Organometallics **1990**, *9*, 1177–1181

Organotransition-Metal Metallacarboranes. 16.[1] Directed Synthesis of Arene-Linked Metal Sandwich Complexes via Controlled Substitution on Boron

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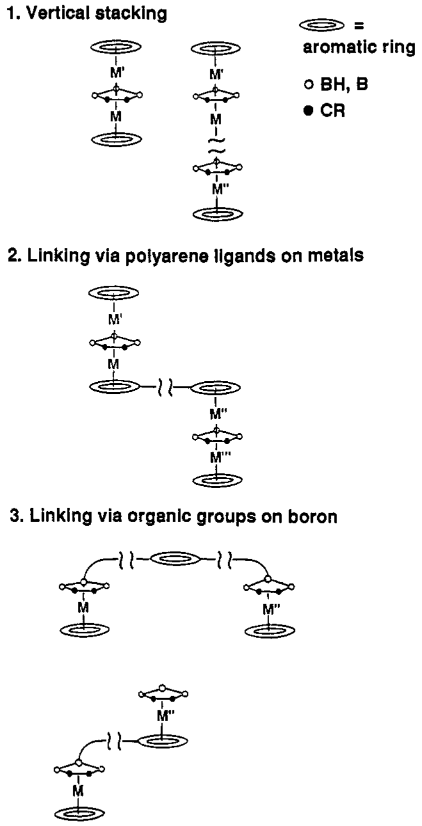
Received September 22, 1989

The synthetic utility of the B(5)-alkylation method described in the preceding article was explored via reactions with dihaloalkylarenes to create phenylene-linked bis(metallacarboranyl) complexes. *nido*-Metallacarboranes of the type $(Et_2C_2B_3H_5)M(ligand)$, where M(ligand) = $Co(C_5Me_5)$, $Fe(C_6Me_6)$, and $Ru(MeC_6H_4CHMe_2)$, were bridge-deprotonated and treated with xylyl bromides to form xylyl-bridged dimetallic species of the general formula $[(ligand)Me(Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$. Thermal reactions of the iron and ruthenium complexes with $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ resulted in η^6 coordination of a $(Et_2C_2B_4H_4)Fe$ unit to the phenylene ring of each complex, forming trimetallic species in which the central C_6 ring serves as a linchpin. A similar reaction of the *B*-benzyl complex $(Et_2C_2B_3H_4\text{-}5\text{-}CH_2C_6H_5)Fe(C_6Me_6)$ gave the benzyl-bridged diiron compound $5\text{-}[(Et_2C_2B_4H_4)Fe(C_6H_5CH_2)]\text{-}(Et_2C_2B_3H_4)Fe(C_6Me_6)$. The new complexes were isolated as air-stable solids in generally high yields and characterized from their ^{11}B and ^1H NMR, infrared, and mass spectra.

Introduction

The carborane ligands *nido*-2,3-$R_2C_2B_4H_4^{2-}$ and *cyclo*-$R_2C_2B_3H_3^{4-}$ form monomeric and oligomeric metal sandwich complexes of unusual stability and structural novelty.[2,3] Although these groups are steric and isoelectronic surrogates for arenes or cyclopentadienide ($C_5R_5^-$), they are much more versatile organometallic building blocks. For example, the small carborane ligands (of which many different C- and B-substituted derivatives are now accessible) form highly stable triple-decker and multilevel sandwich complexes with a variety of transition metals and have recently been shown to stabilize iron(II)–arene and ruthenium(II)–arene complexes that undergo reversible electrochemical oxidation to the metal(III) species.[4] In another recent application, the first known pyrrolyl–metal triple-decker complexes have been prepared by incorporating C_2B_3 bridging rings.[5] The versatility of these ligands can be enhanced still further by derivatizing them via general, reliable reactions with organic and organometallic reagents. This property is especially valuable in the construction of extended molecular systems.

Chart I. Modes of Assembly of Multiunit Sandwich Systems



Several conceptual approaches to the assembly of electron-delocalized multiunit complexes have been under study in our laboratory, as outlined in Chart I. These consist of (1) vertical stacking of metals, aromatic hydrocarbons, and $R_2C_2B_3$ rings as found in triple-decker[2a] and quadruple-decker[6] complexes,[7] (2) linkage of sandwich complexes through polyarenes that are π-coordinated to transition metals,[2b] and (3) linkage of metal–carborane units by means of organic groups bound to the carborane rings, a concept that is the focus of this paper. This last approach, if it is to be useful as a synthetic strategy, requires procedures for selectively attaching organic groups to boron (the carboranyl carbons are in most cases already organosubstituted). We have investigated two methods for accomplishing this: reactions of alkyl halides with C_2B_4 anions prior to metal complexation lead to B(4/6)-monoalkyl derivatives,[8] while similar treatment of metal–C_2B_3

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[1] Part 15: Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics*, preceding paper in this issue.

