene, which afforded respectively CH_2-bridged and xylyl-bridged bis(cobaltacarboranyl) products. Double-decapitation, deprotonation, and metalation of one of the *p*-xylyl-linked species gave a linked bis(triple-decker sandwich) complex.

Introduction

Seven-vertex metallacarborane clusters of the type LM($RR'C_2B_4H_4$) in which LM = Cp*Co, CpCo, (arene)Fe, or (arene)Ru (**1**, Scheme I) are easily converted to *nido*-LM($RR'C_2B_3H_5$) sandwich complexes (**2**).[2,3] These, in turn, are tailorable building blocks that can be used to construct a wide variety of oligomeric and even polymeric systems via (i) metal stacking reactions to create multidecker sandwiches, (ii) linking through the hydrocarbon rings coordinated to the metal atoms, or (iii) linking through organic groups attached to the boron atoms in the C_2B_3 rings.[3] This chemistry has been largely based on the development in this laboratory[4] of synthetic methods for introducing organic and inorganic substituents onto boron positions in complexes of type **2**. Derivatization of the carborane ring is necessary, not only for attaching linking groups but also, as it turns out, to control the electronic properties of the open C_2B_3 face in order to promote the formation of stable, isolable tetradecker sandwiches.[5] Our main approach entails the attack of electrophilic reagents (R″X) such as alkyl halides on the B–B edge of a bridge-deprotonated $LM(RR'C_2B_3H_4)^-$ anion (**2**$^-$) to generate, in most cases, the B(5)–R″ derivative. In recent work it has been found that B(4/6)–monohalo and B(4,6)–dihalo derivatives of $Cp^*Co(Et_2C_2B_3H_5)$ can be prepared in quantitative yield by reactions of the neutral complex with *N*-halosuccinimides.[4d]

Scheme I



While these methods afford a broad range of *boron*-functionalized species, our ability to vary the substituents on the C_2B_3 *carbon* atoms in type **1** and **2** complexes has been sharply limited. In practice, this has been possible only by employing different RC≡CR′ alkynes in the preparation[6] of *nido*-$RR'C_2B_4H_6$ carboranes (the precursors to **1**) from B_5H_9. Owing to this limitation, type **2** complexes having groups other than alkyl or arylalkyl on the ring carbons have been mostly inaccessible. Consequently, we sought a practical synthetic route to "parent" **1** (LM = Cp*Co) in which R = R′ = H, reasoning that the C–H hydrogens should be acidic toward lithium alkyls and hence easily replaceable; the parent compounds could then be converted to their open-faced type **2** counterparts in the usual way. This approach ultimately proved successful and has been employed in

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(1) (a) Part 27: Meng, X.; Sabat, M.; Grimes, R. N. Manuscript in preparation. (b) Part 26: Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. Submitted for publication. (c) Based in part on the Ph.D. Thesis of M.A.B., University of Virginia, 1992.

(2) (a) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 4776. (b) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *Ibid.* **1989**, *111*, 4784.

(3) For recent reviews see: (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Grimes, R. N. *Pure Appl. Chem.* **1991**, *63*, 369. (c) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 261–285.

(4) (a) Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171. (b) Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics* **1990**, *9*, 1177. (c) Piepgrass, K. W.; Grimes, R. N. *Organometallics* **1992**, *11*, 2397. (d) Piepgrass, K. W.; Stockman, K. E.; Sabat, M.; Grimes, R. N. *Organometallics* **1992**, *11*, 2404.

(5) (a) Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 681. (b) Piepgrass, K.; Meng, X.; Hölscher, M.; Sabat, M.; Grimes, R. N. Submitted for publication.

(6) (a) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211. (b) Fessler, M. E.; Spencer, J. T.; Lomax, J. F.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 3069. (c) Boyter, H. A., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 3075. (d) Boyter, H. A., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 3080. (e) Cendrowski-Guillaume, S. M.; Spencer, J. T. *Organometallics* **1992**, *11*, 969.

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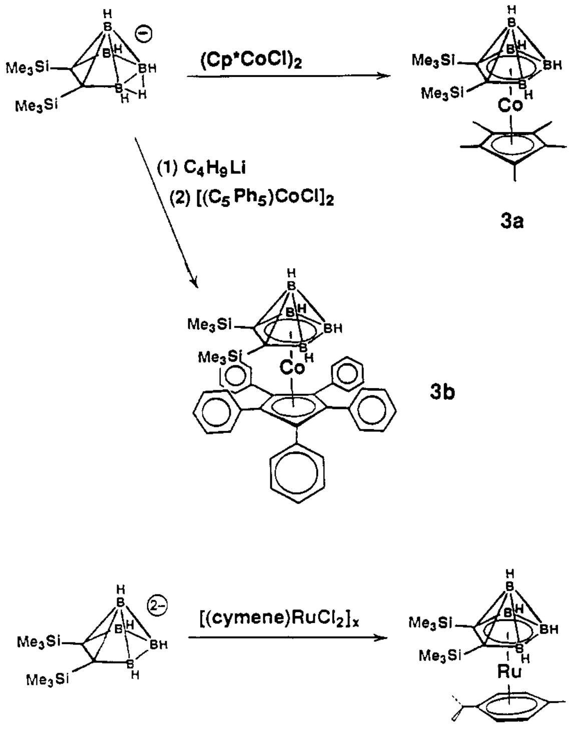
Scheme II



3a

3b

4

the synthesis of a series of monomeric and linked dimeric metallacarborane sandwich complexes as described herein.[7]

Results and Discussion

Synthesis and Desilylation of *C*-(Trimethylsilyl)cobaltacarboranes. Recently, Hosmane et al. reported a route to the unsubstituted *nido*-2,3-$H_2C_2B_4H_6$ carborane via reaction of the *C,C'*-bis(trimethylsilyl) derivative with gaseous HCl.[8] This suggested to us that $LM(C_2B_4H_6)$ parent compounds might be prepared similarly from their *C,C'*-disilyl derivatives. In order to explore this possibility, the new complex $Cp^*Co[(Me_3Si)_2C_2B_4H_4]$ (**3a**), an orange, air-stable crystalline solid, was prepared in high yield from the bis(trimethylsilyl)carborane anion (Scheme II). An analogous synthesis employing the pentaphenylcyclopentadienide(1–) ligand gave orange, air-stable $(\eta^5\text{-}C_5Ph_5)Co[(Me_3Si)_2C_2B_4H_4]$ (**3b**), which to our knowledge marks the first use of the C_5Ph_5 ring system in boron cluster chemistry. The corresponding (cymene)ruthenacarborane sandwich **4** (cymene = *p*-isopropyltoluene) was also synthesized in low yield from the carborane dianion. Characterization of these and other new compounds (vide infra) via NMR, infrared, and mass spectra (Tables I–III and Experimental Section) was straightforward.

In contrast to *nido*-$(Me_3Si)_2C_2B_4H_6$,[8] complex **3a** proved unreactive toward HCl even on prolonged exposure. Moreover, **3a** was unaffected by refluxing for several hours in glacial acetic acid and was similarly inert toward cesium fluoride in THF/aqueous solution. Desilylation was readily accomplished, however, by treatment with tetrabutylammonium fluoride (TBAF) in THF solution, generating the mono(trimethylsilyl) species **5** and/or the unsubstituted (parent) carborane **6a**, the ratio of these products depending on reaction conditions (Scheme III). Like **3a**, both **5** and **6a** were isolated as orange, air-stable crystals.

