

Metallacarborane Staircase Oligomers. Stepwise Assembly via Tetradecker Stacking Reactions^{1,2}

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Abstract: Bis(cobaltacarborane) complexes bridged by fulvalene or 1,4-bis(tetramethylcyclopentadienyl)benzene ligands, and containing reactive carborane C₂B₃ end rings, are effective synthons for the stepwise construction of air-stable multisandwich oligomers and polymers that are soluble in organic solvents. Bridge deprotonation of the end rings followed by coordination of two such units to a central transition metal (Ni^{IV}, Co^{IV}, Co^{III}H) formed multilevel species having a central tetradecker sandwich linked to double-decker end units. The latter groups have exposed C₂B₃ rings on which the same reaction sequence can be repeated to generate progressively larger oligomers. Products having 5–17 metal atoms have been isolated via chromatography on silica and representative complexes characterized via ¹H and ¹¹B NMR, UV-visible, and FAB mass spectra. X-ray diffraction studies established the structures of a 5-cobalt complex, [(Et₂C₂B₃H₃)Co(C₅Me₄)C₆H₄(C₅Me₄)Co(Et₂C₂B₃H-4,5-Cl₂)]₂Co (**4b**), containing a central Co–Co–Co tetradecker sandwich, and a fulvalene-bridged dimer, [(Et₂C₂B₃H₂-4,6-Br₂-5-Me)Co(C₅H₄)]₂ (**2c**). Crystal data for **4b**: *M* = 1632.0; monoclinic, space group *C*2/*c*; *Z* = 4; *a* = 33.57(1) Å, *b* = 8.720(3) Å, *c* = 29.412(5) Å; β = 109.95(2)°; *V* = 8093(4) Å³; *R* = 0.083 for 3250 reflections having *I* > 3.5σ(*I*). Crystal data for **2c**: *M* = 828.9; monoclinic, space group *P*2₁/*n*; *Z* = 2; *a* = 9.956(4) Å, *b* = 13.439(5) Å, *c* = 11.327(4) Å; β = 103.87(2)°; *V* = 1471(2) Å³; *R* = 0.038 for 1477 reflections having *I* > 2σ(*I*).

Introduction

The molecular engineering of new materials having targeted electronic, magnetic, or optical properties is a primary goal of synthetic chemistry, and transition-metal organometallic compounds are playing an increasingly useful role.³ In this context, covalently linked multisandwich polymers constructed from metallocene or metallocene-like building-block complexes⁴ offer the advantage that the intramolecular metal–ligand interactions are constrained by strong bonds, unlike ionic solids in which the spatial arrangement of metals and ligands is difficult to control. Furthermore, the versatility inherent in covalent sandwich polymers is potentially enormous, given the range of possible metal–ligand combinations that might be employed to create new varieties of polysandwich species. As the synthetic state of the art in this area advances, one can envision electronically tunable materials tailored to specific purposes via the choice of metals, adjustment of metal oxidation states, and introduction of substituent groups. This will require highly versatile ligands that form strong π-sandwich bonds to metals, are capable of modification via standard organic methods, and are stable under a wide range of conditions.

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To a remarkable degree, these criteria are satisfied by the large family of sandwich complexes formed by transition or main-group metals with boron–carbon ligands⁵ having five- or six-membered rings⁶ (e.g., C₄B, C₃B₂, C₄B₂) or C₂B₃ carborane units.⁷ In our laboratory, methods have been developed for the systematic construction of double-decker, triple-decker and tetradecker metal–carborane (metallacarborane) sandwiches incorporating different cyclic hydrocarbon or heterocyclic ligands and transition metals of the first, second, and third series.^{1,5,7,8} In collaborative work with W. Siebert and co-workers, “hybrid” sandwich compounds incorporating both diborolyl (C₂B₂) rings and carborane ligands have been synthesized.⁹ As a class, the carborane-based complexes are air-stable, neutral, soluble in organic solvents, and readily derivatized;^{8–10} moreover, at least some paramagnetic metallacarborane sandwiches—notably CoCo and CoRu triple-decker complexes—are Class III mixed-valence systems, i.e., the

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(6) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943; *Pure Appl. Chem.* **1987**, *59*, 947. (b) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 5.3.

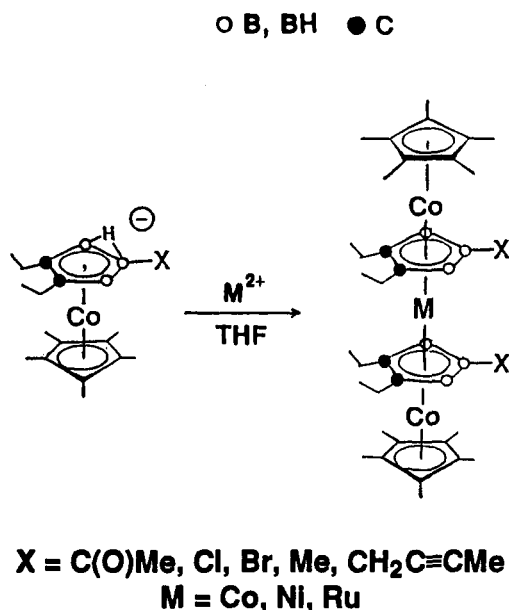
(7) Grimes, R. N. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp 261–285.

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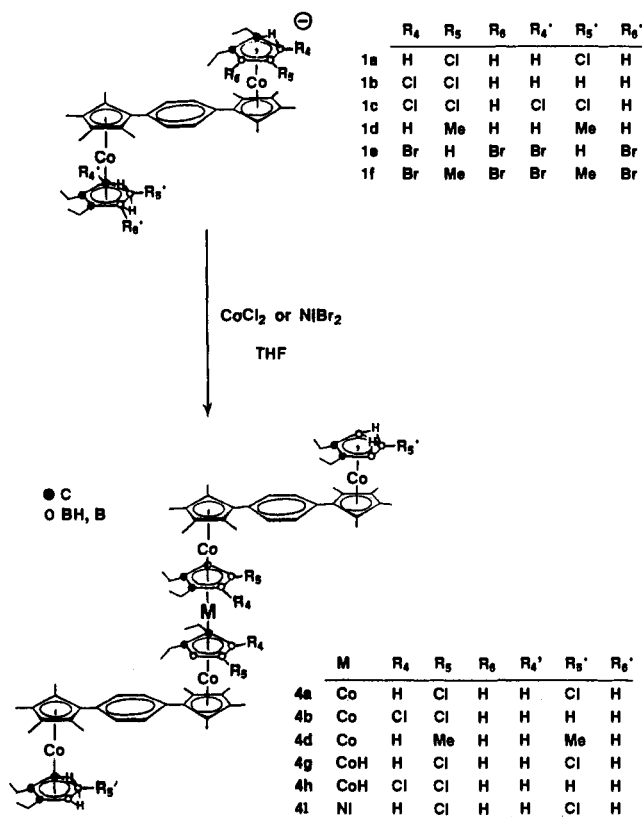
(9) (a) Fessenbecker, A.; Attwood, M. D.; Grimes, R. N.; Stephan, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Inorg. Chem.* **1990**, *29*, 5164. (b) Fessenbecker, A.; Attwood, M. D.; Bryan, R. F.; Grimes, R. N.; Woode, M. K.; Stephan, M.; Zenneck, U.; Siebert, W. *Inorg. Chem.* **1990**, *29*, 5157. (c) Attwood, M. A.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300. (d) Fessenbecker, A.; Stephan, M.; Grimes, R. N.; Pritzkow, H.; Zenneck, U.; Siebert, W. *J. Am. Chem. Soc.* **1991**, *113*, 3061.

