X-ray Crystal Structure of $(\eta^5-C_5H_4CH_3)Re(NO)(PPh_3)(I)$ (4). Irregular deep red prisms of 4^{14} were obtained by recrystallization from CH_2Cl_2 /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, k = 2n) and subsequent least-squares refinement.

A total of 2645 reflections were collected. Corrections were applied and the structure was solved as described for $3e (CH_2Cl_2)_{0.5}$ 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

James H. Davis, Jr., Ekk Sinn, and Russell N. Grimes*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received November 30, 1988

Abstract: This paper describes the systematic preparation and characterization of new families of triple-decker sandwich complexes incorporating formal cyclo-Et₂C₂B₃H₃⁴⁻ bridging ligands, including the first species of this class containing second- or third-row transition metals. Complexes of general formula $(L)M(Et_2C_2B_3H_3)M'(L)$ (M = Ru, Os; M' = Co, Ru; L = cymene [*p*-isopropyltoluene], Cp, or C_5Me_5) were obtained in stepwise fashion via (1) synthesis of $closo-(L)M(Et_2C_2B_4H_4)$ metallacarboranes, (2) "decapitation" (apex BH removal) of these complexes to give nido-(L)M(Et₂C₂B₃H₅), (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 $CpCo(Et_2C_2B_3H_3)FeCp$ was prepared via treatment of $(\eta^6-C_8H_{10})Fe(Et_2C_2B_3H_4)^-$ with Na⁺Cp⁻ and CoCl₂ followed by air oxidation. The reaction of (CO)₃RuCl₂ with (C₅Me₅)- $Co(Et_2C_2B_3H_3)^2$ gave the "pseudo-triple-decker" complex $(C_5Me_5)Co(Et_2C_2B_3H_3)Ru(CO)_3$. The triple-deckers, especially those containing osmium, are susceptible to chlorination by RuCl₃, OsCl₃, 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 ¹¹B and ¹H NMR, infrared, visible-UV, and unit- and high-resolution mass spectra, further supported by X-ray crystallographic analyses of (cymene)Ru- $(Et_2C_2B_3H_3)Ru(cymene)$ (10) and $CpCo(Et_2C_2B_3H_3)Ru(cymene)$ (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 $F_0^2 > 3\sigma(F_0^2)$. 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 $C_2B_4H_8$ are bridge deprotonated, η^5 -coordinated to transition metals to create metallacarborane 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

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Table I. 115.8-MHz ¹¹B FT NMR Data

| compd ^a | $\delta (J_{BH}, Hz)$ | rel areas |
|--|--|-----------|
| $(C_6H_6)Ru(Et_2C_2B_4H_4)$ (1) ^b | 8.70 (151), 3.80 (130), 0.42 (142) | 1:1:2 |
| $(C_{10}H_{14})Ru(Et_2C_2B_4H_4)$ (2) ^b | 7.54 (148), 4.14 (138), 0.54 (148) | 1:1:2 |
| $(C_{10}H_{14})Ru[(PhCH_2)_2C_2B_4H_4]$ (3) ^b | 8.58 (138), 5.10 (127), 1.36 (127) | 1:1:2 |
| $(C_6Me_6)Ru(Et_2C_2B_4H_4)$ (4) ^b | 5.62 (138), 4.50 (150), 1.03 (138) | 1:1:2 |
| $(C_{10}H_{14})Ru(Et_2C_2B_3H_5)$ (5) ^c | 0.48 (138), -3.08 (138) | 1:2 |
| $CpCo(Et_2C_2B_4H_4)$ (6) ^b | 8.52 (150), ^d 2.55 (150) | 1:1 |
| $(C_5Me_5)Co(Et_2C_2B_4H_4)$ (7) ^c | 12.10 (134), 4.28 (162), 2.59 (185) | 1:2:1 |
| $CpCo(Et_2C_2B_3H_5)$ (8) ^{f,g} | 8.87, 2.37 | 1:2 |
| $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (9) ^b | 7.47 (146), 3.94 (134) | 1:2 |
| $(C_{10}H_{14})_2Ru_2(Et_2C_2B_3H_3)$ (10) ^c | 38.10 (127), 4.27 (138) | 1:2 |
| $(C_{10}H_{14})Ru(Et_2C_2B_3H_3)CoCp (11a)^c$ | 47.51 (150), 4.96 (150) | 1:2 |
| $(C_{10}H_{14})Ru(Et_2C_2B_3H_2Cl)CoCp (11b)^{f_g}$ | 35.00, 10.50, -3.40 | 1:1:1 |
| $(C_{10}H_{14})_2 RuOs(Et_2C_2B_3H_3) (12a)^c$ | 23.59 (127), -2.13 (138) | 1:2 |
| $(C_{10}H_{14})_2 RuOs(Et_2C_2B_3H_2Cl)$ (12b) ^c | 21.40 (92), 10.67, ^e -2.35 (127) | 1:1:1 |
| $(C_{10}H_{14})Os(Et_2C_2B_3H_3)CoCp (13a)^c$ | 32.26 (150), -1.45 (138) | 1:2 |
| $(C_{10}H_{14})Os(Et_2C_2B_3H_2Cl)CoCp (13b)^c$ | 28.80 (104), 10.35, ^e -1.03 (138) | 1:1:1 |
| $(CO)_{3}Ru(Et_{2}C_{2}B_{3}H_{3})Co(C_{5}Me_{5})$ (17) ^c | 48.27 (127), 7.14 (138) | 1:2 |

