

X-ray Crystal Structure of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Re}(\text{NO})(\text{PPh}_3)(\text{I})$ (4). Irregular deep red prisms of 4^{14} were obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$. Data were collected as described in Table III. Cell constants and an orientation matrix were obtained from least-squares refinement, using the setting angles of 15 reflections in the range $20^\circ < 2\theta < 26^\circ$. The space group was determined from the systematic absences ($h00, h = 2n; 0k0, k = 2n; 00l, l = 2n$) and subsequent least-squares refinement.

(39) Frenz, B. A. The Enraf-Nonius CAD 4 SDP—A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In *Computing and Crystallography*; Schenk, H.; Olthof-Hazelkamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

A total of 2645 reflections were collected. Corrections were applied and the structure was solved as described for $3e\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ above. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized positions.

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for iodide complex **4** (2 pages); calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

Arene-Metal-Carborane Triple-Decker Sandwiches. Designed Synthesis of Homo- and Heterobimetallic Complexes of Cobalt, Iron, Ruthenium, and Osmium¹

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Abstract: This paper describes the systematic preparation and characterization of new families of triple-decker sandwich complexes incorporating formal *cyclo*- $\text{Et}_2\text{C}_2\text{B}_3\text{H}_3^{4-}$ bridging ligands, including the first species of this class containing second- or third-row transition metals. Complexes of general formula $(\text{L})\text{M}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{M}'(\text{L})$ ($\text{M} = \text{Ru, Os}; \text{M}' = \text{Co, Ru}; \text{L} = \text{cymene [p-isopropyltoluene], Cp, or C}_5\text{Me}_5$) were obtained in stepwise fashion via (1) synthesis of *closo*- $(\text{L})\text{M}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ metal-lacarboranes, (2) "decapitation" (apex BH removal) of these complexes to give *nido*- $(\text{L})\text{M}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$, (3) bridge deprotonation to form the corresponding mono- or dianion, and (4) reaction of the anion with an arene metal halide to generate the desired triple-decker compound. In addition, the cobalt-iron triple-decker $\text{CpCo}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{FeCp}$ was prepared via treatment of $(\eta^6\text{-C}_8\text{H}_{10})\text{Fe}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_4)^-$ with Na^+Cp^- and CoCl_2 followed by air oxidation. The reaction of $(\text{CO})_3\text{RuCl}_2$ with $(\text{C}_5\text{Me}_5)\text{-Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)^{2-}$ gave the "pseudo-triple-decker" complex $(\text{C}_5\text{Me}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{CO})_3$. The triple-deckers, especially those containing osmium, are susceptible to chlorination by RuCl_3 , OsCl_3 , or dichloromethane, forming exclusively the 4-chloro derivatives. All of the characterized triple-decker complexes are air-stable crystalline solids (except for the osmium-ruthenium species, which are air sensitive) and have been structurally characterized from their ^{11}B and ^1H NMR, infrared, visible-UV, and unit- and high-resolution mass spectra, further supported by X-ray crystallographic analyses of (cymene) $\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{cymene})$ (**10**) and $\text{CpCo}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{cymene})$ (**11a**). Crystal data for **10**: mol wt 561.13; space group $P\bar{1}$; $Z = 2$; $a = 10.409$ (3), $b = 11.268$ (5), $c = 12.002$ (4) Å; $\alpha = 96.16$ (3), $\beta = 99.49$ (2), $\gamma = 106.69$ (3)°; $V = 1312$ (2) Å³; $R = 0.043$ for 4777 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **11a**: mol wt 476.92; space group $P2_1/c$; $Z = 4$; $a = 8.808$ (6), $b = 17.708$ (8), $c = 14.194$ (8) Å; $\beta = 103.50$ (4)°; $V = 2153$ (4) Å³; $R = 0.058$ for 3289 reflections having $F_o^2 > 3\sigma(F_o^2)$.

A primary goal in our research is the tailored synthesis of electron-delocalized organometallic oligomers and polymers, and our overall strategy entails the construction of progressively larger polymetallic systems via systematic, controlled methods.² The ultimate objective is to develop preparative routes to substances having specified structure-correlated properties (e.g., conducting polymers) via the assembly of selected metals and ligands. In earlier work we demonstrated¹⁻³ that arene and small carborane ligands, in combination with transition metals, form stable, robust

complexes that are amenable to chemical modification and in some cases exhibit reversible electrochemical changes in metal oxidation states;⁴ moreover, reasonably general syntheses of such complexes, and their small *nido*-carborane precursors, are now available.²

In our approach, B- and C-substituted derivatives of the *nido*-2,3-dicarbahexaborane $\text{C}_2\text{B}_4\text{H}_8$ are bridge deprotonated, η^3 -coordinated to transition metals to create metallocarborane clusters, and subsequently incorporated into larger carborane-metal-arene systems that are stabilized by the carborane units. In recent publications we have described synthetic routes to mono-, bis- and tris(carboranyl) derivatives that have been specifically tailored as ligands for this purpose and have aryl, polaryl, or alkyl substituents.⁵ With these materials in hand, we have undertaken to develop methods for converting them into arene-metal-carborane double- and triple-decker sandwich complexes incorporating

(1) Organotransition-Metal Metallocarboranes. 12. (a) For part 11, see: Whelan, T.; Spencer, J. T.; Pourian, M. R.; Grimes, R. N. *Inorg. Chem.* **1987**, *26*, 3116. (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.

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(3) (a) Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 328. (b) Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 323. (c) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335. (d) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1985**, *4*, 896. (e) Swisher, R. G.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1985**, *4*, 882 and references therein.

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Table I. 115.8-MHz ¹¹B FT NMR Data

compd ^a	δ (J _{BH} , Hz)	rel areas
(C ₆ H ₆)Ru(Et ₂ C ₂ B ₄ H ₄) (1) ^b	8.70 (151), 3.80 (130), 0.42 (142)	1:1:2
(C ₁₀ H ₁₄)Ru(Et ₂ C ₂ B ₄ H ₄) (2) ^b	7.54 (148), 4.14 (138), 0.54 (148)	1:1:2
(C ₁₀ H ₁₄)Ru[(PhCH ₂) ₂ C ₂ B ₄ H ₄] (3) ^b	8.58 (138), 5.10 (127), 1.36 (127)	1:1:2
(C ₆ Me ₆)Ru(Et ₂ C ₂ B ₄ H ₄) (4) ^b	5.62 (138), 4.50 (150), 1.03 (138)	1:1:2
(C ₁₀ H ₁₄)Ru(Et ₂ C ₂ B ₃ H ₅) (5) ^c	0.48 (138), -3.08 (138)	1:2
CpCo(Et ₂ C ₂ B ₄ H ₄) (6) ^b	8.52 (150), ^d 2.55 (150)	1:1
(C ₅ Me ₅)Co(Et ₂ C ₂ B ₄ H ₄) (7) ^c	12.10 (134), 4.28 (162), 2.59 (185)	1:2:1
CpCo(Et ₂ C ₂ B ₃ H ₅) (8) ^{f,g}	8.87, 2.37	1:2
(C ₅ Me ₅)Co(Et ₂ C ₂ B ₃ H ₅) (9) ^b	7.47 (146), 3.94 (134)	1:2
(C ₁₀ H ₁₄) ₂ Ru ₂ (Et ₂ C ₂ B ₃ H ₅) (10) ^c	38.10 (127), 4.27 (138)	1:2
(C ₁₀ H ₁₄)Ru(Et ₂ C ₂ B ₃ H ₅)CoCp (11a) ^c	47.51 (150), 4.96 (150)	1:2
(C ₁₀ H ₁₄)Ru(Et ₂ C ₂ B ₃ H ₅ Cl)CoCp (11b) ^{f,g}	35.00, 10.50, -3.40	1:1:1
(C ₁₀ H ₁₄) ₂ RuOs(Et ₂ C ₂ B ₃ H ₅) (12a) ^c	23.59 (127), -2.13 (138)	1:2
(C ₁₀ H ₁₄) ₂ RuOs(Et ₂ C ₂ B ₃ H ₅ Cl) (12b) ^c	21.40 (92), 10.67, ^e -2.35 (127)	1:1:1
(C ₁₀ H ₁₄)Os(Et ₂ C ₂ B ₃ H ₅)CoCp (13a) ^c	32.26 (150), -1.45 (138)	1:2
(C ₁₀ H ₁₄)Os(Et ₂ C ₂ B ₃ H ₅ Cl)CoCp (13b) ^c	28.80 (104), 10.35, ^e -1.03 (138)	1:1:1
(CO) ₃ Ru(Et ₂ C ₂ B ₃ H ₅)Co(C ₅ Me ₅) (17) ^c	48.27 (127), 7.14 (138)	1:2

^aShifts relative to BF₃·OEt₂, positive values downfield. ^bDichloromethane solution. ^c*n*-Hexane solution. ^dOverlapping signals. ^eSinglet. ^fCDCl₃ solution. ^gCoupling not resolved.

first-, second-, or third-row transition elements. Triple-decker complexes having *cyclo*-RR'C₂B₃H₃ middle rings and C₅R₅ or arene end rings⁶ are attractive candidates as construction units for the preparation of large multimetal systems, because of their stability under a variety of conditions, electron delocalization, and accessibility: as we describe below, it is now possible to prepare families of such species in which the metals, end rings, and/or substituents on the C₂B₃ ring can be varied.