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

[3] Recent reviews: (a) Grimes, R. N. *Pure Appl. Chem.* **1987**, *59*, 847. (b) Grimes, R. N. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; Molecular Structure and Energetics 5; VCH: New York, 1988; Chapter 11, pp 235–263.

[4] Merkert, J. M.; Geiger, W. E., Jr.; Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1989**, *8*, 1580.

[5] Chase, K. J.; Grimes, R. N. *Organometallics* **1989**, *8*, 2492.

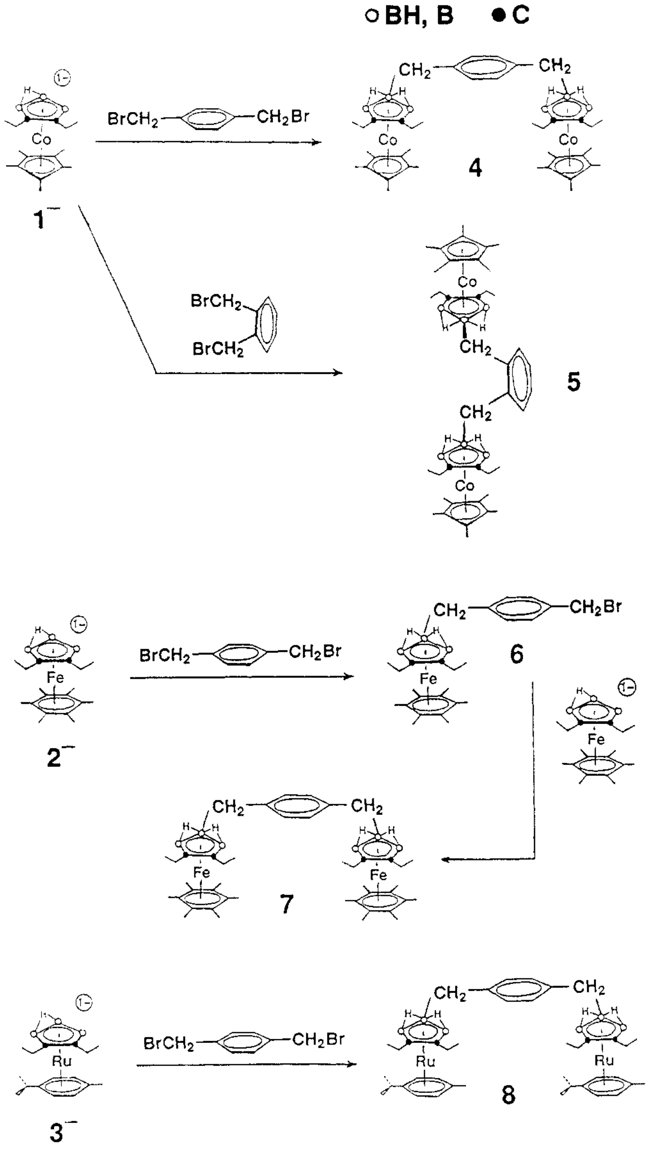
[6] Fessenbecker, A.; Siebert, W.; Attwood, M. D.; Grimes, R. N. To be submitted for publication.

[7] A number of triple-decker, quadruple-decker, and larger stacked complexes have been constructed from organoboron ligands having C_3B_2, C_2B_2S, and C_4B rings; for leading references see: (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.

[8] Davis, J. H., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 4213.

0276-7333/90/2309-1177$02.50/0

Scheme I



complexes produces exclusively B(5)-substituted products, which can be further B-alkylated as desired. The latter route, which was elaborated in the preceding article,[1] can be exploited to link two or more metal complex units with electron-delocalized organic moieties. Here we describe the application of this method in the controlled synthesis of arene-linked multiunit complexes.

Results and Discussion

Synthesis of Xylyl-Bridged Complexes. Reactions of bis(haloalkyl)arenes and 2 molar equiv of a $(Et_2C_2B_3H_4)M(ligand)^-$ anion (1^-, 2^-, or 3^-), employed as the Li^+ salt in THF solution, to synthesize phenylene-linked bis(metallacarborane) complexes are shown in Scheme I. The alkylations proceed stepwise, forming initially a *B*(*5*)-bromoxylyl monomer that interacts with a second metal–carborane anion to give the target compounds **4**, **5**, **7**, and **8** in good yield. This sequence was established through the isolation of the 5-[(*p*-(α-bromoxylyl)] derivative of the cobalt complex (**1c** in the preceding paper) and the corresponding iron compound **6** in the present work.