^aShifts relative to BF₃·OEt₂, positive values downfield. ^bDichloromethane solution. ^cn-Hexane solution. ^dOverlapping signals. ^cSinglet. ^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 C_2B_3 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-C₃B₂, 1,2- and 1,4-C₄B₂, or C₄B 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) $M(R_2C_2B_4H_4)$ 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- C_4H_9Li to give stable Na⁺Li⁺(RR'C_2B_4H_4)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 $nido-(L)M(RR'C_2B_3H_5)$ metallacarboranes; in the latter case the

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(11) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire,





dianion can be obtained with $n-C_4H_9Li$ alone, as described below. The metallacarborane dianions, in turn, have given us an entry to the planned synthesis of MC_2B_4 clusters of second- and third-row transition metals, a class of metallacarboranes of which the only previously reported examples are $(Et_3P)_2Pt(R_2C_2B_4H_4)$ $(R = H, Me)^{12}$ and $(CO)_3Os[(Me_3Si)_2C_2B_4H_4]^{.13}$ 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

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⁽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.
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Table II. 300-MHz ¹H FT NMR Data

compd 1

2

3

4

5

| 00-MITZ II II TAMK Data | |
|--|-------------------|
| δ ^{a-c} | rel areas |
| 5.35 s (C_6H_6), 2.45 m (CH_2), 2.37 m (CH_2), 1.22 m (CH_3) | 6:2:2:6 |
| 5.31 d (C_6H_4), 5.22 d (C_6H_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 | 2:2:1:2:2:3:6:6 |
| $(CHMe_2), 1.20 \text{ m} (CH_3CH_2)$ | |
| 7.15 m (C_6H_5), 5.00 d (C_6H_4), 4.98 d (C_6H_4), 3.95 d (PhCH ₂), 3.88 d (PhCH ₂), 2.40 m (CHMe ₂), 2.01 s | 10:2:2:2:1:3:6 |
| $(CH_{3}C_{6}H_{4}), 1.08 d (CHMe_{2})$ | |
| 2.24 m (CH ₂), 2.19 m (CH ₂), 2.15 s (C_6Me_6), 1.17 m (CH ₃) | 2:2:18:6 |
| 5.41 d (C_6H_4), 5.33 d (C_6H_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 | 2:2:1:2:3:2:6:6:2 |
| $(CHMe_2)$, 1.09 m (CH_3CH_2) , -5.54 s $(B-H-B)$ | |
| 4.78 s (C_5H_5), 2.68 m (CH_2), 2.44 m (CH_2), 1.29 m (CH_3) | 5:2:2:6 |

- (CHMe₂), 1.09 m (C 4.78 s (C₅H₅), 2.68 m (CH₂), 2.44 m (CH₂), 1.29 m (CH₃ 6
- 7 2.51 m (CH₂), 2.28 m (CH₂), 1.77 s (C₅Me₅), 1.19 m (CH₃)
- 8 4.66 s (C₅H₅), 2.13 m (CH₂), 1.94 m (CH₂), 1.18 m (CH₃), -6.01 br (B-H-B)
- 2.09 m (CH₂), 1.89 m (CH₂), 1.76 s (C₅Me₅), 1.10 m (CH₃), -5.54 br (B-H-B) 10
- 4.96 d (C_6H_4), 4.84 d (C_6H_4), 2.58 m ($CHMe_2$), 2.54 q (CH_2), 2.00 s ($CH_3C_6H_4$), 1.33 t (CH_3CH_2), 1.19 d 4:4:2:4:6:6:12 (CHMe₂) 11a 4.92 d (C₆H₄), 4.81 d (C₆H₄), 4.46 s (C₅H₅), 2.78 m (CH₂), 2.64 m (CH₂), 2.53 m (CHMe₂), 1.97 s 2:2:5:2:2:1:3:6:6 $(CH_{3}C_{6}H_{4})$, 1.48 m $(CH_{3}CH_{2})$, 1.18 d $(CHMe_{2})$ 4.91 d (C_6H_4) , 4.82 d (C_6H_4) , 4.49 s (C_5H_5) , 2.28–2.85 m (CH_2) , 2.02 s $(CHMe_2)$, 1.47 m $(CH_3C_6H_4)$, 1.20 d 11b
- 2:2:5:5:3:6:6 (CHMe₂) 12a 5.16 d (C₆H₄), 5.04 d (C₆H₄), 5.00 d (C₆H₄), 4.90 d (C₆H₄), 2.46–2.75 m (CH₂), 2.10 s (CHMe₂), 2.00 s 2:2:2:2:6:3:3:6:6:6
- $(CH_3C_6H_4)$, 1.29 m $(CH_3C_6H_4)$, 1.22 d $(CHMe_2)$, 1.19 d $(CHMe_2)$ 5.31 d (C_6H_4) , 5.19 d (C_6H_4) , 5.18 d (C_6H_4) , 5.10 d (C_6H_4) , 5.06 br (C_6H_4) , 5.02 d (C_6H_4) , 2.45-2.73 m 12b 1:2:1:1:2:1:6:3:3:18 (CH₂, CHMe₂), 2.14 s (CH₃C₆H₄), 2.00 s (CH₃C₆H₄), 1.18-1.26 m (CHMe₂) 2:2:5:2:2:1:3:6:6 5.21 d (C₆H₄), 5.15 d (C₆H₄), 4.55 s (C₅H₅), 2.95 m (CH₂), 2.74 m (CH₂), 2.48 m (CHMe₂), 2.17 s 13a (CHMe₂), 1.45 m (CH₃), 1.20 d (CHMe₂) 2:2.15:6 17 2.78 m (CH₂), 2.50 m (CH₂), 1.69 s (C₅Me₅), 1.40 m (CH₃)
- ^a CDCl₃ 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 $CoCl_2$, NaC_5R_5 (R = H or Me), and Na⁺Et₂C₂B₄H₅⁻ via a modification of the method originally reported⁸⁶ 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-

