(*m*-carborane-9-yl) ether, phenyl *m*-carboran-9-yl ether, and 9-hydroxy-*m*-carborane. Ether was removed under vacuum, and the residual oil was chromatographed on silica 40/100 μ (15 × 200 mm column) first with hexane, to give 9-chloro-*m*-carborane (0.164 g; 63% yield), mp 220–222 °C (hexane), and then with a benzene–hexane (1:1) mixture, to give 0.036 g (ca. 10%) of a mixture of phenyl *m*-carboran-9-yl ether (for the mass spectrum see ref 22) and bis(*m*-carboran-9-yl) ether.[22] The ratio of the two components of this mixture was determined by GC-MS analysis. Finally, elution with ether gave 9-hydroxy-*m*-carborane (0.024 g; 10%), mp 326–328 °C (benzene–heptane).

The aqueous solution was acidified with 15% HCl, and the mixture was treated with aqueous bromine, to give 2,4,6-tribromophenol, which was filtered out, dried, and sublimed under vacuum: yield 0.130 g (27%); mp 92–94 °C.

7. Reaction of Phenyl(*m*-carboran-9-yl)bromonium Tetrafluoroborate with NaF. A mixture of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate (0.05 g; 0.13 mmol), sodium fluoride (0.013 g; 0.38 mmol), dichloromethane (1 mL), and water (1 mL) was vigorously stirred under reflux for 5 h. GLC and GC-MS analyses of the organic layer (9-iodo-*m*-carborane as internal standard) showed the formation of benzene, bromobenzene (exact yields were not determined; ca. 10% and 70%, respectively), 9-fluoro-*m*-carborane (45% yield), and 9-bromo-*m*-carborane (8% yield). No fluorobenzene was found among the reaction products (GC-MS).

8. Reaction of 1 with NaF. A mixture of **1** (0.05 g; 0.15 mmol), sodium fluoride (0.018 g; 0.43 mmol), dichloromethane (1 mL), and water (1 mL) was vigorously stirred under reflux for 5 h. GLC and GC-MS analyses of the organic layer (9-iodo-*m*-carborane as internal standard) showed the formation of benzene, chlorobenzene (exact yields were not determined; ca. 10% and 70%, respectively), 9-fluoro-*m*-carborane (50%), and 9-chloro-*m*-carborane (10%). Again, formation of fluorobenzene (GC-MS) did not occur.

9. Reaction of 1 with Pyridine. A solution of **1** (1.00 g; 2.9 mmol) in pyridine (10 mL) was refluxed for 9 h. Pyridine was removed under vacuum, and the residue was treated with ether, giving an oil that solidified only after a minimum of five reprecipitations with ether from acetone. The yield of pyridinium tetrafluoroborate was 0.083 g (68%); mp 210–225 °C (ethanol; see ref 1). Combined ether and ether–acetone solutions were evaporated to dryness. The remaining residue was washed with benzene, to give boric acid (0.174 g; 9.5% yield), which was identified by IR spectroscopy. The benzene solution was extracted with 10% acetic acid. Combined acidic solutions were treated with 10% NaOH, and the mixture was extracted with ether. Evaporation of ether gave a mixture of α-, β-, and γ-phenylpyridines (0.008 g; 2% yield; identified by TLC comparison, with authentic samples). The remaining benzene solution (after extraction of phenylpyridines) was filtered through alumina and reduced to dryness. The solid residue was washed with hexane, to give crystalline zwitterionic B–N-bonded pyridinium 7,9-dicarba-*nido*-undecaborate, which was purified by vacuum sublimation: yield 0.326 g (53%); mp 163–165 °C (see refs 9 and 29). Evaporation of the hexane solution and vacuum sublimation of the residue gave 9-chloro-*m*-carborane (0.133 g; 25% yield), mp 220–222 °C.