Although TBAF is widely used in organic chemistry for removal of silyl protecting groups, in our work we found unexpectedly[9] that it functions *catalytically*; e.g., 0.01 equiv of TBAF effects quantitative conversion of **3a** to **5** and **6a** (the latter in 40% yield) in less than 1 min. As our primary research objectives in this study were synthetic, we did not undertake a study of the catalytic mechanism per se. We did, however, conduct some experiments that are relevant to the function of the TBAF reagent. The reaction is solvent dependent—it is not observed in chloroform solution, for example—and the substitution of other $NR_4^+F^-$ reagents (R = Me, Et) for TBAF gave much slower formation of **5** and **6a**. When the reaction with TBAF was conducted in THF-d_8, partial introduction of deuterium at the cage carbon positions was detected; however, the presence of water in the system (present in the commercial TBAF reagent and in all except the most rigorously dried laboratory THF) appears essential. The choice of capping ligand on the metal does not appear crucial, as the pentaphenylcyclopentadienyl complex **3b** was also found to undergo TBAF-catalyzed desilylation (albeit more slowly than **3a**), forming the parent complex **6b**.

Lithiation and C-Alkylation of $Cp^*Co(H_2C_2B_4H_4)$. The principal objects of our interest were unsubstituted species such as **6a**, whose cage C–H hydrogens were expected to be acidic and hence easily replaceable by organic substituents. This proved to be the case, as treatment with *n*-butyllithium in THF does generate the lithio complex $Li^+Cp^*Co(C_2B_4H_5)^-$, which exhibits a deep purple color in solution. This species was not isolated but was employed in situ in reactions with alkyl halides, as described below.

The CH-deprotonation of **6a** by butyllithium is reminiscent of similar chemistry exhibited by the icosahedral carboranes[11] 1,2- and 1,7-$C_2B_{10}H_{12}$ (*o*- and *m*-carborane, respectively) and by smaller homologues as well, e.g., 2,4-$C_2B_5H_7$[12] and 1,6-$C_2B_4H_6$.[13] In order to compare the deprotonation of **6a** with that of other carborane clusters, competitive experiments were conducted in which equimolar quantities of that complex and *o*- or *m*-carborane were combined in THF solution and treated with 1 equiv of butyllithium. In both cases, subsequent addition of excess ethyl iodide and separation of the products afforded only the *C*-ethylcarborane derivatives (identified from their proton NMR and mass spectra) and unreacted **6a** (eqs 1 and 2). Clearly, while the

$$\mathbf{6a} + 1,2\text{-}C_2B_{10}H_{12} \xrightarrow[2\,\text{EtI}]{1\,\text{BuLi}} \mathbf{6a} + 1\text{-Et-}1,2\text{-}C_2B_{10}H_{11} \qquad (1)$$

$$\mathbf{6a} + 1,7\text{-}C_2B_{10}H_{12} \xrightarrow[2\,\text{EtI}]{1\,\text{BuLi}} \mathbf{6a} + 1\text{-Et-}1,7\text{-}C_2B_{10}H_{11} \qquad (2)$$

parent cobaltacarborane **6a** exhibits protonic character at its cage carbons sufficient to allow C-lithiation, it is nevertheless significantly less acidic than the icosahedral carboranes. It is also of interest to compare this complex with 12-vertex cobaltacarboranes. Although the direct analogue $Cp^*Co(C_2B_9H_{11})$ evidently has not been prepared, it has been reported[14] that treatment of $CpCo(C_2B_9H_{11})$ with *n*-BuLi in THF resulted in butylation at the Cp ring rather than the carborane ligand. However, when

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(7) A preliminary report of a portion of this work has appeared: Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 2836.

(8) Hosmane, N. S.; Islam, M. S.; Burns, E. G. *Inorg. Chem.* **1987**, *26*, 3236.

(9) Fluoride-promoted C–Si cleavage is well-known in organic chemistry,[10] but in all prior reports of which we are aware, its function is stoichiometric, not catalytic.

(10) Furin, G. G.; Vyazankina, O. A.; Gostevsky, B. A.; Vyazankin, N. S. *Tetrahedron* **1988**, *44*, 2675.

(11) (a) For an overview, see: Grimes, R. N. *Carboranes*; Academic Press: New York, 1970. Leading primary references: (b) Grafstein, D.; Bobinski, J.; Dvorak, J.; Smith, H. F.; Schwartz, N. N.; Cohen, M. S.; Fein, M. M. *Inorg. Chem.* **1963**, *2*, 1120. (c) Heying, T. L.; Ager, J. W.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097. (d) Zakharkin, L. I.; Stanko, V. I.; Klimova, A. I.; Chapovskii, Yu. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 2236. (e) Zakharkin, L. I.; Kazantsev, A. V. *Zh. Obshch. Khim.* **1967**, *37*, 1211.

(12) Olsen, R. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 5072.

(13) Olsen, R. R.; Grimes, R. N. *Inorg. Chem.* **1971**, *10*, 1103.

(14) Zakharkin, L. I.; Bikkineev, R. Kh. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2128.