2:2:15:6

5:2:2:1:2

2:2:15:6:2

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 |
| 2 | m, 1215 m, 1110 w, 1054 w, 1019 m, 970 m 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, |
| 4 | 1222 vw, 1011 vw, 976 vw 3817 w 3676 w 2530 w 2410 c 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 |
| 6 | m, 1124 m, 1018 m $2593 \le 2551 \le 2115$ br 1714 ch 1630 c 1567 ch 1257 m |
| U | 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 |
| c | m, 1222 w, 1068 vw, 1011 m, 969 m |
| 8 | 3831 m, 3810 m, $36/6$ m, 2959 m, $291/$ m, 2868 m, 2516 m, 2368 m, 2333 m, 1700 s, 1560 s, 1520 s, 1412 m, 1242 |
| | m, 2506 m, 2555 m, 1700 s, 1500 s, 1559 s, 1412 m, 1245 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 |
| 10 | 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 |
| | sii, 1555 s, 1204 iii, 1215 iii, 1117 m, 1008 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 sn, 2509 w, 2362 w, 1700 m, 1560 s, 1525 m, 1250 |
| 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 1557 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, |
| | m. 1124 w. 1075 w. 1018 m. 976 m |
| 41 or | m, r = v + v + v + v + v + v + v + v + v + v |
| = shou | lder, br = broad. |
| 51100 | |
| bining | monometallic arene-metal and arene-metal-carborane |
| units t | o form triple-decker species. As shown in Scheme II, the |
| nido-r | uthenacarborane complex 5 was singly deprotonated to |
| genera | te the monoanion 5 ⁻ . Removal of the second bridging proton |
| forme | d the orange-red dianion 5^{2-} , which was reacted with |
| (cyme | ne)ruthenium dichloride to give the diruthenium sandwich |
| (η ⁶ -Μ | $eC_6H_4CHMe_2)_2Ru_2(Et_2C_2B_3H_3)$ (10), obtained as dark |
| orange | e air-stable crystals. Alternatively, treatment of the mo- |
| noanic | on 5 ⁻ with CoCl ₂ and NaC ₅ H ₅ gave the heterobimetallic |
| triple- | Becker sandwich CpCo($Et_2C_2B_3H_3$)Ru(η° -MeC ₆ H ₄ CHMe ₂) |
| -(IIA), | 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 $CpCo(Et_2C_2B_3H_3)^{2-1}$ dianion 8^{2-} 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



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

Similar chemistry was employed to generate heterobimetallic mium-containing triple-deckers. Thus, the reaction of 5^{2-} with symene) osmium dichloride produced yellow crystalline (η^{6} $eC_6H_4CHMe_2$ $Ru(Et_2C_2B_3H_3)Os(\eta^6-MeC_6H_4CHMe_2)$ (12a), companied by its 4-chloro derivative 12b, a golden, slightly r-sensitive crystalline solid. Under the usual conditions of nthesis followed by workup in dichloromethane (see Experiental Section), the latter species was isolated in much larger eld, indicating that the propensity of 12a to chlorination is greater an that of 10 or 11a (whose chlorinated derivatives were not served to form under comparable conditions). Investigation vealed that 12b formed on exposure of 12a to CH₂Cl₂ during orkup. However, even in nonhalogenated solvents 12b was ptained as a byproduct unless extremely pure [(cymene)OsCl₂]₂ as employed, owing to the presence of OsCl₃ in that reagent. irect treatment of 12a with OsCl₃ generates 12b rapidly and antitatively.