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Scheme II



Scheme III



pentadienyl groups. Significantly, this same feature has been observed, with dihedral angles of 47–55°, in each of the three previous metallacarborane complexes containing the (C₅-Me₄)₂C₆H₄ ligand for which X-ray structural data is available.^{8b,14b} The tilt is undoubtedly a consequence of steric interaction between the phenylene ring and nearby methyl groups, and it appears to have electronic consequences, as noted below.

Complexes 4g, 4h, and 4i, in which M is CoH or Ni, contain formal 42-electron tetradecker and 18-electron double-decker systems and are evidently diamagnetic, as indicated by their ¹H and ¹¹B NMR spectra (Tables I and II), which are essentially composites of the spectra of their monomeric (nonlinked) double-decker and tetradecker components.^{1,8a,b} Compounds 4a, 4b, and 4d, where M = Co(IV), have 41-electron tetradecker stacks and

Scheme IV

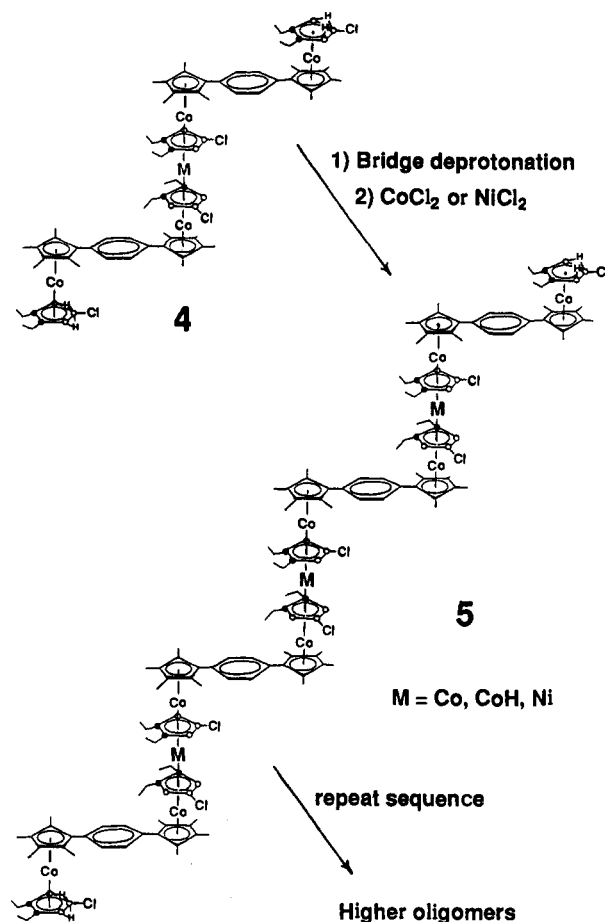


exhibit NMR spectra in which only the signals from the diamagnetic double-decker portions of the molecule are clearly discernible. These findings imply that, despite the apparent delocalization in CoCoCo tetradeckers (vide supra), the tetradecker sandwich unit in 4-type complexes is electronically insulated from the end groups, a conclusion that is supported by cyclic voltammetry on these species.¹² Given the out-of-plane tilt of the linking phenylene rings discussed above, π -overlap of the phenylene MOs with those of the cyclopentadienyl rings is surely inhibited, blocking intersandwich metal-metal electronic communication through the phenylene system; however, this would not rule out the possibility of weak through-space interaction.

The reactive C₂B₃ end rings in 4 complexes, like those in the precursor 1, can be bridge deprotonated and the sequence in Scheme III repeated to generate still larger oligomers of the type [(Et₂C₂B₃H₄Cl)Co(C₅Me₄)]₂[(C₅Me₄)Co(Et₂C₂B₃H₂Cl)M-(Et₂C₂B₃H₂Cl)Co(C₅Me₄)]_n(C₆H₄)_{n+1}, where M = Co, CoH, or Ni (Scheme IV). The products isolated thus far, all soluble in organic solvents, have $n = 1-5$, corresponding to species having 5–17 metal atoms; thus the 11-cobalt ($n = 3$) complex 5a was prepared from the pentacobalt species 1a. A proposed structure for the 11-cobalt oligomers is shown in Scheme IV with an arbitrarily depicted staircase conformation.

Deprotonation of the tetrachloro complex 1c with (Me₂Si)₂NLi followed by reaction with CoCl₂ gave a product mixture whose FAB mass spectra suggested the presence of oligomers analogous to 5a. During workup of the mixture, crystals of a minor product (6) were obtained and X-ray data were collected. Although the crystal quality was poor and did not permit a definitive structure determination, refinement was possible sufficiently to establish

