tations. Precession photography was employed in the case of **10** to identify crystals satisfactory for data collection. Relevant crystal data and experimental parameters for both compounds are listed in Table IV. Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle diffractometer. The θ–2θ scan technique was used as previously described[26] to record the intensities for all nonequivalent reflections within the ranges of θ given in Table IV. Scan widths were calculated as $(A + B \tan \theta)$, where A is estimated from the mosaicity of the crystal and allows for the increase in peak width due to $K\alpha_1$–$K\alpha_2$ splitting.

The intensities of three standard reflections showed no greater fluctuations during data collection than those expected from Poisson statistics. The raw intensity data were collected for Lorentz-polarization effects and absorption. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics ($\rho = 0.05$),[27] were used in the final refinement of the structural parameters.

Solution and Refinement of the Structures. For both compounds, three-dimensional Patterson syntheses were used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[26] Anisotropic temperature factors were introduced for the non-hydrogen atoms. Additional Fourier difference functions permitted location of all hydrogen atoms in the case of **10** and of the hydrogens bound to boron in **11a**. In the latter case, the remaining hydrogens were placed in calculated positions for four cycles of least-squares refinement and thereafter held fixed.

The models converged to the R values given in Table IV. Final difference Fourier maps were featureless. Listings of the observed and calculated structure factors together with positional and thermal parameters and calculated mean planes are available as supplementary material.

Acknowledgment. We thank Kathy Fonda and Dr. Martin Attwood for assistance in recording the ^{11}B NMR spectra and Dr. Mike Kinter for the high-resolution mass spectra. The support of the National Science Foundation (Grant No. CHE 87-21657) and the U.S. Army Research Office is gratefully acknowledged.

Supplementary Material Available: Tables of positional and thermal parameters and mean planes for **10** and **11a** (9 pages); calculated and observed structure factors for **10** and **11a** (56 pages). Ordering information is given on any current masthead page.

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(26) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

(27) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

Fulvalene- and Polyarene-Transition Metal-Carborane Complexes as Building Blocks for Multilevel Arrays. Stepwise Synthesis and Structural Characterization of Polymetallic Linked Sandwiches[1]

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Abstract: The designed synthesis and structural elucidation of a series of linked double-decker and triple-decker arene–metal–carborane complexes, in which the sandwich moieties are linked either directly or via bridging phenylene or biphenylene groups, are reported. The reaction of fulvalenide dianion $[(C_5H_4)_2{}^{2-}]$ with $CoCl_2$ and the $Et_2C_2B_4H_5^-$ ion generated $[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$ (**1**), the first known fulvalene–metal–carborane sandwich species, as air-stable orange crystals. "Double-decapitation" (removal of the apex BH units) of **1** gave yellow air-stable $[(Et_2C_2B_3H_5)Co(C_5H_4)]_2$ (**3**). The interaction of the 1,4-bis(tetramethylcyclopentadienyl)phenylene dianion $[Me_4C_5–C_6H_4–C_5Me_4]^{2-}$ with $CoCl_2$ and the carborane ion produced orange $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2C_6H_4$ (**4**), which on double-decapitation gave yellow $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2C_6H_4$ (**6**), both compounds isolated as air-stable crystals. Similar treatment of the $[Me_4C_5–(C_6H_4)_2–C_5Me_4]^{2-}$ dianion gave orange crystals of $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2(C_6H_4)_2$ (**7**), which was decapitated to generate yellow $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)_2$ (**9**); again, both species are air-stable. Linked triple-decker complexes (the first examples of this genre) were prepared via a different approach, involving reactions of $[Me_4C_5–(C_6H_4)_n–C_5Me_4]^{2-}$ anions with $CoCl_2$ followed by $(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$, which gave emerald green air-stable $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2(C_6H_4)_n$ (**10**, $n = 1$; **11**, $n = 2$). A fulvalene-bridged bis(triple-decker) complex, emerald air-stable crystalline $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5H_4)]_2$ (**12**), was prepared via the reaction of fulvalenide dianion with the $(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ anion and $CoCl_2$. The complexes were structurally characterized from their ^{11}B and ^{1}H NMR, IR, UV–visible, and mass spectra, supported by X-ray crystallographic studies on **1**, **6**, and **10**. Crystal data for **1**: mol wt 504.87; space group *Pbca*; $Z = 4$; $a = 6.764$ (3), $b = 13.135$ (4), $c = 29.22$ (2) Å; $V = 2596$ (3) Å^3; $R = 0.037$ for 1547 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **6**: mol wt 673.58; space group $P2_1/c$; $Z = 2$; $a = 14.702$ (6), $b = 8.746$ (2), $c = 15.003$ (3) Å; $\beta = 103.35$ (3)°; $V = 1877$ (2) Å^3; $R = 0.082$ for 2098 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **10**: mol wt 1310.0; space group $P\bar{1}$; $Z = 1$; $a = 11.094$ (3), $b = 12.062$ (4), $c = 12.823$ (3) Å; $\alpha = 78.00$ (3), $\beta = 74.77$ (3), $\gamma = 69.78$ (2)°; $V = 1541$ (2) Å^3; $R = 0.056$ for 3842 reflections having $F_o^2 > 3\sigma(F_o^2)$.

In an accompanying article[2] we describe the tailored syntheses of double- and triple-decker arene–metal–carborane sandwich complexes from *nido*-$R_2C_2B_4H_6$ reagents, one purpose of which is to provide stable, versatile, electron-delocalized building-block units for use in construction of larger electronically active oligomers and polymers. In this paper we report on the next stage in the development of this idea, which entails the preparation of linked sandwiches via rational methods. Compounds of this type are envisioned as precursors to still larger species, as will be discussed. However, we are concerned here primarily with the preparation, structures, and electronic properties of linked-sandwich oligomers that contain up to four metal centers in stable bonding environments and can adopt variable oxidation states. Systems meeting these criteria are uncommon in metal–arene chemistry, and their

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(1) Organotransition-Metal Metallacarboranes. 13. (a) For part 12, see ref 2. (b) Presented in part at the Third Chemical Congress of North America, Toronto, Canada, June 1988, Abstract INOR 73, and the First Boron-USA Workshop, Southern Methodist University, Dallas, TX, April 1988, Abstract TM25.

(2) Davis, J. H., Jr.; Sinn, E.; Grimes, R. N., preceding paper in this issue.