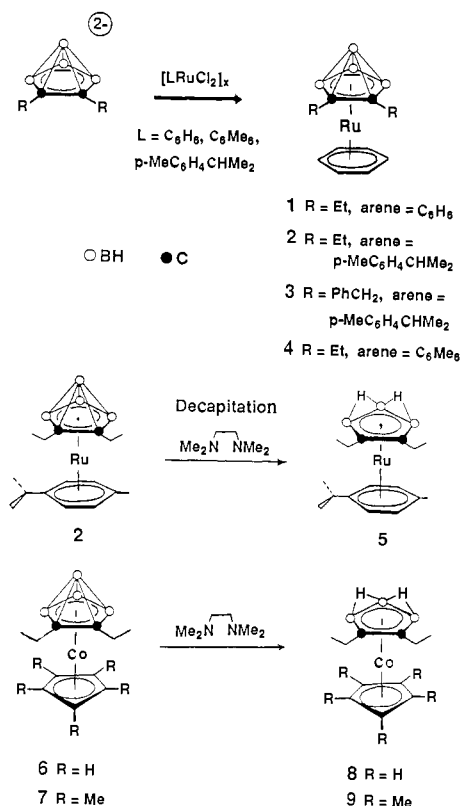
Although isomers of the dicobalt metallacarboranes⁷ Cp₂Co₂RR'C₂B₃H₃ (the first examples of electrically neutral triple-decker complexes) were prepared in this laboratory 16 years ago⁸ and numerous derivatives have been characterized, general methods for preparing carborane-based triple-deckers have not been available. (Closely related triple- and multiple-decker complexes incorporating 1,3-C₂B₂, 1,2- and 1,4-C₂B₂, or C₂B bridging ligands have, however, been reported, particularly from the Siebert and Herberich groups.⁹) In this paper we report tailored syntheses of R₂C₂B₃H₃-bridged triple-decker sandwiches having arene end rings and describe the structural and spectroscopic characterization of a number of such complexes. The accompanying paper¹⁰ details the further extension of this chemistry to linked double- and triple-decker systems.

Results and Discussion

Preparation of Arene-Metal-Carborane Sandwich Complexes.

As starting building-block units for use in triple-decker synthesis, compounds of the type (arene)M(R₂C₂B₄H₄) were synthesized as depicted in Scheme I. Several preparative routes were explored, but where feasible we preferred the reactions of arene metal halides with carborane dianions, as in the synthesis of the ruthenium complexes 1-4, which were isolated via chromatography on silica. In this approach we have taken note of the recent discovery¹¹ by Hosmane and co-workers that *nido*-RR'C₂B₄H₆ carboranes can be doubly deprotonated via reaction with NaH followed by *n*-C₄H₉Li to give stable Na⁺Li⁺(RR'C₂B₄H₄)²⁻ double salts. We found that not only is this reaction sequence generally applicable to our *nido*-carborane starting materials, but it also works with *nido*-(L)M(RR'C₂B₃H₅) metallacarboranes; in the latter case the

Scheme I



dianion can be obtained with *n*-C₄H₉Li alone, as described below. The metallacarborane dianions, in turn, have given us an entry to the planned synthesis of MC₂B₄ clusters of second- and third-row transition metals, a class of metallacarboranes of which the only previously reported examples are (Et₃P)₂Pt(R₂C₂B₄H₄) (R = H, Me)¹² and (CO)₃Os[(Me₃Si)₂C₂B₄H₄].¹³ This approach¹⁴ to arene-metal-carborane sandwiches has the advantage that only two reacting species are involved, thereby minimizing the formation of side products, and is an efficient route to such compounds in that the arene is bound to the metal prior to the introduction of the carborane substrate. Compounds 1 and 4 were obtained as colorless, air-stable crystals, while 2 and 3 were

(6) Grimes, R. N. *Coord. Chem. Rev.* **1979**, *28*, 47.

(7) Viewed as seven-vertex pentagonal-bipyramidal MM'C₂B₃ clusters, the metals occupy the apical (1,7) vertices and the carbon atoms are in equatorial (2,3 or 2,4) locations.

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

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

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(11) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600.

(12) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 1186.

(13) Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* **1984**, *3*, 1119.

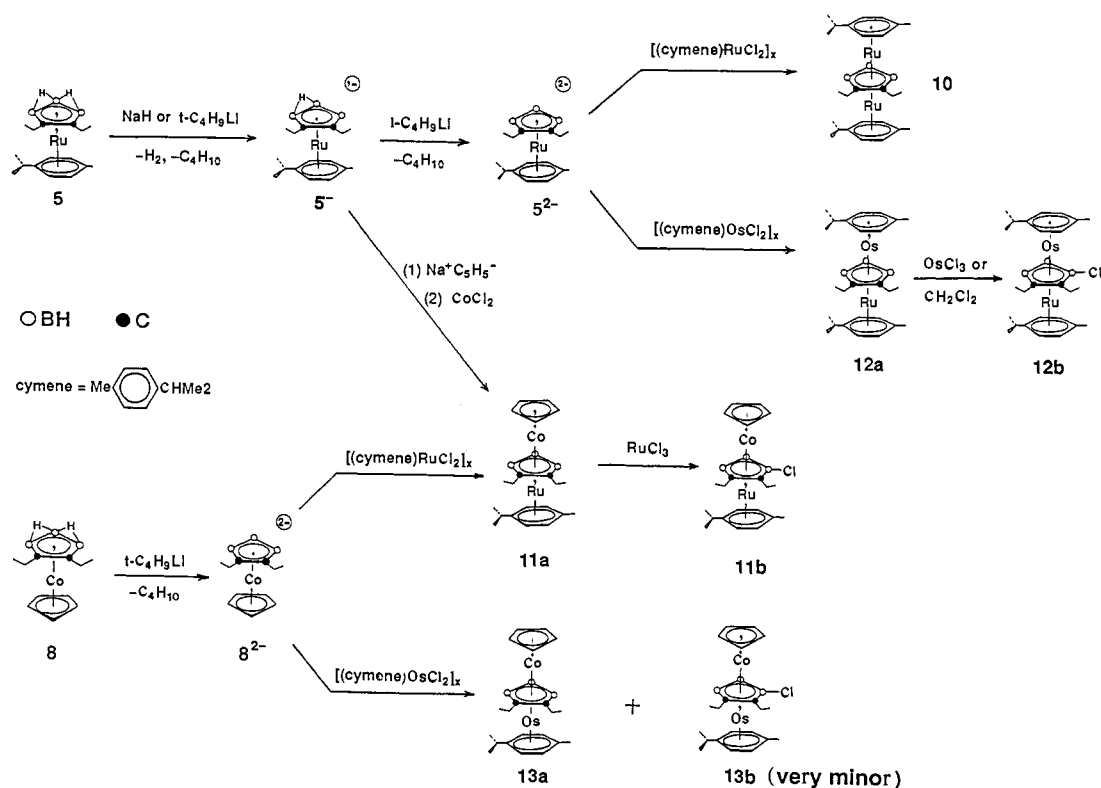
(14) A similar method has been utilized to prepare (arene)FeC₂B₃H₁₁ icosahedral clusters. See: Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77.

Table II. 300-MHz ¹H FT NMR Data

compd	δ^a - ^c	rel areas
1	5.35 s (C ₆ H ₆), 2.45 m (CH ₂), 2.37 m (CH ₂), 1.22 m (CH ₃)	6:2:2:6
2	5.31 d (C ₆ H ₄), 5.22 d (C ₆ H ₄), 2.58 m (CHMe ₂), 2.42 m (CH ₂), 2.38 m (CH ₂), 2.08 s (CH ₃ C ₆ H ₄), 1.41 m (CHMe ₂), 1.20 m (CH ₃ CH ₂)	2:2:1:2:2:3:6:6
3	7.15 m (C ₆ H ₅), 5.00 d (C ₆ H ₄), 4.98 d (C ₆ H ₄), 3.95 d (PhCH ₂), 3.88 d (PhCH ₂), 2.40 m (CHMe ₂), 2.01 s (CH ₃ C ₆ H ₄), 1.08 d (CHMe ₂)	10:2:2:2:2:1:3:6
4	2.24 m (CH ₂), 2.19 m (CH ₂), 2.15 s (C ₆ Me ₆), 1.17 m (CH ₃)	2:2:18:6
5	5.41 d (C ₆ H ₄), 5.33 d (C ₆ H ₄), 2.58 m (CHMe ₂), 2.10 m (CH ₂), 2.09 s (CH ₃ C ₆ H ₄), 1.94 m (CH ₂), 1.21 d (CHMe ₂), 1.09 m (CH ₃ CH ₂), -5.54 s (B-H-B)	2:2:1:2:3:2:6:6:2
6	4.78 s (C ₅ H ₅), 2.68 m (CH ₂), 2.44 m (CH ₂), 1.29 m (CH ₃)	5:2:2:6
7	2.51 m (CH ₂), 2.28 m (CH ₂), 1.77 s (C ₅ Me ₅), 1.19 m (CH ₃)	2:2:15:6
8	4.66 s (C ₅ H ₅), 2.13 m (CH ₂), 1.94 m (CH ₂), 1.18 m (CH ₃), -6.01 br (B-H-B)	5:2:2:1:2
9	2.09 m (CH ₂), 1.89 m (CH ₂), 1.76 s (C ₅ Me ₅), 1.10 m (CH ₃), -5.54 br (B-H-B)	2:2:15:6:2
10	4.96 d (C ₆ H ₄), 4.84 d (C ₆ H ₄), 2.58 m (CHMe ₂), 2.54 q (CH ₂), 2.00 s (CH ₃ C ₆ H ₄), 1.33 t (CH ₃ CH ₂), 1.19 d (CHMe ₂)	4:4:2:4:6:6:12
11a	4.92 d (C ₆ H ₄), 4.81 d (C ₆ H ₄), 4.46 s (C ₅ H ₅), 2.78 m (CH ₂), 2.64 m (CH ₂), 2.53 m (CHMe ₂), 1.97 s (CH ₃ C ₆ H ₄), 1.48 m (CH ₃ CH ₂), 1.18 d (CHMe ₂)	2:2:5:2:2:1:3:6:6
11b	4.91 d (C ₆ H ₄), 4.82 d (C ₆ H ₄), 4.49 s (C ₅ H ₅), 2.28-2.85 m (CH ₂), 2.02 s (CHMe ₂), 1.47 m (CH ₃ C ₆ H ₄), 1.20 d (CHMe ₂)	2:2:5:5:3:6:6
12a	5.16 d (C ₆ H ₄), 5.04 d (C ₆ H ₄), 5.00 d (C ₆ H ₄), 4.90 d (C ₆ H ₄), 2.46-2.75 m (CH ₂), 2.10 s (CHMe ₂), 2.00 s (CH ₃ C ₆ H ₄), 1.29 m (CH ₃ C ₆ H ₄), 1.22 d (CHMe ₂), 1.19 d (CHMe ₂)	2:2:2:2:6:3:3:6:6:6
12b	5.31 d (C ₆ H ₄), 5.19 d (C ₆ H ₄), 5.18 d (C ₆ H ₄), 5.10 d (C ₆ H ₄), 5.06 br (C ₆ H ₄), 5.02 d (C ₆ H ₄), 2.45-2.73 m (CH ₂ , CHMe ₂), 2.14 s (CH ₃ C ₆ H ₄), 2.00 s (CH ₃ C ₆ H ₄), 1.18-1.26 m (CHMe ₂)	1:2:1:1:2:1:6:3:3:1:8
13a	5.21 d (C ₆ H ₄), 5.15 d (C ₆ H ₄), 4.55 s (C ₅ H ₅), 2.95 m (CH ₂), 2.74 m (CH ₂), 2.48 m (CHMe ₂), 2.17 s (CHMe ₂), 1.45 m (CH ₃), 1.20 d (CHMe ₂)	2:2:5:2:2:1:3:6:6
17	2.78 m (CH ₂), 2.50 m (CH ₂), 1.69 s (C ₅ Me ₅), 1.40 m (CH ₃)	2:2:15:6