Table I. 300-MHz ^1H FT NMR Data

compd	δ[a–c]
$(C_5Me_5)Co[(Me_3Si)_2C_2B_4H_4]$ (**3a**)	1.80 s (C_5Me_5), 0.40 s ($SiMe_3$)
$(C_5Ph_5)Co[(Me_3Si)_2C_2B_4H_4]$ (**3b**)	7.1 m (C_5Ph_5), 0.2 s ($SiMe_3$)
$(C_5Ph_5)Co[(Me_3Si)_2C_2B_3H_5]$ (**3c**)	7.1 m (C_5Ph_5), 0.15 s ($SiMe_3$), –5.4 br s (B–H–B)
$(C_{10}H_{14})Ru[(Me_3Si)_2C_2B_4H_4]$ (**4**)	5.2 m (cymene C_6H_4), 2.2 s (cymene CMe_3), 1.2 t (cymene isopropyl CH), 0.4 s (CH_3), 0.2 s ($SiMe_3$), 0.1 s ($SiMe_3$)
$(C_5Me_5)Co[(Me_3Si)C_2B_4H_5]$ (**5**)	5.25 br s (cage CH), 1.80 s (C_5Me_5), 0.30 s ($SiMe_3$)
$(C_5Me_5)Co(C_2B_4H_6)$ (**6a**)	5.05 br s (cage CH), 1.80 s (C_5Me_5)
$(C_5Ph_5)Co(C_2B_4H_6)$ (**6b**)	7.10 m (C_5Ph_5), 5.61 br s (cage CH)
$(C_5Me_5)Co(EtC_2B_4H_5)$ (**7**)	4.7 br s (cage CH), 2.7 m (CH_2), 2.4 m (CH_2), 1.81 s (C_5Me_5), 1.2 t (CH_3)
$(C_5Me_5)Co[(PhCH_2)EtC_2B_4H_4]$ (**8**)	7.0 m (C_6H_5), 4.0 q (CH_2), 3.6 q (CH_2), 2.6 m (CH_2), 2.4 m (CH_2), 1.81 s (C_5Me_5), 1.1 m (CH_3)
$(C_5Me_5)Co[(Me_3Si)_2C_2B_3H_5]$ (**9a**)	1.80 s (C_5Me_5), 0.20 s ($SiMe_3$), –5.88 br s (B–H–B)
$(C_5Me_5)Co[(Me_3Si)_2C_2B_3H_4Cl]$ (**9b**)	1.80 s (C_5Me_5), 0.20 s ($SiMe_3$), –3.91 br s (B–H–B)
$(C_5Me_5)Co[(Me_3Si)C_2B_3H_6]$ (**10a**)	4.5 br s (cage CH), 1.80 s (C_5Me_5), 0.15 s ($SiMe_3$), –5.79 br s (B–H–B)
$(C_5Me_5)Co[(Me_3Si)C_2B_3H_5Cl]$ (**10b**)	4.5 br s (cage CH), 1.80 s (C_5Me_5), 0.15 s ($SiMe_3$), –3.77 br s (B–H–B)
$(C_5Me_5)Co(C_2B_3H_7)$ (**11a**)	4.3 br s (cage CH), 1.80 s (C_5Me_5), –5.66 br s (B–H–B)
$(C_5Me_5)Co(C_2B_3H_6Cl)$ (**11b**)	4.2 br s (cage CH), 1.80 s (C_5Me_5), –3.53 br s (B–H–B)
$(C_5Me_5)Co(ClC_2B_3H_6)$ (**12**)	4.3 br s (cage CH), 1.85 s (C_5Me_5), –5.56 br s (B–H–B)
$[(C_5Me_5)Co(C_2B_4H_5)]_2CH_2$ (**13**)[d]	5.08 br s (cage CH), 2.40 t (CH_2), 1.85 s (C_5Me_5), 1.82 s (C_5Me_5)
p-$[(C_5Me_5)Co(C_2B_4H_5)CH_2]_2C_6H_4$ (**14a**)[d]	6.9 s (C_6H_4), 5.1 br s (cage CH), 4.7 br s (cage CH), 4.1 t (CH_2), 3.6 t (CH_2), 2.7 t (CH_2), 2.5 t (CH_2), 1.85 s (C_5Me_5), 1.65 s (C_5Me_5)
p-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (**14b**)[d]	6.9 s (C_6H_4), 2.6 t (CH_2), 2.5 t (CH_2), 2.3 dd (CH_2), 0.20 s ($SiMe_3$), 1.80 s (C_5Me_5), 1.70 s (C_5Me_5)
m-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (**15**)[d]	7.1 s (C_6H_4), 6.8 s (C_6H_4), 6.7 s (C_6H_4), 2.7 m (CH_2), 2.5 m (CH_2), 2.3 dd (CH_2), 0.30 s ($SiMe_3$), 1.80 s (C_5Me_5), 1.70 s (C_5Me_5)
o-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (**16**)[d]	7.0 s (C_6H_4), 6.8 s (C_6H_4), 2.6 m (CH_2), 2.5 m (CH_2), 2.2 dd (CH_2), 0.25 s ($SiMe_3$), 1.80 s (C_5Me_5), 1.65 s (C_5Me_5)
p-$[(C_5Me_5)Co((SiMe_3)C_2B_3H_5)CH_2]_2C_6H_4$ (**17**)[d]	7.0 s (C_6H_4), 2.6 m (CH_2), 1.80 s (C_5Me_5), 1.70 s (C_5Me_5), 0.15 s ($SiMe_3$), –5.8 br s (B–H–B)
$[(C_5Me_5)_2Co_2((SiMe_3)C_2B_3HCl_2)CH_2]_2C_6H_4$ (**18**)	6.83 s (C_6H_4), 6.80 s (C_6H_4), 2.6 m (CH_2), 2.4 m (CH_2), 1.80 s (C_5Me_5), 1.70 s (C_5Me_5), 0.45 s ($SiMe_3$)

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [c] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [d] Mixture of isomers (see text).

Table II. 115.8-MHz ^{11}B FT NMR Data

compd	δ (J_{BH}, Hz)[a–c]	rel areas
3a	10.1, 9.1, –3.1 (158)	1:2:1
3b	16.8, 11.1, 3.2	1:2:1
4	19.0, 8.4, 6.3	1:1:2
5	12.8 (141), 5.9, 4.5, –2.0 (156)	1:1:1:1
6a	13.0 (141), 3.6 (152), –0.6 (142)	1:2:1
7	12.9 (116), 4.2, 2.5, 0.5	1:1:1:1
11a	5.6, 3.9 (155)	1:2
12	7.5 (148), 5.1 (163), 3.5 (157)	1:1:1
13	12.1, 3.4, –1.3	1:2:1
14a	15.5, 13.2, 3.1, –0.9	1:1:1:1
14b	11.9, 4.6, –1.2	1:2:1
15	12.0, 5.4, –2.0 (116)	1:2:1
16	12.0, 5.4, –1.8	1:2:1
17	6.2, 3.5	1:2
18	58.6, 53.7, 15.2, 5.8	1:1:1:1

[a] Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. [b] Dichloromethane solution. [c] H–B coupling constant in Hz is given in parentheses, when resolved.

the reaction was conducted in diethyl ether the carborane CH was lithiated.[14]

As anticipated, the synthesis of *C*-alkyl or *C*,*C'*-dialkyl derivatives of **6a** via lithiation and reaction with alkyl halides was straightforward, as demonstrated by the preparation of the *C*-monoethyl complex **7** and its subsequent conversion to the *C*-ethyl-*C'*-benzyl derivative **8** (Scheme IV). These chiral products were, of course, obtained as racemic mixtures, of which only one enantiomer is shown for each complex.

Synthesis and Derivatization of *nido*-Cp*Co(RR'C$_2$B$_3$H$_3$) Sandwich Complexes. As noted in the Introduction, the utility of small metallacarborane complexes as synthons for constructing multilevel and linked sandwich structures requires the conversion of *closo*-MC_2B_4 clusters to *nido*-MC_2B_3 species via base-induced removal of the apex boron ("decapitation"). Complexes **3a**, **5**, and **6a** exhibited similar behavior, reacting easily with tetramethylethylenediamine (TMEDA) to give the corresponding *nido*-cobaltacarborane products Cp*Co(RR'$C_2B_3H_5$) (**9a**, R = R' = $SiMe_3$; **10a**, R = $SiMe_3$, R' = H; **11a**, R = R' = H) in high yield as yellow air-stable solids (Scheme V). The pentaphenylcyclopentadienyl complex **3b** similarly decapitated to form the orange nido complex (η^5-C_5Ph_5)Co[$(Me_3Si)_2C_2B_3H_5$] (**3c**). Compounds **9a**, **10a**, and **11a** were readily converted to their B(5)–chloro derivatives **9b**, **10b**, and **11b** via bridge deprotonation followed by treatment with methanesulfonyl chloride, as depicted in Scheme V. Like other *nido*-cobaltacarboranes,[2,3] the bridge-deprotonated anions of these complexes can be metalated at the C_2B_3 open face to generate triple-decker sandwiches, as described below.

In an attempt to chlorinate the closo complex **6a** via treatment with butyllithium followed by methanesulfonyl chloride, the *C*-chloro nido species **12** was obtained in 41% yield as the only isolable product. The same product was obtained when *N*-chlorosuccinimide was employed as the chlorinating agent. Evidently the replacement of a CH hydrogen atom by chlorine in **6a** renders the apical BH unit particularly susceptible to base attack and removal.