0002-7863/89/1511-4784$01.50/0

Scheme I

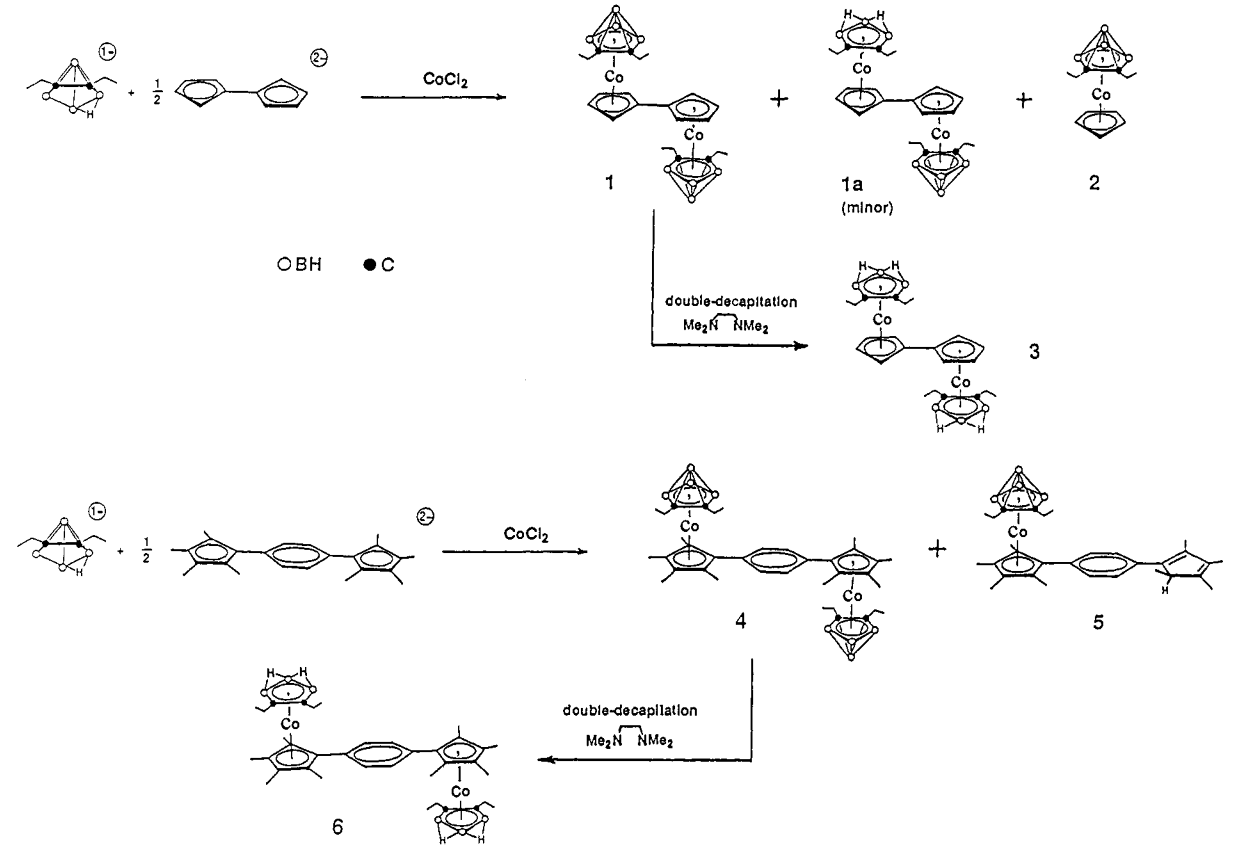

Table I. 115.8-MHz ^{11}B FT NMR Data

compd^{a}	δ (J_{BH}, Hz)	rel areas
$[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$ (**1**)^{b}	10.24 (138), 9.13 (140), 2.82 (122)	1:1:2
$(Et_2C_2B_4H_4)(Et_2C_2B_3H_5)Co_2(C_5H_4)_2$ (**1a**)^{b}	12.16 (192), 9.99 (179), [3.28, 2.48, 2.10]^{c}	1:1:5
$[(Et_2C_2B_3H_5)Co(C_5H_4)]_2$ (**3**)^{b}	3.94 (123), 2.46 (150)	1:2
$[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2(C_6H_4)$ (**4**)^{d}	12.00,^{e} 3.4^{e}	1:2
$[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)$ (**6**)^{d}	6.27 (141), 3.42 (109)	1:2
$[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2(C_6H_4)_2$ (**7**)^{f}	13.73,^{e} 5.00^{e}	1:2
$(Et_2C_2B_4H_4)Co(C_5Me_4)(C_6H_4{-}C_6H_5)$ (**8**)^{f}	13.60 (119), 5.24 (83)	1:2
$[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)_2$ (**9**)^{f}	7.21 (149), 4.61 (185)	1:2
$[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2C_6H_4$ (**10**)^{f}	47.15,^{e} 6.94^{e}	1:2
$[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2(C_6H_4)_2$ (**11**)^{f}	47.25,^{e} 5.93^{e}	1:2
$[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5H_4)]_2$ (**12**)^{f}	46.60,^{e} 6.23^{e}	1:2

^{a}Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. ^{b}Dichloromethane solution. ^{c}Overlapping signals. ^{d}$CDCl_3$ solution. ^{e}Coupling not resolved. ^{f}*n*-Hexane solution.

availability in this work opens new opportunities for probing metal-metal interactions in covalently bonded organometallic networks.

Results and Discussion

Synthesis and Structure of Bis(cobaltacarboranyl) Fulvalene Complexes. The fulvalenide dianion $[(C_5H_4)_2^{2-}]$ exhibits electron delocalization between the rings and is known to form isolable bimetallic complexes.[3] Hence an attractive synthetic target for our purposes was $[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$ (**1**), which can be described as a dimer of $(Et_2C_2B_4H_4)CoCp$ (**2**, identical with **6** in the preceding paper[2]), an exceedingly robust red crystalline compound; the *C,C'*-dimethyl analogue of **2** was reported some time ago.[4] Accordingly, the reaction of the diethylcarborane monoanion $Et_2C_2B_4H_5^-$ with $CoCl_2$ and fulvalenide dianion gave orange crystalline **1** accompanied by **2** and a minor product, yellow $(Et_2C_2B_4H_4)(Et_2C_2B_3H_5)Co_2(C_5H_4)_2$ (**1a**), a "monodecapitated" derivative of **1** in which one apex BH has been removed (Scheme

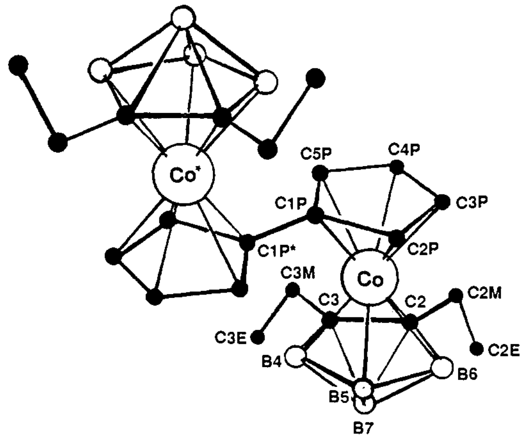

Figure 1. PLUTO drawing of the molecular structure of $[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$ (**1**) (hydrogen atoms are omitted for clarity). Starred atoms are the symmetry equivalents of their unstarred counterparts.

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[3] Leading references: (a) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82 and references therein. (b) Huffman, M. A.; Newman, D. A.; Tilset, M.; Tolman, W. B.; Vollhardt, K. P. C. *Ibid.* **1986**, *5*, 1926. (c) Lacoste, M.; Astruc, D.; Garland, M.; Varret, V. *Organometallics* **1988**, *7*, 2253 and references therein.