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

compd^{a-c}	δ (J_{BH}, Hz)	rel areas
p-$[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (**4**)	23.41, 0.33	1:2
o-$[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (**5**)^d	22.22, -0.73	1:2
$(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2C_6H_4CH_2Br)$ (**6**)^e	21.20, -3.81	1:2
p-$[(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (**7**)^e	19.99, -4.62	1:2
p-$[(MeC_6H_4CHMe_2)Ru\text{-}(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (**8**)	16.10, -4.04 (99)	1:2
5-$[(Et_2C_2B_4H_4)Fe(C_6H_5CH_2)]\text{-}(Et_2C_2B_3H_4)Fe(C_6Me_6)$ (**9**)	5.07, 2.81, 0.32	1:1:5
5-$[(Et_2C_2B_3H_5)Fe(C_6H_5CH_2)]\text{-}(Et_2C_2B_3H_4)Fe(C_6Me_6)$ (**10**)	2.47 (126), -0.55 (132)	2:1
p-$[(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2(C_6H_4)Fe(Et_2C_2B_4H_4)$ (**11**)	18.21, 8.17, 1.65, -3.04	1:1:4:4
p-$[(MeC_6H_4CHMe_2)Ru(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2(C_6H_4)\text{-}Fe(Et_2C_2B_4H_4)$ (**12**)	16.60, 8.32, 4.14, 1.83, -3.92	1:1:2:2:4

[a] Shifts relative to $BF_3{\cdot}OEt_2$, positive values downfield. [b] *n*-Hexane solution. [c] H-B coupling constant is given in parentheses, when resolved. [d] Chloroform solution. [e] Dichloromethane solution.

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

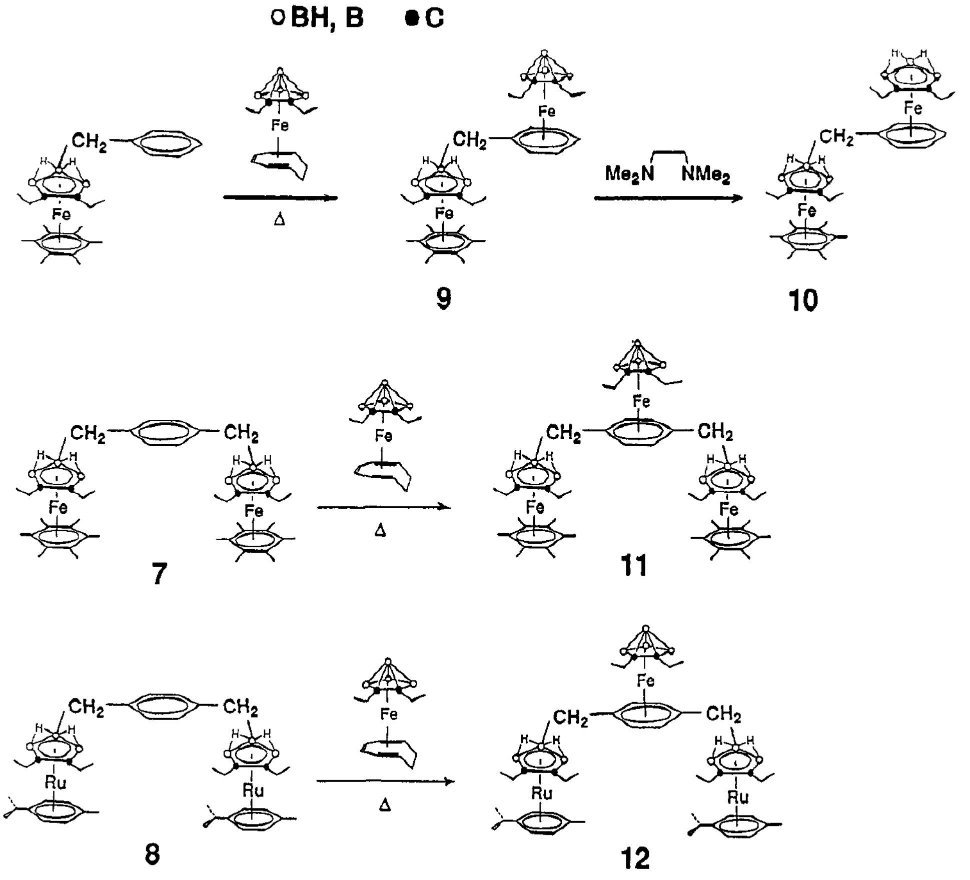
compd	δ^{a-c}
4	6.93 s (C_6H_4), 2.17 br s (CH_2), 2.08 m (CH_2), 1.86 m (CH_2), 1.77 s (C_5Me_5), 1.02 m (CH_3), -5.6 br s (B-H-B)
5	6.95 m (C_6H_4), 6.90 m (C_6H_4), 2.52 br s (B-CH_2), 2.19 m (CH_2), 1.83 s (C_5Me_5), 1.81 m (CH_2), 1.03 m (CH_3), -5.4 br s (B-H-B)
6	6.87 s (C_6H_4), 4.46 s (CH_2Br), 2.17 s (C_6Me_6), 1.90 m (CH_2), 1.73 m (CH_2), 0.95 t (CH_3), -6.03 br s (B-H-B)
7	6.85 s (C_6H_4), 2.24 s (B-CH_2), 2.15 s (C_6Me_6), 1.86 m (CH_2), 1.69 m (CH_2), 0.95 t (CH_3), -6.05 br s (B-H-B)
8	6.95 s (xylyl C_6H_4), 5.07 q (cymene C_6H_4), 2.59 m (isopropyl CH), 2.20 s (B-CH_2), 2.16 s (isopropyl Me), 2.07 m (CH_2), 1.91 m (CH_2), 1.23 d (cymene Me), 1.03 t (CH_3), -4.59 br s (B-H-B)
9	5.31 m (C_6H_5), 5.16 m (C_6H_5), 2.62 m (CH_2), 2.35 m (CH_2), 2.17 s (C_6Me_6), 2.16 br s (B-CH_2), 1.27 m (CH_3), -6.52 br s (B-H-B)
10	5.09 m (C_6H_5), 2.38 m (CH_2), 2.15 s (C_6Me_6), 2.14 br s (B-CH_2), 1.12 m (CH_3), -6.50 br s (B-H-B)
12	5.15 br s (cymene C_6H_4), 5.02 s (xylyl C_6H_4), 2.58 m (CH_2, isopropyl CH), 2.30 m (CH_2), 2.18 s (cymene Me), 2.10 br s (B-CH_2), 2.02 m (CH_2), 1.85 m (CH_2), 1.26 d (isopropyl Me), 1.22 m (C_2B_3 Me), 0.99 m (C_2B_4 Me), -4.99 br s (B-H-B)