^aCDCl₃ solution. ^bShifts relative to (CH₃)₄Si. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. ^cB-H_{terminal} resonances are broad quartets and mostly obscured by other signals.

Scheme II



colorless oils; in the case of **2** slight sensitivity to air was noted.

The corresponding reaction of (cymene)osmium dichloride (cymene = *p*-isopropyltoluene) did not yield an analogous osmacarborane; however, as described below, this reagent was useful in the synthesis of osmium-containing triple-deckers. The cyclopentadienylcobalt complexes **6** and **7**, both isolated as orange air-stable crystals, were prepared from CoCl₂, NaC₅R₅ (R = H or Me), and Na⁺Et₃C₂B₄H₅⁻ via a modification of the method originally reported^{8b} for the synthesis of CpCoMe₂C₂B₄H₄.

In order to utilize *closo*-metallacarborane complexes such as **1-4** as stacking units in the preparation of larger sandwiches, they must first be "decapitated", i.e., the apex BH unit removed.² This

is readily accomplished via treatment with wet *N,N,N',N'*-tetramethylethylenediamine (TMEDA), as illustrated by the formation of the ruthenium complex **5** and the cobalt complexes **8** and **9** (Scheme I). Compound **5** is a colorless oil and, in contrast to its precursor **2**, is very air stable; the decapitated cobalt complex **8** is a slightly air-sensitive oil, while its pentamethyl counterpart **9** was isolated as extremely air-stable lemon yellow crystals. The characterization of compounds **1-9** via ¹¹B and ¹H FT NMR (Tables I and II), infrared (Table III), visible-ultraviolet, and mass spectroscopy (Experimental Section) was straightforward.

Synthesis of Homo- and Heterobimetallic Triple-Decker Sandwich Complexes. Several methods were employed in com-

Table III. Infrared Absorptions (cm⁻¹, CCl₄ Solutions vs CCl₄)^a

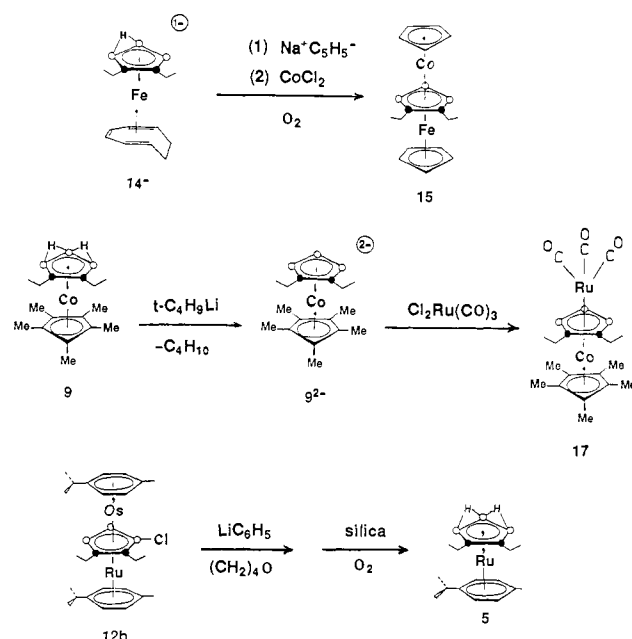
compd	absorptions
1	3845 m, 3817 m, 3676 s, 3641 m, 2551 s, 2368 s, 2326 m, 1700 s, 1560 vs, 1532 vs, 1518 sh, 1503 m, 1419 m, 1265 m, 1215 m, 1110 w, 1054 w, 1019 m, 970 m
2	3838 w, 3803 w, 3676 w, 2966 s, 2924 vs, 2868 m, 2537 vs, 1693 s, 1560 s, 1539 m, 1250 m, 1222 w, 1124 w, 1011 m
3	3838 m, 3817 m, 3669 m, 2973 w, 2931 m, 2860 w, 2537 w, 2375 m, 2333 m, 1700 s, 1560 s, 1532 s, 1419 m, 1257 w, 1222 vw, 1011 vw, 976 vw
4	3817 w, 3676 w, 2530 w, 2410 s, 2361 m, 2340 m, 1595 m, 1553 vs, 1264 m, 1215 m, 1110 w, 1054 w, 1012 m, 978 m
5	3838 m, 3810 m, 3676 m, 2966 m, 2931 m, 2853 m, 2607 vw, 2375 m, 2319 m, 1700 s, 1560 s, 1532 s, 1426 s, 1257 m, 1124 m, 1018 m
6	2593 w, 2551 w, 2115 br, 1714 sh, 1630 s, 1567 sh, 1257 m, 1222 m, 1103 w, 1068 w, 1011 m, 970 m
7	3845 m, 3824 m, 3676 m, 2980 m, 2924 m, 2860 vw, 2544 m, 2368 m, 2333 m, 1700 s, 1560 s, 1539 s, 1419 m, 1271 m, 1222 w, 1068 vw, 1011 m, 969 m
8	3831 m, 3810 m, 3676 m, 2959 m, 2917 m, 2868 m, 2516 m, 2368 m, 2333 m, 1700 s, 1560 s, 1539 s, 1412 m, 1243 m, 1209 w, 1068 vw, 1004 w
9	3838 m, 3810 m, 3669 m, 2966 m, 2924 m, 2860 m, 2523 m, 2361 w, 2333 w, 1701 s, 1560 s, 1539 s, 1271 m, 1208 m, 1082 vw, 1004 m, 976 m
10	3824 w, 3877 w, 2959 m, 2882 m, 2474 m, 2361 w, 1595 m, sh, 1533 s, 1264 m, 1215 m, 1117 m, 1068 w, 1004 m, 969 m
11a	3824 w, 3803 w, 3669 w, 2973 m, 2924 m, 2860 w, 2481 m, 1728 w, 1700 m, 1560 m, 1532 sh, 1257 m, 1222 w, 1110 w, 1075 w, 1004 m, 969 w
11b	3845 w, 3824 w, 3801 w, 3677 m, 3071 w, 2959 s, 2931 s, 2860 sh, 2509 w, 2362 w, 1700 m, 1560 s, 1525 m, 1250 vs, 1131 sh, 1096 vs, 1025 vs
12b	3655 w, 3585 w, 2966 vs, 2924 vs, 2868 m, 2495 m, 2361 w, 1939 w, 1567 w, 1454 m, 1384 w, 1250 w, 997 w, 934 w
13a	3782 w, 3641 w, 2966 m, 2931 m, 2853 m, 2481 m, 2354 w, 1574 w, 1264 w, 1208 w, 1117 w, 1004 m, 976 w
13b	3852 w, 3592 w, 2973 w, 2931 w, 2495 w, 2389 w, 2298 w, 1581 sh, 1546 s, 1257 m, 1208 m, 1124 w, 1060 w, 1004 m, 976 m
15	3831 w, 3683 w, 2966 m, 2917 m, 2882 w, 2509 m, 2534 w, 2333 w, 1581 sh, 1546 s, 1257 m, 1215 w, 1131 w, 1075 w, 990 m, 976 w
17	3803 w, 3739 w, 3683 w, 2980 m, 2938 m, 2903 sh, 2509 m, 2066 vs, 1996 vs, 1581 m, 1539 s, 1377 m, 1264 m, 1215 m, 1124 w, 1075 w, 1018 m, 976 m

^aLegend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

binning monometallic arene-metal and arene-metal-carborane units to form triple-decker species. As shown in Scheme II, the *nido*-ruthenacarborane complex **5** was singly deprotonated to generate the monoanion **5⁻**. Removal of the second bridging proton formed the orange-red dianion **5²⁻**, which was reacted with (cymene)ruthenium dichloride to give the diruthenium sandwich (η^6 -MeC₆H₄CHMe₂)₂Ru₂(Et₂C₂B₃H₃) (**10**), obtained as dark orange air-stable crystals. Alternatively, treatment of the monoanion **5⁻** with CoCl₂ and NaC₅H₅ gave the heterobimetallic triple-decker sandwich CpCo(Et₂C₂B₃H₃)Ru(η^6 -MeC₆H₄CHMe₂) (**11a**), an emerald green, very air-stable crystalline solid.