10. Reaction of 1 with PPh$_3$. An acetone solution (3 mL) of **1** (0.20 g; 0.58 mmol) and triphenylphosphine (0.31 g; 1.18 mmol) in a quartz tube was irradiated with UV light (Soviet-made PRK-2 mercury lamp) for 38 h. GLC analysis of the reaction mixture showed the presence of benzene (ca. 1% yield) and the absence of *m*-carborane among the reaction products. The ^{31}P NMR spectrum of the reaction mixture showed no formation of triphenyl(*m*-carboran-9-yl)phosphonium tetrafluoroborate (for the spectrum see ref 3). Treatment of the mixture with ether led to the precipitation of tetraphenylphosphonium tetrafluoroborate (0.232 g; 95% yield), mp 348–351 °C (acetone–ether; see ref 30). The ether solution was reduced to ca. 5 mL and treated with methyl iodide (0.5 mL), and the resulting mixture was refluxed for 1.5 h, to remove excess PPh$_3$. The methyltriphenylphosphonium iodide formed was filtered out, the mother liquor evaporated, and the remaining solid extracted with hexane. The hexane solution was filtered through alumina and evaporated, to give 9-chloro-*m*-carborane (0.086 g; 82% yield), mp 220–222 °C (hexane).

11. Reaction of Phenyl(*m*-carboran-9-yl)bromonium Tetrafluoroborate with NaCl. A mixture of phenyl(*m*-carboran-9-yl)bromonium tetrafluoroborate (0.049 g; 0.13 mmol), sodium chloride (0.02 g; 0.34 mmol), chloroform (1 mL), and water (1 mL) was vigorously stirred under reflux for 1 h. GLC analysis of the organic phase (iodobenzene as internal standard) showed the formation of only bromobenzene and 9-chloro-*m*-carborane in quantitative yields.

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Organotransition-Metal Metallacarboranes. 18.[1] η^6,η^5-Benzyltetramethylcyclopentadienide(1−) as a Bridging Ligand in Multilevel Iron–Cobalt Sandwich Complexes

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Received September 26, 1990

Benzyltetramethylcyclopentadiene ($Me_4C_5CH_2Ph$) was prepared in high yield from commercial reagents and deprotonated with butyllithium to give the red title anion, which was converted to the orange sandwich complex $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)$ (**1**) via reaction with $CoCl_2$ and $Na^+Et_2C_2B_4H_5^-$ in THF. Decapitation (apex BH removal) of **1** with wet TMEDA gave yellow $(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (**2**), which in turn was bridge-deprotonated and reacted with $CoCl_2$ and the title anion to give a burgundy-colored triple-decker complex, $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (**3**). The thermal cyclooctatriene-displacement reaction of **1** with $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ produced an orange bimetallic species, $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**4**). Similar treatment of **3** with the same cyclooctatriene–ferracarborane reagent gave the iron–dicobalt complex $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (**5**) and the diiron–dicobalt species $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (**6**), both isolated as red oils. Complex **2** was benzylated at the B(5) location on the open face by bridge deprotonation to give the anion **2**$^-$, followed by reaction with benzyl bromide to form the yellow solid derivative $(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**7**). Mono- and bis(ferracarboranyl) derivatives of **7** were prepared by thermal displacement of cyclooctatriene from $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ by **7** to give primarily $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**8**) and a small amount of $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**9**). The monoiron species **8** consisted almost entirely of one isomer (**8a**), having the iron coordinated to the *B*-benzyl unit; the alternative isomer (**8b**), in which the iron is bonded to the cyclopentadienyl benzyl group, was detected in only trace amounts in NMR spectra. The much higher reactivity in **7** of the *B*-benzyl vs the cyclopentadienyl benzyl group toward iron coordination suggests deactivation of the latter by the adjacent cobalt atom.

Introduction

Bimetallic[2] and polymetallic[3] linked sandwich complexes are attracting increasing attention, in part because they provide a bridge between molecular chemistry and materials science and also because they have potential for utilization in novel electronic devices. In our research, a current focus of interest is the design

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0020-1669/91/1330-1765\$02.50/0

Table I. 115.8-MHz ^{11}B FT NMR Data[a-c]