[4] Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

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

compd	δ^{a-c}	rel areas
1	4.94 m (C_5H_4), 4.90 m (C_5H_4), 2.31 m (CH_2), 2.18 m (CH_2), 1.14 m (CH_3)	2:2:2:2:6
1a	4.98 m (C_5H_4), 4.92 m (C_5H_4), 4.87 m (C_5H_4), 4.82 m (C_5H_4), 2.35 m (CH_2), 2.18 m (CH_2), 1.90 m (CH_2), 1.75 m (CH_2), 1.18 m (CH_3), 1.02 m (CH_3)	2:2:2:2:2:2:2:2:6:6
3	4.88 m (C_5H_4), 4.86 m (C_5H_4), 1.94 m (CH_2), 1.83 m (CH_2), 1.04 m (CH_3), −6.04 s, br (B–H–B)	2:2:2:2:6:2
4	7.62 s (C_6H_4), 2.52 m (CH_2), 2.31 m (CH_2), 1.91 s (C_5Me_4), 1.88 s (C_5Me_4), 1.17 m (CH_3)	2:2:2:6:6:6
6	7.55 s (C_6H_4), 2.06 m (CH_2), 1.90 m (CH_2), 1.84 s, br (C_5Me_4), 1.09 m (CH_3), −5.50 s, br (B–H–B)	2:2:2:12:6:2
7	7.70 s, br (C_6H_4), 2.52 m (CH_2), 2.32 m (CH_2), 1.90 s (C_5Me_4), 1.86 s (C_5Me_4), 1.16 m (CH_3)	4:2:2:6:6:6
8	7.68 m (C_6H_4, C_6H_5), 7.48 m (C_6H_5), 7.39 m (C_6H_5), 2.45 m (CH_2), 2.24 m (CH_2), 1.84 s (C_5Me_4), 1.82 s (C_5Me_4), 1.17 m (CH_3)	6:2:1:2:2:6:6:6
9	7.68 m (C_6H_4), 2.07 m (CH_2), 1.88 m (CH_2), 1.84 s, br (C_5Me_4), 1.09 m (CH_3), −5.82 s, br (B–H–B)	4:2:2:12:6:2
10	7.54 s (C_6H_4), 4.83 m (C_6H_4), 4.60 m (C_6H_4), 2.60[d] m (CH_2, $CHMe_2$), 2.35 m (CH_2), 1.97 s (CH_3), 1.78 s (C_5Me_4), 1.73 s (C_5Me_4), 1.35 m (CH_3), 1.20 d ($CHMe_2$)	2:2:2:3:2:3:6:6:6:6
11	7.64 s, br (C_6H_4), 4.95 m (C_6H_4), 4.84 m (C_6H_4), 2.70 m ($CHMe_2$), 2.69 m (CH_2), 2.38 m (CH_2), 1.98 s (CH_3), 1.80 s (C_5Me_4), 1.77 s (C_5Me_4), 1.38 m (CH_3), 1.20 d ($CHMe_2$)	4:2:2:1:2:2:3:6:6:6:6
12	4.82 m (C_6H_4), 4.80 m (C_5H_4), 4.70 m (C_6H_4), 4.40 m (C_5H_4), 2.45 m ($CHMe_2$), 2.08[d] m (CH_2), 1.87 s (CH_3), 1.17 m (CH_3), 1.12 d ($CHMe_2$)	2:2:2:1:4:3:6:6

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. 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] Overlapping resonances.

Table III. Infrared Absorptions (cm^{-1}, CCl_4 Solutions vs CCl_4)[a]

compd	absorptions
1	3831 w, 3817 w, 3676 m, 2973 vs, 2931 s, 2875 s, 2565 vs, 2361 w, 1700 m, 1567 m, 1525 m, 1454 m, 1337 m, 1257 w, 1222 w, 1117 w, 1068 w, 955 w, 934 w
1a	3845 m, 3817 m, 3676 m, 2966 m, 2924 m, 2853 m, 2551 m, 2361 m, 2333 m, 1700 s, 1560 s, 1539 s, 1412 m, 1264 m, 1124 m, 1096 m, 1011 m
3	3845 s, 3817 s, 3676 s, 2980 w, 2938 w, 2558 m, 2368 m, 2347 m, 1707 s, 1616 s, 1560 vs, 1539 s, 1426 m, 1257 w, 1222 w, 1005 m, 976 w
4	3845 m, 3824 m, 3676 m, 2368 m, 2333 m, 1700 m, 1560 s, 1532 s, 1419 m, 1257 m, 1208 m, 1110 w, 1075 w, 1004 m, 976 m
6	3845 m, 3824 m, 3676 m, 2966 vw, 2931 vw, 2375 m, 2333 m, 1700 m, 1560 m, 1532 m, 1426 m, 1243 vw, 1222 vw, 1032 vw, 983 vw
7	3831 m, 3817 m, 3676 s, 2537 vw, 2368 m, 2333 m, 1707 s, 1567 s, 1532 s, 1419 m, 1264 w, 1222 w, 1011 w, 976 vw
8	3838 m, 3810 m, 3676 m, 2973 w, 2933 w, 2853 vw, 2544 m, 2368 m, 2333 m, 1700 s, 1560 s, 1532 s, 1426 m, 1271 m, 1208 m, 1124 vw, 1068 vw, 1011 m, 976 m
9	3838 m, 3810 m, 3676 s, 2368 m, 2340 m, 1700 s, 1560 s, 1539 s, 1419 s, 1257 vw, 1215 vw, 1011 vw, 983 vw
10	2959 s, 2924 s, 2903 sh, 2860 w, 2467 vs, 2375 m, 2333 w, 1595 m, 1546 s, 1250 m, 1215 m, 1004 m, 976 w
11	3838 m, 3810 m, 3683 m, 2966 w, 2931 w, 2868 w, 2467 w, 2361 m, 2333 m, 1700 m, 1560 s, 1532 s, 1412 m, 1250 m, 1215 w, 1005 m, 976 w
12	3845 m, 3824 m, 3669 s, 2966 vw, 2931 vw, 2481 vw, 2361 m, 2340 m, 1693 s, 1560 s, 1532 s, 1419 s, 1257 m, 1229 m, 1004 m, 976 w

[a] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

I). The reaction is inherently inefficient, owing to the presence of both fulvalenide and cyclopentadienide ions in THF solution[5] and also to the propensity of **1** to undergo decapitation. However, **1** was obtained in quantity sufficient for full characterization.

The structure of **1**, the first reported fulvalene–metallacarborane complex, was assigned from its ^{11}B and ^1H NMR spectra (which closely resemble those of **2**[2] and its *C,C′*-dimethyl counterpart[4]) and its infrared, visible–UV, and mass spectra and was subsequently confirmed by X-ray diffraction. The spectroscopic data are listed in Tables I–III and in the Experimental Section. The molecular geometry of **1** is shown in Figure 1, and details of the data collection, bond distances, and selected bond angles are given in Tables IV and V. To our knowledge, this structure determination is the first reported for a bimetallic fulvalene complex in which the metals are not otherwise linked; **1** is also apparently

Table IV. Experimental X-ray Diffraction Parameters and Crystal Data on **1**, **6**, and **10**

	1	**6**	**10**
M_r	504.87	673.58	1310.0
space group	*Pbca*	$P2_1/c$	$P\bar{1}$
a, Å	6.764 (3)	14.702 (6)	11.094 (3)
b, Å	13.135 (4)	8.746 (2)	12.062 (4)
c, Å	29.22 (2)	15.003 (3)	12.823 (3)
α, deg			78.00 (3)
β, deg		103.35 (3)	74.77 (3)
γ, deg			69.78 (2)
V, Å^3	2596 (3)	1877 (2)	1541 (2)
μ, cm^{-1} (Mo Kα)	13.55	9.42	12.27
D(calcd), g cm^{-3}	1.60	1.19	1.41
A[a]	0.65	0.65	0.65
B[a]	0.35	0.35	0.35
2θ range, deg	1.5–54	1.5–50	1.5–48
reflectns obsd	2801	3428	4999
reflectns refined	1547	2098	3842
R	0.037	0.082	0.056
R_w	0.049	0.087	0.064
max shift in final cycle	0.05	0.07	0.07
largest peak in final diff map, e/Å	0.68	1.92	0.97
esd unit weight	1.3	2.8	1.8
Z	4	2	1

[a] See ref 2.