The cobalt-ruthenium sandwich **11a** was also prepared by a different route, involving the addition of the CpCo(Et₂C₂B₃H₃)²⁻ dianion **8²⁻** to (cymene)ruthenium dichloride as shown. This result is significant with respect to designed synthesis, as it demonstrates that some flexibility is achievable in the construction of sandwich complexes of desired composition. As a result of observations on the synthesis of osmium-ruthenium complexes (*vide infra*), we suspected that osmium or ruthenium halides were capable of effecting chlorine substitution on boron; accordingly, we treated **11a** with RuCl₃ in acetone and obtained the 4-chloro derivative **11b**, also a green air-stable solid, in high yield (Scheme II). Complex **11a** is an exceedingly robust material, as demonstrated by its unreactivity toward hexamethylbenzene at high temperature

Scheme III



or under ultraviolet light; this observation contrasts sharply with the facile displacement of cymene from (cymene)ruthenium dichloride by hexamethylbenzene at 180 °C.¹⁵ Compounds **10**, **11a**, and **11b** were fully characterized spectroscopically (Tables I-III and Experimental Section), and the assigned structures were confirmed by X-ray crystallographic analyses of **10** and **11a** as described below.

Similar chemistry was employed to generate heterobimetallic osmium-containing triple-deckers. Thus, the reaction of **5²⁻** with (cymene)osmium dichloride produced yellow crystalline (η^6 -MeC₆H₄CHMe₂)Ru(Et₂C₂B₃H₃)Os(η^6 -MeC₆H₄CHMe₂) (**12a**), accompanied by its 4-chloro derivative **12b**, a golden, slightly air-sensitive crystalline solid. Under the usual conditions of synthesis followed by workup in dichloromethane (see Experimental Section), the latter species was isolated in much larger yield, indicating that the propensity of **12a** to chlorination is greater than that of **10** or **11a** (whose chlorinated derivatives were not observed to form under comparable conditions). Investigation revealed that **12b** formed on exposure of **12a** to CH₂Cl₂ during workup. However, even in nonhalogenated solvents **12b** was obtained as a byproduct unless extremely pure [(cymene)OsCl₂]₂ was employed, owing to the presence of OsCl₃ in that reagent. Direct treatment of **12a** with OsCl₃ generates **12b** rapidly and quantitatively.

A cobalt-osmium sandwich, CpCo(Et₂C₂B₃H₃)Os(η^6 -MeC₆H₄CHMe₂) (**13a**), was formed, together with the minor 4-chlorinated product **13b**, by reaction of **8²⁻** with (cymene)osmium dichloride. The osmium-cobalt triple-deckers, like their ruthenium-cobalt counterparts **11a** and **11b**, form beautiful emerald green crystals, which appear to be stable in air over extended periods.

In order to provide an "all-first-transition series" heterobimetallic triple-decker for comparative purposes, the iron-cobalt sandwich complex CpCo(Et₂C₂B₃H₃)FeCp (**15**) was prepared from the previously described¹⁶ cyclooctatrienyl ferracarborane (η^6 -C₈H₁₀)Fe(Et₂C₂B₃H₃) (**14**) as shown in Scheme III. In this reaction, a CpCo unit was coordinated to the C₂B₃ ring as intended, but in addition the cyclooctatriene ligand was displaced from iron by cyclopentadiene; although replacement of Fe-complexed C₈H₁₀ by *arenes* has been routinely employed in our laboratory,² we had not previously observed the substitution of this ligand by C₅H₅⁻. Complex **15** is a paramagnetic (29-electron),

(15) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

(16) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1983**, *2*, 506.

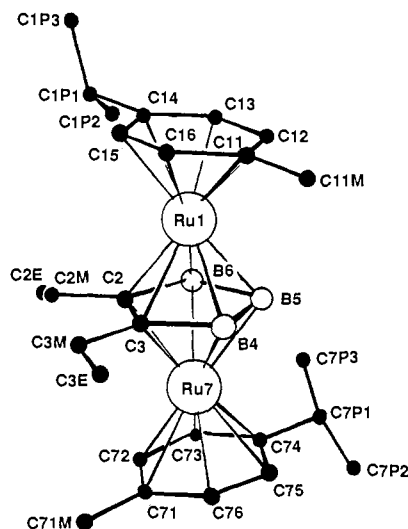


Figure 1. PLUTO drawing of the molecular structure of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$ (**10**) (hydrogen atoms are omitted for clarity).

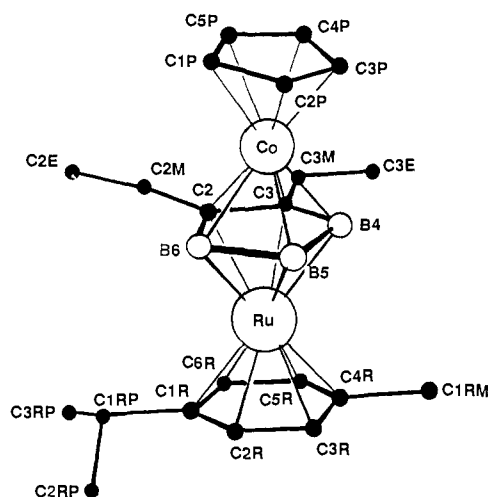


Figure 2. PLUTO drawing of the molecular structure of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}$ (**11a**), with hydrogens omitted.

black-brown air-stable crystalline solid, which exhibits no useful NMR spectra but was characterized from its UV-visible and mass spectra. Curiously, when the analogous *closo*-ferracarborane ($\eta^6\text{-C}_8\text{H}_{10}$) $\text{Fe}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_6)$ (**16**) was treated with $\text{Na}^+\text{C}_5\text{H}_5^-$, no reaction was observed.

A different synthetic approach to bimetallic complexes was explored via the reaction of the dark red $(\text{C}_5\text{Me}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)^{2-}$ dianion **9**²⁻ with $\text{Cl}_2\text{Ru}(\text{CO})_3$, which afforded the "pseudo-triple-decker" complex $(\text{CO})_3\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Co}(\eta^5\text{-C}_5\text{Me}_5)$ (**17**) as emerald air-stable crystals (Scheme III). In addition to the NMR and mass spectroscopic data that define the $\text{RuC}_2\text{B}_3\text{Co}$ cluster in **17**, the presence of CO ligands on ruthenium is clearly evident in the strong C–O stretching bands near 2000 cm^{-1} in the IR spectrum. Compounds of type **17** (of which there is one earlier analogue, $(\text{CO})_3\text{Fe}(\text{Me}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}$, prepared several years ago¹⁷) have potential utility as stacking modules, if the carbonyl groups can be displaced by arene-metal and/or arene-carborane units; this possibility is under investigation.

In an attempt to replace the chlorine substituent on **12b** with phenyl, the complex was treated with phenyllithium in THF solution. Surprisingly, the only product isolated following column chromatography on silica was the double-decker sandwich **5** (Scheme III), obtained in nearly quantitative yield. In contrast,

Table IV. Experimental X-ray Diffraction Parameters and Crystal Data on **10** and **11a**

	10	11a
M_r	561.13	476.92
space group	$P\bar{1}$	$P2_1/c$
a , Å	10.409 (3)	8.808 (6)
b , Å	11.268 (5)	17.708 (8)
c , Å	12.002 (4)	14.194 (8)
α , deg	96.16 (3)	
β , deg	99.49 (2)	103.50 (4)
γ , deg	106.69 (3)	
V , Å ³	1312 (2)	2153 (4)
μ , cm ⁻¹ (Mo $K\alpha$)	11.32	14.87
$D(\text{calcd})$, g cm ⁻³	1.42	1.47
A^a	0.65	0.65
B^a	0.35	0.35
2θ range, deg	1.5–54	1.5–54
reflectns obsd	5216	4652
reflectns refined	4777	3289
R	0.043	0.058
R_w	0.061	0.081
max shift in final cycle	0.42	0.02
largest peak in final diff map, e/Å	0.70	0.95
esd unit weight	2.0	2.4
Z	2	4

^aSee text.