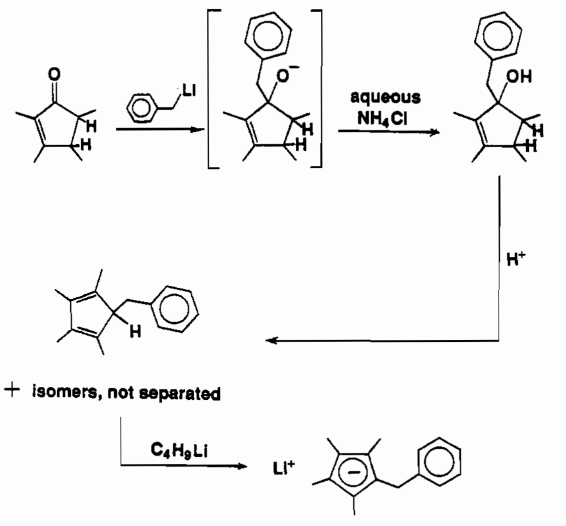
compound	δ (J_{BH}, Hz)	rel areas
$(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)$ (**1**)	13.38 (136), 4.09 (134)	1:2
$(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (**2**)	6.88 (140), 3.89 (129)	1:2
$(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (**3**)	61.44, 9.41	1:2
$(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**4**)	13.55 (141), 7.83 (150), 6.28, 4.34 (162),[d] 1.84 (152)[d]	1:1:1:3:2
$(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (**5**)	61.31, 8.81,[d] 6.54,[d] 1.89,[d] –0.75[e]	1:2:1:3
$(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (**6**)	5.94,[d] 4.39,[d] 0.96,[d] (114)	3:3:5
$(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**7**)	22.33, –0.09 (80)	1:2
$(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**8a**)	20.4,[f] [5.16, 4.25], 0.83	1:3:3
$(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**9**)	5.8,[d,f] 1.7[d,f]	5:6

[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] Superimposed/overlapped resonances. [e] Shoulder. [f] Broad resonance.

and construction of multiunit metal sandwich complexes that incorporate cyclic planar C_2B_3 or pyramidal C_2B_4 carborane units together with C_6 (arene) or C_5 (cyclopentadienyl) aromatic hydrocarbon ligands.[1a,b,4,5] The carborane ligands serve a multifold purpose: to provide electronic stabilization for unusual or otherwise unstable structures (e.g., multidecker complexes); to promote electron delocalization between metal centers; and to serve as points of attachment for external functional groups and for intermolecular linkage of sandwich units. One of our objectives is the controlled, stepwise assembly of electron-delocalization oligomers and polymers containing multidecker sandwich units whose metal atoms are capable of communicating with each other electronically. To this end, we have explored the use of a variety of polycyclic aromatic hydrocarbons as linking groups,[4b,6] including fulvalenide ($[C_5H_4]_2^{2-}$) and bis(cyclopentadienyl)polyphenylenide ions, which have led to the synthesis of some novel species including the first examples of fulvalene-bridged bis(metallacarborane) complexes and linked triple-decker sandwiches.[4b]

In the systems we have examined, the metal–hydrocarbon moieties are in most cases either $(\eta^6\text{-}C_6R_6)M^{2+}$ or $(\eta^5\text{-}C_5R_5)M'^{2+}$, where M and M′ are iron-group and cobalt-group metals, respectively; either type, and indeed most transition elements, readily bond to the carborane ligands (this is, in fact, one of the major virtues of the carboranes in organometallic synthesis). Heterometallic species incorporating both kinds of the above metal–ligand groups in the same molecule are of interest, and in fact we have recently reported a few such complexes: these include Fe–Co triple-decker sandwiches[4a,7] as well as *B*-benzyl or *B*-xylyl cobalt–carborane π-complexes whose aryl rings are η^6-coordinated to iron atoms.[1b] However, from the standpoint of designed synthesis, it is desirable to have other, more general approaches to the mixed-metal species. We were attracted to the concept of a simple, readily accessible bicyclic hydrocarbon ligand which easily coordinates to both iron- and cobalt-series metals and which can be used as a template on which to build polymetallic multisandwich arrays. We have found that the benzyltetramethylcyclopentadienide ion satisfies these criteria very well, and here report its synthesis and utilization in metal sandwich chemistry.