Table I. 300-MHz ¹H FT NMR Data

compound	$\delta^{a,b,c}$
[(Et ₂ C ₂ B ₃ H ₄ -5-Cl)Co(C ₅ Me ₄) ₂ C ₆ H ₄ (1a)]	7.64 s (C ₆ H ₄), 2.05 m (CH ₂), 1.88 s, 1.84 s (C ₅ Me ₄), 1.04 t (ethyl CH ₃), -3.86 b s (B-H-B)
(Et ₂ C ₂ B ₃ H ₃ -4,5-Cl ₂)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H ₅) (1b)	7.59 s (C ₆ H ₄), 2.04 m (CH ₂), 1.91 s, 1.86 s, 1.84 s, 1.79 s, 1.75 s (C ₅ Me ₄), 1.08 m (ethyl CH ₃), -1.88 b s, -3.63 b s, -5.83 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₃ -4,5-Cl ₂)Co(C ₅ Me ₄) ₂ C ₆ H ₄ (1c)]	7.60 s (C ₆ H ₄), 2.06 m (CH ₂), 1.91 s, 1.86 s, 1.79 s, 1.75 s (C ₅ Me ₄), 1.08 m (ethyl CH ₃), -1.88, -3.63 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Me)Co(C ₅ Me ₄) ₂ C ₆ H ₄ (1d)]	7.64 s (C ₆ H ₄), 2.12 m (CH ₂), 1.89 s, 1.79 s (C ₅ Me ₄), 1.08 t (ethyl CH ₃), 0.19 s (B-CH ₃), -5.16 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₃ -4,6-Br ₂)Co(C ₅ Me ₄) ₂ C ₆ H ₄ (1e)]	7.47 s (C ₆ H ₄), 2.19 m, 2.06 m (CH ₂), 1.87 s, 1.75 s (C ₅ Me ₄), 1.10 t (ethyl CH ₃), -3.40 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₂ -4,6-Br ₂ -5-Me)Co(C ₅ Me ₄) ₂ C ₆ H ₄ (1f)]	7.69 s (C ₆ H ₄), 2.17 m (CH ₂), 1.91 s, 1.70 s (C ₅ Me ₄), 1.11 t (ethyl CH ₃), 0.05 b s (B-CH ₃), -2.89 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Me)Co(C ₅ H ₄) ₂ (2a)]	4.77 s, 4.71 s (C ₅ H ₄), 1.92 m, 1.77 m (CH ₂), 1.02 t (ethyl CH ₃), 0.34 s (B-CH ₃), -5.29 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₃ -4,6-Br ₂)Co(C ₅ H ₄) ₂ (2b)]	4.95 s, 4.94 s, 4.853 s, 4.847 s (C ₅ H ₄), 2.19 m, 1.93 m (CH ₂), 1.03 t (ethyl CH ₃), -3.34 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₂ -4,6-Br ₂ -5-Me)Co(C ₅ H ₄) ₂ (2c)]	4.79 s, 4.70 s (C ₅ H ₄), 2.09 m, 1.89 m (CH ₂), 1.01 t (ethyl CH ₃), 0.54 s (B-CH ₃), -2.73 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Cl)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H ₂ -5-Cl)] ₂ -Co (4a)	8.03 s (C ₆ H ₄), 2.00 m (CH ₂), ^d 1.84 s, 1.81 s (C ₅ Me ₄), 1.01 t (ethyl CH ₃), ^d -3.86 b s (B-H-B) ^d
[(Et ₂ C ₂ B ₃ H ₃)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H-4,5-Cl ₂)] ₂ Co (4b)	8.00 s (C ₆ H ₄), 2.00 m (CH ₂), ^d 1.81 s (C ₅ Me ₄), 1.03 t (ethyl CH ₃), ^d -5.86 b s (B-H-B) ^d
[(Et ₂ C ₂ B ₃ H ₃ -5-Me)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H ₂ -5-Me)] ₂ -Co (4d)	7.66 b s (C ₆ H ₄), 2.06 b s (CH ₂), 1.80 s, 1.74 s (C ₅ Me ₄), 1.02 b s (ethyl CH ₃), -0.17 s (B-CH ₃), -5.22 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Cl)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H ₂ -5-Cl)] ₂ -CoH (4g)	7.53 d, 7.45 d (C ₆ H ₄), 2.65 m, 2.05 m (CH ₂), 1.85 s, 1.82 s, 1.81 s, 1.62 s (C ₅ Me ₄), 1.44 t, 1.09 t (ethyl CH ₃), -5.85 b s (B-H-B), -8.04 b s (CoH)
[(Et ₂ C ₂ B ₃ H ₃)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H-4,5-Cl ₂)] ₂ CoH (4h)	7.56 d, 7.51 d (C ₆ H ₄), 2.98 m, 2.40 m, 2.15 m (CH ₂), ^e 2.02 m, 1.90 m (CH ₂), ^d 1.854 s, 1.847 s, 1.82 s, 1.80 s (C ₅ Me ₄), ^d 1.614 s, 1.607 s, 1.52 s, 1.51 s (C ₅ Me ₄), ^e 1.35 t, 1.09 m (ethyl CH ₃), -5.84 b s (B-H-B), ^d -8.16 b s (CoH) ^e
[(Et ₂ C ₂ B ₃ H ₄ -5-Cl)Co(C ₅ Me ₄)C ₆ H ₄ (C ₅ Me ₄)Co(Et ₂ C ₂ B ₃ H ₂ -5-Cl)] ₂ -Ni (4i)	7.59 s, 7.56 s, 7.47 s, 7.45 s (C ₆ H ₄), 2.32 m, 2.04 m (CH ₂), 1.87 s, 1.80 s, 1.68 s, 1.61 s (C ₅ Me ₄), 1.24 t, 1.04 t (ethyl CH ₃), -3.86 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Me)Co(C ₅ H ₄) ₂ Co(Et ₂ C ₂ B ₃ H ₂ -5-Me)] ₂ Co (7)	4.87 b s (C ₅ H ₄), 2.35 b m, 2.27 b m (CH ₂), 1.27 b s (ethyl CH ₃), 0.62 b s (B-CH ₃), -4.95 b s (B-H-B)
[(Et ₂ C ₂ B ₃ H ₄ -5-Me)Co(C ₅ H ₄) ₂ Co ₃ (Et ₂ C ₂ B ₃ H ₂ -5-Me) ₂ (C ₅ H ₄) ₂ (8)]	4.94 b s, 4.92 b s (C ₅ H ₄), 2.45 b s (CH ₂), 1.24 b s (ethyl CH ₃), 0.56 b s, 0.52 b s (B-CH ₃), -5.05 b s (B-H-B)

^a CDCl₃ solution. ^b Shifts relative to (CH₃)₄Si. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, b = broad. ^c B-H_{terminal} resonances are broad quartets and mostly obscured by other signals. ^d Signals assigned to diamagnetic (C₅Me₄)Co(C₂B₃) end groups. ^e Signals assigned to central tetradeccker stack.

Table II. 115.8-MHz ¹³B FT NMR Data

compound	δ (J _{BH} , Hz) ^{a,b,c}	rel areas
1a	19.5, -1.4	1:2
1c	16.7, 8.5, -2.1	1:1:1
1e	8.9, 1.8	2:1
1f	4.9 ^c	
2a	18.8, -0.3	1:2
2b	8.3, 1.8	2:1
4a ^d	20.0, 4.0, -0.5	1:1:1
4g	47.7 f 20.0, ^e 6.9 f 4.0, ^e -0.5 ^e	1:1:1:1:2
4h	47.7 f 7.1, ^{e,f} 4.0, ^e -0.5 ^e	1:1:2:2
4i	79.7 f 19.6, 7.7, 4.7, ^c -1.3 ^e	1:1:1:1:2
7	19.9, 0.84	1:2

^a Proton-decoupled; shifts relative to BF₃·OEt₂, positive values downfield. ^b Dichloromethane solution. ^c Very broad resonance. ^d Only resonances of the diamagnetic C₂B₃ end rings were observed (see text). ^e Resonance assigned to end rings. ^f Resonance assigned to central tetradeccker stack.

the atom connectivities.²⁰ As shown in Figure 2, the complex is a tetradeccker dimer that forms a closed loop containing six cobalt atoms, linked at both ends by phenylene rings. Unfortunately, at this writing we have been unable to further characterize this interesting species, but we hope eventually to develop a rational synthesis of 6-type dimers and explore their reactivity and electronic properties.

(20) Crystal data: space group *P* $\bar{1}$; *Z* = 1; *a* = 12.782(8) Å; *b* = 13.613(8) Å; *c* = 16.27(1) Å; α = 111.40(5)°; β = 91.06(6)°; γ = 116.27(6)°; *V* = 2307 Å³. A limited data set (to $2\theta = 46^\circ$) was collected on very poorly diffracting crystals.

Table III. Experimental X-ray Diffraction Parameters and Crystal Data

compound	4b	2c
emp form.	Co ₅ Cl ₄ C ₇₂ B ₁₂ H ₁₀₈ ·C ₇ H ₈	Co ₂ Br ₄ C ₂₄ B ₆ H ₃₈
form. wt	1632.0	828.9
cryst color, habit	black needle	yellow-brown prism
cryst dim (mm)	0.42 × 0.21 × 0.14	0.46 × 0.32 × 0.24
space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	33.57(1)	9.956(4)
<i>b</i> , Å	8.720(3)	13.439(5)
<i>c</i> , Å	29.412(5)	11.327(4)
β , deg	109.95(2)	103.87(2)
<i>V</i> , Å ³	8093(4)	1471(2)
<i>Z</i>	4	2
μ , cm ⁻¹ (Mo K α)	11.76	65.22
transmission factors	0.87–1.00	0.61–1.00
<i>D</i> (calcd), g cm ⁻³	1.333	1.871
$2\theta_{\max}$	46.0	50.0
reflectns measured	6083	2710
reflectns observed	3250 ^a	1477 ^b
<i>R</i>	0.083	0.038
<i>R</i> _w	0.102	0.043
largest peak in final diff map, e/Å ³	2.92	0.60

^a *I* > 3.50 σ (*I*). ^b *I* > 2.00 σ (*I*).