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

The linked complexes whose proposed structures are depicted in Scheme I are yellow, air-stable crystalline solids that were structurally characterized from their ^{11}B and ^1H NMR, infrared, and mass spectra (Tables I–III and Experimental Section). In each case, the proton-coupled boron NMR spectra are very similar to those of their monomer precursors[1] **1**, **2**, and **3**, exhibiting 1:2 patterns with the unique B(5) resonance appearing as a singlet, reflecting alkyl substitution at that position. In all four compounds, both the ^{11}B and ^1H NMR spectra reflect the idealized C_{2v} symmetry of the proposed geometry. We note here the significant advantages of alkylation at B(5): the highly symmetrical products exhibit readily interpretable NMR patterns, and only a single isomer is obtained in each case, avoiding the complications (i.e., lower individual yields and the need for separation of stereoisomers) that would result from asymmetric (B(4/6)) substitution.

Linkage via Metal–Arene π-Coordination to *B*-(Alkylaryl) Complexes. Earlier studies in this laboratory[9] demonstrated that thermal reactions of

Scheme II



$(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ complexes with arenes result in displacement of the cyclooctatriene ligand by the arene, giving $(R_2C_2B_4H_4)Fe$(arene) products. As this type of reaction has proved generally successful in our research (for example, working with a variety of monoarenes and polyarenes[3]), we explored its application to the aryl-containing complexes described above and in the accompanying paper. Our rationale was that η^6 coordination of $(R_2C_2B_4H_4)Fe$ fragments to the arene ring in such species could furnish an additional synthetic pathway for linking metal–carborane sandwich units. As a trial experiment, the *B*(5)-benzyl derivative $(C_6Me_6)Fe(Et_2C_2B_3H_4\text{-}5\text{-}CH_2Ph)$ (**2e** in the preceding article) was treated with $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ to give the dimetallic linked species **9** as a yellow solid (Scheme II). The reaction of **9** with wet TMEDA (tetramethylethylenediamine) afforded the "decapitated"[3] complex **10**. The proposed structures of **9** and **10** are consistent with their unit- and high-resolution mass spectra as well as their ^{11}B and ^1H NMR spectra, which exhibit features characteristic of both constituent metallacarborane fragments.[1] Also significant is a substantial upfield shift of the phenyl protons in **9** and **10** (relative to the signals in the uncomplexed precursor), which is a consequence of π-coordination of the C_6 ring to iron.