Table V. Bond Distances (Å) and Selected Bond Angles (Deg) in **1**

Bond Distances

Co–C1p	2.035 (3)	C1p–C1p*	1.474 (6)	C3–C3m	1.503 (5)
Co–C2p	2.019 (4)	C1p–C2p	1.423 (6)	C3–B4	1.562 (6)
Co–C3p	2.038 (4)	C1p–C5p	1.414 (5)	C3–B7	1.771 (6)
Co–C4p	2.061 (4)	C2p–C3p	1.419 (6)	B4–B5	1.676 (6)
Co–C5p	2.059 (4)	C3p–C4p	1.401 (6)	B4–B7	1.782 (6)
Co–C2	2.007 (4)	C4p–C5p	1.414 (6)	B5–B6	1.657 (6)
Co–C3	2.020 (3)	C2–C2m	1.517 (5)	B5–B7	1.730 (6)
Co–B4	2.093 (4)	C2–C3	1.470 (5)	B6–B7	1.785 (6)
Co–B6	2.081 (4)	C2–B6	1.553 (5)	C2m–C2e	1.502 (6)
Co–B5	2.117 (5)	C2–B7	1.774 (6)	C3m–C3e	1.441 (7)

Bond Angles

C5p–C1p–C2p	107.6 (3)	C2–C3–C3m	122.9 (3)
C5p–C1p–C1p*	126.8 (4)	C2–C3–B4	112.3 (3)
C2p–C1p–C1p*	125.6 (4)	C3m–C3–B4	124.6 (3)
C3p–C2p–C1p	107.6 (4)	C3m–C3–B7	134.5 (3)
C4p–C3p–C2p	108.4 (4)	C3m–C3–Co	134.4 (3)
C3p–C4p–C5p	107.9 (4)	B7–C3–Co	91.1 (2)
C1p–C5p–C4p	108.5 (4)	C3–B4–B5	104.4 (3)
C2m–C2–B6	123.4 (3)	B7–B4–Co	88.4 (2)
C2m–C2–B7	135.7 (3)	B6–B5–B4	105.8 (3)
C3–C2–C2m	123.7 (3)	B7–B5–Co	89.0 (2)
C3–C2–B6	112.6 (3)	C2–B6–B5	104.9 (3)
C2m–C2–Co	133.0 (3)	B7–B6–Co	88.7 (2)
B7–C2–Co	91.3 (2)	C2E–C2m–C2	112.6 (3)
		C3E–C3m–C3	116.4 (4)

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[5] Pittman, C. U.; Surynarayanan, B. *J. Am. Chem. Soc.* **1976**, *96*, 7916.

the first structurally characterized cobalt–fulvalene complex. The compound crystallizes in an orthorhombic lattice with a required center of symmetry, so that the fulvalene $C_{10}H_8$ ring system is constrained to be planar. The central fulvalene carbon–carbon distance (C1p–C1p*) is 1.474 (6) Å, a value that is within the normal range found in fulvalene–metal π-complexes[6] and is consistent with a degree of multiple bonding between the rings. The bond lengths and angles within the $CpCoC_2B_4$ units exhibit no significant differences from those of the closely related complex[7] $CpCo(Me_2C_2B_4H_4)$ and, moreover, are typical of *closo*-seven-vertex metallacarborane cages. The calculated mean planes of the C_2B_3 and fulvalenide rings are nearly parallel (dihedral angle 3.12°), and the distances of these planes from the cobalt atom are 1.564 and 1.650 Å, respectively.

As was discussed in the preceding paper,[2] the construction of higher order stacked sandwich complexes from MC_2B_4 cluster units requires decapitation (apex BH removal) to create open C_2B_3 faces. In the present case, treatment of **1** with wet *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) resulted in "double-decapitation" to give $[(Et_2C_2B_3H_5)Co(C_5H_4)]_2$ (**3**) as air-stable yellow crystals. This observation is of interest because earlier attempts in our laboratory and others[8] to double-decapitate complexes of the type $(R_2C_2B_4H_4)_2M$ (in which two carborane ligands are coordinated to a common metal atom) have resulted in removal of only one BH group. In those species, it is apparent that the first decapitation effectively deactivates the apex BH unit of the remaining C_2B_4 cage toward base attack. In the case of **1**, whose carborane ligands are more remote from each other and are coordinated to different metal centers, this effect is not observed; the two carborane ligands are independently decapitated, and the conversion to **3** proceeds readily and in high yield.

Synthesis and Structure of Phenylene- and Biphenylene-Linked Complexes. The difficulties inherent in working with the fulvalenide ligand (e.g., its instability and coexistence with $C_5H_5^-$ in solution) led us to explore more tractable bicyclic or polycyclic aromatic hydrocarbons as linking agents for our systems. In earlier work, Spencer and Grimes[9] prepared complexes employing fluorene (*o,o′*-diphenylenemethane) as a bridging ligand via thermal reactions; for purposes of the present investigation, we utilized only low-energy (room temperature or below) routes in order to better control the course of the reactions. After unsuccessful experiments with 9,9-bifluorenyl $[(C_{10}H_{12})_2]$, the phenylene-linked bis(tetramethylcyclopentadienide) dianions $[(Me_4C_5)-(C_6H_4)_n-(C_5Me_4)]^{2-}$ were selected as suitable candidates in view of their accessibility, electron delocalization, and stability in solution. As is depicted in Scheme I, the reaction of the monophenylene-bridged dianion with the carborane monoanion and $CoCl_2$ produced orange crystals of $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2C_6H_4$ (**4**) and an unstable minor product that decomposed on workup and was identified from its mass spectrum as a monocobalt species, $[(Et_2C_2B_4H_4)Co(C_5Me_4)-C_6H_4-C_5Me_4H$ (**5**). Double-decapitation of **4** with TMEDA proceeded easily, giving the desired product, yellow crystalline $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2C_6H_4$ (**6**), in quantitative yield.

Given that **6** is a key compound in our overall synthetic strategy, since its double-open-ended geometry is amenable in principle to metal complexation at both ends, an X-ray diffraction study was conducted that confirmed the proposed structure (Figure 2 and Tables IV and VI). As was observed in **1**, previously discussed, and **10**, described below, the **6** molecule is crystallographically centrosymmetric. The phenylene ring is tilted by 47° relative to the cyclopentadienyl ring plane, which can be understood in terms of relief of crowding by the adjacent methyl units. The bond distances and angles in the $(Et_2C_2B_3H_5)Co(C_5Me_4)$ portion of the molecule are closely similar to those observed in other crystallographically characterized metallacarboranes containing a *nido*-$M(R_2C_2B_3H_5)$ group.[10]

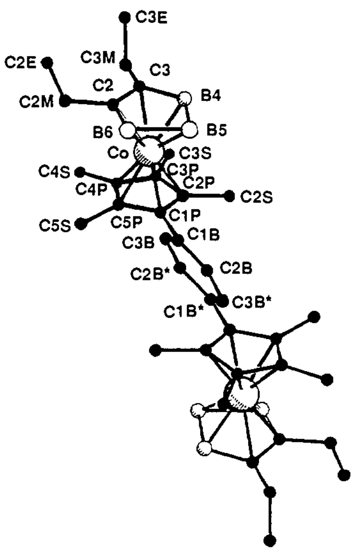

Figure 2. PLUTO drawing of the molecular structure of $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2C_6H_4$ (**6**), with hydrogens omitted.