Synthesis of Fulvalene-Bridged Dimers and Oligomers

The preparative approach shown in Schemes III and IV appears applicable to other carborane-based systems involving different combinations of metals, polycyclic hydrocarbon bridges, and R substituents and may be capable of extension to much higher

Table IV. Bond Distances and Selected Bond Angles for $[(Et_2C_2B_3H_3)Co(C_5Me_4)C_6H_4(C_5Me_4)Co(Et_2C_2B_3H-4,5-Cl_2)]_2Co$ (**4b**)

Bond Distances, Å			
Co1-C2	2.15(1)	CL5-B5	1.80(1)
Co1-C3	2.22(1)	C1S-C2S	1.56(6)
Co1-B4	2.12(1)	C1S-C6S	1.31(6)
Co1-B5	2.06(1)	C2-C2M	1.50(2)
Co1-B6	2.08(1)	C2-C3	1.48(2)
Co2-C2	2.07(1)	C2-B6	1.55(2)
Co2-C3	2.07(1)	C2S-C3S	1.21(5)
Co2-C1R1	2.13(1)	C2M-C2E	1.47(2)
Co2-C1R2	2.09(1)	C2AM-C2A	1.53(2)
Co2-C1R3	2.06(1)	C2AM-C2AE	1.51(2)
Co2-C1R4	2.05(1)	C2A-C3A	1.42(1)
Co2-C1R5	2.08(1)	C2A-B6A	1.50(2)
Co2-B4	2.11(1)	C3M-C3	1.52(2)
Co2-B5	2.06(1)	C3M-C3E	1.54(2)
Co2-B6	2.10(1)	C3-B4	1.56(2)
Co3-C2A	2.09(1)	C3S-C4S	1.46(4)
Co3-C3A	2.10(1)	C3A-C3AM	1.46(2)
Co3-C3R1	2.06(1)	C3A-B4A	1.57(2)
Co3-C3R2	2.08(1)	C3AM-C3AE	1.54(2)
Co3-C3R3	2.07(1)	C4S-C5S	1.16(4)
Co3-C3R4	2.08(1)	C5S-C6S	1.17(5)
Co3-C3R5	2.06(1)	C1R1-C1R2	1.41(1)
Co3-B4A	2.06(1)	C1R1-C1R5	1.44(1)
Co3-B5A	2.05(2)	C1R1-C2R1	1.49(1)
Co3-B6A	2.05(2)	C1M2-C1R2	1.51(2)
CL4-B4	1.78(1)	C1R2-C1R3	1.42(1)
C1R3-C1M3	1.49(1)	C1R4-C1M4	1.50(1)
C1R3-C1R4	1.43(1)	C3M2-C3R2	1.51(2)
C1R4-C1R5	1.43(1)	C3R2-C3R3	1.41(1)
C1R5-C1M5	1.51(2)	C3R3-C3M3	1.49(1)
C2R1-C2R2	1.42(2)	C3R3-C3R4	1.42(1)
C2R1-C2R6	1.37(2)	C3R4-C3M4	1.50(1)
C2R2-C2R3	1.39(2)	C3R4-C3R5	1.43(1)
C2R3-C2R4	1.39(1)	C3R5-C3M5	1.50(2)
C2R4-C2R5	1.42(1)	B4-B5	1.69(2)
C2R4-C3R1	1.49(1)	B4A-B5A	1.87(2)
C2R5-C2R6	1.38(2)	B5-B6	1.75(2)
C3R1-C3R2	1.47(1)	B5A-B6A	1.82(2)
C3R1-C3R5	1.40(1)		
Selected Bond Angles, deg			
Co1-C2-C2M	130.6(7)	C3M-C3-B4	124(1)
Co2-C2-C2M	131.0(7)	Co3-C3A-C3AM	127.7(7)
C2M-C2-C3	118(1)	C2A-C3A-C3AM	125(1)
C2M-C2-B6	127(1)	C2A-C3A-B4A	115(1)
C3-C2-B6	114.6(9)	C3AM-C3A-B4A	119(1)
C2-C2M-C2E	115(1)	C3A-C3AM-C3AE	114(1)
C2A-C2AM-C3AE	112(1)	Co1-B4-CL4	133.3(7)
Co3-C2A-C2AM	127.7(7)	B4A-B5A-B6A	97(1)
C2AM-C2A-C3A	121(1)	Co2-C1R1-C2R1	131.4(7)
C2AM-C2A-B6A	121(1)	Co3-C3R1-C2R4	129.9(7)
C3A-C2A-B6A	117(1)	Co2-B4-CL4	128.6(7)
C3-C3M-C3E	117(1)	CL4-B4-C3	126(1)
Co2-C3-C3M	127.9(8)	CL4-B4-B5	127(1)
Co1-C3-C3M	136.0(8)	C3-B4-B5	107(1)
C2-C3-C3M	124(1)	C3A-B4A-B5A	104(1)
C2-C3-B4	112(1)	Co1-B5-CL5	130.7(6)
CL5-B5-B4	129.7(9)	Co2-B5-CL5	127.6(6)
CL5-B5-B6	127.2(8)	C2-B6-B5	104.0(8)
B4-B5-B6	103.1(9)	C2A-B6A-B5A	107(1)

molecular weight oligomers and polymers, provided solubility problems can be avoided. The bis(cobaltacarboranyl)fulvalene complex **2** (Scheme 1) is of interest as a possible precursor to conducting polymers, since one might reasonably expect metal-metal communication to be facilitated by the delocalized fulvalene π -system. In order to explore this idea, we modified the earlier low-yield synthesis^{8b} of **2** to allow its preparation on a 3-gram scale in ca. 35% yield; derivatives of **2** were then synthesized and employed in tetradecar stacking reactions to construct fulvalene-bridged oligomers. The preparation of the *B5,B5'*-dimethyl and *B4,B6,B4',B6'*-tetrabromo derivatives **2a** and **2b** was similar to that of the phenylene-linked complexes **1c** and **1d**, as described

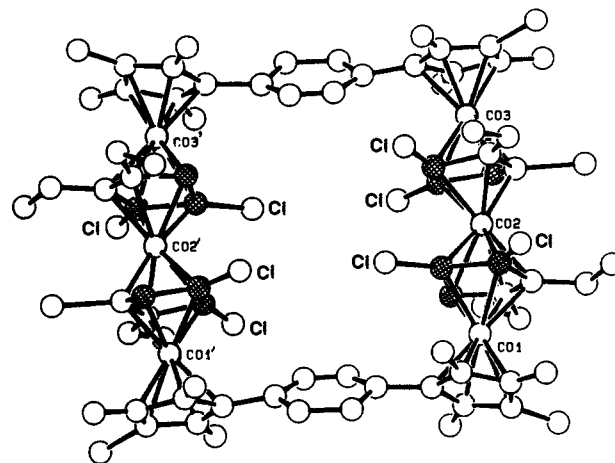


Figure 2. Molecular structure of **6** (boron atoms shaded).²⁰

Table V. Bond Distances and Selected Bond Angles for $[(Et_2C_2B_3H_2-4,6-Br_2-5-Me)Co(C_5H_4)]_2$