Corresponding reactions of the xylyl-bridged diiron and diruthenium complexes **7** and **8** proceeded similarly to give the trimetallic species **11** and **12**, respectively, as shown in Scheme II. The structural characterization of these compounds from spectroscopic data was straightforward, aided by the high symmetry, which simplified interpretation of the NMR data (vide supra). As with **9**, the ^{11}B and ^1H NMR patterns in **11** and **12** closely resemble those of the original compounds **7** and **8** with $(Et_2C_2B_4H_4)Fe$

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

compd	abs
4	2960 vs, 2958 vs, 2925 vs, 2914 vs, 2910 vs, 2909 vs, 2867 vs, 2865 vs, 2495 vs, 2492 vs, 2362 vs, 2337 vs, 1734 vs, 1700 vs, 1696 vs, 1684 vs, 1653 s, 1558 vs, 1539 vs, 1506 vs, 1456 vs
5	2958 s, 2923 s, 2881 s, 2851 s, 2506 s, 2361 s, 1700 s, 1685 s, 1653 s, 1559 s, 1507 s, 1457 s
6	3010 m, 2955 vs, 2919 vs, 2857 s, 2474 s, 1929 m, 1218 m, 1066 m, 1011 m, 949 w, 892 m, 866 w, 822 m, 774 m, 742 m, 652 m
7	3010 w, 2960 s, 2908 vs, 2865 s, 2495 s, 2481 s, 1958 w, br, 1500 s, 1443 s, 1379 s, 1265 w, 1216 m, 1064 m, 1008 m, 899 m, 841 m, 770 s
8	3043 w, 2959 s, 2923 s, 2865 s, 2823 m, 2485 s, 1898 m, br, 1851 w, 1732 w, 1593 w, 1531 m, 1504 s, 1494 m, 1463 s, 1446 s, 1377 s, 1227 s, 1196 w, 1133 w, 1084 w, 1053 m, 1032 m, 1008 w, 947 w, 895 s, 859 m, 842 s, 804 m, 777 s, 746 w
9	2922 m, 2853 m, 1467 s, 1462 s, 1453 s, 1450 s, 1446 s, 1435 s, 1428 s, 1422 s, 1417 s, 1415 s, 1379 s, 1365 s
10	2494 m, 2479 m, 2477 m, 2442 m, 2431 m, 1964 m, 1957 m, 1954 m, 1950 m, 1940 m, 1937 m, 1934 m, 1931 m, 1920 m, 1916 m, 1914 m, 1906 m, 1903 m, 1900 m, 1898 m, 1893 m, 1887 m, 1886 m, 1874 m, 1864 m, 1861 m, 1858 m, 1443 m, 1377 m
11	2962 s, 2923 m, 2918 m, 2868 s, 2856 s, 2850 s, 2516 s, 2361 s, 2340 s, 2337 s, 1265 m, 739 m, 668 m
12	2965 vs, 2961 vs, 2925 vs, 2886 vs, 2881 vs, 2868 vs, 2858 vs, 2855 vs, 2850 vs, 2530 vs, 2524 vs, 2518 vs, 2361 s, 2339 vs, 2337 vs, 1734 vs, 1700 s, 1696 vs, 1685 vs, 1653 s, 1636 vs, 1559 s, 1539 vs, 1507 vs, 1457 vs

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

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(9) (a) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1983**, *2*, 506. (b) Swisher, R. G.; Sinn, E.; Butcher, R. J.; Grimes, R. N. *Organometallics* **1985**, *4*, 882. (c) Spencer, J. T.; Grimes, R. N. *Organometallics* **1987**, *6*, 323, 328 and references therein. (d) Attwood, M. D.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300.

peaks superimposed. Again, the observation of strong upfield shifts of the phenylene proton resonances in these complexes is diagnostic of metal–ring coordination and supports the structural assignments.

The isolation of **11** and **12** is an illustration of true directed synthesis, in which two previously developed reaction types, B(5)-alkylation and Fe–arene complexation via η^6-C_8H_{10} displacement, have been combined to provide a route to novel complexes of specific design. The products themselves are of interest in that the benzene ring in the center provides an anchor for three distinct metal–carborane units, two of them via σ-bonds through methylene groups and the third via an η^6–Fe bonding interaction. We have found that the presence of CH_2 spacer units between the carborane and arene rings is essential for the formation of trimetallic complexes of this type; species incorporating two metallacarborane clusters linked *directly* by a C_6H_4 ring[2b] *do not* undergo thermal reactions with $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ to yield trimetallic complexes.[10] It has not yet been established whether electronic or steric factors are primarily responsible for the "deactivation" of the linking phenylene ring in such species, although inspection of models suggests that steric crowding plays a significant role.