Table VI. Bond Distances (Å) and Selected Bond Angles (Deg) in **6**

Bond Distances					
Co–B4	2.03 (1)	C1p–C5p	1.43 (1)	C2b–C3b*	1.40 (1)
Co–B5	2.05 (1)	C1p–C1b	1.50 (1)	C2–C3	1.43 (2)
Co–B6	1.96 (1)	C2p–C3p	1.42 (1)	C2–B6	1.32 (2)
Co–C2	2.06 (1)	C2p–C2s	1.53 (2)	C2–C2m	1.54 (2)
Co–C3	2.10 (1)	C3p–C4p	1.40 (2)	C2m–C2e	1.52 (2)
Co–C1p	2.020 (9)	C3p–C3s	1.61 (1)	C3–C3m	1.48 (2)
Co–C2p	2.08 (1)	C4p–C5p	1.43 (1)	C3–B4	1.52 (2)
Co–C3p	2.03 (1)	C4p–C4s	1.50 (1)	C3m–C3e	1.51 (2)
Co–C4p	2.09 (1)	C5p–C5s	1.56 (1)	B4–B5	1.77 (2)
Co–C5p	2.03 (1)	C1b–C2b	1.41 (1)	B5–B6	2.02 (2)
C1p–C2p	1.40 (1)	C1b–C3b	1.38 (1)		

Bond Angles			
C5p–C1p–C1b	127 (1)	C4p–C5p–C5s	125 (1)
C2p–C1p–C5p	109 (1)	C5s–C5p–Co	132 (1)
C2p–C1p–C1b	124 (1)	C3b–C1b–C2b	119 (1)
C1b–C1p–Co	132.3 (8)	C3b–C1b–C1p	122 (1)
C1p–C2p–C3p	107 (1)	C2b–C1b–C1p	119 (1)
C1p–C2p–C2s	128 (1)	C3b–C2b–C1b	119 (1)
C3p–C2p–C2s	125 (1)	C2m–C2–Co	126 (1)
C2s–C2p–Co	127 (1)	B6–C2–C3	120 (1)
C4p–C3p–C2p	110 (1)	B6–C2–C2m	118 (1)
C4p–C3p–C3s	126 (1)	C3–C2–C2m	122 (1)
C2p–C3p–C3s	124 (1)	C2e–C2m–C2	109 (1)
C3s–C3p–Co	127 (1)	C2–C3–C3m	124 (1)
C3p–C4p–C5p	106 (1)	C2–C3–B4	114 (1)
C3p–C4p–C4s	127 (1)	C3m–C3–B4	121 (1)
C5p–C4p–C4s	127 (1)	C3m–C3–Co	128 (1)
C4s–C4p–Co	131 (1)	C3–C3m–C3e	114 (1)
C1p–C5p–C4p	108 (1)	C3–B4–B5	109 (1)
C1p–C5p–C5s	126 (1)	B4–B5–B6	92 (1)
		C2–B6–B5	106 (1)

In attempting the synthesis of the corresponding biphenylene-linked complexes, we found that $Me_4C_5-(C_6H_4)_2-C_5Me_4$, when prepared by the literature procedure,[11] forms an inseparable mixture with $Me_4C_5-C_6H_4-C_6H_5$. The reaction of a solution of the mixed hydrocarbons anions with the carborane ion and $CoCl_2$ formed the desired product, orange $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2(C_6H_4)_2$ (**7**), accompanied by the

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[6] Drago, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280.

[7] Weiss, R.; Bryan, R. F. *Acta Crystallogr., Sect. B* **1977**, *B33*, 589.

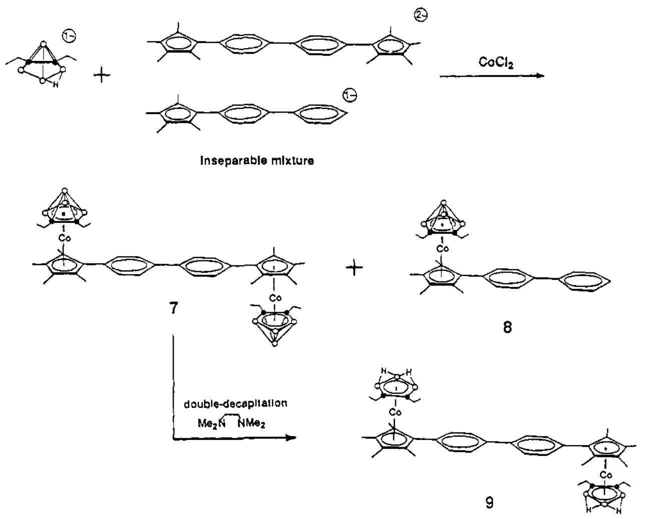
[8] Hosmane, N. S., private communication.

[9] Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 323, 328.

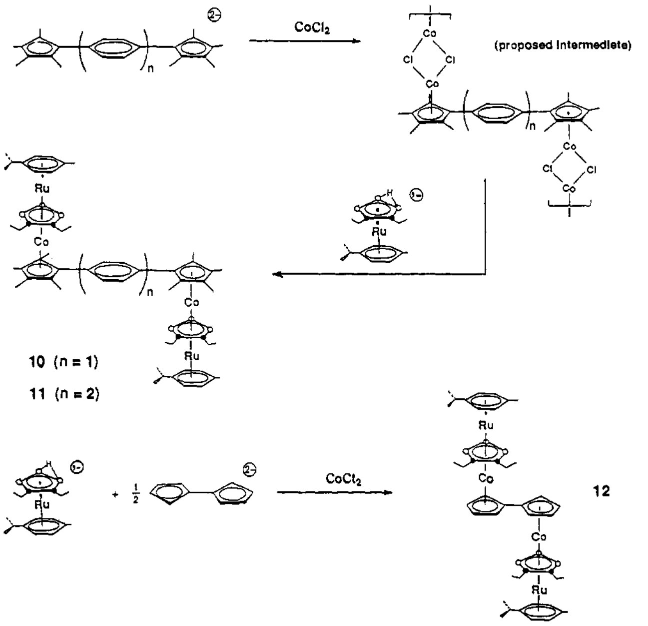
[10] (a) *nido*-$(5-B_9H_{12}OC_4H_8)$-1,2,3-$Co(Me_2C_2B_3H_5)$: Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1928. (b) *nido,closo*-$(Me_2C_2B_3H_5)Co(Me_2C_2B_4H_3C_5H_4CoCp)$: Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447. (c) μ-HgCl-*nido*-1,2,3-$(C_5Me_5)CoMe_2C_2B_3H_4$ and μ-Hg-(*nido*-1,2,3-$CpCoMe_2C_2B_3H_4)_2$: Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863. (d) *nido*-1,2,3-$(CO)_3FeC_2B_3H_7$: Brennan, J. P.; Grimes, R. N.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1973**, *12*, 2266.

[11] Bunel, E. E.; Campos, P.; Ruz, J.; Valle, L.; Chadwick, I.; Santa Ana, M.; Gonzalez, G.; Manriquez, J. M. *Organometallics* **1988**, *7*, 474.

Scheme II



Scheme III



monocobalt complex $(Et_2C_2B_4H_4)Co(C_5Me_4)-C_6H_4-C_6H_5$ (**8**, Scheme II). As in the case of **4**, complex **7** was readily decapitated to generate the double-open-ended species $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)_2$ (**9**) as yellow crystals.

Preparation of Linked Triple-Decker Complexes. Our original strategy for synthesizing oligomeric multidecker sandwich complexes envisioned the addition of metal–ligand units to decapitated linked complexes such as **3**, **6**, and **9**, via bridge deprotonation followed by reaction with arene metal halides; such an approach would parallel the corresponding reactions of $CpCo(Et_2C_2B_3H_4)^-$, which readily generate monomeric triple-deckers.[2,4] However, in our hands this approach did not lead to isolation of the desired linked species. Tetradeprotonation of **3**, **6**, and **9** with 4 equiv of *n*-butyllithium appeared to proceed readily, but subsequent treatment with (cymene)ruthenium dichloride gave no characterizable products. Accordingly, an alternative route was developed, in which a linked-hydrocarbon dianion is treated with $CoCl_2$ to form a dimetalated intermediate whose postulated structure, based on the geometry previously proposed[12] for $[CoCl_2(C_5Me_5)]_2$, is shown in Scheme III. Reactions of these species (n = 1, 2) with the $(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ anion[2] yielded the respective linked triple-decker products $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2(C_6H_4)_n$ (**10**, n = 1; **11**, n = 2).