The NMR, infrared, and mass spectra of these compounds support the assigned structures. In common with other type **2** cobaltacarboranes having electron-withdrawing substituents at B(5), the chlorinated species **9a**, **10a**, and **11a** are likely precursors to tetradecker complexes via stacking reactions with transition metal halides.[5] This is supported by the proton NMR spectra on these compounds, which exhibit B–H–B signals between δ –3.5 and –3.9, well within the range previously shown to be diagnostic for complexes capable of tetradecker stacking.[5]

Linkage of Cobaltacarborane Cluster Units via C-Alkylation. The preparation of *C*-alkyl derivatives of the parent complex **6a**, described above, opened the way to synthesis of linked systems via reactions with alkyl dihalides. As a sterically rigorous test of this approach, we treated the *C*-monolithio derivative of **6a** with dibromomethane and obtained the yellow-orange methylene-bridged species **13** in low yield (Scheme VI). Not surprisingly,

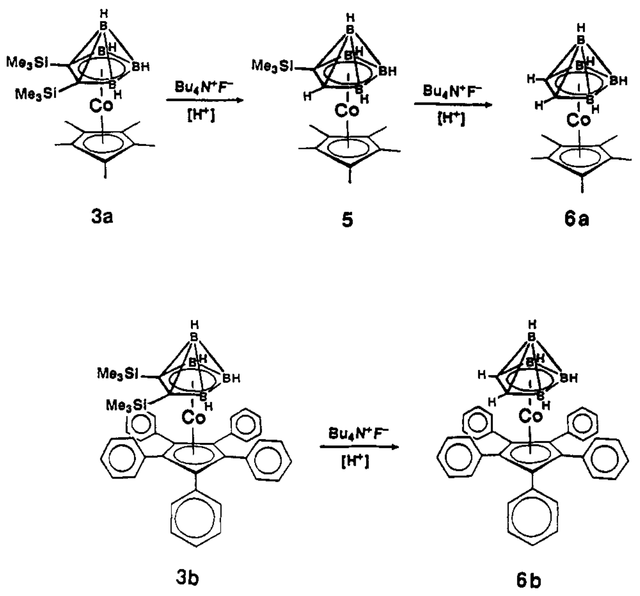
Table III. Infrared Absorptions (cm^{-1}; Neat Films on KBr Plates)[a,b]

compd	absorptions
3a	2956 s, 2919 s, 2854 m, 2536 vs, 1453 m, 1376 m, 1247 s, 1099 w, 1026 m, 838 vs, 757 m, 690 m
3b	3058 m, 2957 m, 2899 m, 2558 s, 2344 w, 1602 w, 1503 m, 1445 m, 1410 m, 1249 m, 1162 w, 1077 w, 841 vs, 741 s, 699 s
3c	3057 w, 2924 s, 2854 m, 2526 w, 1600 w, 1444 m, 1241 m, 1074 m, 1074 w, 1029 w, 830 m, 743 m, 700 s
4	2955 vs, 2925 vs, 2853 s, 2537 s, 1734 w, 1457 m, 1381 w, 1247 s, 837 vs, 758 w, 680 m
5	2961 s, 2919 s, 2854 m, 2536 vs, 2343 w, 1475 m, 1377 s, 1247 s, 1172 w, 1127 w
6a	3040 w, 2965 m, 2917 s, 2849 m, 2540 vs, 1473 s, 1376 s, 1261 m, 1180 w, 1090 w, 1013 m, 820 m, 679 m
6b	3219 br m, 2558 m, 2361 w, 2339 w, 1437 br vs, 1179 w, 1085 w, 699 m
7	2966 s, 2917 s, 2873 m, 2533 vs, 2360 w, 1737 w, 1475 m, 1453 m, 1382 s, 1118 w
8	2963 s, 2920 s, 2857 m, 2532 vs, 1733 w, 1454 s, 1381 s, 1030 m, 872 m, 700 s
9a	2958 s, 2922 s, 2854 m, 2540 m, 2342 w, 1869 w, 1376 m, 1243 s, 1074 w, 911 m, 832 vs, 750 m
9b	2956 s, 2922 s, 2854 m, 2525 s, 1889 w, 1452 m, 1330 m, 1247 m, 1085 m, 827 s, 752 w
10a	2958 s, 2910 s, 2519 vs, 1861 m, 1377 s, 1245 s, 1077 m, 834 s
10b	2956 m, 2922 m, 2854 w, 2525 m, 1889 w, 1237 m, 1084 m, 827 s
11a	2960 m, 2913 s, 2852 m, 2527 vs, 1855 w, 1364 s, 1031 m, 848 m, 767 w
11b	2923 vs, 2853 s, 2529 s, 2362 w, 1895 w, 1457 m, 1376 s, 1031 m, 871 w, 819 w, 756 w
12	2920 m, 2854 w, 2540 s, 1859 w, 1384 vs, 1031 m, 909 m, 740 s
13	2917 vs, 2849 s, 2536 m, 2343 w, 1457 m, 1363 w, 1030 w, 843 w
14a	2918 s, 2857 m, 2539 vs, 1858 w, 1513 m, 1473 s, 1457 s, 1381 vs, 1265 w, 1029 m, 871 m, 843 m, 738 m
14b	2957 m, 2918 m, 2864 w, 2531 vs, 2360 w, 1473 w, 1457 w, 1380 w, 1248 m, 1129 w, 1059 w, 1028 w, 839 vs
15	2956 vs, 2920 s, 2858 m, 2547 vs, 1607 w, 1475 m, 1380 m, 1248 s, 1060 m, 839 vs, 690 m
16	2958 s, 2919 s, 2856 m, 2539 vs, 1473 m, 1456 m, 1408 w, 1248 s, 1129 m, 1060 m, 1028 m, 949 w, 838 vs, 757 s
17	2924 s, 2920 s, 2854 m, 2522 s, 1861 w, 1542 w, 1515 w, 1456 m, 1380 m, 1333 w, 1245 s, 1093 m, 1029 w, 891 w, 833 vs
18	2957 vs, 2913 vs, 2472 s, 1449 s, 1378 vs, 1245 s, 1513 w, 1473 m, 1448 s, 1428, 1379 vs, 1245 s

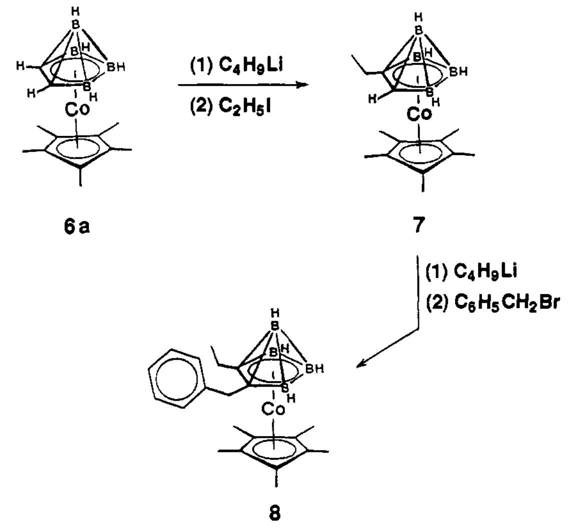
[a] Microcrystalline films obtained by evaporation of solutions. [b] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

given the steric constraints in the vicinity of the methylene bridge, the formation of **13** was inefficient and substantial **6a** was recovered. The proposed structure of **13** is clearly supported by its mass spectrum and NMR spectra, but the observation of two nearly superimposed, but distinct, Cp* signals in the proton NMR reveals the presence of more than one isomer. This is readily explained in stereochemical terms, as there are two possible modes for the bridged structure, i.e., the optically inactive meso isomer and the chiral form which is present as a d,l pair (Scheme VI). The differences in magnetic environments in the isomers are too small to be otherwise detectable, as seen for example in the observation of only one set of ^{11}B NMR resonances. These isomers are chemically almost indistinguishable and were inseparable on chromatographic columns.