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

Bond Distances			
Ru1–Ru7	3.478 (2)	Ru7–C71'	2.20 (3)
Ru1–C2	2.225 (4)	Ru7–C72	2.223 (5)
Ru1–C3	2.244 (5)	Ru7–C73	2.191 (5)
Ru1–B4	2.228 (5)	Ru7–C74	2.178 (6)
Ru1–B5	2.212 (6)	Ru7–C75	2.22 (1)
Ru1–B6	2.205 (6)	Ru7–C75'	2.02 (6)
Ru1–C11	2.189 (5)	Ru7–C76	2.218 (6)
Ru1–C12	2.159 (5)	Ru7–C76'	2.12 (4)
Ru1–C13	2.181 (5)	C2–C3	1.480 (6)
Ru1–C14	2.250 (5)	C2–C2M	1.498 (6)
Ru1–C15	2.217 (5)	C2–B6	1.574 (7)
Ru1–C16	2.209 (5)	C3–C3M	1.507 (7)
Ru7–C2	2.216 (4)	C3–B4	1.582 (7)
Ru7–C3	2.211 (5)	B4–B5	1.739 (8)
Ru7–B4	2.223 (6)	B5–B6	1.707 (8)
Ru7–B5	2.187 (6)	C2M–C2E	1.49 (1)
Ru7–B6	2.229 (5)	C3M–C3E	1.494 (9)
Ru7–C71	2.296 (5)	C11–C12	1.386 (9)
		C11–C16	1.457 (9)
		C11–C11M	1.526 (8)
		C12–C13	1.425 (8)
		C13–C14	1.425 (7)
		C14–C15	1.409 (8)
		C14–C1P1	1.510 (7)
		C15–C16	1.353 (9)
		C1P1–C1P3	1.508 (8)
		C1P1–C1P2	1.52 (1)
		C71–C76	1.38 (1)
		C71–C71M	1.46 (2)
		C71–C72	1.47 (1)
		C72–C73	1.408 (9)
		C73–C74	1.410 (9)
		C74–C75	1.43 (1)
		C74–C7P1	1.49 (1)
		C75–C76	1.43 (1)

Bond Angles			
C3–C2–C2M	119.8 (4)	C15–C14–C13	116.6 (5)
C3–C2–B6	113.1 (4)	C15–C14–C1P1	120.6 (5)
C2M–C2–B6	127.1 (4)	C13–C14–C1P1	122.8 (5)
C2M–C2–Ru1	129.2 (3)	C1P1–C14–Ru1	131.9 (4)
C2M–C2–Ru1	127.7 (3)	C16–C15–C14	123.7 (5)
Ru7–C2–Ru1	103.1 (2)	C15–C16–C11	120.2 (5)
C2–C3–C3M	120.2 (4)	C1P3–C1P1–C14	110.3 (5)
C2–C3–B4	112.6 (4)	C1P3–C1P1–C1P2	111.1 (5)
C3M–C3–B4	127.2 (4)	C14–C1P1–C1P2	113.7 (5)
C3M–C3–Ru7	128.0 (3)	C76–C71–C71M	120 (1)
C3M–C3–Ru1	129.3 (3)	C76–C71–C72	115.4 (7)
Ru7–C3–Ru1	102.6 (2)	C71M–C71–C72	124 (1)
C3–B4–B5	104.9 (4)	C73–C72–C71	122.8 (6)
Ru7–B4–Ru1	102.8 (2)	C72–C73–C74	119.3 (6)
B6–B5–B4	103.5 (4)	C73–C74–C75	119.3 (8)
Ru7–B5–Ru1	104.5 (2)	C73–C74–C7P1	124.8 (7)
C2–B6–B5	105.8 (4)	C73–C74–Ru7	71.7 (3)
Ru1–B6–Ru7	103.3 (2)	C75–C74–Ru7	72.4 (5)
C2E–C2M–C2	116.1 (5)	C75–C74–C7P1	115.9 (7)
C3E–C3M–C3	116.1 (5)	C7P1–C74–Ru7	128.9 (6)
C12–C11–C16	117.7 (5)	C76–C75–C74	119.6 (9)
C12–C11–C11M	119.8 (6)	C71–C76–C75	123.5 (8)
C16–C11–C11M	122.4 (6)	C74–C7P1–C7P2	113.1 (7)
C11M–C11–Ru1	127.9 (4)	C74–C7P1–C7P3	111.5 (7)
C11–C12–C13	121.1 (5)	C7P2–C7P1–C7P3	108.6 (6)
C12–C13–C14	120.7 (5)		

12b failed to react on prolonged reflux with LiAlH_4 . At present we do not have a satisfactory rationale for this degradation of **12b**, but it is apparent that the binding of osmium to the C_2B_3 face is weaker than that of cobalt or ruthenium; this is also suggested

(17) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343.

by the relatively higher air sensitivity of the osmium complexes in comparison to their ruthenium analogues.

Crystallographic Studies of Diruthenium and Cobalt-Ruthenium Triple-Decker Complexes. The characterization of compounds **10-13** as triple-decker sandwiches (also describable as seven-vertex 1,7,2,3-MM'C₂B₃ metallocarborane clusters) is consistent with their ¹¹B and ¹H NMR spectra (Tables I and II) and is further supported by X-ray crystallographic studies on **10** and **11a**. Data collection parameters, bond distances, and bond angles for both compounds are presented in Tables IV-VI, and the molecular structures are depicted in Figures 1 and 2, respectively. Each complex incorporates a planar C₂B₃ central ring (formally Et₂C₂B₃H₃⁴⁻) which is η⁵-coordinated to two metal ions as shown. Both structures exhibit metal-carborane and metal-arene bond distances and angles that are in the normal ranges for cobalt and ruthenium, respectively, and the end rings are tilted away from the ring carbons on the central C₂B₃ unit (presumably in relief of ring-ethyl steric interactions), with dihedral angles of 6.2° (mean cymene-carborane) in **10**, and corresponding angles of 6.2° (cymene-carborane) and 6.4° (cymene-Cp) in **11a**. The observed pentagonal-bipyramidal MM'C₂B₃ cage geometry in these molecules is consistent with the presence of 16 skeletal electrons (corresponding to closo geometry for seven-vertex clusters); in the language of metal-sandwich chemistry, both species are 30-electron triple-decker complexes, as reflected in their observed diamagnetism and NMR spectra.

The metal-carborane and metal-hydrocarbon binding is symmetrical in both species, with each atom located nearly over the centroids of its coordinated ligands. In comparing these structures with those reported for other arene-ruthenaboranes and arene-ruthenacarboranes,¹⁸ we find no notable differences in the metal-arene or metal-cage interactions.

The structures of **10** and **11a** are similar to those of CpCo(2,3-MeC₂B₃H₄)CoCp,^{8a} CpCo(2,4-MeC₂B₃H₄)CoCp,¹⁹ and CpCo[2,3-(C₃H₄)C₂B₃H₃]CoCp,²⁰ the only C₂B₃-bridged triple-deckers to have been structurally characterized prior to this work. The principal differences between the present and earlier structures are ascribable to the larger covalent radius of Ru²⁺ compared to Co³⁺, although the carborane C2-C3 bond is slightly longer in **10** [1.480 (6) Å] and in **11a** [1.46 (1) Å] than in CpCo(2,3-MeC₂B₃H₄)CoCp [1.441 (7) Å].^{8a} This trend implies a reduction in C-C bond order as cobalt is replaced by ruthenium in C₂B₃-bridged triple-decker systems, suggesting slightly stronger interaction between the metal and the carboranyl carbons (and hence delocalization of electron density out of the C-C bond) in the case of ruthenium. By way of comparison, it is useful to note that when there is only *one* metal bound to the C₂B₃ face, the carboranyl C-C bond length is quite short, as illustrated in the present work by the "double-decapitated" complex [(Et₂C₂B₃H₅)Co(C₅Me₅)]₂(C₆H₄) (compound **6** in the following article¹⁰) in which the value is 1.43 (2) Å.

The closely related borole^{9c} and diborolene^{9a,b} complexes, which feature C₄B and C₃B₂ rings, respectively, furnish a number of examples of triple-decker (or larger) sandwiches on which crystal structures are available. While none of these contain ruthenium or osmium, several platinum-iron and platinum-nickel species,²¹