Bond Distances, Å			
Br1-B4	1.958(9)	C2-C3	1.43(1)
Br2-B6	1.97(1)	C2-B6	1.51(1)
Co-C2	2.060(7)	C3-C3M	1.51(1)
Co-C3	2.076(8)	C3-B4	1.53(1)
Co-C1R1	2.065(7)	C3M-C3E	1.51(1)
Co-C1R2	2.048(7)	C4-B5	1.57(1)
Co-C1R3	2.045(8)	C1R1-C1R1'	1.57(1)
Co-C1R4	2.082(8)	C1R1-C1R2	1.41(1)
Co-C1R5	2.095(8)	C1R1-C1R5	1.41(1)
Co-B4	2.032(9)	C1R1-C1R3	1.43(1)
Co-B5	2.01(1)	C1R3-C1R4	1.42(1)
Co-B6	2.033(9)	C1R4-C1R5	1.41(1)
C2M-C2	1.51(1)	B4-B5	1.81(1)
C2M-C2E	1.53(1)	B5-B6	1.79(1)
Selected Bond Angles, deg			
C2-C2M-C2E	112.2(7)	C1R1'-C1R1-C1R2	124(1)
Co-C2-C2M	125.4(5)	C1R1'-C1R1-C1R5	125(1)
C2M-C2-C3	122.6(7)	Br1-B4-C3	127.1(6)
C2M-C2-B6	122.6(7)	Br1-B4-B5	124.2(6)
C3-C2-B6	114.4(7)	Br1-B4-Co	126.1(5)
Co-C3-C3M	126.1(5)	C3-B4-B5	108.1(7)
C2-C3-C3M	125.4(7)	Co-B5-C4	127.3(7)
C2-C3-B4	113.3(7)	C4-B5-B4	132.2(7)
C3M-C3-B4	120.7(7)	C4-B5-B6	132.5(8)
C3-C3M-C3E	111.7(7)	B4-B5-B6	95.2(6)
Co-C1R1-C1R1'	126.3(7)	Br2-B6-Co	125.4(2)
C2-B6-B5	108.9(7)	Co-B6-C2	69.3(4)
Br2-B6-C2	127.3(7)	Co-B6-B5	63.1(4)
BR2-B6-B5	122.9(6)		

above. However, the *B5,B5'*-dimethyl-*B4,B6,B4',B6'*-tetrabromo complex **2c** was obtained only by bromination of **2a**, in contrast to its phenylene-linked counterpart **1d**; attempts to prepare **2c** via methylation of **2b** gave only decomposition.

Further support to the spectroscopic characterization of these dimers was provided by an X-ray structural analysis of **2c**, establishing that the C_{10} fulvalene system is planar, as expected, and that the cobaltacarborane units occupy transoid locations. Information on the crystal structure and data collection information is listed in Table III, bond distances and angles are given in Table V, and an ORTEP drawing of the structure is presented in Figure 3. The structural parameters of the *nido*-(C_2B_3)Co cluster in **2c** are close to those found in other complexes of this class.¹⁹ Of more direct interest here is the fulvalene-cobaltacarborane interaction, for which the only crystallographically defined precedent is the *closo* species^{8b} $[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$. Detailed comparison between the latter structure and the open cage (*nido*) system **2c** is not straightforward, in view of the different carborane ligands in these molecules as well as the fact

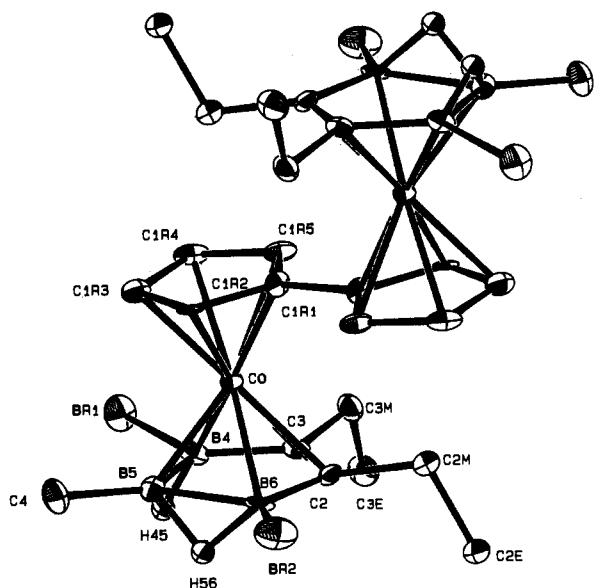


Figure 3. Molecular structure of **2c** with 30% thermal ellipsoids (hydrogens omitted).

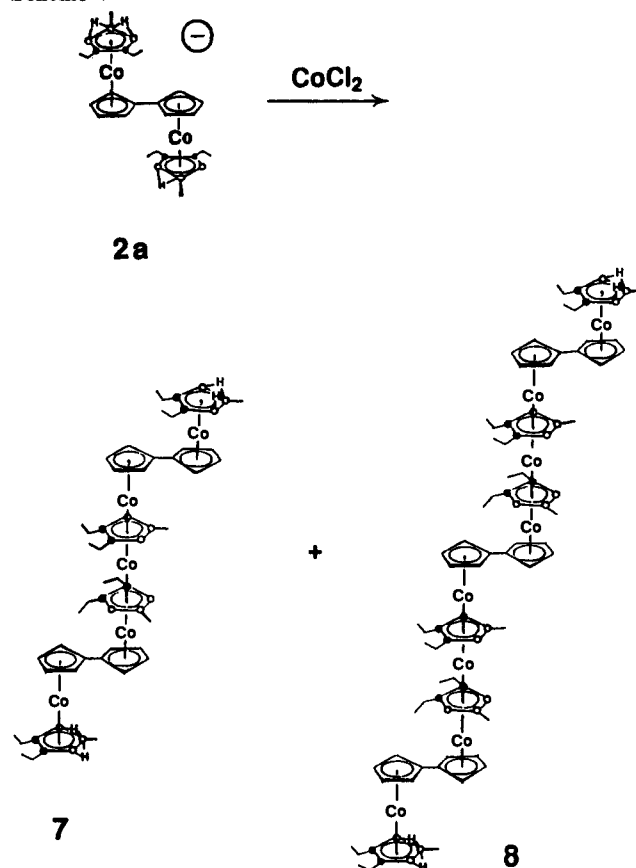
that the earlier molecule is unsubstituted while **2c** bears bromine and methyl substituents. With respect to the fulvalene ligands in these two complexes, there are no particularly striking differences although one can point to a somewhat longer central C—C bond (C1R1—C1R1') in **2c** (1.57(1) vs 1.474(6) Å in the CoC₂B₄ cluster) and a greater tilt angle of the C₅ ring relative to the C₂B₃ plane in **2c** (7.21 vs 3.12°). Perhaps more significant is the fact that both species have planar fulvalene units and are centrosymmetric with the metals on opposite sides of the C₁₀ plane.