Scheme III



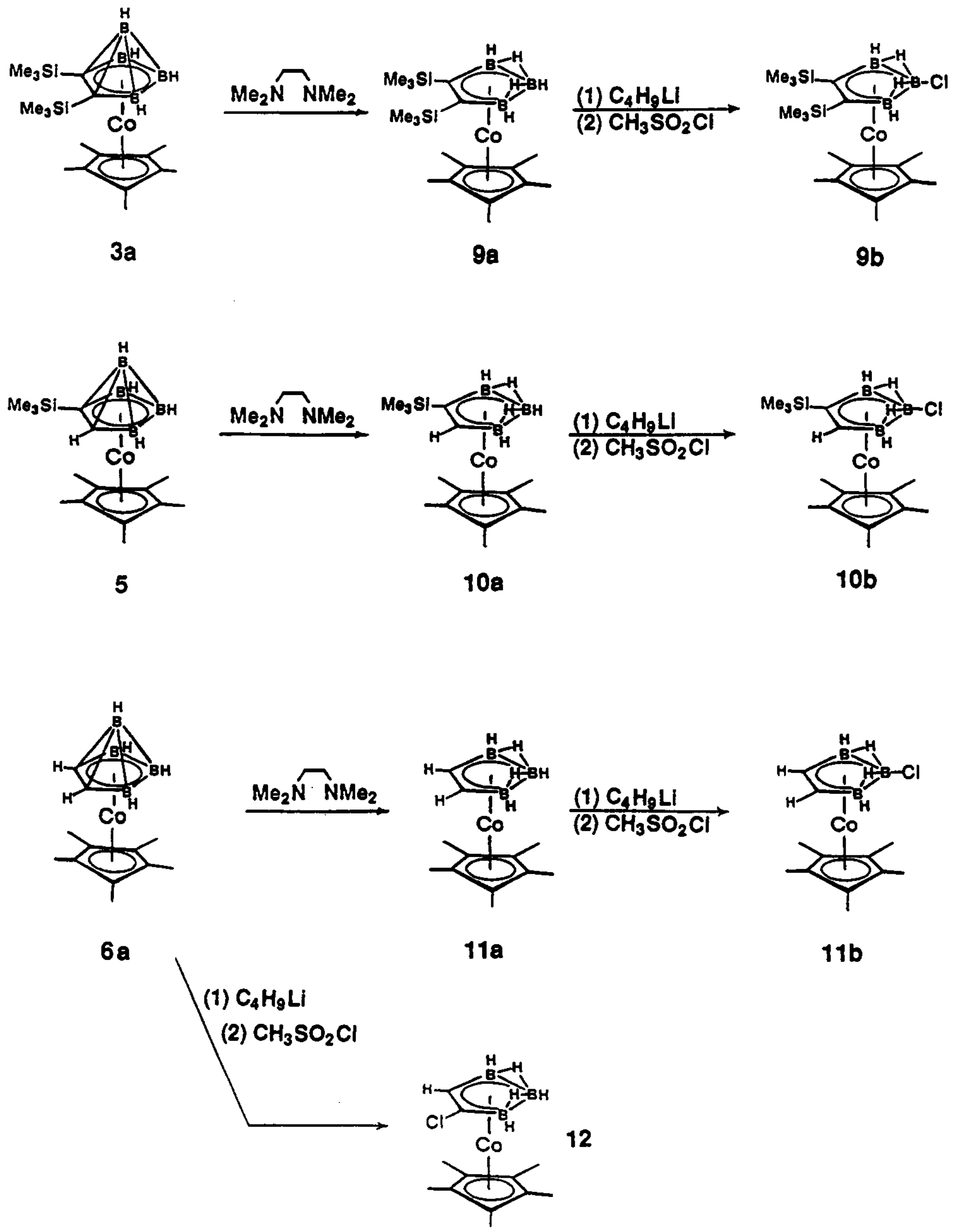
Scheme IV



A family of xylyl-linked complexes was prepared in similar fashion. Reactions of the parent cluster **6a** and the mono(*C*-trimethylsilyl) derivative **5** with *p*-dibromoxylene afforded respectively **14a** and **14b**, both as air-stable orange crystals. Owing to regeneration of **6a** via competitive reprotonation of the anion, the isolated yield of **14b** was considerably higher than that of **14a** (73 vs 12%). The corresponding treatment of **5** with *m*- and *o*-dibromoxylene generated the respective products **15** and **16** in 15 and 42% isolated yields. In each of these complexes, as in the methylene-linked complex **13**, the observation of two Cp* proton NMR resonances (and two cage CH signals in the case of **14a**) reflects the presence of two isomers which are assumed to be d,l/meso mixtures. Again, these isomers are not otherwise easily distinguishable, as shown, for example, by the single SiMe$_3$ proton NMR signal recorded for compounds **14b**, **15**, and **16**.

This chemistry can be combined with methods previously developed for metal complexation and construction of multidecker sandwiches, affording considerable versatility in designed synthesis. As an illustration, the *p*-xylyl-linked bis(cobaltacarborane) **14b** was "double-decapitated" to give the bis(*nido*-cobaltacarboranyl) species **17**, isolated as a yellow air-stable solid (Scheme VII). The latter complex in turn was bridge-deprotonated and treated with the dimer of Cp*CoCl to generate the xylyl-bridged bis(triple-decker) compound **18**, isolated as a dark red air-stable solid. Complex **18** was found to be a tetrachloro derivative, as shown, on the basis of mass spectroscopic and NMR evidence. Chlorination during workup in dichloromethane is not uncommon in *closo*-cobaltacarborane complexes[2] and is the presumed origin of the halogenation in this instance. The placement of chlorine substituents on the cages cannot be determined from spectroscopic data; moreover, the ^{11}B NMR spectrum indicates that at least two isomers are present, probably

Scheme V



differing in the patterns of halogenation at the six available boron sites. The assigned triple-decker geometry is supported by the presence of low-field ^{11}B NMR peaks, a well-established characteristic of C_2B_3-bridged sandwich structures.[2]

Concluding Remarks

This study extends and complements previous work in this laboratory on the controlled synthesis of multicage/multidecker metallacarborane systems, since derivatization at the cage carbon positions is now a synthetic option along with the previously developed methods[2-5] for substitution at boron, multidecker metal stacking, and variations or combinations of these strategies. As a group, these reactions allow the tailored construction of a virtually unlimited variety of linked, stacked, and functionalized multimetal complexes for which chemical and thermal stability can be expected in most instances. The very recent development[6e] of a rapid, high-yield, room-temperature route to the precursor *nido*-2,3-RR′$C_2B_4H_6$ carboranes (recently extended to a large (~35 g) scale in our laboratory) further extends the accessibility of these powerful ligands to organometallic chemists. In the following article,[15] we employ our combined C- and B-substitution approaches in the synthesis of specific organometallic sandwich target compounds.