A cobalt-osmium sandwich, $CpCo(Et_2C_2B_3H_3)Os(\eta^6 [eC_6H_4CHMe_2]$ (13a), was formed, together with the minor chlorinated product 13b, by reaction of $8^{2^{-}}$ with (cymene)osmium chloride. The osmium-cobalt triple-deckers, like their rutheum-cobalt counterparts 11a and 11b, form beautiful emerald een crystals, which appear to be stable in air over extended riods.

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 $(\eta^6-C_8H_{10})$ Fe(Et₂C₂B₃H₅) (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 cyclopentadienide; although replacement of Fecomplexed C_8H_{10} by arenes has been routinely employed in our laboratory,² we had not previously observed the subrogation of this ligand by $C_5H_5^-$. Complex 15 is a paramagnetic (29-electron),

⁽¹⁵⁾ Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. Inorg. Svnth. 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 $(MeC_6H_4CHMe_2)_2Ru_2(Et_2C_2B_3H_3)$ (10) (hydrogen atoms are omitted for clarity).



Figure 2. PLUTO drawing of the molecular structure of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)CoCp$ (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 $(\eta^6-C_8H_{10})$ Fe(Et₂C₂B₄H₆) (16) was treated with Na⁺C₅H₅⁻, no reaction was observed.

A different synthetic approach to bimetallic complexes was explored via the reaction of the dark red $(C_5Me_5)Co(Et_2C_2B_3H_3)^{2-}$ dianion 9²⁻ with $Cl_2Ru(CO)_3$, which afforded the "pseudo-triple-decker" complex (CO)₃Ru(Et_2C_2B_3H_3)Co(η^5 -C₅Me₅) (17) as emerald air-stable crystals (Scheme III). In addition to the NMR and mass spectroscopic data that define the RuC₂B₃Co 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, (CO)₃Fe(Me₂C₂B₃H₃)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 | PĪ | $P2_1/c$ |
| 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 α) | 11.32 | 14.87 |
| $D(\text{calcd}), \text{ g cm}^{-3}$ | 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 D | istances | | | - | |
|-----------|--|---------------|---------------|--------------|------|-------------|----------|
| Rui-Ru7 | 3.478 (2) | Ru7-C71′ | 2.20 (3) | C11-C16 | | 1.457 | (9) |
| Ru1–C2 | 2.225 (4) | Ru7-C72 | 2.223 (5) | C11-C11 | М | 1.526 | (8) |
| Ru1–C3 | 2.244 (5) | Ru7-C73 | 2.191 (5) | C12-C13 | | 1.425 | (8) |
| Ru1-B4 | 2.228 (5) | Ru7-C74 | 2.178 (6) | C13-C14 | | 1.425 | (7) |
| Ru1-B5 | 2.212 (6) | Ru7-C75 | 2.22 (1) | C14-C15 | | 1.409 | (8) |
| Ru1-B6 | 2 205 (6) | Ru7-C75' | 2 02 (6) | C14-C1P | 1 | 1 510 | (7) |
| Ru1-C11 | 2 189 (5) | Ru7 - C76 | 2 218 (6) | C15-C16 | - | 1 353 | à |