Table VI. Bond Distances (Å) and Selected Bond Angles (Deg) in **11a**

Bond Distances					
Ru-Co	3.297 (3)	Co-B6	2.080 (8)	C3-B4	1.57 (1)
Ru-C2	2.228 (6)	Co-C1p	2.038 (7)	B4-B5	1.74 (1)
Ru-C3	2.208 (6)	Co-C2p	2.001 (7)	B5-B6	1.72 (1)
Ru-B4	2.215 (7)	Co-C3p	2.009 (8)	C2m-C2e	1.55 (1)
Ru-B5	2.207 (7)	Co-C4p	2.066 (8)	C3m-C3e	1.61 (1)
Ru-B6	2.230 (7)	Co-C5p	2.091 (8)	C1r-C6r	1.37 (1)
Ru-C1r	2.251 (7)	C1p-C5p	1.39 (2)	C1r-C2r	1.40 (1)
Ru-C2r	2.159 (7)	C1p-C2p	1.40 (1)	C1r-C1rp	1.52 (1)
Ru-C3r	2.148 (7)	C2p-C3p	1.40 (1)	C2r-C3r	1.39 (1)
Ru-C4r	2.188 (7)	C3p-C4p	1.35 (1)	C3r-C4r	1.39 (1)
Ru-C5r	2.209 (7)	C4p-C5p	1.38 (1)	C4r-C5r	1.40 (1)
Ru-C6r	2.240 (7)	C2-C3	1.46 (1)	C4r-C1rm	1.53 (1)
Co-C2	2.043 (6)	C2-C2m	1.537 (9)	C5r-C6r	1.42 (1)
Co-C3	2.044 (6)	C2-B6	1.54 (1)	C1rp-C3rp	1.45 (2)
Co-B4	2.072 (7)	C3-C3m	1.519 (9)	C1rp-C2rp	1.49 (1)
Co-B5	2.095 (8)				
Bond Angles					
C3-C2-C2m	119.7 (6)	C2-C2m-C2e	113.3 (7)		
C3-C2-B6	113.5 (6)	C3-C3m-C3e	111.8 (7)		
C2m-C2-B6	126.8 (6)	C6r-C1r-C2r	117.5 (7)		
C2m-C2-Co	129.8 (4)	C2r-C1r-C1rp	123 (1)		
C2m-C2-Ru	129.0 (4)	C6r-C1r-C1rp	119 (1)		
Co-C2-Ru	101.0 (3)	C1rp-C1r-Ru	133.0 (5)		
C2-C3-C3m	120.3 (6)	C3r-C2r-C1r	121.7 (7)		
C2-C3-B4	113.2 (5)	C4r-C3r-C2r	121.2 (7)		
C3m-C3-Co	130.7 (4)	C3r-C4r-C5r	117.8 (7)		
C3m-C3-Ru	127.6 (4)	C3r-C4r-C1rm	122 (1)		
C3m-C3-B4	126.6 (6)	C5r-C4r-C1rm	121 (1)		
Co-C3-Ru	101.6 (2)	C1rm-C4r-Ru	128.8 (6)		
C3-B4-B5	104.8 (5)	C4r-C5r-C6r	120.4 (7)		
Co-B4-Ru	100.5 (3)	C1r-C6r-C5r	121.5 (7)		
B6-B5-B4	102.2 (5)	C2rp-C1rp-C1r	107.8 (8)		
Co-B5-Ru	100.0 (3)	C3rp-C1rp-C1r	116.6 (8)		
C2-B6-B5	106.3 (6)	C3rp-C1rp-C2rp	110.0 (8)		
Co-B6-Ru	99.7 (3)				

viz., CpM(MeEt₂C₃B₂Et₂)Pt(Et₂MeC₃B₂Et₂) and [CpM(MeEt₂C₃B₂Et₂)₂]Pt (M = Fe, Ni), are noteworthy as multidecker complexes incorporating third-row transition elements. A dirhodium triple-decker with a 1,4-diborabenzene bridging ligand, (C₅Me₅)₂Rh₂(H₄C₄B₂Me₂)²⁺, has been prepared and crystallographically characterized.²²

General Observations

The synthetic work described here exploits the reactivity of (L)M(R₂C₂B₃H₄)²⁻ dianions toward arene metal dihalides as a route to designed homo- and heterobimetallic triple-decker complexes. The availability of the dianions is the key to incorporating second- and third-row transition elements into arene-metal-carborane double- and triple-decker sandwiches, since the corresponding (L)M(R₂C₂B₃H₄)⁻ monoanions (which were employed in the synthesis of the original dicobalt triple-deckers⁸) do not react with arene metal halides to generate multidecker species. However, monoanions such as **5**⁻ on treatment with CoCl₂ and C₅H₅⁻ do produce triple-decker products, as was described above (Scheme II).

The triple-decker sandwiches reported herein are of interest in two respects, both of which will be further developed in subsequent papers. As indicated in the introduction, they are envisioned as modules for the construction of much larger multidecker and linked systems, including polymers; the following article¹⁰ describes a step toward this goal in the synthesis and characterization of linked double- and triple-decker sandwiches having several metal centers. The second aspect of these monomeric and oligomeric complexes deserving attention is their electronic structure and behavior, particularly in respect to electron delocalization, communication between metals, and redox chemistry. Studies directed at these questions, currently in progress,

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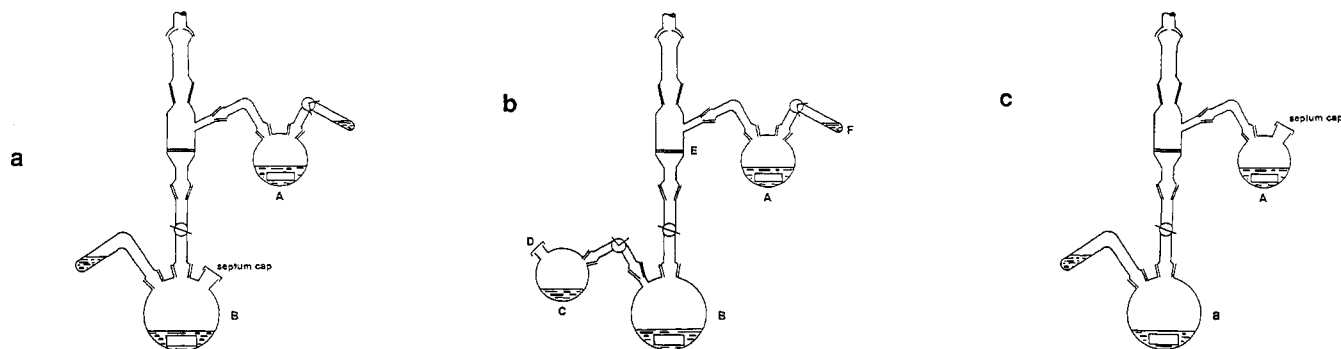


Figure 3. Apparatus for synthesis of arene-metal-carborane complexes.

are strengthened considerably by the fact that we now have available a family of structurally related complexes in which the metals are systematically varied. Moreover, the synthetic routes described here are expected to facilitate the preparation of many other homo- and heteromultimetal complexes as required.

Experimental Section

Instrumentation. ^{11}B (115.8 MHz) and ^1H (300 MHz) NMR spectra were acquired on Nicolet NT-360 and GE QE300 spectrometers, respectively, and visible-ultraviolet spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with an HP Vectra computer interface. Unit-resolution mass spectra were obtained on a Finnegan MAT 4600 GC/MS spectrometer using perfluorotributylamine (FC43) as a calibration standard. Simulated mass spectra based on natural isotopic abundances were calculated on an AT&T 3B5 computer using the program MASPEC by R. N. Grimes. In all cases, strong parent envelopes were observed, and the calculated and observed unit-resolution spectral patterns were in close agreement. High-resolution mass measurements were obtained on a Finnegan MAT 8230 instrument using an SSX 300 data system with perfluorokerosene as a reference standard. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer. Column chromatography was conducted on silica gel 60 (Merck), and thick-layer chromatography was carried out on precoated silica gel plates (Merck).

Materials. 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. *nido*-2,3-Diethyl-2,3-dicarbaheptaborane(8) ($\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$) and the corresponding 2,3-dibenzyl derivative were prepared as described elsewhere.^{23,3a} Sodium hydride was used as a 50% dispersion in mineral oil. *tert*-Butyllithium and sodium cyclopentadienide were purchased as standard solutions from Aldrich.

Synthesis of $\text{Na}^+\text{Li}^+(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)^{2-}$ ($\text{R} = \text{Et}$ or CH_2Ph). A 2- to 3-fold molar excess of NaH suspension in oil was placed in a two-neck 100-mL round-bottom flask (A, Figure 3a) and washed with *n*-hexane to remove the oil. The flask was equipped with a stirring bar and a sidearm containing the diethyl- or dibenzylcarborane and was fitted to the reaction apparatus as shown. The entire apparatus was evacuated on a vacuum line, 50 mL of tetrahydrofuran (THF) was condensed onto the NaH at liquid nitrogen temperature, and the liquid nitrogen was removed. While the solvent was still cold, the carborane was added from the sidearm as the solution was stirred. Following warming of the solution to room temperature with evolution of hydrogen (ca. 30 min), it was filtered in vacuo into flask B. The clear, colorless filtrate containing the carborane monoanion was cooled to -78°C , and an equimolar quantity of *tert*-butyllithium (1.7 M *n*-pentane solution) was added to the carborane solution via a syringe through the rubber septum. The initially canary yellow solution was warmed to room temperature and stirred for ca. 15 min, during which time the color faded to pale golden yellow. The solution of carborane dianion prepared in this manner was used in subsequent metallacarborane syntheses as described below.

Synthesis of (Arene)Ru($\text{R}_2\text{C}_2\text{B}_4\text{H}_4$) Complexes (1–4). The general procedure was as follows. To a stirred THF solution of the $\text{R}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$ ($\text{R} = \text{Et}$ or CH_2Ph) was added, at room temperature, an equimolar amount (based on starting carborane) of the solid (arene)RuCl₂ reagent via a tip tube attached to the reactor flask. The (arene)RuCl₂ gradually dissolved, giving a deep orange-brown solution which was stirred overnight. The solution was opened to the air and the contents placed in a

250-mL round-bottom flask. The THF was removed by rotary evaporation, leaving a brown tar which was extracted into 100-mL of dichloromethane and suction-filtered through 1 in. of silica gel on a sintered glass disk. The silica was washed with CH_2Cl_2 until the effluent was colorless, and the resulting orange-brown solution was again rotary evaporated, leaving a sticky yellow-brown solid which was taken up in a minimal volume of 2:1 *n*-hexane/ CH_2Cl_2 . Elution with the same mixed solvent on a silica column produced one pale yellow band, which was collected and evaporated to give a colorless to pale yellow oil, characterized as 1, 2, 3, or 4. In the cases of 1 and 4, dissolving the oil in a minimal volume of *n*-hexane followed by cooling overnight to 0°C gave pure crystalline solid products. For the individual compounds, details of the preparations follow:

(C_6H_6)Ru($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$) (1). $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$ (0.35 g, 2.7 mmol) and (C_6H_6)RuCl₂ (0.680 g, 2.7 mmol) gave 0.320 g (1.04 mmol, 39% yield based on carborane employed) of 1. Exact mass: calcd for $^{102}\text{Ru}^{12}\text{C}_{12}^{11}\text{B}_4^1\text{H}_{20}^+$, 310.0974; found, 310.0988. Visible-UV absorptions (nm, in CH_2Cl_2): 272 (100%), 280 (97%), 288 (93%), 314 (73%).