Experimental Section

Instrumentation and Analysis. All operations were conducted in vacuum apparatus unless otherwise stated. ^{11}B (115.8 MHz) and ^{1}H (300 MHz) NMR spectra were acquired on Nicolet NT-360 or GE QE300 spectrometers, and unit-resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Infrared spectra were recorded on a Mattson Cygnus FTIR spectrometer. All new products gave unit-resolution mass spectra exhibiting strong parent envelopes and intensity patterns in good agreement with calculated spectra based on natural isotopic distributions. In addition, the fragmentations exhibited in the unit-resolution spectra are consistent with the proposed structures, e.g., loss of ligand or M(ligand) units from the parent ions. Elemental analyses were provided by E&R Microanalytical Laboratory, Corona, NY 11368.

Materials. The carborane 2,3-$(Me_3Si)_2C_2B_4H_6$ was prepared as described previously.[16] Reagent grade dichloromethane and *n*-hexane

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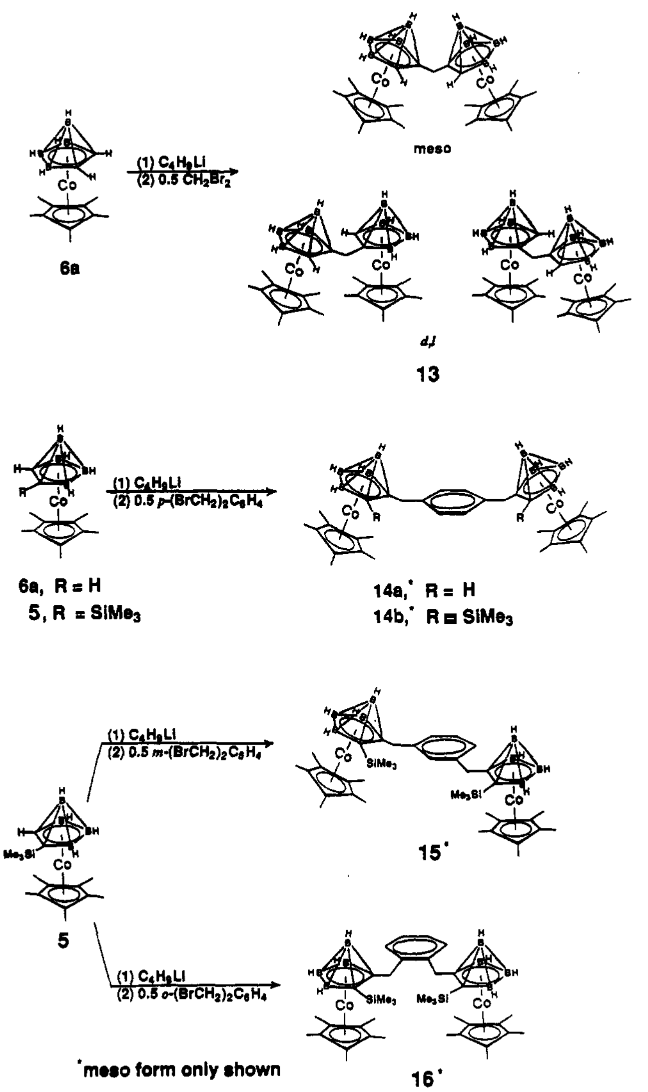
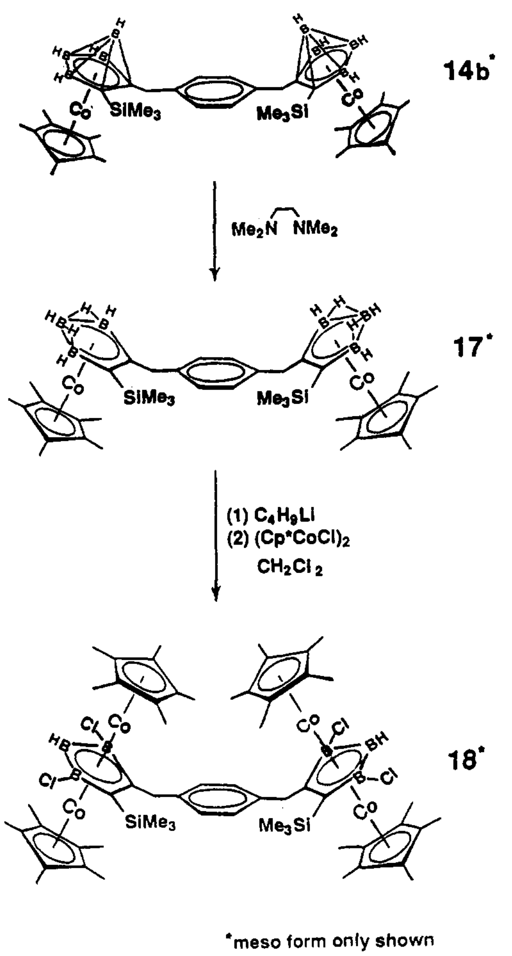
[15] Benvenuto, M. A.; Sabat, M.; Grimes, R. N. *Inorg. Chem.*, following paper in this issue.

Scheme VI



Scheme VII



were stored over molecular sieves, and THF was stored over benzophenone/Na and distilled immediately prior to use.

Synthesis of $(C_5Me_5)Co[(Me_3Si)_2C_2B_4H_4]$ (3a). A solution of LiC_5Me_5 was prepared by addition of excess *n*-butyllithium (1.7 M in hexane) to 262 mg (1.67 mmol) of C_5Me_5H in dry THF. This solution was stirred for 1 h and added to anhydrous $CoCl_2$ (217 mg, 1.67 mmol) in THF, and the combined solution was stirred for 45 min. To this was added a solution of $Na^+(Me_3Si)_2C_2B_4H_5^-$ (prepared via reaction of 368 mg (1.67 mmol) of the neutral carborane with excess NaH in 50 mL of THF), and the mixture was stirred for 16 h. The reactor was opened in air, the solution rotary-evaporated to dryness, the residue dissolved in dichloromethane, and the solution filtered through 2 cm of silica gel. The eluent was evaporated to dryness, and the residue was taken up in 2:1 hexane/dichloromethane and eluted through a silica column. The second band obtained was bright orange **3a** (0.532 g, 1.29 mmol, 77%). Exact mass: calcd for $^{59}Co^{28}Si_2{}^{12}C_{18}{}^{11}B_4{}^{1}H_{37}{}^+$, *m/z* 412.2138; found, 412.2137.