General Observations

A continuing theme in the work described in this series of papers is the development of reliable synthetic methods for preparing organotransition-metal–carborane complexes suitable as building-block units and for linking and/or stacking them in desired patterns to create new types of organometallic networks. The chemistry reported here demonstrates that regiospecific B(5)-alkylation is a useful tool in such synthesis. Moreover, its utility is further extended by combining it with previously known metallacarborane reactions, such as cyclooctatriene displacement from $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ by arene rings. Other approaches to linked and stacked multiunit systems are under study and will be reported in subsequent publications.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in earlier publications in this series.[1] All new products gave unit-resolution mass spectra in good agreement with calculated spectra, supported by high-resolution mass measurements. In addition, the fragmentations exhibited in the unit-resolution spectra are consistent with the proposed structures, e.g., loss of ligand or M(ligand) units from the parent ions.

Synthesis of *p*-$[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (4). In an evacuated system, complex **1**[2a] (0.159 g, 0.51 mmol) was deprotonated in THF solution at −78 °C via addition of 20 mL (0.51 mmol) of 2.5 M *tert*-butyllithium in hexane, as previously described.[2a] To the solution was added from a tip-tube 67 mg (0.26 mmol) of α,α'-dibromo-*p*-xylene. The solution turned red-brown; when it was stirred for 24 h, it faded to yellow-brown. The flask was opened to the air, and the solvent was removed by rotary evaporation to give a brown solid, which was extracted with dichloromethane and the extract filtered through silica to give a yellow solution that on evaporation produced **4** as yellow needles (0.137 g, 0.19 mmol, 74%). Exact mass: calcd for $^{59}Co_2{}^{13}C_2{}^{12}C_{38}{}^{11}B_6{}^{1}H_{66}{}^{+}$, 732.4454; found, 732.4522.

Synthesis of *o*-$[(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (5). By the procedure above, 0.165 g (0.52 mmol) of **1** was deprotonated in THF with an equimolar quantity of 1.7 M *tert*-butyllithium, and 70 mg (0.26 mmol) of α,α'-dibromo-*o*-xylene was added, producing a red-brown solution. When it was stirred for 24 h, the solution faded to yellow and a canary yellow solid precipitated. Evaporation of the THF solution gave a yellow solid, which was extracted with a large volume of chloroform to produce a yellow solution. Filtration through glass wool followed by slow evaporation gave 0.150 g (0.21 mmol, 79%) of **5** as yellow crystals. Compound **5** is insoluble in THF, ether, or alkanes and is only very slighly soluble in chloroform. Exact mass: calcd for $^{59}Co_2{}^{13}C_2{}^{12}C_{38}{}^{11}B_6{}^{1}H_{66}{}^{+}$, 732.4454; found, 732.4522.

Synthesis of $(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2C_6H_4CH_2Br)$ (6) and *p*-$[(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (7). The above procedure was followed to deprotonate 0.212 g (0.63 mmol) of **2** with an equimolar amount of *tert*-butyllithium in THF, which produced a color change from red to orange on stirring for 10 min at room temperature. The flask was recooled to −78 °C, and 83 mg of α,α'-dibromo-*p*-xylene was added, causing the color to change from red to orange within a few minutes. When it was stirred at room temperature for 12 h, the solution turned yellow and a fine yellow solid precipitated. The THF was removed by evaporation; the residue was dissolved in dichloromethane and filtered through silica gel. The solution was chromatographed on a silica column in 50/50 dichloromethane–hexane, giving two yellow bands, which were collected as yellow solids and characterized as **6** (85 mg, 0.164 mmol, 26%) and **7** (0.119 g, 0.153 mmol, 49%). Exact mass for **6**: calcd for $^{56}Fe^{12}C_{26}{}^{11}B_3{}^{1}H_{40}{}^{81}Br^{+}$, 522.1922; found, 522.1916. Exact mass for **7**: calcd for $^{56}Fe_2{}^{12}C_{44}{}^{11}B_6{}^{1}H_{72}{}^{+}$, 778.4891; found, 778.4898.