($\text{MeC}_6\text{H}_4\text{CHMe}_2$)Ru($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$) (2). $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$ (0.41 g, 3.1 mmol) and (C_6H_6)RuCl₂ (0.955 g, 3.1 mmol) gave 0.657 g (1.80 mmol, 58% yield) of 2. Exact mass: calcd for $^{102}\text{Ru}^{12}\text{C}_{16}^{11}\text{B}_4^1\text{H}_{28}^+$, 366.1600; found, 366.1627. Visible-UV absorptions (nm, in CHCl_3): 244 (100%), 264 (60%), 302 (28%), 320 (28%).

($\text{MeC}_6\text{H}_4\text{CHMe}_2$)Ru($(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_4$) (3). $(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_6$ (0.98 g, 3.8 mmol) and ($\text{MeC}_6\text{H}_4\text{CHMe}_2$)RuCl₂ (1.2 g, 3.8 mmol) gave 0.310 g (0.63 mmol, 17% yield) of 3. Exact mass: calcd for $^{102}\text{Ru}^{12}\text{C}_{26}^{11}\text{B}_4^1\text{H}_{32}^+$, 490.1913; found, 490.1922. Visible-UV absorptions (nm, in CHCl_3): 270 (100%), 283 (88%), 310 (23%).

(C_6Me_6)Ru($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$) (4). $\text{Et}_2\text{C}_2\text{B}_4\text{H}_6$ (0.12 g, 0.91 mmol) and (C_6Me_6)RuCl₂ (0.31 g, 0.91 mmol) gave 0.12 g (0.30 mmol, 33% yield) of 4. Exact mass: calcd for $^{102}\text{Ru}^{12}\text{C}_{18}^{11}\text{B}_4^1\text{H}_{32}^+$, 394.1913; found, 394.1923. Visible-UV absorptions (nm, in CHCl_3): 252 (100%), 282 (47%), 324 (19%), 320 (28%).

Synthesis of ($\text{MeC}_6\text{H}_4\text{CHMe}_2$)Ru($\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$) (5). A 50-mg sample of 2 was dissolved in 5 mL of tetramethylethylenediamine (TMEDA) in an open 50-mL round-bottom flask. After addition of 2 drops of water (required in order to effect apex BH removal), a reflux condenser was attached and the pale yellow solution was refluxed at 150°C for 1 h, during which the liquid became dark brown and opaque. After removal of the solvent by rotary evaporation, the tan solid residue was extracted into a minimal volume of *n*-hexane and chromatographed in hexane on a silica column. One bright yellow band was eluted, which on evaporation of solvent gave 5 as a colorless oil, 48 mg (0.14 mmol, 88% yield based on starting 2). Exact mass: calcd for $^{102}\text{Ru}^{12}\text{C}_{16}^{11}\text{B}_3^1\text{H}_{29}^+$, 356.1586; found, 356.1585. Visible-UV absorptions (nm, in CH_2Cl_2): 288 (88%), 278 (100%).

Synthesis of CpCo($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$) (6). A solution of $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5^-$ in THF, prepared from 2.03 g (15 mmol) of the neutral carborane, was filtered and frozen in liquid nitrogen, and 1.94 g (15 mmol) of CoCl_2 was added. Following addition of 7.5 mL of 2.0 M $\text{Na}^+\text{C}_5\text{H}_5^-$, the mixture was warmed to room temperature with continuous stirring. The solution gradually became deep brown-yellow and copious amounts of gas were evolved. After the solution was stirred overnight, the reactor was opened to air and 100 mL of 1.5 M aqueous HCl was added together with 20 mL of acetone. After stirring for 30 min, the organic solvents were removed on a rotary evaporator, leaving the colorless aqueous phase and a brown sludge. The solution was decanted and the brown sludge was taken up in dichloromethane and dried over MgSO_4 . After filtration and rotary evaporation, a black solid remained which was column chromatographed on silica in 50:50 *n*-hexane/toluene to give two bands. The first band was identified from its mass spectrum as yellow ($\text{Et}_2\text{C}_2\text{B}_3\text{H}_5$)Co(H)($\text{Et}_2\text{C}_2\text{B}_4\text{H}_4$) (analogous to the previously reported tetra-*C*-methyl derivative²⁴). The second band, on evaporation of solvent,

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gave 1.2 g of orange crystalline **6** (4.7 mmol, 32%). Exact mass: calcd for $^{59}\text{Co}^{12}\text{C}_{11}^{11}\text{B}_4^{1}\text{H}_{19}^+$, 254.1191; found, 254.1191. Visible-UV absorptions (nm, in CHCl_3): 270 (100%), 424 (7%).

Synthesis of $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_4)$ (7**).** The apparatus depicted in Figure 3b was charged with 1.0 g (7.3 mmol) of $\text{C}_5\text{Me}_5\text{H}$ in flask C, 0.95 g (7.3 mmol) of CoCl_2 in flask B, 1.1 g (24 mmol) of NaH in flask A, and 1.31 g (9.9 mmol) of $\text{Et}_2\text{C}_2\text{B}_3\text{H}_6$ in the sidearm F and evacuated. THF (50 mL) was condensed into C at liquid nitrogen temperature and then warmed to room temperature to give a yellow solution, which was isolated from the remainder of the apparatus by closing the stopcock. THF (50 mL) was similarly condensed into B, and the solution was warmed to room temperature. The stopcock between B and C was opened and 4.3 mL of 1.7 M *tert*-butyllithium (7.3 mmol) in pentanes was added slowly to C via a syringe through septum D; this produced LiC_5Me_5 as a grayish tan precipitate. After 1 h of stirring to ensure complete reaction, the slurry in C was slowly added dropwise to flask B. The solution in B slowly became green-blue and finally olive green after all of the reagent had been added. The combined solution was stirred for 1 h, during which time flask A was warmed to allow deprotonation of the carborane and formation of the $\text{Et}_2\text{C}_2\text{B}_3\text{H}_5^-$ anion. The solution in A was then added to B through a sintered glass filter (E), upon which the solution in B immediately changed to deep orange-brown. The combined solution was stirred overnight and then opened to the air, and the solvent was removed by evaporation to give an orange solid. Chromatography of the solid on a silica column in 2:1 *n*-hexane/ CH_2Cl_2 gave one orange band which on evaporation of solvent was crystalline **7**, 1.8 g (5.6 mmol, 77%). Exact mass: calcd for $^{59}\text{Co}^{12}\text{C}_{16}^{11}\text{B}_4^{1}\text{H}_{29}^+$, 324.1974; found, 324.1974. Visible-UV absorptions (nm, in CHCl_3): 292 (100%), 248 (19%), 418 (3%).

Synthesis of $(\eta^5\text{-C}_5\text{R}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_5)$ (8**, R = H; **9**, R = Me).** The procedure followed was identical with that employed in the preparation of **5**, except that the reaction was conducted at room temperature. For **8**, 0.19 g (0.76 mmol) of **6** and 4 mL of TMEDA gave 0.15 g (0.61 mmol, 81%) of **8** as a yellow oil. Exact mass: calcd for $^{59}\text{Co}^{12}\text{C}_{11}^{11}\text{B}_3^1\text{H}_{20}^+$, 244.1176; found, 244.1181. Visible-UV absorptions (nm, in CHCl_3): 260 (87%), 290 (100%), 386 (22%), 424 (17%). For **9**, 0.59 g (1.8 mmol) of **7** and 8 mL of TMEDA with 4 drops of water gave 0.49 g (1.6 mmol, 87%) of yellow crystalline **9**. Exact mass: calcd for $^{59}\text{Co}^{12}\text{C}_{16}^{11}\text{B}_3^1\text{H}_{30}^+$, 314.1959; found, 314.1962. Visible-UV absorptions (nm, in CHCl_3): 248 (33%), 284 (100%), 428 (8%).

Synthesis of the Dianions $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3^{2-})$ (5²⁻**) and $(\text{C}_5\text{R}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3^{2-})$ (**8²⁻**, R = H; **9²⁻**, R = Me).** Flask A in the apparatus shown in Figure 3c was charged with **5**, **8**, or **9** and evacuated, and 50 mL of THF was condensed into the flask at liquid nitrogen temperature. The cold bath was removed, and 2 mol equiv of 1.7 M *tert*-butyllithium in pentane was added to the cold solution (via syringe) with stirring. On warming to room temperature, the initially yellow solution changed to red-orange or red. After stirring at room temperature for ca. 15 min, the solution containing the dianion was filtered through a coarse frit into flask B, to which was attached a side tube containing an arene metal dihalide reagent. Addition of the latter reagent to flask B via rotation of the side tube, with subsequent stirring overnight followed by chromatography on silica (in dichloromethane except where otherwise stated), afforded the triple-decker sandwich compounds **10**–**13**. Details of these syntheses follow.

$(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$ (10**).** The reaction of 0.44 mmol of **5²⁻** and 0.159 g (0.44 mmol) of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{RuCl}_2$ gave 0.120 g (0.20 mmol, 46%) of orange crystalline **10**. Exact mass: calcd for $^{102}\text{Ru}_2^{12}\text{C}_{26}^{11}\text{B}_3^1\text{H}_{41}^+$, 590.1562; found, 590.1575. Visible-UV absorptions (nm, in CHCl_3): 450 (2%), 366 (8%), 260 (100%).