Scheme I



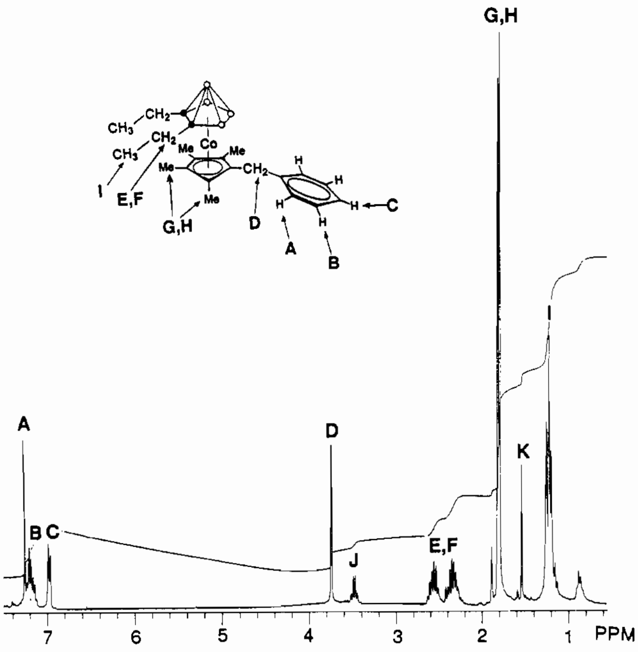


Figure 1. 300-MHz ^{1}H FT NMR spectrum of **1** in $CDCl_3$ solution, showing assignments of resonances A–I. Other signals: J, Et_2O; K, water. B–H resonances are broad quartets, mostly obscured by C–H signals.

Results and Discussion

Synthesis of Benzyltetramethylcyclopentadiene. The neutral hydrocarbon $Me_4HC_5CH_2C_6H_5$, which to our knowledge has not previously been reported, was straightforwardly obtained in a

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

compd	δ^{a-c}
1	7.21 m (C_6H_5), 7.19 m (C_6H_5), 6.98 m (C_6H_5), 3.77 s (benzyl CH_2), 2.58 m (ethyl CH_2), 2.34 m (ethyl CH_2), 1.81 s (C_5Me_4), 1.79 s (C_5Me_4), 1.22 m (ethyl CH_3)
2	7.23 m (C_6H_5), 7.15 m (C_6H_5), 7.04 m (C_6H_5), 3.65 s (benzyl CH_2), 2.13 m (ethyl CH_2), 1.92 m (ethyl CH_2), 1.78 s (C_5Me_4), 1.12 m (ethyl CH_3), −6.0 s, br (B−H−B)
3	7.14 m (C_6H_5), 7.11 m (C_6H_5), 6.91 m (C_6H_5), 3.59 s (benzyl CH_2), 2.59 m (ethyl CH_2), 1.62 s (C_5Me_4), 1.57 s (C_5Me_4), 1.55 m (ethyl CH_3)
4	5.22 m (C_6H_5), 5.17 m (C_6H_5), 3.74 s (benzyl CH_2), 2.61 m (ethyl CH_2), 2.37 m (ethyl CH_2), 1.87 s (C_5Me_4), 1.77 s (C_5Me_4), 1.25 m (ethyl CH_3)
5	7.15 m (C_6H_5),[d] 7.08 m (C_6H_5),[d] 6.91 m (C_6H_5),[d] 5.18 m (C_6H_5,[e] 3.68 s (benzyl CH_2), 3.58 s (benzyl CH_2), 2.65 (ethyl CH_2), 2.61 m (ethyl CH_2), 2.39 m (ethyl CH_2), 1.67 s (C_5Me_4), 1.62 s (C_5Me_4), 1.57 s (C_5Me_4), 1.54 s (C_5Me_4), 1.28 m (ethyl CH_3)
6	5.18 m (C_6H_5), 3.60 s (benzyl CH_2), 2.64 m (ethyl CH_2), 2.40 m (ethyl CH_2), 1.68 s (C_5Me_4), 1.65 m (ethyl CH_3), 1.55 s (C_5Me_4), 1.28 m (ethyl CH_3)
7	7.35 m (C_6H_5), 7.20 m (C_6H_5), 7.03 m (C_6H_5), 3.67 s (*C*-benzyl CH_2), 2.30 s, br (*B*-benzyl CH_2), 2.13 m (ethyl CH_2), 1.90 m (ethyl CH_2), 1.82 s (C_5Me_4), 1.78 s (C_5Me_4), 1.07 m (ethyl CH_3), −5.2 s, br (B−H−B)
8a	7.30 m (C_6H_5),[d] 7.20 m (C_6H_5),[d] 7.03 m (C_6H_5),[d] 5.30 m (C_6H_5),[e] 5.22 m (C_6H_5),[e] 3.67 m (*C*-benzyl CH_2), 2.64 (ethyl CH_2), 2.38 m (ethyl CH_2), 2.25 s, br (*B*-benzyl CH_2), 2.15 m (ethyl CH_2), 1.90 m (ethyl CH_2), 1.83 s (C_5Me_4),[f] 1.80 s (C_5Me_4), 1.78 s (C_5Me_4), 1.25 m (ethyl CH_3), 1.05 m (ethyl CH_3)
9	5.30 m (C_6H_5), 5.25 m (C_6H_5), 3.68 s (*C*-benzyl CH_2), 2.68 m (ethyl CH_2), 2.40 m (ethyl CH_2), 2.30 s, br (*B*-benzyl CH_2), 2.17 m (ethyl CH_2), 1.85 s (ethyl CH_3), 1.81 m (C_5Me_4), 1.25 s (ethyl CH_3), 1.07 s (ethyl CH_3), −5.5 s, br (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. [c] B–$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [d] Uncomplexed phenyl ring. [e] Complexed phenyl ring. [f] Overlapping singlets.