Conversion of the fulvalene complexes to multisandwich species was explored via reactions involving a variety of metal reagents and conditions. Ultimately, we focused on the dimethyl complex **2a** as the synthon of choice, and the most definitive results were obtained from its interaction with CoCl₂. Following procedures similar to those used to prepare the phenylene-linked oligomers described above, complexation of the deprotonated anion **2a**⁻ afforded the 5-cobalt and 8-cobalt products **7** and **8**, isolated as brown air-stable solids (Scheme V) and characterized from NMR and mass spectral data. As in the type **4** (phenylene-linked) oligomers, the NMR signals arising from the paramagnetic CoCoCo stacks in **7** and **8** are not interpretable, but those of the diamagnetic (Et₂C₂B₃H₄Me)Co(C₅H₄) groups are readily identifiable. In contrast to the phenylene-linked complexes, whose proton NMR spectra suggest little or no communication between the central tetradecar sandwich and the outer groups, the NMR signals of the outer (C₂B₃)Co units in **7** and **8** are significantly shifted relative to those of their precursor **2a**. This implies a degree of interstack electronic communication in these species, although the fact that the paramagnetism appears confined to the central stack argues against complete delocalization. Studies on the electronic properties of these and related polymetallic complexes are in progress.

Concluding Remarks

This work demonstrates the viability of tetradecar stacking as an approach to controlled oligomer- and polymer-building utilizing small metallacarborane sandwich synthons. Given the wide choices available in metal ions, derivatized carborane ligands, and suitable organic polycycles as potential linking groups—as well as the general stability and solubility of the products—this chemistry appears capable of extension to a considerable variety of polysandwich systems. Moreover, as we have already noted, the prospects are good that such compounds (or solid-state

Scheme V



materials derived from them) can be tailored to exhibit specific desired properties, since methods for their regiospecific functionalization are now available. Owing to recent dramatic improvements in the synthesis of R₂C₂B₄H₆ *nido*-carboranes, allowing their preparation in 40-gram lots^{25b,15b} under benign conditions (cold solutions)^{15a} and drawing on the huge U.S. Government stockpile of B₅H₉,⁵ the development of this chemistry on a practical scale seems feasible. Of course, well-defined high molecular weight polymers of this type have yet to be produced, and it remains to be determined what happens as one proceeds to very large systems. Nonetheless, in light of the problems often encountered in trying to build metal-hydrocarbon multidecker sandwich polymers²¹ (including product air sensitivity or instability), the advantages afforded by metallacarborane sandwich chemistry warrant further investigation, which is continuing.

The task of assembling multimetallic molecules or networks from metallacarboranes can be approached in a number of ways other than the sandwich-forming procedure described here. Two of these—direct linkage of clusters via covalent bonds involving B or C atoms²² and the synthesis of solid-state metallocenium metallacarboranide salts²³—are presently under study in our laboratory.

Experimental Section

Instrumentation. ¹¹B (115.8 MHz) and ¹H (300 MHz) NMR spectra were acquired on Nicolet NT-360 or GE QE300 spectrometers, and visible-ultraviolet spectra were recorded on a Hewlett-Packard 8452A Diode Array Spectrophotometer with an HP Vectra Computer Interface. Unit-resolution mass spectra of the bimetallic starting complexes **1a-f**

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(23) Meng, X.; Waterworth, S.; Sabat, M.; Grimes, R. N. *Inorg. Chem.*, In press.

and 2a–c were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. In all cases, strong parent envelopes were observed, and the calculated and observed unit-resolution spectral patterns were in close agreement. Fast-atom bombardment (FAB) negative-ion mass spectra of high molecular weight products were acquired in a 3-nitrobenzyl alcohol matrix. Elemental analyses were obtained either in this department on a Perkin-Elmer 2400 CHN Analyzer using cyclohexanone (2,4-dinitrophenyl)-hydrazine as a standard or by E&R Microanalytical Laboratory, Corona, NY 11368.

Materials and Procedures. Dichloromethane and *n*-hexane were anhydrous grade and were stored over 4-Å molecular sieves prior to use. THF was distilled from sodium–benzophenone immediately prior to use. Column chromatography was conducted on silica gel 60 (Merck), and thick-layer chromatography was carried out on precoated silica gel plates (Merck). Unless otherwise indicated, all syntheses were conducted under vacuum or an atmosphere of nitrogen. Workup of products was conducted in air using benchtop procedures.

Synthesis of *p*-(C₃Me₄H)₂C₆H₄. The literature synthesis of this hydrocarbon²⁴ is reported to give the product in 18% yield, but we have obtained nearly quantitative yields via a modified procedure, as follows. *p*-Dibromobenzene (8.53 g, 36.2 mmol) was placed in a 500-mL flask containing a stirring bar, which was evacuated and refilled with dry N₂ three times. Degassed anhydrous diethyl ether (150 mL) and 20 mL of 2.5 M *n*-butyllithium were added (dropwise in the latter case) via syringe under N₂. After the solution was stirred for 20 min, forming a white precipitate, 5.0 g (36 mmol) of 2,3,4,5-tetramethyl-2-cyclopentenone (Aldrich) was added dropwise via syringe, and the solution was refluxed for 1 h. The solution was cooled to room temperature and an additional 20 mL of *n*-butyllithium was added, forming a white precipitate. The mixture was stirred for 1 h. Another 5-g portion of the cyclopentenone reagent was added dropwise, causing the precipitate to dissolve. After the solution was stirred for 1 h at room temperature and then refluxed for 30 min, the solution was cooled to room temperature and quenched twice with 200 mL of aqueous saturated NH₄Cl. The aqueous phase was extracted twice with 30 mL of diethyl ether, and the combined ether fraction was dried over MgSO₄. The solution was concentrated to ca. 30 mL via rotary evaporation, and 1.57 g of *p*-toluenesulfonic acid monohydrate was added. After 10 min of stirring, a precipitate was observed. The stirring was continued for 2 h, after which sufficient ether was added to dissolve all of the precipitate. The ether solution was washed three times with ca. 200 mL of water in a 1000-mL separation funnel and then was dried over MgSO₄ and rotary-evaporated to give the yellow solid product (9.7 g, nearly quantitative yield). This compound was converted as required to the bis(*cis*-cobaltacarboranyl) complex [(Et₂C₂B₄H₄)Co(C₃Me₄)₂C₆H₄] and then to the bis(*nido*-cobaltacarboranyl) species [(Et₂C₂B₃H₃)Co(C₃Me₄)₂C₆H₄] (1) as described earlier.^{8b}

Synthesis of [(Et₂C₂B₃H₄-5-Cl)Co(C₃Me₄)₂C₆H₄] (1a). A three-neck round-bottom flask was fitted with a septum and stirring bar and charged with 0.345 g (0.51 mmol) of 1 and 70 mL of dry THF, and 1.13 mmol (2.22 equiv) of (Me₃Si)₂NLi was added via syringe. The mixture was stirred for 30 min at room temperature, following which 0.136 g (1.19 mmol) of CH₃SO₂Cl was added via syringe and the solution was stirred for 4–5 h. The solvent was removed via rotary-evaporation, the residue was extracted with CH₂Cl₂, and the solution was filtered through 2 cm of silica and washed with that solvent until the washings were colorless. The orange filtrate was column-chromatographed on silica to give 0.360 g (0.48 mmol, 95% yield) of orange crystalline 1a. Note: Deprotonation of 1 with *n*-butyllithium instead of (Me₃Si)₂NLi gave lower yields (ca. 70%) of the desired product.

Syntheses of (Et₂C₂B₃H₃-4,5-Cl₂)Co(C₃Me₄)₂C₆H₄ (1b) and [(Et₂C₂B₃H₃-4,5-Cl₂)Co(C₃Me₄)₂C₆H₄] (1c). The procedure used to prepare 1a was employed, except that *n*-butyllithium (1 equiv) was used to effect the deprotonation of 0.420 g (0.62 mmol) of 1. Following the initial washing through silica, the solution contained three compounds, as detected by NMR and mass spectra: unreacted 1, the mono-*B*5-chloro derivative of 1, and 1a. The solution was placed in a 100-mL round-bottom flask, and 50 mL of dry THF was added in vacuo; the above procedure (addition of *n*-butyllithium and CH₃SO₂Cl) was repeated, with chromatography on silica affording 0.250 g (0.34 mmol, 54%) of 1b. The tetrachloro derivative 1c was prepared from 1a by the same method, giving the orange solid product in 50% yield.