| Ru1-C12 | 2 159 (5) | Ru7-C76' | 2.210(0) | | P3 | 1 508 | |
| Ru1-C13 | 2.137(3) | C_{2}^{2} | 1.480(6) | | P2 | 1.500 | (1) |
| Ru1-C14 | 2.101 (5) | $C_2 - C_2 M$ | 1.408 (6) | C_{11} | 1 4 | 1 28 (| |
| Ru1 = C15 | 2.230(3) | $C_2 = C_2 M$ | 1.496 (0) | C71-C71 | м | 1.30 (| 3 |
| Ru1 - C15 | 2.217(3) | $C_2 = D_0$ | 1.374(7) | C71_C71 | 141 | 1.40 (| 27 |
| Ru1 - C10 | 2.209(3) | | 1.507 (7) | C71-C72 | | 1.4/ (| <u>.</u> |
| Ru = C2 | 2.210 (4) | C3-B4 | 1.582 (7) | C72-C73 | | 1.408 | (9) |
| Ru/-C3 | 2.211 (5) | B4~B5 | 1./39 (8) | C/3-C/4 | | 1.410 | (9) |
| Ru/-B4 | 2.223 (6) | B2~B6 | 1.707 (8) | C74-C75 | | 1.43 (| (1) |
| Ru7-B5 | 2.187 (6) | C2M-C2E | 1.49 (1) | C74-C7P | 1 | 1.49 (| (1) |
| Ru7-B6 | 2.229 (5) | C3M-C3E | 1.494 (9) | C75-C76 | | 1.43 (| (1) |
| Ru7–C71 | 2.296 (5) | C11-C12 | 1.386 (9) | | | | |
| | | Bond | Angles | | | | |
| C3-C2 | -C2M | 1198 (4) | C15-C14-C | 13 | 116 | 6 (5) | |
| C3-C2 | -B6 | 1131 (4) | C15-C14-C | 1 P 1 | 120 | 6 (5) | |
| C2M-0 | ~2-B6 | 1271(4) | C13 - C14 - C | 101 | 120 | 8 (5) | |
| C2M-0 | | 127.1(7) | C1P1-C1A | .D.1 | 121 | | |
| C2M-0 | 2^{-1} 2 | 127.2(3) | | Nu1 | 121. | 7 (5) | |
| Du7 C | 2-Kui 2 Dul | 127.7(3) | | 14 | 120 | $\gamma(3)$ | |
| C1 C2 | 2-Ku1 | 103.1(2) | | | 110 | 2 (5) | |
| C2-C3- | | 120.2(4) | CIP3-CIPI | -014 | 110. | 3 (3) | |
| 02-03 | B4 | 112.6 (4) | CIP3-CIPI | -CIP2 | 111. | 1 (5) | |
| C3M-C | 3-B4 | 127.2 (4) | CI4-CIPI- | CIP2 | 113. | 7 (5) | |
| C3M-0 | 23-Ru7 | 128.0 (3) | C76-C71-C | 71 M | 120 | (1) | |
| C3M-0 | 23-Rul | 129.3 (3) | C76-C71-C | 272 | 115. | .4 (7) | |
| Ru7–C | 3-Ru1 | 102.6 (2) | C71M-C71 | -C72 | 124 | (1) | |
| C3-B4- | -B5 | 104.9 (4) | C73-C72-C | 271 | 122. | .8 (6) | |
| Ru7–B | 4–Rul | 102.8 (2) | C72-C73-C | 274 | 119. | .3 (6) | |
| B6-B5- | -B4 | 103.5 (4) | C73-C74-C | 275 | 119. | .3 (8) | |
| Ru7-B | 5-Rul | 104.5 (2) | C73-C74-C | C7P1 | 124. | .8 (7) | |
| C2-B6- | -B5 | 105.8 (4) | C73-C74-R | Lu7 | 71, | 7 (3) | |
| Ru1-B | 6–Ru7 | 103.3 (2) | C75-C74-R | Lu7 | 72, | 4 (5) | |
| C2E-C | 2M-C2 | 116.1 (5) | C75-C74-C | C7P1 | 115. | 9 (7) | |
| C3E-C | 3M-C3 | 116.1 (5) | C7P1-C74- | Ru7 | 128. | 9 (6) | |
| C12-C | 11-C16 | 117.7 (5) | C76-C75-C | 74 | 119. | 6 (9) | |
| C12-C | 11-C11M | 119.8 (6) | C71-C76-C | 275 | 123. | 5 (8) | |
| C16-C | 11-C11M | 122.4 (6) | C74-C7P1- | C7P2 | 113. | 1 (7) | |
| CIIM- | -C11-Ru1 | 127.9 (4) | C74-C7P1- | C7P3 | 111. | 5 (7) | |
| C11-C | 12-C13 | 121.1 (5) | C7P2-C7P1 | -C7P3 | 108 | 6 (6) | |
| C12-C | 13-014 | 120.7 (5) | 0/12 0/11 | | | | |
| 012 0 | 10 014 | | | | | | |