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

compd	absorptions
1	2969 s, 2931 s, 2916 s, 2873 vs, 2533 m, 1603 vs, 1495 s, 1489 vs, 1475 s, 1470 s, 1458 s, 1453 s, 1434 vs, 1432 vs, 1427 vs, 1380 s, 1075 vs, 1064 vs, 1029 s, 872 s, 725 s, 702 s, 668 vs
2	3028 vs, 2961 m, 2925 m, 2868 s, 2528 m, 2510 m, 1865 s, 1604 vs, 1547 s, 1544 s, 1537 s, 1531 vs, 1524 vs, 1495 s, 1478 s, 1475 s, 1467 s, 1461 s, 1453 s, 1435 vs, 1428 vs, 1380 s, 1369 s, 1075 vs, 1053 vs, 1030 s, 930 s, 908 vs, 784 s, 744 s, 729 s, 701 m
3	3031 vs, 3027 vs, 3025 vs, 2971 s, 2967 s, 2962 s, 2925 s, 2923 s, 2918 s, 2911 s, 2906 s, 2881 vs, 2871 vs, 2857 vs, 2829 vs, 2826 vs, 2823 vs, 2470 s, 2361 s, 2340 vs, 2337 vs, 2332 vs, 1603 vs, 1494 vs, 1478 vs, 1475 vs, 1469 vs, 1461 vs, 1452 vs, 1447 vs, 1432 vs, 1378 s, 1368 vs, 1075 vs, 1072 vs, 1070 vs, 818 s, 701 vs, 668 s
4	2968 s, 2932 vs, 2912 vs, 2908 vs, 2872 vs, 2533 s, 1473 vs, 1465 vs, 1456 vs, 1452 vs, 1437 vs, 1430 vs, 1420 vs, 1413 vs, 1380 vs, 1063 vs, 1028 vs, 873 vs
5	2965 s, 2928 s, 2917 s, 2908 s, 2907 s, 2880 vs, 2871 vs, 2856 vs, 2830 vs, 2533 s, 2468 s, 1495 vs, 1473 vs, 1452 s, 1432 vs, 1413 vs, 1378 s, 1261 vs, 1093 vs, 1088 vs, 1085 vs, 1072 vs, 1065 vs, 1051 vs, 1028 s, 998 vs, 874 vs, 816 s, 702 vs
6	2962 s, 2925 m, 2880 vs, 2870 s, 2854 s, 2532 s, 2470 vs, 1475 vs, 1467 vs, 1461 vs, 1453 vs, 1451 vs, 1447 vs, 1432 vs, 1428 vs, 1423 vs, 1378 s, 1063 vs, 1027 vs, 1014 vs, 816 vs
7	3024 vs, 2961 vs, 2926 vs, 2909 vs, 2883 vs, 2880 vs, 2867 vs, 2496 vs, 2495 vs, 2492 vs, 2361 s, 2340 s, 2337 s, 2334 s, 2332 s, 2307 vs, 1918 vs, 1869 vs
8a	3084 m, 3062 m, 3027 m, 2963 vs, 2928 vs, 2869 s, 2526 vs, 1918 m, 1602 m, 1583 m, 1576 m, 1558 m, 1517 s, 1495 s, 1454 vs, 1430 m, 1413 m, 1379 s, 1224 m, 1075 m, 1064 m, 1052 m, 1029 s, 1013 m, 997 m, 895 m, 874 s, 832 m, 811 m, 791 m, 778 m, 732 s, 701 s, 603 m
9	3072 w, 3069 w, 3066 w, 3060 w, 3017 w, 2963 vs, 2927 vs, 2870 s, 2855 s, 2530 vs, 1517 m, 1496 w, 1454 s, 1413 m, 1378 m, 1222 w, 1063 w, 1054 w, 1029 w, 1013 w, 997 m, 895 m, 874 m, 834 w, 792 w, 728 w, 668 w, 659 w