Synthesis of [(Et₂C₂B₃H₄-5-Me)Co(C₃Me₄)₂C₆H₄] (1d). A 250-mL three-neck flask was charged with 0.400 g (0.593 mmol) of 1, 50 mL of THF was introduced, and 1.2 mmol of *n*-butyllithium was added via syringe to the cold solution. After the solution was stirred for 30 min at room temperature, 0.170 g (1.2 mmol) of methyl iodide was added via syringe and the mixture was stirred for 4 h. The solvent was removed via rotary-evaporation, the residue was extracted with CH₂Cl₂, and the solution was filtered through 2 cm of silica and washed with that solvent until the washings were colorless. The yellow-orange solution was rotary-evaporated to dryness, giving 0.420 g (0.593 mmol, 100% yield) of crystalline 1d.

Synthesis of [(Et₂C₂B₃H₃-4,6-Br₂)Co(C₃Me₄)₂C₆H₄] (1e). A 100-mL three-neck flask fitted with a sidearm was charged with 0.150 g (0.223 mmol) of 1, and 0.160 g (0.899 mmol) of *N*-bromosuccinimide (NBS) was placed in the sidearm. The apparatus was evacuated, 50 mL of THF was transferred into it, and the mixture was warmed to room temperature. The sidearm was rotated to drop the NBS into the THF solution, and the mixture was stirred overnight, after which the solvent was removed by rotary-evaporation. The residue was extracted with CH₂Cl₂ and the solution was chromatographed on a silica column, giving one yellow band, which was 1e (0.220 g, 0.223 mmol, 100% yield).

Synthesis of [(Et₂C₂B₃H₂-4,6-Br₂-5-Me)Co(C₃Me₄)₂C₆H₄] (1f). A 0.220-g (0.222 mmol) sample of 1e was placed in a 100-mL three-neck flask, and 50 mL of THF was added in vacuo. *n*-Butyllithium was added via syringe to the cold solution, which was then warmed to room temperature and stirred for 30 min. Methyl iodide (2 equiv) was added via syringe, and the mixture was stirred for 3 h. The solvent was removed by rotary-evaporation, the residue was extracted with CH₂Cl₂, and the solution was chromatographed on silica to give one yellow band, which was 1f (0.202 g, 0.199 mmol, 90% yield).

Improved Syntheses of [(Et₂C₂B₄H₄)Co(C₃H₄)₂] and [(Et₂C₂B₃H₃)Co(C₃H₄)₂] (2). The procedure described in an earlier paper^{8b} was modified by combining the fulvalene dianion, CoCl₂, and Et₂C₂B₄H₅⁻ in THF solution at liquid nitrogen temperature, warming the mixture slowly to -78 °C, and warming to 0 °C over 5 h with stirring, followed by warming to room temperature overnight. This afforded 0.900 g (1.78 mmol, 36% yield) of [(Et₂C₂B₄H₄)Co(C₃H₄)₂] from 5.0 mmol of dicyclopentadiene, 10 mmol of CoCl₂, and 10 mmol of Et₂C₂B₄H₆. Decapitation of this complex with TMEDA^{8b} gave 0.775 g (1.59 mmol, 89%) of [(Et₂C₂B₃H₃)Co(C₃H₄)₂] (2).

Syntheses of [(Et₂C₂B₃H₄-5-Me)Co(C₃H₄)₂] (2a), [(Et₂C₂B₃H₃-4,6-Br₂)Co(C₃H₄)₂] (2b), and [(Et₂C₂B₃H₂-4,6-Br₂-5-Me)Co(C₃H₄)₂] (2c). The procedure described above for the preparation of the corresponding phenylene-linked complexes 1d and 1e was employed with the parent fulvalene complex^{8b} 2 as starting material. Deprotonation of 0.380 g (0.782 mmol) of 2 with 1.56 mmol of *n*-butyllithium followed by reaction with 0.222 g (1.56 mmol) of methyl iodide gave 0.340 mg (0.66 mmol, 84%) of 2a. The bromination of 2 to form 2b was nearly quantitative (97%). The synthesis of the dimethyltetrahalo derivative 2c required a modification in the procedure, since the method used to prepare the analogous phenylene-linked complex 1f (*i.e.*, methylation of the tetrabromo compound) led only to decomposition and did not give 2c. To circumvent the problem, the methylation of 2 was conducted first, forming 2a, and 0.78 mmol of that compound was brominated with NBS, as in the preparation of 1f. This sequence afforded the desired 2c (0.62 g, 0.75 mmol, 96% yield). Anal. for 2c. Calcd for Co₂Br₄C₂₄B₆H₃₈: C, 34.78; H, 4.62. Found: C, 34.40; H, 5.12.

Syntheses of Phenylene-Linked Multisandwich Complexes [(Et₂C₂B₃H₄-5-Cl)Co(C₃Me₄)C₆H₄(C₃Me₄)Co(Et₂C₂B₃H₂-5-Cl)]₂Co (4a), [(Et₂C₂B₃H₃)Co(C₃Me₄)C₆H₄(C₃Me₄)Co(Et₂C₂B₃H₂-4,5-Cl₂)]₂Co (4b), [(Et₂C₂B₃H₄-5-Me)Co(C₃Me₄)C₆H₄(C₃Me₄)Co(Et₂C₂B₃H₂-5-Me)]₂Co (4d), and [(Et₂C₂B₃H₄-5-Cl)Co(C₃Me₄)C₆H₄(C₃Me₄)Co(Et₂C₂B₃H₂-5-Cl)]₂Ni (4f). The 5-cobalt and higher oligomers were all prepared via bridge deprotonation of a bimetallic starting complex followed by reaction with CoCl₂ or NiCl₂. For the synthesis of 4a, a 0.336-g (0.452 mmol) sample of 1a was dissolved in 100 mL of THF, 0.9 equiv of (Me₃Si)₂NLi was added at 0 °C, and the solution was stirred at room temperature for 50 min. CoCl₂ (1 equiv) was added, the mixture was stirred for 4 h, the flask was opened to the air, and the solvent was removed by rotary evaporation to give a dark residue which was dissolved in 1:1 CH₂Cl₂/hexane and eluted on a silica column using the same solvent. Four bands were collected, of which the first was yellow 1a (0.217 g, 65% recovery); the second was dark brown 4a (75 mg (0.048 mmol), 61% yield based on 1a consumed), containing a small amount (ca. 10%) of the corresponding diamagnetic species 4g; the third was an apparent 8-cobalt complex, [(Et₂C₂B₃H₄-5-Cl)Co(C₃Me₄-C₆H₄-C₃Me₄)Co₃(Et₂C₂B₃H₂-5-Cl)]₂-

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(C₅Me₄)₂C₆H₄, MW 2335 (FAB mass spectrum), 35 mg; and the fourth was the 11-cobalt complex **5a**, 15 mg. Anal. for **4a**. Calcd for C₅Cl₄C₇₂B₁₂H₁₀₈: C, 56.16; B, 8.42; H, 7.07. Found: C, 56.38; B, 8.31; H, 7.09. MS base peaks for **4a**, 1539 (FAB neg ion), calcd MW 1539.9; for **5a**, 3133 (FAB neg ion), calcd MW 3134.6. UV-visible absorptions (nm): for **4a**, 434 (88%), 296 (100%); for **5a**, 434 (97%), 296 (100%).