12b failed to react on prolonged reflux with LiAlH₄. 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 metallacarborane 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 $Et_2C_2B_3H_3^{4-}$) which is η^5 -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 $MM'C_2B_3$ 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 30electron 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 areneruthenacarboranes,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- $(2,3-MeC_2B_3H_4)CoCp$,^{8a} CpCo $(2,4-MeC_2B_3H_4)CoCp$,¹⁹ and $CpCo[2,3-(C_3H_4)C_2B_3H_3]CoCp,^{20}$ the only C_2B_3 -bridged tripledeckers 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 C_2B_3 face, the carboranyl C-C bond length is quite short, as illustrated in the present work by the "double-decapitated" complex $[(Et_2C_2B_3H_5)Co(C_5Me_4)]_2(C_6H_4)$ (compound 6 in the following article¹⁰) in which the value is 1.43 (2) Å.

The closely related borole9c and diborolene9a,b complexes, which feature C_4B and C_3B_2 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 I | 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) | Clr-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) | Clr-Clrp | 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-C1rr | n 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) | Clrp-C3 | rp 1.45 (2) |
| Co-B4 | 2.072 (7) | C3-C3m | 1.519 (9) | C1rp-C2 | rp 1.49 (1) |
| Co-B5 | 2.095 (8) | | | - | - |
| | | Dand | A | | |
| <u></u> | 31 C1- | 1107(6) | Angles | 2. 1 | 122(7) |
| C3-C | 2 - C 2 m | 119.7(0) | $C_2 = C_2 m = C_2$ | 2e 1 3a 1 | 13.3(7) |
| C3-C | -2-D0 | 113.3 (0) | | 3e 1 3e 1 | 11.0(7) 17.5(7) |
| C2m | -C2-Б0 -C2-Со | 120.8(0) | $C_{0} = C_{1} = C_{0}$ | 21 I | 23(1) |
| C2m | -C2-C0 | 129.0(4) | C_{21} - C_{1r-C} | 1rp 1 | $\frac{23(1)}{10(1)}$ |
| C211 | -C2-Ru | 129.0(4) | C_{1rn} | $\frac{11}{2}$ 1 | $\frac{17}{330}(5)$ |
| C0-0 | 2^{-} Ku 2^{-} C2m | 101.0(3) | $C_{1p} = C_{1r} = C_{1r}$ | 1 m 1 | 217(7) |
| C2-C | 23-C3III | 120.3(0) | $C_{1} = C_{2} = C_{1}$ | 2r 1 | 21.7(7) |
| C2-C | -C3-Ca | 130.7(4) | $C_{r}^{-}C_{r-C}^{-}$ | 5r 1 | 178(7) |
| C3m | -C3-Ru | 127.6(4) | $C_{3r} - C_{4r} - C$ | 1rm 1 | 22 (1) |
| C3m | -C3-B4 | 126.6 (6) | C5r - C4r - C | 1rm 1 | $\frac{22}{21}$ (1) |
| | ~3_Ru | 120.0(0) | $C_{1rm} = C_{4r}$ | Ru 1 | 28 8 (6) |
| C3-F | 84-R5 | 101.0(2) 104.8(5) | C4r - C5r - C | 6r 1 | 20.0(0) |
| Co-F | 34-Ru | 104.0(3) | C_{1r} | 5r 1 | 21.5(7) |
| B6-F | 35-R4 | 100.3(5) | C2rn-C1rn- | -C1r = 1 | 07.8(8) |
| Co-F | 35-Ru | 100.0(3) | C3rp-C1rp- | -C1r 1 | 16.6 (8) |
| C2-F | 36-B5 | 106.3 (6) | C3rp-C1rp- | -C2rp 1 | 10.0 (8) |
| Co-F | 36-Ru | 99.7 (3) | -orp onp | | |
| 00 L | | | | | |

viz., CpM(MeEt₂C₃B₂Et₂)Pt(Et₂MeC₃B₂Et₂) and [CpM- $(MeEt_2C_3B_2Et_2)]_2$ 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, $(C_5Me_5)_2Rh_2(H_4C_4B_2Me_2)^{2+}$, has been prepared and crystallo-graphically characterized.²²

General Observations

The synthetic work described here exploits the reactivity of $(L)M(R_2C_2B_4H_4)^{2-}$ 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-metalcarborane double- and triple-decker sandwiches, since the corresponding $(L)M(R_2C_2B_3H_4)^-$ 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 $CoCl_2$ and $C_5H_5^$ 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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⁽²²⁾ Herberich, G. E.; Hessner, B.; Huttner, G.; Zsolnai, L. Angew. Chem., Int. Ed. Engl. 1981, 20, 472.



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 ^{1}H (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-dicarbahexaborane(8) ($Et_2C_2B_4H_6$) 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*-Butyl-lithium and sodium cyclopentadienide were purchased as standard solutions from Aldrich.

Synthesis of Na⁺Li⁺($R_2C_2B_4H_4$)²⁻ (R = Et or CH₂Ph). 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 tertbutyllithium (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($R_2C_2B_4H_4$) Complexes (1-4). The general procedure was as follows. To a stirred THF solution of the $R_2C_2B_4H_4^{2-}$ (R = 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:

 (\tilde{C}_6H_6) Ru(Et₂C₂B₄H₄) (1). Et₂C₂B₄H₆ (0.35 g, 2.7 mmol) and (C₆-H₆)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 ¹⁰²Ru¹²C₁₂¹¹B₄¹H₂₀⁺, 310.0974; found, 310.0988. Visible–UV absorptions (nm, in CH₂Cl₂): 272 (100%), 280 (97%), 288 (93%), 314 (73%).

(MeC₆H₄CHMe₂)Ru(Et₂C₂B₄H₄) (2). Et₂C₂B₄H₆ (0.41 g, 3.1 mmol) and (C₆H₆)RuCl₂ (0.955 g, 3.1 mmol) gave 0.657 g (1.80 mmol, 58% yield) of 2. Exact mass: calcd for 102 Ru¹²C₁₆¹¹B₄¹H₂₈⁺, 366.1600; found, 366.1627. Visible–UV absorptions (nm, in CHCl₃): 244 (100%), 264 (60%), 302 (28%), 320 (28%).

 $(MeC_6H_4CHMe_2)Ru[(PhCH_2)_2C_2B_4H_4]$ (3). $(PhCH_2)_2C_2B_4H_6$ (0.98 g, 3.8 mmol) and $(MeC_6H_4CHMe_2)RuCl_2$ (1.2 g, 3.8 mmol) gave 0.310 g (0.63 mmol, 17% yield) of 3. Exact mass: calcd for $^{102}Ru^{12}C_{26}^{11}B_4^{-1}H_{32}^{+}$, 490.1913; found, 490.1922. Visible–UV absorptions (nm, in CHCl₃): 270 (100%), 283 (88%), 310 (23%).