Table VII. Bond Distances (Å) and Selected Bond Angles (Deg) in **10**

Bond Distances					
Ru–C2	2.233 (8)	Co–C34	2.040 (8)	C24–C28	1.47 (1)
Ru–C3	2.272 (8)	Co–C35	2.016 (8)	C25–C26	1.42 (2)
Ru–B4	2.20 (1)	C2–C3	1.52 (1)	C28–C30	1.52 (2)
Ru–B5	2.18 (1)	C2–C2m	1.54 (1)	C28–C29	1.52 (1)
Ru–B6	2.24 (1)	C2–B6	1.55 (1)	C31–C35	1.40 (1)
Ru–C21	2.26 (1)	C2m–C2e	1.47 (2)	C31–C32	1.44 (1)
Ru–C22	2.217 (9)	C3–C3m	1.46 (1)	C31–C31m	1.50 (1)
Ru–C23	2.143 (9)	C–Cl1	1.69 (2)	C32–C33	1.44 (1)
Ru–C24	2.209 (8)	C–Cl2	1.69 (2)	C32–C32m	1.48 (1)
Ru–C25	2.19 (1)	C3–B4	1.56 (1)	C33–C34	1.42 (1)
Ru–C26	2.23 (1)	C3m–C3e	1.50 (2)	C33–C33m	1.51 (1)
Co–C2	2.068 (8)	B4–B5	1.67 (2)	C34–C41	1.48 (1)
Co–C3	2.087 (8)	B5–B6	1.75 (1)	C34–C35	1.48 (1)
Co–B4	2.07 (1)	C20–C21	1.52 (2)	C35–C35m	1.47 (1)
Co–B5	2.11 (1)	C21–C22	1.34 (2)	C41–C42	1.39 (1)
Co–B6	2.06 (1)	C21–C26	1.44 (2)	C41–C43	1.40 (1)
Co–C31	2.079 (8)	C22–C23	1.45 (2)	C42–C43*	1.37 (1)
Co–C32	2.103 (8)	C23–C24	1.43 (1)	C42–C43	1.37 (1)
Co–C33	2.048 (8)	C24–C25	1.41 (1)		

Bond Angles			
C3–C2–C2m	118.5 (8)	C35–C31–C32	109.0 (7)
C3–C2–B6	113.7 (7)	C35–C31–C31m	125 (1)
C2m–C2–B6	127.8 (8)	C32–C31–C31m	126 (1)
C2e–C2m–C2	115 (1)	C31–C32–C33	107.2 (8)
C3m–C3–C2	112.2 (8)	C31–C32–C32m	125.5 (9)
C3m–C3–B4	128.6 (8)	C33–C32–C32m	127 (1)
C2–C3–B4	109.1 (7)	C34–C33–C32	109.4 (8)
C3–C3m–C3e	115 (1)	C34–C33–C33m	126.3 (8)
C3–B4–B5	109.8 (7)	C32–C33–C33m	124.1 (9)
B4–B5–B6	102.0 (7)	C33–C34–C41	126.5 (7)
C2–B6–B5	105.4 (7)	C33–C34–C35	105.9 (7)
C22–C21–C26	120 (2)	C41–C34–C35	127.4 (8)
C22–C21–C20	123 (2)	C31–C35–C35m	126.6 (8)
C26–C21–C20	116 (2)	C31–C35–C34	108.4 (7)
C21–C22–C23	121 (1)	C35m–C35–C34	124.7 (8)
C24–C23–C22	122 (1)	C42–C41–C43	115.3 (7)
C25–C24–C23	115 (1)	C42–C41–C34	124.1 (7)
C25–C24–C28	124 (1)	C43–C41–C34	120.6 (7)
C23–C24–C28	121.0 (9)	C43–C42*–C41*	121.3 (7)
C24–C25–C26	123 (1)	C42–C43*–C41*	123.4 (7)
C25–C26–C21	119 (1)	C41–C42–C43*	121.3 (7)
C24–C28–C30	114 (1)	C41–C43–C42*	123.4 (7)
C24–C28–C29	109 (1)	Cl2–C–Cl1	116 (1)
C30–C28–C29	111 (1)		

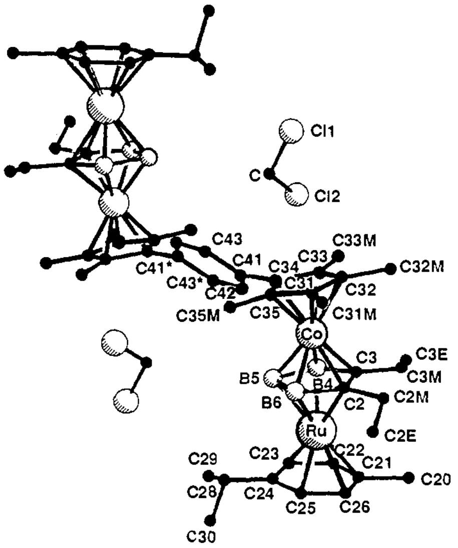


Figure 3. PLUTO drawing of the molecular structure of $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2C_6H_4\cdot 2CH_2Cl_2$ (**10**), with hydrogens omitted.

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(12) Koelle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980.

Compounds **10** and **11** were isolated as emerald green air-stable crystals, whose NMR and mass spectra are consistent with the structures indicated. This geometry was established via a crystallographic study on **10**, the relevant data for which are presented in Tables IV and VII. As shown in Figure 3, the molecule crystallizes with a center of symmetry so that the two sandwich stacks extend in opposite directions from the central C_6H_4 ring. The asymmetric unit also contains a molecule of dichloromethane solvent. The central phenylene ring is tilted by 51° with respect to each of the cyclopentadienyl planes, probably in relief of steric crowding between the central ring and the adjacent methyl groups. The structural parameters of the identical ruthenium–cobalt sandwich units are similar to those of the corresponding monomer $CpCo(Et_2C_2B_3H_3)Ru(\eta^6\text{-}MeC_6H_4CHMe_2)$ (compound **11a** in the preceding article[2]). The cyclopentadienyl and cymene planes are tilted with respect to the C_2B_3 ring plane by 6.2 and 7.7°, respectively, in a direction away from the C–Et groups; these dihedral angles may be compared with the corresponding values of 6.2 and 6.4° in the monomeric complex.[2] One possibly significant difference in these two structures is in the carboranyl C2–C3 distance, whose value of 1.52 (1) Å in **10** is not only longer than that in the monomer [1.46 (1) Å][2] but is the longest yet observed in C_2B_3-bridged triple-decker sandwiches.[13] If the long C–C bond in **10** can be taken as reflecting low bond order, in line with the discussion in the preceding paper,[2] this may indicate depletion of electron density in the CoC_2B_3Ru cluster via interaction with the polycyclic hydrocarbon ligand. This effect may be augmented by the presence of methyl substituents on the C_5 rings in **10**, which probably serves to strengthen the $Co–C_5Me_5$ bonding interaction and hence weaken the cobalt–carborane link. The variation of the carborane C–C bond length in small metallacarborane complexes is useful in correlating molecular and electronic structures and has been discussed previously.[13c]

The bis(triple-decker) counterpart of the fulvalene complex **3** was prepared in a manner analogous to the syntheses of **10** and **11**. The reaction of fulvalenide dianion with the $(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ anion and $CoCl_2$ gave $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5H_4)]_2$ (**12**) as an emerald green air-stable solid. The characterization of **12** from its NMR and mass spectra was straightforward, as the ^{11}B and ^1H NMR patterns are very similar to those of the monomeric counterpart $CpCo(Et_2C_2B_3H_3)Ru(\eta^6\text{-}MeC_6H_4CHMe_2)$ (a minor byproduct in the present synthesis) whose structural characterization is reported elsewhere.[2] Compound **12** is noteworthy as the first species that we are aware of in which two triple-decker sandwich units are directly linked; the incorporation of fulvalene into a triple-decker system is also novel. With four metal centers in a framework that is expected to exhibit substantial electron delocalization, one can anticipate an extensive redox chemistry with multiple reversible oxidations and reductions. For example, recent observations on related arene–transition metal–carborane complexes in collaboration with W. E. Geiger and associates have revealed the first iron- and ruthenium–arene sandwich species that undergo reversible oxidation;[14] it is highly likely that similar stabilizaton by the cyclocarborane rings occurs in **12** and related stacked systems.