$(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}$ (11a**).** The reaction of 1.60 mmol of **8²⁻** and 0.479 g (1.60 mmol) of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2$ gave a green solid, which on chromatography in 1:4 dichloromethane/toluene produced several minor bands and one major green band. Slow evaporation of this latter material from dichloromethane solution gave 0.382 g (8.0 mmol, 50%) of green crystalline **11a**. Exact mass: calcd for $^{102}\text{Ru}^{59}\text{Co}^{12}\text{C}_{21}^{11}\text{B}_3^1\text{H}_{32}^+$, 478.1152; found, 478.1160. Visible-UV absorptions (nm, in CHCl_3): 618 (2%), 456 (3%), 352 (10%), 294 (100%), 236 (40%).

Alternate Synthesis of **11a from **5⁻**.** A solution of the (cymene)ruthenium(carborane) monoanion **5⁻** was prepared from 0.130 g (0.37 mmol) of **5** by addition of 1.0 equiv of *tert*-butyllithium in *n*-pentane, following the same procedure as was employed to generate the dianion (vide supra) except for the ratio of reagents. The dark yellow solution was filtered into flask B (Figure 3a) and frozen in liquid nitrogen. After addition of 50 mg (0.37 mmol) of CoCl_2 from the sidearm and 0.37 mmol of NaCp via syringe, the solution was allowed to warm and stirred ov-

ernight at room temperature, with workup as described above to give 65 mg (0.14 mmol, 38%) of green crystalline **11a**.

$(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{OsRu}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)$ (12a**) and $(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{OsRu}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_2\text{-4-Cl})$ (**12b**).** The reaction of 0.96 mmol of **5²⁻** and 0.380 g (0.96 mmol) of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{OsCl}_2$, prepared by the method of Cabeza and Maitlis,²⁵ gave a brown solid whose mass spectrum indicated the presence of **12a** only. However, chromatography of this material in dichloromethane produced a major and a minor orange band. The major band, on evaporation, gave 0.25 g (0.35 mmol, 37%) of yellow crystalline **12b**, while the minor band was **12a** (5 mg, 0.02 mmol, <1% yield). Exact mass for **12b**: calcd for $^{190}\text{Os}^{102}\text{Ru}^{59}\text{Co}^{12}\text{C}_{25}^{11}\text{B}_3^1\text{H}_{40}^+$, 713.1759; found, 713.1798. Visible-UV absorptions (nm, in CH_2Cl_2): 420 (1%), 338 (10%), 276 (28%), 246 (100%).

$(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{CoCp}$ (13a**) and $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_2\text{-4-Cl})\text{CoCp}$ (**13b**).** The reaction of 1.02 mmol of **8²⁻** and 0.403 g (1.02 mmol) of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{OsCl}_2$ gave a green solid which on chromatography in dichloromethane gave three green bands, of which the major one was dissolved in hexane and cooled to 0 °C overnight to give 0.184 g (0.33 mmol, 32%) of green crystalline **13a**. A minor band (<5 mg) was identified as **13b** from its mass spectrum but not further characterized. Exact mass for **13a**: calcd for $^{190}\text{Os}^{59}\text{Co}^{12}\text{C}_{21}^{11}\text{B}_3^1\text{H}_{32}^+$, 566.1701; found, 566.1710. Visible-UV absorptions (nm, in CH_2Cl_2): for **13a**, 586 (1%), 328 (9%), 284 (38%), 266 (37%), 234 (100%); for **13b**, 594 (2%), 290 (31%), 270 (29%), 262 (30%), 234 (100%).

Synthesis of $\text{CpCo}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{FeCp}$ (15**).** A solution of $\text{Li}^+(\text{Et}_2\text{C}_2\text{B}_3\text{H}_4)\text{Fe}(\eta^5\text{-C}_8\text{H}_{10})^-$ (**14⁻**) was prepared in a manner analogous to that of **5⁻** from 0.117 g (0.42 mmol) of **14⁻** with 0.25 mL (0.42 mmol) of 1.7 M *tert*-butyllithium in pentane. The anion solution was filtered into flask B (Figure 3a) and frozen in liquid nitrogen. CoCl_2 (54 mg, 0.42 mmol) was added from the sidearm, and 0.42 mmol of NaCp (2.0 M solution in THF) was introduced via syringe. The solution was thawed, stirred overnight, and rotary evaporated to give a black solid. Chromatography of the solid on silica in 3:1 *n*-hexane/toluene eluted two very small yellow bands (unidentified) and a major brown band. Evaporation of the latter solution gave 15 mg (0.04 mmol, 20%) of brown-black crystalline **15**. Exact mass for **15**: calcd for $^{59}\text{Co}^{59}\text{Fe}^{12}\text{C}_{16}^{11}\text{B}_3^1\text{H}_{23}^+$, 363.0760; found, 363.0767. Visible-UV absorptions (nm, in CH_2Cl_2): 504 (0.5%), 448 (1%), 388 (9%), 308 (100%), 276 (45%).

Synthesis of $(\text{C}_5\text{Me}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)\text{Ru}(\text{CO})_3$ (17**).** A solution of $\text{Li}^+(\text{C}_5\text{Me}_5)\text{Co}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_3)^{2-}$ (**9²⁻**) was generated from 0.42 g (1.3 mmol) of **9** and 2.6 mmol of *tert*-butyllithium in pentane (1.7 M solution). The solution was filtered into flask B (Figure 3c), and 0.33 g (1.3 mmol) of $(\text{CO})_3\text{RuCl}_2$ was added to the stirred solution at room temperature. The solution immediately became burgundy but changed to brown on stirring for 2 h. The flask was opened to the air and the solvent removed by evaporation, leaving a brown solid. Column chromatography on silica in 50:50 *n*-hexane/dichloromethane gave a green band, which on evaporation afforded 0.104 g (0.21 mmol, 35% yield based on **9** consumed) of green **17**. An orange band was also collected and identified as **9** (0.130 g, 0.65 mmol). Crystals of **17** can be obtained by slow cooling of an *n*-hexane solution overnight. Exact mass for **17**: calcd for $^{102}\text{Ru}^{59}\text{Co}^{16}\text{O}_3^{12}\text{C}_{19}^{11}\text{B}_3^1\text{H}_{28}^+$, 498.0687; found, 498.0709. Visible-UV absorptions (nm, in CH_2Cl_2): 590 (1%), 474 (3%), 326 (20%), 234 (100%).

Reaction of **11a with RuCl_3 .** A 10-mg (0.020 mmol) sample of **11a** and 10 mg (0.050 mmol) of anhydrous RuCl_3 were dissolved in 15 mL of acetone and 0.5 mL of water in a flask open to the air. The green solution became black-green on stirring. After 2 h the solvent was removed, leaving a black solid which was extracted with CH_2Cl_2 and filtered through 2 cm of silica. Evaporation of the green filtrate gave 10 mg (93%) of **11b** as a black-green solid. Visible-UV absorptions (nm, in CHCl_3): 628 (3%), 304 (38%), 262 (34%), 234 (100%).

Reaction of **12b with LiC_6H_5 .** A solution of 0.190 g (0.27 mmol) of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{OsRu}(\text{Et}_2\text{C}_2\text{B}_3\text{H}_2\text{-4-Cl})$ (**12b**) in 20 mL of THF was placed in a 100-mL round-bottom flask fitted with a septum and stirred under N_2 . To the stirred solution was added via syringe 0.13 mL (0.27 mmol) of LiC_6H_5 as a 2.0 M solution in *n*-hexane. After 2 h of stirring with no apparent color change, the flask was opened to the air and the solution was filtered through silica and evaporated to give yellow **5**, whose purity was established via thin-layer chromatography and mass spectrometry. No **12b** or other compounds were detected.

X-ray Structure Determinations on **10 and **11a**.** 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. In each case, crystals were examined under the polarizing microscope and found acceptable; these were mounted on glass fibers in random orien-

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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 described²⁶ to record the intensities for all non-equivalent 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.

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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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Fulvalene- and Polyarene-Transition Metal-Carborane Complexes as Building Blocks for Multilevel Arrays. Stepwise Synthesis and Structural Characterization of Polymetallic Linked Sandwiches¹

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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 $(\eta^6-MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$, which gave emerald green air-stable $[(\eta^6-MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)Co(\eta^5-Me_4C_5)]_2(C_6H_4)_n$ (**10**, $n = 1$; **11**, $n = 2$). A fulvalene-bridged bis(triple-decker) complex, emerald air-stable crystalline $[(\eta^6-MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)Co(\eta^5-C_5H_4)]_2$ (**12**), was prepared via the reaction of fulvalenide dianion with the $(\eta^6-MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_4)^-$ anion and $CoCl_2$. The complexes were structurally characterized from their ¹¹B and ¹H 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) Å³; $R = 0.037$ for 1547 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **6**: mol wt 673.58; space group *P2₁/c*; $Z = 2$; $a = 14.702$ (6), $b = 8.746$ (2), $c = 15.003$ (3) Å; $\beta = 103.35$ (3)°; $V = 1877$ (2) Å³; $R = 0.082$ for 2098 reflections having $F_o^2 > 3\sigma(F_o^2)$. Crystal data for **10**: mol wt 1310.0; space group *P1̄*; $Z = 1$; $a = 11.094$ (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) Å³; $R = 0.056$ for 3842 reflections having $F_o^2 > 3\sigma(F_o^2)$.

In an accompanying article² 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

(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.

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