 $(C_6Me_6)Ru(Et_2C_2B_4H_4)$ (4). $Et_2C_2B_4H_6$ (0.12 g, 0.91 mmol) and $(C_6Me_6)RuCl_2$ (0.31 g, 0.91 mmol) gave 0.12 g (0.30 mmol, 33% yield) of 4. Exact mass: calcd for $^{102}Ru^{12}C_{18}^{-11}B_4^{-1}H_{32}^{-+}$, 394.1913; found, 394.1923. Visible–UV absorptions (nm, in CHCl₃): 252 (100%), 282 (47%), 324 (19%), 320 (28%).

Synthesis of $(MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_5)$ (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 ¹⁰²Ru¹²C₁₆¹¹B₃¹¹H₂₉⁺, 356.1586; found, 356.1585. Visible–UV absorptions (nm, in CH₂Cl₂): 288 (88%), 278 (100%).

Synthesis of $CpC_0(Et_2C_2B_4H_4)$ (6). A solution of $Et_2C_2B_4H_5^-$ 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 CoCl₂ was added. Following addition of 7.5 mL of 2.0 M Na⁺C₅H₅⁻, 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 MgSO4. 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 $(Et_2C_2B_3H_5)Co(H)(Et_2C_2B_4H_4)$ (analogous to the previously reported tetra-C-methyl derivative²⁴). The second band, on evaporation of solvent,

⁽²³⁾ Boyter, H. A., Jr.; Swisher, R. G.; Sinn, E.; Grimes, R. N. Inorg. Chem. 1985, 24, 3810.

gave 1.2 g of orange crystalline 6 (4.7 mmol, 32%). Exact mass: calcd for ${}^{59}Co^{12}C_{11}{}^{11}B_4{}^{1}H_{19}{}^{+}$, 254.1191; found, 254.1191. Visible–UV absorptions (nm, in CHCl₃): 270 (100%), 424 (7%).

Synthesis of $(\eta^5 - C_5 Me_5)Co(Et_2 C_2 B_4 H_4)$ (7). The apparatus depicted in Figure 3b was charged with 1.0 g (7.3 mmol) of C₅Me₅H in flask C, 0.95 g (7.3 mmol) of CoCl₂ in flask B, 1.1 g (24 mmol) of NaH in flask A, and 1.31 g (9.9 mmol) of $Et_2C_2B_4H_6$ 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 LiC₅Me₅ 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 $Et_2C_2B_4H_5^-$ 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/CH₂Cl₂ gave one orange band which on evaporation of solvent was crystalline 7, 1.8 g (5.6 mmol, 77%). Exact mass: calcd for ${}^{59}Co^{12}C_{16}{}^{11}B_4{}^{11}H_{29}{}^+$, 324.1974; found, 324.1974. Visible-UV absorptions (nm, in CHCl₃): 292 (100%), 248 (19%), 418 (3%).

Synthesis of $(n^5 \cdot C_5 R_5)Co(Et_2 C_2 B_3 H_5)$ (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 $^{59}Co^{12}C_{11}^{11}B_3^{11}H_{20}^{+}$, 244.1176; found, 244.1181. Visible–UV absorptions (nm, in CHCl₃): 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 $^{59}Co^{12}C_{16}^{11}B_3^{11}H_{30}^{+}$, 314.1959; found, 314.1962. Visible–UV absorptions (nm, in CHCl₃): 248 (33%), 284 (100%), 428 (8%).

Synthesis of the Dianions (MeC₆H₄CHMe₂)Ru(Et₂C₂B₃H₃²⁻) (5²⁻) and (C₅R₅)Co(Et₂C₂B₃H₃²⁻) (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.

 $(MeC_6H_4CHMe_2)_2Ru_2(Et_2C_2B_3H_3)$ (10). The reaction of 0.44 mmol of 5²⁻ and 0.159 g (0.44 mmol) of $(MeC_6H_4CHMe_2)RuCl_2$ gave 0.120 g (0.20 mmol, 46%) of orange crystalline 10. Exact mass: calcd for $^{102}Ru_2^{12}C_{26}^{11}B_3^{11}H_{41}^{+}$, 590.1562; found, 590.1575. Visible–UV absorptions (nm, in CHCl_3): 450 (2%), 366 (8%), 260 (100%).

(MeC₆H₄CHMe₂)Ru(Et₂C₂B₃H₃)CoCp (11a). The reaction of 1.60 mmol of 8²⁻ and 0.479 g (1.60 mmol) of (MeC₆H₄CHMe₂)RuCl₂ 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 ¹⁰²Ru⁵⁹Co¹²C₂₁¹¹B₃H₃₂⁺, 478.1152; found, 478.1160. Visible–UV absorptions (nm, in CHCl₃): 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 overnight at room temperature, with workup as described above to give 65 mg (0.14 mmol, 38%) of green crystalline **11a**.