Conclusions

This work demonstrates that controlled routes to specifically designed arene–metal–carborane linked systems are feasible, and provides further evidence of the versatility of the $Et_2C_2B_4H_4^{2-}$ and $Et_2C_2B_3H_5^{2-}$ ligands in transition-metal organometallic chemistry. Among the large tasks ahead are the detailed exploration of the electronic structures and redox chemistry of this class of multimetal complexes and the further extension of the synthetic principles described in these papers to larger oligomers and ultimately to polymers. We hope to report on progress in both of these areas in subsequent papers.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in the preceding paper.[2] All new compounds gave unit-resolution electron-impact mass spectra exhibiting strong parent envelopes that closely matched the intensities calculated from natural isotopic abundances.

Syntheses of $[(Et_2C_2B_4H_4)Co(C_5H_4)]_2$ (1) and $(Et_2C_2B_4H_4)(Et_2C_2B_3H_5)Co_2(C_5H_4)_2$ (1a). In a reaction apparatus configured as in Figure 3b of the accompanying paper,[2] 0.25 g of NaH (50% dispersion in mineral oil, washed twice with *n*-hexane to remove the oil) was placed in flask A, while flask B was charged with 0.467 g (3.6 mmol) of anhydrous $CoCl_2$. The apparatus was evacuated on a vacuum line, and ca. 50 mL of THF was distilled into each of flasks A, B, and C. A 2.0 M solution of NaC_5H_5 (1.78 mL, 3.6 mmol) was added via syringe to flask C through a rubber septum. The solution was cooled to −78 °C and a solution of I_2 (0.46 g, 1.8 mmol) in 10 mL of dry THF was added incrementally, over a 1-h period, via syringe to the cooled, stirred solution in flask C. The resulting pale tan solution containing dihydrofulvalene[5] was warmed to −60 °C and *carefully* maintained at that temperature (±5 °C) for 1 h. Addition of 2.1 mL of 1.7 M *tert*-butyllithium in pentanes (3.6 mmol) produced a slight color change to peach yellow, after which the solution was warmed to −30 °C over 1 h. A solution of $Na^+Et_2C_2B_4H_5^-$ (0.468 g, 3.6 mmol) in THF was prepared in flask A via addition of $Et_2C_2B_4H_6$ from the sidearm to the stirred solution of NaH in THF over 1 h, monitored by the evolution of H_2. A liquid nitrogen bath was placed around flask B containing the $CoCl_2$ solution, and the fulvalenide and carborane ion solutions in flasks C and A, respectively, were added in turn to B through the sintered glass filter E. The mixture was warmed to room temperature, during which process the purple solution became orange-brown and noncondensible gas was evolved. After the mixture was stirred overnight at room temperature, the reaction vessel was opened to the air, 100 mL of 1.2 M HCl and 10 mL of acetone were added, and the mixture was stirred in air for 1 h, after which time the organic solvent phase was removed by rotary evaporation to leave an orange aqueous phase (I_2) and a brown solid. The aqueous layer was discarded and the brown solid was collected by filtration, dissolved in a minimum volume of toluene, and eluted on a silica column in toluene to give four orange bands of which the first was identified spectroscopically as the known compound[2] $CpCo(Et_2C_2B_4H_4)$ (**2**). The second (major) band was collected and chromatographed on a silica thick-layer plate in 1:1 *n*-hexane/toluene, which eluted two orange crystalline products, R_f 0.35 and 0.11. These compounds were characterized respectively as **1** (87 mg, 0.17 mmol) and **1a** (3 mg, 0.006 mmol). Exact mass for **1a**: calcd for $^{59}Co_2{}^{12}C_{22}{}^{11}B_7{}^1H_{37}{}^+$, 496.2211; found, 496.2223. Visible–UV absorptions (nm, in CH_2Cl_2): for **1**, 430 (4%), 370 (12%), 318 (52%), 284 (100%), 244 (75%); for **1a**, 324 (15%), 286 (28%), 270 (40%), 234 (100%), 204 (44%).

Synthesis of $[(Et_2C_2B_3H_5)Co(C_5H_4)]_2$ (3). A 77-mg (0.15 mmol) sample of **1** was dissolved in 5 mL of TMEDA in a 50-mL round-bottom flask equipped with a stir bar, and 0.5 mL of water and 5 mL of THF were added. The solution was stirred in air for 30 min, during which the solution changed from orange to golden yellow. The solvents were removed in vacuo to give a golden solid, which was column chromatographed on silica in 50:50 (v/v) *n*-hexane/dichloromethane, producing one dark yellow band. Slow evaporation of the eluate gave **3** as an orange crystalline solid (70 mg, 0.14 mmol, 97%). Exact mass for **3**: calcd for $^{59}Co_2{}^{12}C_{22}{}^{11}B_6{}^1H_{38}{}^+$, 486.2196; found, 486.2200. Visible–UV absorptions (nm, in CH_2Cl_2): 378 (14%), 336 (31%), 286 (100%), 272 (89%), 244 (61%).

Synthesis of $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2C_6H_4$ (4). In an apparatus of the type employed in the preceding synthesis, flasks A, B, and C were charged respectively with 0.32 g of NaH (50% mineral oil dispersion), 0.390 g (3.0 mmol) of $CoCl_2$, and 0.490 g (1.5 mmol) of 1,4-bis(2,3,4,5-tetramethylcyclopenta-1,5-dienyl)benzene, and 50 mL of THF was distilled into each flask. A 2.5-mL volume of *n*-butyllithium in hexanes (2.5 M) was introduced into C, causing a vigorous reaction with precipitation of a copious amount of gray-tan solid. After this slurry (containing the $(C_5Me_4)_2C_6H_4^{2-}$ dianion) was stirred for 10 min at room temperature, it was added *slowly* over a 30-min period to the $CoCl_2$ solution in B. During this addition the solution became blue-green and finally olive. The solution in B was stirred for 1 h, during which time the carborane anion $Et_2C_2B_4H_5^-$ (3.0 mmol) was prepared in flask A as described in the preceding synthesis. The solution in A was filtered in vacuo into B, causing the latter solution to immediately turn dark brown-orange. The solution was stirred for 2 h, the flask was opened to the air, and the solvent was removed by rotary evaporation to give a crude residue whose mass spectrum revealed the presence of compounds **4** and

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(13) (a) Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046. (b) Robinson, W. T.; Grimes, R. N. *Inorg. Chem.* **1975**, *14*, 3056. (c) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10.

(14) Merkert, J. M.; Geiger, W. E., Jr.; Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics*, in press.

5. Column chromatography of this material on silica in 50:50 *n*-hexane/dichloromethane gave two major orange bands, the first of which was collected as an orange-brown oil and characterized as $[(Et_2C_2B_4H_4)Co(C_5Me_4)-C_6H_4-C_5Me_4H$ (**5**, 0.170 g, 0.33 mmol, 22%). Attempts at further purification of this material led to gross decomposition. The second band was recovered as orange crystalline **4**, 0.290 g (0.41 mmol, 27%). Exact mass for **4**: calcd for $^{59}Co_2{}^{12}C_{36}{}^{11}B_8{}^{1}H_{56}{}^{+}$, 694.3791; found, 694.3796. Visible–UV absorptions (nm, in CH_2Cl_2): 426 (4%), 304 (100%), 245 (45%).