Synthesis of *p*-$[(MeC_6H_4CHMe_2)Ru(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2C_6H_4$ (8). A 0.432-g (0.122-mmol) sample of **3** was deprotonated as in the previous cases, and the solution of 3^- was stirred at room temperature for 15 min, during which time the color changed from yellow to orange. The reactor was cooled to −78 °C, 0.161 g (0.061 mmol) of α,α'-dibromo-*p*-xylene was added, and the solution was warmed with stirring to room temperature, producing a red-orange solution that turned yellow after 30 min. The solution was stirred overnight, after which the THF was removed by evaporation to leave a pale yellow solid that was not readily soluble in hexane and therefore was filtered through silica as a dichloromethane solution. Subsequent column chromatography of the solution on silica gave 0.378 g (0.466 mmol, 76%) of **8** as a light yellow solid. Exact mass: calcd for $^{100}Ru_2{}^{12}C_{40}{}^{11}B_6{}^{1}H_{64}{}^{+}$, 814.3661; found, 814.3690.

Synthesis of 5-$[(Et_2C_2B_4H_4)Fe(C_6H_5CH_2)](Et_2C_2B_3H_4)Fe(C_6Me_6)$ (9). A 47-mg (0.11-mmol) quantity of dry solid $(C_6Me_6)Fe(Et_2C_2B_3H_4\text{-}5\text{-}CH_2Ph)$ (**2e** in the accompanying paper) was placed in a thick-walled Carius tube together with 64 mg (0.22 mmol) of $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$[11] in a minimal volume of dichloromethane. The tube was evacuated on a vacuum line, leaving a dry solid, and was flame-sealed while under vacuum, following which it was placed in an oven at 195 °C for 2 h, removed, and cooled. The reaction tube was opened, the contents were extracted with dichloromethane, and the solution was filtered through silica to give a dark orange-brown solution. After solvent removal by rotary evaporation, the residue was dissolved in 50/50 dichloromethane–hexane and chromatographed on a silica gel plate. Four bands were observed, consisting (top to bottom) of C_8H_8, $(C_6Me_6)Fe(Et_2C_2B_3H_4\text{-}5\text{-}CH_2Ph)$, $(Et_2C_2B_4H_4)Fe(C_8H_{10})$, and **9** as identified via mass spectroscopy. The lowest band was extracted with dichloromethane, and solvent was removed to give 39 mg (0.064 mmol, 58%) of yellow solid **9**. Exact mass: calcd for $^{56}Fe_2{}^{12}C_{31}{}^{11}B_7{}^{1}H_{53}{}^{+}$, 614.3497; found, 614.3493.

Synthesis of 5-$[(Et_2C_2B_3H_5)Fe(C_6H_5CH_2)](Et_2C_2B_3H_4)Fe(C_6Me_6)$ (10). Compound **9** (27 mg, 0.044 mmol) was refluxed for 90 min in 5 mL of wet TMEDA (tetramethylethylenediamine) open to the atmosphere. The TMEDA was evaporated, the yellow residue extracted with dichloromethane, the extract filtered through silica, and the solvent removed. The residue was dissolved in dichloromethane and the solution chromatographed on a silica gel plate in 50/50 dichloromethane–hexane, giving one major band, which was collected and the solvent removed to give 22 mg (0.036 mmol, 83%) of yellow solid **10**. Exact mass: calcd for $^{56}Fe_2{}^{12}C_{31}{}^{11}B_6{}^{1}H_{50}{}^{+}$, 600.3169 (parent − 4H); found, 600.3121.

Synthesis of *p*-$[(C_6Me_6)Fe(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CH_2)]_2(C_6H_4)Fe(Et_2C_2B_4H_4)$ (11). The procedure employed in the synthesis of **9** was followed with use of 74 mg (0.095 mmol) of

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[10] Davis, J. H., Jr.; Grimes, R. N. Unpublished observations.

[11] Maynard, R. B.; Swisher, R. G.; Grimes, R. N. *Organometallics* 1983, *2*, 500.

7 and 55 mg (0.19 mmol) of the iron cyclooctatriene complex. Workup as before gave 9 mg of product, corresponding to ca. 10% yield. Exact mass: calcd for $^{56}Fe_3{}^{12}C_{50}{}^{11}B_{10}{}^{1}H_{86}{}^{+}$, 964.5708; found, 964.5714.