 $(MeC_6H_4CHMe_2)_2OsRu(Et_2C_2B_3H_3)$ (12a) and $(MeC_6H_4CHMe_2)_2OsRu(Et_2C_2B_3H_2-4-Cl)$ (12b). The reaction of 0.96 mmol of 5^{2-} and 0.380 g (0.96 mmol) of $(MeC_6H_4CHMe_2)OsCl_2$, 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, <[% yield]). Exact mass for 12b: calcd for $1^{90}Os^{10}Ru^{35}Cl^{13}Cl^2C_25^{11}B_3^{1}H_{40}^{-+}$, 713.1759; found, 713.1798. Visible– UV absorptions (nm, in CH_2Cl_2): 420 (1%), 338 (10%), 276 (28%), 246 (100%).

(MeC₆H₄CHMe₂)Os(Et₂C₂B₃H₃)CoCp (13a) and (MeC₆H₄CHMe₂)-Os(Et₂C₂B₃H₂-4-Cl)CoCp (13b). The reaction of 1.02 mmol of 8^{2-} and 0.403 g (1.02 mmol) of (MeC₆H₄CHMe₂)OsCl₂ 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 ¹⁹⁰Os⁵⁹Co¹²C₂₁ ¹¹B₃¹¹H₃₂⁺, 566.1701; found, 566.1710. Visible–UV absorptions (nm, in CH₂Cl₂): 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 CpCo(Et₂C₂B₃H₃)FeCp (15). A solution of Li⁺- $(Et_2C_2B_3H_4)Fe(\eta^5-C_8H_{10})^-$ (14⁻) was prepared in a manner analogous to that of 5⁻ from 0.117 g (0.42 mmol) of 14¹⁶ 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. CoCl₂ (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 brownblack crystalline 15. Exact mass for 15: calcd for ⁵⁹Co⁵⁶Fe¹²C₁₆¹¹B₃¹H₂₃⁺, 363.0760; found, 363.0767. Visible-UV absorptions (nm, in CH2Cl2): 504 (0.5%), 448 (1%), 388 (9%), 308 (100%), 276 (45%)

Synthesis of $(C_3Me_3)Co(Et_2C_2B_3H_3)Ru(CO)_3$ (17). A solution of $Li^+_2(C_5Me_3)Co(Et_2C_2B_3H_3)^{2-}$ (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 (CO)_3RuCl₂ 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 $10^2Ru^{59}Co^{16}O_3^{12}C_{19}^{-11}B_3^{-1}H_{28}^{+}$, 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 RuCl₃. A 10-mg (0.020 mmol) sample of **11a** and 10 mg (0.050 mmol) of anhydrous RuCl₃ 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 CHCl₃): 628 (3%), 304 (38%), 262 (34%), 234 (100%).

Reaction of 12b with LiC₆**H**₅. A solution of 0.190 g (0.27 mmol) of $(MeC_6H_4CHMe_2)_2OsRu(Et_2C_2B_3H_2-4-Cl)$ (**12b**) in 20 mL of THF was placed in a 100-mL round-bottom flask fitted with a septum and stirred under N₂. To the stirred solution was added via syringe 0.13 mL (0.27 mmol) of LiC₆H₅ 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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⁽²⁵⁾ Cabeza, J. A.; Maitlis, P. M. J. Chem. Soc., Dalton Trans. 1975, 573.

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 -2 θ scan technique was used as previously described²⁶ 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 $\sigma(F_0^2)$ 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

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6. 197.

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.

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

James H. Davis, Jr., Ekk Sinn, and Russell N. Grimes*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received November 30, 1988

Abstract: The designed synthesis and structural elucidation of a series of linked double-decker and triple-decker arenemetal-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 CoCl₂ 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 CoCl₂ 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 $[(\eta^6 - MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5 - Me_4C_5)]_2(C_6H_4)_n$ (10, n = 1; 11, n = 2). A fulvalene-bridged bis(triple-decker) complex, emerald air-stable crystalline $[(\eta^6-MeC_6H_4CHMe_2)Ru(Et_2C_2B_3H_3)Co(\eta^5-C_5H_4)]_2$ (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 CoCl₂. 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 $P2_1/c$; Z = 2; a = 14.702 (6), b = 8.746 (2), c = 15.003 (3) Å; $\beta = 103.35$ (3)°; V = 1877 (2) 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 $P\overline{1}$; 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) Å³; R = 0.082 for 2098 reflections having $F_o^2 > 3\sigma(F_o^2)$. = 0.056 for 3842 reflections having $F_0^2 > 3\sigma(F_0^2)$.

In an accompanying article² we describe the tailored syntheses of double- and triple-decker arene-metal-carborane sandwich complexes from nido-R₂C₂B₄H₆ 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

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