Synthesis of $(C_5Ph_5)Co[(Me_3Si)_2C_2B_4H_4]$ (3b). Pentaphenylcyclopentadienyl bromide (0.868 g, 1.65 mmol) was dissolved in THF in vacuo, and butyllithium (1.65 mmol in hexane) was added via syringe and the solution stirred for 1 h. This solution was slowly added in vacuo to a solution of $CoCl_2$ (0.215 g, 1.65 mmol) in THF, and the reaction mixture was stirred for 45 min. A previously prepared solution of $Na^+(Me_3Si)_2C_2B_4H_5^-$ in THF (obtained by deprotonation of 1.65 mmol of the carborane with NaH) was filtered in vacuo through a fritted disk into the above reaction mixture. The mixture was stirred for 16 h and opened in air, and the workup procedure described for **3a** was followed. The third band to elute from the silica gel column was red-orange **3b** (0.320 g, 0.443 mmol, 27%). Anal. Calcd for $CoSi_2C_{43}B_4H_{47}$: C, 71.51; H, 6.56. Found: C, 71.24; H, 6.33.

Conversion of 3b to $(C_5Ph_5)Co[(Me_3Si)_2C_2B_3H_5]$ (3c). A solution of **3b** (0.050 mmol) in 12 mL of TMEDA was prepared, 2 drops of water were added via pipet, and the solution was stirred in air for 1.5 h. The solvent was removed under vacuum, the product was suction-filtered through 2 cm of silica gel with hexane and then with CH_2Cl_2, and the latter fraction was dried to give **3c** (30 mg, 0.042 mmol, 85%). Anal. Calcd for $CoSi_2C_{43}B_3H_{48}$: C, 72.50; H, 6.79. Found: C, 73.97; H, 7.13.

Synthesis of $(C_{10}H_{14})Ru[(Me_3Si)_2C_2B_4H_4]$ (4). A solution of $Na^+(Me_3Si)_2C_2B_4H_5^-$ in THF was prepared by deprotonation of 0.240 g (1.09 mmol) of the carborane with NaH and filtered in vacuo. To this solution was added 0.436 mL (1.09 mmol) of butyllithium in hexane and the mixture stirred for 15 min to form the carborane dianion. $(C_{10}H_{14})RuCl_2$ (0.334 g, 1.09 mmol) was added to the dianion solution, and the solution was stirred for 16 h. The mixture was opened in air and evaporated to dryness, the residue was taken up in acetone, and the new mixture was suction filtered through 2 cm of silica. The solvent was removed, the solid was dissolved in 9:1 hexane/CH_2Cl_2, and the solution was chromatographed on a silica TLC plate, affording **4** as a pale yellow oil (38 mg, 0.084 mmol, 8%).

Synthesis of $(C_5Me_5)Co[(Me_3Si)C_2B_4H_5]$ (5). A solution of 154 mg (0.374 mmol) of **3a** in 30 mL of THF was cooled to 0 °C in air, 0.04 mL of 1 M Bu_4NF was added, the solution was stirred for 5 min, and solvent was removed at 0 °C. The product was taken up in 2:1 hexane/CH_2Cl_2 and eluted through a silica column to give two orange bands, of which the first was recovered **3a** (23 mg, 14%) and the second was **5** (0.109 g, 86%). Exact mass: calcd for $^{59}Co^{28}Si^{12}C_{15}{}^{11}B_4{}^{1}H_{29}{}^+$, *m/z* 340.1742; found, 340.1766.

Synthesis of $(C_5Me_5)Co(C_2B_4H_6)$ (6a). The procedure used for preparing **5** was followed except that only 3 mL of THF solvent was employed, giving a 10-fold increase in concentration. The second band eluted on silica gel was **6a** (70 mg, 0.26 mmol, 70%). Exact mass: calcd for $^{59}Co^{12}C_{12}{}^{11}B_4{}^{1}H_{21}{}^+$, *m/z* 268.1347; found, 268.1337.

Synthesis of $(C_5Ph_5)Co(C_2B_4H_6)$ (6b). A sample of **3b** (0.203 g, 0.281 mmol) was dissolved in 6.2 mL of THF in air, and Bu_4NF (0.03 mL of 1 M in THF) was added. After the solution was stirring for 3 min, the solvent was removed and the residue worked up as for **5** and **6a**, affording

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(16) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359.

6b as the fourth band eluted from a silica column (32 mg, 0.055 mmol, 20%). Anal. Calcd for $CoC_{37}B_3H_{31}$: C, 76.91; H, 5.41. Found: C, 76.70; H, 5.68.

Synthesis of $(C_5Me_5)Co(EtC_2B_4H_5)$ (7). A 97-mg (0.363 mmol) sample of **6a** was dissolved in THF in vacuo, and an equimolar amount of butyllithium was added via syringe producing an immediate color change from orange to purple. After the mixture was stirred for 15 min, 0.726 mmol of ethyl iodide was added and the solution stirred for 3.5 h. The solution was opened to air and rotary-evaporated to dryness, the solid was dissolved in CH_2Cl_2, the mixture was filtered through 2 cm of silica, and the solvent was removed to give **7** (0.106 g, 0.359 mmol, 99%). Exact mass: calcd for $^{59}Co^{12}C_{14}{}^{11}B_4{}^{1}H_{25}{}^{+}$, *m/z* 296.1660; found, 296.1647.

Synthesis of $(C_5Me_5)Co[(PhCH_2)EtC_2B_4H_4]$ (8). A 41-mg (0.139 mmol) sample of **7** was dissolved in THF in vacuo, and an equimolar amount of butyllithium was added. After the solution was stirred for 30 min, 0.278 mmol of benzyl bromide was added and the mixture stirred overnight. The solution was opened to air and rotary-evaporated to dryness, the solid was dissolved in CH_2Cl_2, and the solution was again evaporated to dryness. The residue was taken up in 2:1 hexane/CH_2Cl_2 and chromatographed on a silica column to give, as the third band to elute, a mixture of **7** and **8**. Subsequent elution of this material on a silica plate in the same solvent gave one broad band, of which the first and last portions were collected separately; the first part was pure **8** (14 mg, 0.039 mmol, 28%).

Synthesis of $(C_5Me_5)Co[(Me_3Si)_2C_2B_3H_5]$ (9a). A solution of 0.100 g (0.243 mmol) of **3a** in 30 mL of TMEDA containing 3 drops of water was stirred for 1.5 h, the solution was evaporated to dryness, the residue was dissolved in hexane, and the solution was eluted through a silica gel column. The first band to elute was yellow **9a** (97 mg, 0.241 mmol, 99%). Anal. Calcd for $CoSi_2C_{18}B_3H_{38}$: C, 53.78; H, 9.53. Found: C, 54.97; H, 10.00.

Synthesis of $(C_5Me_5)Co[(Me_3Si)_2C_2B_3H_4Cl]$ (9b). A 0.596 g (1.48 mmol) sample of **9a** was dissolved in dry THF, an equimolar amount of butyllithium was added via syringe, the solution was stirred for 15 min, and $MeSO_2Cl$ (2.96 mmol) was added via syringe. After the mixture was stirred for 2.5 h, the solvent was removed, the residue was taken up in hexane, and the solution was eluted on a silica gel column, giving as the second band orange **9b** (0.216 g, 0.495 mmol, 34%).

Synthesis of $(C_5Me_5)Co[(Me_3Si)C_2B_3H_6]$ (10a). The procedure employed in the preparation of **9a** was followed, using **5** (0.264 g, 0.777 mmol) as starting material and 14.0 mL of TMEDA containing 4 drops of water. The isolated yield of **10a** was 0.221 g (0.670 mmol, 86%).