Synthesis of *p*-[(MeC$_6$H$_4$CHMe$_2$)Ru(2,3-Et$_2$C$_2$B$_3$H$_4$-5-CH$_2$)]$_2$(C$_6$H$_4$)Fe(Et$_2$C$_2$B$_4$H$_4$) (12). The procedure employed in the synthesis of 9 and 11 was followed with use of 83 mg (0.10 mmol) of 8 and 60 mg (0.21 mmol) of the iron cyclooctatriene complex. The reaction was conducted at 150 °C for 30 min followed by 180 °C for 90 min. Workup as described above gave 22 mg (0.02 mmol, 22%) of brown solid **12**. The unit-resolution mass spectrum of 12 exhibits a broad parent ion envelope between m/z 1005 and 988 that closely matches the intensity pattern calculated from natural isotope distributions, with the high-mass peak corresponding to $^{104}Ru_2{}^{56}Fe^{13}C^{12}C_{45}{}^{11}B_{10}{}^{1}H_{78}{}^{+}$). Major fragments appear at P − 130 (loss of $Et_2C_2B_4H_4$) and P − 186 (loss of $Fe(Et_2C_2B_4H_4)$).

Acknowledgment. We thank Dr. Mike Kinter for the high-resolution mass spectra and Kevin Chase for several of the boron NMR spectra. The support of the National Science Foundation (Grant No. CHE 87-21657) and the U.S. Army Research Office is gratefully acknowledged.

Monodemethylation of a Coordinated Ditelluroether. Synthesis and X-ray Structure of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$]

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Received September 22, 1989

When [Pd{*o*-C$_6$H$_4$(TeMe)$_2$}I$_2$] is heated for short periods in dimethyl sulfoxide or the solution allowed to stand for several days at room temperature, monodemethylation occurs with the formation of the title complex, the structure of which was established by a single-crystal X-ray study. Crystal data for [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$] at room temperature: monoclinic, a = 11.142 (2) Å, b = 20.785 (2) Å, c = 19.596 (4) Å, β = 92.66 (2)°, Z = 4, space group $P2_1/n$, and R_w = 0.045 for 4467 data ($F > 3\sigma(F)$). The structure is based on a tetrameric unit containing an eight-membered ring (Pd$_4$Te$_4$) in which each square-planar-coordinated Pd atom is surrounded by one I and three Te atoms. The Te atom that does not have a methyl group attached is bonded to two Pd atoms and is part of the ring. Some spectroscopic properties of the title complex are reported and discussed. Realkylation does not occur on treatment of the tetramer with MeI.

Introduction

S-Dealkylation of metal-coordinated thioether groups has been observed in many systems,[1] the first report of such a process being over 100 years ago.[2] Detailed investigations have been carried out on a number of nickel(II), palladium(II), and platinum(II) systems, including those with the ligands *o*-C$_6$H$_4$(AsMe$_2$)(SMe),[3] PhP(*o*-C$_6$H$_4$SMe)$_2$,[4] *o*-C$_6$H$_4$(PPh$_2$)(SMe), and *o*-C$_6$F$_4$(PPh$_2$)(SMe),[5] the dealkylation occurring upon heating the complex in a high-boiling solvent such as *N*,*N*-dimethylformamide or dimethyl sulfoxide (DMSO) and being promoted by the addition of nucleophiles such as I$^-$ and CNS$^-$. Mechanistically the dealkylation is thought to be similar to Zeisel ether cleavage,[5,6] and the reaction can often (but not always) be reversed by treatment of the resulting thiolate complex with alkylating agents.[1-7] Similar Se-dealkylation of coordinated selenoether functions has been reported.[6,8] Dealkylation of coordinated dithio-[9] and diselenoethers[10] occurs either on pyrolysis or on heating in DMSO solution, but the reactions are complicated by the presence of several potential sites of R–S(Se) bond cleavage. Much less is known about tellurium ligands,[11] and chelating bidentate telluroether complexes have been reported only recently.[12,13] Complexes of telluride (RTe$^-$) groups have been prepared from RTeTeR or NaTeR and suitable metal substrates,[14] and the complex [Pt(PPh$_3$)$_2$(*o*-C$_6$H$_4$Te$_2$)] has been structurally characterized.[15] Here we report the first example of monodealkylation of a coordinated ditelluroether and the structure of the unusual tetrameric product.

Experimental Section

Physical measurements were made as described previously.[12,13]

Preparation of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$]. [Pd{*o*-C$_6$H$_4$(TeMe)$_2$}I$_2$][13] (0.1 g) was dissolved in DMSO (5 cm^3) and heated on a water bath for 3 h. A black solid separated out over this period. This was filtered off, washed with DMSO and diethyl ether, and dried in vacuo; yield 0.065 g, 81%. Anal. Calcd for $C_{28}H_{28}I_4Pd_4Te_8$: C, 14.5; H, 1.2. Found: C, 14.2; H, 1.2.

X-ray Structure Analysis. Dark, air-stable, rectangular plates of [{Pd(*o*-C$_6$H$_4$(TeMe)Te)I}$_4$] were obtained during an attempt to obtain the ditelluroether complex from DMSO solution

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