Synthesis of $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2C_6H_4$ (6). The procedure described above for the conversion of **1** to **3** was employed to convert **4** to **6**. The reaction of 0.285 g (0.36 mmol) of **4** gave 0.280 g (0.36 mmol) of isolated yellow crystalline **6**, corresponding to 100% yield. Exact mass for **6**: calcd for $^{59}Co_2{}^{12}C_{36}{}^{11}B_6{}^{1}H_{58}{}^{+}$, 674.3761; found, 674.3797. Visible–UV absorptions (nm, in CH_2Cl_2): 422 (3%), 332 (13%), 250 (100%).

Synthesis of $[(Et_2C_2B_4H_4)Co(C_5Me_4)]_2(C_6H_4)_2$ (7) and $(Et_2C_2B_4H_4)Co(C_5Me_4)-C_6H_4-C_6H_5$ (8). The tetracyclic ligand 1,12-bis(tetramethylcyclopentadienyl)biphenyl $[(C_5Me_5H)_2C_{12}H_8$ (A)] was prepared according to the literature procedure,[11] which, however, gave a mixture of the desired compound (A) and a side product, 1-(tetramethylcyclopentadienyl)biphenyl $[(C_5Me_5H)C_{12}H_9$ (B)] in an A:B ratio of ~60:40 as determined from proton NMR. These compounds proved inseparable via either crystallization or column chromatography on silica, the latter procedure causing extensive decomposition of both compounds. Consequently, for our synthetic purposes the mixture was employed as such, on the assumption that the organometallic derivatives of the two components would be separable; this proved to be the case. A 2.14-g sample of the mixture, corresponding to 3.8 mmol of A and 2.5 mmol of B, was placed in flask C in the apparatus shown in Figure 3b, and the procedure described above for the preparation of **4** was followed, employing 5.94 mL of 1.7 M *tert*-butyllithium in hexanes (1 equiv per each acidic proton on the two hydrocarbons), 1.31 g (10.1 mmol) of $CoCl_2$, and 1.33 g (10.1 mmol) of $Et_2C_2B_4H_6$. Workup of the products as described for **4** via chromatography of the crude product on silica in 2:1 dichloromethane-/*n*-hexane gave two orange bands, the first of which on evaporation of solvent afforded orange crystalline **7**, 0.580 g (0.75 mmol, 20%). The second band was identified as $(Et_2C_2B_4H_4)Co(C_5Me_4)-C_6H_4-C_6H_5$ (**8**), obtained as an orange oil, 0.220 g (0.34 mmol, 14%). Exact mass for **7**: calcd for $^{59}Co_2{}^{12}C_{42}{}^{11}B_8{}^{1}H_{60}{}^{+}$, 770.4103; found, 770.4150. Exact mass for **8**: calcd for $^{59}Co^{12}C_{27}{}^{11}B_4{}^{1}H_{35}{}^{+}$, 462.2443; found, 462.2451. Visible–UV absorptions (nm, in CH_2Cl_2): for **7**, 248 (54%), 278 (89%), 302 (100%); for **8**, 274 (90%), 302 (100%), 420 (5%).

Synthesis of $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)_2$ (9). Decapitation of **7** (0.160 g, 0.20 mmol) by the method described above for the corresponding conversion of **1** to **3** gave 0.150 g (0.19 mmol, 95%) of yellow crystalline **9**. Exact mass for **9**: calcd for $^{59}Co_2{}^{12}C_{42}{}^{11}B_6{}^{1}H_{62}{}^{+}$, 750.4074; found, 750.4122. Visible–UV absorptions (nm, in CH_2Cl_2): 248 (48%), 292 (100%), 374 (2%), 440 (1.5%).

Synthesis of $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2C_6H_4$ (10). The procedure was identical with that employed in the preparation of **4**, except that the anion $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ (5^- in the preceding paper[2]) was used in place of $Et_2C_2B_4H_5^-$. A 0.879-g (2.50 mmol) sample of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$ and 0.40 g (1.3 mmol) of 1,4-bis(tetramethylcyclopentadienyl)benzene were separately deprotonated with *n*-butyllithium and $CoCl_2$ was reacted with the hydrocarbon anion as described for **4** above. Subsequent reaction with the ruthenium complex anion and workup via the procedure outlined earlier gave, following chromatography on silica in dichloromethane, one green band which on evaporation of solvent afforded emerald crystals of **10**, 0.145 g (0.130 mmol, 11%). Visible–UV absorptions (nm, in CH_2Cl_2): 620 (1.5%), 464 (18%), 324 (77%), 238 (100%).

Synthesis of $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}Me_4C_5)]_2(C_6H_4)_2$ (11). The preparation of **11** was identical with that of **10** except that the hydrocarbon reagent employed was the mixture (A and B) described above in the synthesis of **7**. A 0.110-g sample of the hydrocarbon mixture, containing 0.19 mmol of A and 0.13 mmol of B, was utilized together with 0.180 g (0.51 mmol) of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$, 0.066 g (0.51 mmol) of $CoCl_2$, and 0.51 mmol of *tert*-butyllithium for each of the two deprotonations required (vide supra). Workup as before, with chromatography of the product mixture on a silica column in dichloromethane, gave two green bands. Each of these bands, on TLC analysis, yielded two bands; of the four bands, three were obtained in quantities too small for characterization, but one of these (R_f 0.60), obtained from the second column band, was isolated as emerald crystals of **11**, 30 mg (13%). Visible–UV absorptions (nm, in CH_2Cl_2): 250 (72%), 286 (74%), 332 (100%), 620 1.3%).

Synthesis of $[(\eta^6\text{-}MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5\text{-}C_5H_4)]_2$ (12). The procedure employed was analogous to the preparation of **1**, with the anion $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ used in place of $Et_2C_2B_4H_5^-$. A 0.570-g (1.60 mmol) sample of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$ was deprotonated with an equivalent amount of *tert*-butyllithium in pentane, and the fulvalenide dianion was generated as described above from 1.6 mmol of NaCp in THF and 0.8 mmol of I_2. The combination of these reagents with 1.6 mmol of $CoCl_2$ and subsequent workup gave, on column chromatography on silica, two green bands of which the first proved to be $CpCo(Et_2C_2B_3H_3)Ru(\eta^6\text{-}MeC_6H_4CHMe_2)$ (**11a** in the preceding article[2]), yield 30 mg. The second band was emerald crystalline **12**, 155 mg (0.16 mmol, 20%). Visible–UV absorptions (nm, in CH_2Cl_2): 246 (100%), 282 (92%), 322 (89%), 452 (22%), 640 (1.5%).

X-ray Structure Determinations on 1, 6, and 10. Single crystals of each compound were grown by slow evaporation from dichloromethane at 0 °C, to which hexane had been added until slight turbidity appeared. The procedures employed in data collection and refinement were as described in the accompanying paper.[2]

Solution and Refinement of the Structures. For each compound, three-dimensional Patterson syntheses were used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. Full matrix least-squares calculations were carried out as described elsewhere, and anisotropic temperature factors were introduced. Further Fourier difference syntheses now permitted location of the hydrogen atoms in **1**. In **10**, all of the non-methyl hydrogens were located, but the methyl hydrogen positions were calculated. In **6**, only the B–H terminal hydrogens were found, and all others, including those in the B–H–B bridges, were placed in calculated positions. Full matrix least-squares refinement was carried out as previously described.[15] Anisotropic temperature factors were introduced for the non-hydrogen atoms.

The models converged to the *R* values given in Table IV. Final difference Fourier maps were featureless. Listings of the observed and calculated structure factors are available together with thermal parameters as supplementary material.

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Supplementary Material Available: Tables of thermal parameters and mean planes for **1**, **6**, and **10** (15 pages); calculated and observed structure factors for **1**, **6**, and **10** (52 pages). Ordering information is given on any current masthead page.

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[15] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.