Synthesis of $(C_5Me_5)Co[(Me_3Si)C_2B_3H_5Cl]$ (10b). The procedure employed in the preparation of **9b** was followed, using **10a** (0.210 g, 0.637 mmol), an equimolar quantity of butyllithium, and 1.27 mmol of $MeSO_2Cl$. The isolated yield of **10b** was 81 mg (0.222 mmol, 33%).

Synthesis of $(C_5Me_5)Co(C_2B_3H_7)$ (11a). The procedure employed in the preparation of **9a** was followed, using **6a** (0.078 g, 0.292 mmol) as starting material and 14.0 mL of TMEDA containing 2 drops of water. The isolated yield of **11a** was 54 mg (0.210 mmol, 72%).

Synthesis of $(C_5Me_5)Co(C_2B_3H_6Cl)$ (11b). The procedure employed in the preparation of **9b** was followed, using **11a** (0.167 g, 0.648 mmol), an equimolar quantity of butyllithium, and 2.62 mmol of $MeSO_2Cl$. The isolated yield of **11b** was 0.116 g (0.397 mmol, 61%).

Synthesis of $(C_5Me_5)Co(ClC_2B_3H_6)$ (12). A 0.122 g (0.456 mmol) sample of **6a** was dissolved in dry THF, an equimolar amount of butyllithium was added via syringe, the solution was stirred for 15 min, and $MeSO_2Cl$ (0.912 mmol) was added via syringe. After the mixture was stirred for 1 h, the solvent was removed, the residue was taken up in hexane, and the solution was suction filtered through 2 cm of silica gel, followed by washing with CH_2Cl_2. The hexane fraction was evaporated to dryness, affording **12** (55 mg, 0.188 mmol, 41%).

Synthesis of $[(C_5Me_5)Co(C_2B_4H_5)]_2CH_2$ (13). A solution of **6a** (0.200 g, 0.748 mmol) in THF was prepared in vacuo, and butyllithium (0.748 mmol) in hexane was added via syringe, producing an immediate color change from bright orange to purple. After the solution was stirred for 15 min, 0.374 mmol of CH_2Br_2 was added in vacuo and the mixture was stirred for 15 h. The mixture was opened to the air and evaporated to dryness, the residue taken up in 2:1 hexane/CH_2Cl_2, and the solution was eluted through a silica gel column in the same solvent. The second band to elute was recovered **6a**, and the fourth band was yellow-orange **13** (24 mg, 0.044 mmol, 6%). Anal. Calcd for $Co_2C_{25}B_8H_{42}$: C, 54.90; B, 15.81; H, 7.74. Found: C, 54.75; B, 16.13; H, 7.87.

Synthesis of *p*-$[(C_5Me_5)Co(C_2B_4H_5)CH_2]_2C_6H_4$ (14a). A solution of **6a** (0.578 g, 2.16 mmol) in THF was prepared in vacuo, butyllithium (2.16 mmol) in hexane was added, and the purple solution was stirred for 1 h. *p*-Dibromoxylene was added in vacuo, and the mixture was stirred for 16 h. The mixture was opened to the air and evaporated to dryness, the residue was taken up in CH_2Cl_2, and the solution was suction filtered through a silica gel column, first with CH_2Cl_2 and then with methanol. The CH_2Cl_2 fraction was evaporated to dryness, the solid was redissolved in 1:1 hexane/CH_2Cl_2, and the solution was eluted through silica gel. The fourth band to elute was **14a** (0.168 g, 0.264 mmol, 12%). Anal. Calcd for $Co_2C_{32}B_8H_{48}$: C, 60.33; B, 13.57; H, 7.59. Found: C, 60.38; B, 12.88; H, 7.49.

Synthesis of *p*-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (14b). The procedure used in the preparation of **14a** was followed using **5** (1.058 g, 3.115 mmol) with an equimolar amount of butyllithium and 0.411 g (1.557 mmol) of *p*-dibromoxylene. The isolated yield of **14b** was 0.889 g (1.138 mmol, 73%). Anal. Calcd for $Co_2Si_2C_{38}B_8H_{64}$: C, 58.41; B, 11.07; H, 8.26. Found: C, 59.41; B, 10.46; H, 8.63.

Synthesis of *m*-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (15). The procedure used in the preparation of **14b** was followed using **5** (0.312 g, 0.919 mmol) with an equimolar amount of butyllithium and 0.121 g (0.459 mmol) of *m*-dibromoxylene. The isolated yield of **15** was 55 mg (0.141 mmol, 15%). Anal. Calcd for $Co_2Si_2C_{38}B_8H_{64}$: C, 58.41; H, 8.26. Found: C, 59.65; H, 8.75.

Synthesis of *o*-$[(C_5Me_5)Co((SiMe_3)C_2B_4H_4)CH_2]_2C_6H_4$ (16). The procedure used in the preparation of **14b** was followed using **5** (0.187 g, 0.551 mmol) with an equimolar amount of butyllithium and 0.077 g (0.275 mmol) of *o*-dibromoxylene. The isolated yield of **16** was 90 mg (0.115 mmol, 42%). Anal. Calcd for $Co_2Si_2C_{38}B_8H_{64}$: C, 58.41; B, 11.07; H, 8.26. Found: C, 58.43; B, 10.90; H, 8.48.

Synthesis of *p*-$[(C_5Me_5)Co((SiMe_3)C_2B_3H_5)CH_2]_2C_6H_4$ (17). A solution of 0.105 g (0.134 mmol) of **14b** in 20 mL of TMEDA containing 3 drops of water was stirred for 1 h in air, the solution was evaporated to dryness, the residue was dissolved in 2:1 hexane/CH_2Cl_2, and the solution was eluted through a silica gel column. The first band to elute was bright yellow **17** (24 mg, 0.031 mmol, 23%). Anal. Calcd for $Co_2Si_2C_{38}B_6H_{66}$: C, 59.91; B, 8.51; H, 8.73. Found: C, 60.18; B, 8.28; H, 8.56.

Synthesis of $[(C_5Me_5)_2Co_2((SiMe_3)C_2B_3HCl_2)CH_2]_2C_6H_4$ (18). To a solution of 0.646 mmol of pentamethylcyclopentadiene in THF was added butyllithium (0.646 mmol) in vacuo; the mixture was stirred for 1 h and added dropwise to 84 mg (0.646 mmol) of $CoCl_2$, and the new mixture was stirred for 45 min. During this procedure, **17** (0.246 g, 0.323 mmol) was deprotonated in THF via addition of 0.646 mmol of butyllithium in hexane; this solution was added slowly to the $(Cp^*CoCl)_2$ solution, and the mixture was stirred for 16 h. The solution was rotary-evaporated, and the residue was suction-filtered through 2 cm of silica gel with CH_2Cl_2 followed by acetone and finally methanol. The CH_2Cl_2 fraction was taken up in 1:1 hexane/CH_2Cl_2 and chromatographed on a silica column. The second and third bands to elute were red-black, not characterized; the third band was **18** (68 mg, 0.060 mmol, 18%). The mass spectrum exhibits a strong parent envelope (base peak at *m/z* 1283) in good agreement with the calculated pattern. Anal. Calcd for $Co_4Cl_4Si_2C_{58}B_6H_{86}$: C, 54.34; H, 6.76. Found: C, 55.41; H, 7.13.

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