The same procedure employing **1b** (0.200 g, 0.27 mmol) as the starting material and 0.5 equiv of CoCl₂ gave on workup 62 mg (0.04 mmol, 30%) of **4b**. A small quantity of the diamagnetic (CoH) complex **4h** was also observed, identified via ¹¹B and ¹H NMR spectra. Similar treatment of **1d** (0.420 g, 0.598 mmol) gave 0.290 g of **1d** (69% recovery) and 30 mg of **4d** (22% based on **1d** consumed). MS base peaks: for **4b**, 1539 (FAB neg ion), calcd MW 1539.9; for **4d**, 1458 (FAB neg ion), calcd MW 1458.3. Anal. for **4d**. Calcd for C₅C₇₆B₁₂H₁₂₀: C, 62.60; H, 8.29. Found: C, 62.16; H, 8.64. UV-visible absorptions (nm) for **4d**: 586 (8%), 398 (44%), 294 (100%), 270 (72%).

The nickel tetracobalt complex **4i** was synthesized in an analogous manner from **1a** (90 mg, 0.12 mmol) and *n*-butyllithium (0.125 mmol), followed by reaction of the **1a**⁻ monoanion with 13 mg (0.060 mmol) of NiBr₂. In contrast to the syntheses of the pentacobalt species **4a**–**d**, this latter reaction was run at 55 °C for 6 h followed by 16 h at room temperature. Workup as before gave 68 mg of **1a** (76% recovery) and 14 mg of **4i** (63% yield based on starting material consumed). MS base peak for **4i**, 1539 (FAB neg ion); calcd MW, 1539.7. Anal. for **4b**. Calcd for C₅Cl₄C₇₂B₁₂H₁₀₈: C, 56.16; H, 7.07. Found: C, 56.33; H, 8.01.

Synthesis of Higher Phenylene-Linked Oligomers from Pentacobalt Complexes. The above procedure was followed using 0.260 g (0.17 mmol) of **4a**, 1 equiv of (Me₃Si)₂NLi, and 1 equiv of CoCl₂ in THF. Workup gave 0.140 mmol (53% recovery) of **4a**, 60 mg (48% yield based on **4a** consumed) of the 11-cobalt complex **5a**, and 10 mg (8%) of a 17-cobalt complex (MW from FAB mass spectrum 4727; calcd 4729) that is formulated as two 8-cobalt multisandwich units (vide supra) coordinated to a central Co³⁺. Anal. for **5a**. Calcd for Co₁₁Cl₉C₁₄₄B₂₄H₂₁₂: C, 55.18; H, 6.82. Found: C, 55.54; H, 7.35. Anal. for 17-Co product. Calcd for Co₁₇Cl₁₂C₂₁₆B₃₆H₃₁₆: C, 54.86; H, 6.73. Found: C, 51.54; H, 6.84.

Synthesis of a "Closed-Loop" Tetradecamer Dimer, [(Et₂C₂B₂H-4,5-Cl₂)₂Co₃(C₅Me₄)₂]₂(C₆H₄)₂ (6**).** A 100-mg (0.123 mmol) sample of **1c** and 16 mg (0.123 mmol) of CoCl₂ were placed in a 250-mL flask and evacuated. THF (150 mL) was condensed into the flask and 2 equiv of lithium bis(trimethylsilyl)amide was added dropwise via syringe under an atmosphere of N₂ at 0 °C. This produced a color change from green to orange and then dark brown. After the mixture was stirred overnight at room temperature, the solvent was removed via rotary evaporation and the residue was extracted with 1:1 CH₂Cl₂/hexane. The solution was eluted on a silica column, giving three bands of which the first was unreacted **1c**. The second band exhibited a mass spectrum consistent with a tetrachloro 5-cobalt complex corresponding to two **1c** units coordinated to cobalt but was not otherwise characterized. FAB mass spectra of the third band revealed a mixture of 8- and 11-cobalt complexes, higher oligomers, and **6**. During workup of this solution in air, a crystal was obtained on which X-ray diffraction data was obtained and the structure solved,²⁰ identifying the compound as **6**. Attempts at further characterization have thus far been unsuccessful.

Synthesis of Fulvalene-Bridged Multisandwich Complexes. The experimental setup and procedure described above for the preparation of **4a**, **4b**, and **4d** were employed to generate **7** and **8** from the bimetallic fulvalene complex **2a**. Deprotonation of 0.410 g (0.80 mmol) of **2a** with 0.32 mL of 2.5 M *n*-butyllithium in hexane (0.80 mmol), followed by

reaction of the anion with 52 mg (0.40 mmol) of CoCl₂ gave a product mixture that was chromatographed on silica to give three bands. The first band was yellow **2a** (0.254 g, 62% recovery); the second band was the brown 5-cobalt complex **7** (86 mg, 0.079 mmol, 53% based on **2a** consumed); and the third band was the brown 8-cobalt complex **8** (45 mg, 18% based on **2a** consumed). MS base peaks: for **7**, 1083 (CI), 1083 (FAB neg ion), calcd MW 1081.6; for **8**, 1652 (FAB neg ion), calcd MW 1649.8. Anal. for **7**. Calcd for Co₅C₄₈B₁₂H₈₀: C, 53.31; H, 7.46. Found: C, 53.10; H, 7.53. Anal. for **8**. Calcd for Co₈C₇₂B₁₈H₁₁₈: C, 52.42; H, 7.21. Found: C, 52.24; H, 7.29. UV-visible absorptions (nm): for **7**, 384 (100%), 324 (86%), 280 (97%); for **8**, 574 (14%), 360 (100%), 326 (92%), 290 (82%); at low concentration the 280-nm peak is most intense and the other peaks appear at 326 (85%), 440 (34%), 522 (19%), and 604 (9%).

X-ray Structure Determinations on **2c and **4b**.** Measurements were carried out on a Rigaku AFC6S diffractometer at -120 °C using Mo K α radiation. Table III lists information on the data collections and structure determinations. In both cases, unit-cell dimensions were obtained using the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored, showing no significant variation. Absorption corrections were applied using the Ψ scanning of several reflections. All calculations were performed employing the TEXSAN crystallographic software package.²⁵ The structures were solved by direct methods (SIR88).²⁶ Full-matrix least-squares calculations with anisotropic thermal displacement parameters for all non-hydrogen atoms gave the final residuals reported in Table V (supplementary material). In the case of **4b**, only weak diffraction was observed. An inspection of difference Fourier maps revealed several diffuse peaks that were attributed to a disordered toluene solvent molecule. For both structures, hydrogen atoms were either located from difference Fourier maps or placed in calculated positions and were included as fixed contributions to the structure factors. The final difference Fourier map for **4b** showed a peak ca. 2.1 e/Å³ high in the vicinity of Co3, while the corresponding map for **2c** was essentially featureless. Scattering factors were those of Cromer and Waber²⁷ with anomalous dispersion corrections from Ibers and Hamilton.²⁸

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Supplementary Material Available: Tables of experimental details, atomic coordinates, thermal displacement parameters, and calculated mean planes (13 pages); calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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