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

one-pot, three-step synthesis from commercially available 2,3,4,5-tetramethylcyclopent-2-enone, as outlined in Scheme I. The compound was obtained as a yellow oil consisting of several isomers which were evident in the proton NMR spectrum; separation of these isomers was unnecessary for our purposes, since the subsequent deprotonation of the mixture by butyllithium produced a monoisomeric anion as shown.

Synthesis of Mono- and Dicobalt Sandwich Complexes. Coordination of a $(Et_2C_2B_4H_4)Co$ unit to the $Me_4C_5CH_2Ph^-$ anion was achieved by addition of the latter species to $CoCl_2$ (which generated the postulated intermediate $[ClCo(Me_4C_5CH_2Ph)]_x$), followed by $Et_2C_2B_4H_5^-$, forming $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)$ (**1**) in high yield as a yellow oil (Scheme II). Compound **1** and all other new products were isolated via column and/or preparative plate chromatography and characterized from their ^{11}B and ^1H NMR, infrared, and mass spectra (Tables I–III and Experimental Section), augmented by previously reported X-ray crystallographic structure determinations on related complexes.[8] Assignment of NMR signals was straightforward, as depicted for **1** in Figure 1. Discussion of the spectra of similar small metallacarborane derivatives has been presented in earlier papers.[1a,b,4a,b] "Decapitation"[5] of **1** with wet tetramethylethylenediamine (TMEDA) gave almost quantitatively the bifunctional building-block complex $(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (**2**) (also a yellow oil), which can undergo further metal coordination at its C_2B_3 and phenyl rings, as was subsequently demonstrated.

Bridge deprotonation of **2** with C_4H_9Li took place easily to give the **2**$^-$ anion, which on treatment with $CoCl_2$ and $Me_4C_5CH_2Ph^-$ gave the symmetrically capped triple-decker complex $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (**3**), isolated as a deep crimson oil. Complex **3** is structurally analogous to the crystallographically characterized[8f–h] dicobalt triple-deckers $Cp_2Co_2(RR'C_2B_3H_3)$ and exhibits a low-field ^{11}B resonance (δ ca. +60) which is characteristic of $Co(C_2B_3)Co$ clusters.[4b,9] However, **3** differs from most previously reported triple-decker complexes in having the capability of additional metal complexation via its benzyl rings; this aspect is further developed below.

Coordination of $(Et_2C_2B_4H_4)Fe$ to *B*-Benzylcobaltacarborane Complexes. The addition of an iron–carborane unit to the phenyl group in **1** was accomplished via thermal displacement of cyclooctatriene from $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$, a technique used extensively in our group as a route to arene–ferracarborane complexes.[5,6a,c,10] The reaction of the iron cyclooctatriene reagent[11] with **1** in a sealed tube at 200 °C gave $(Et_2C_2B_4H_4)Co$-

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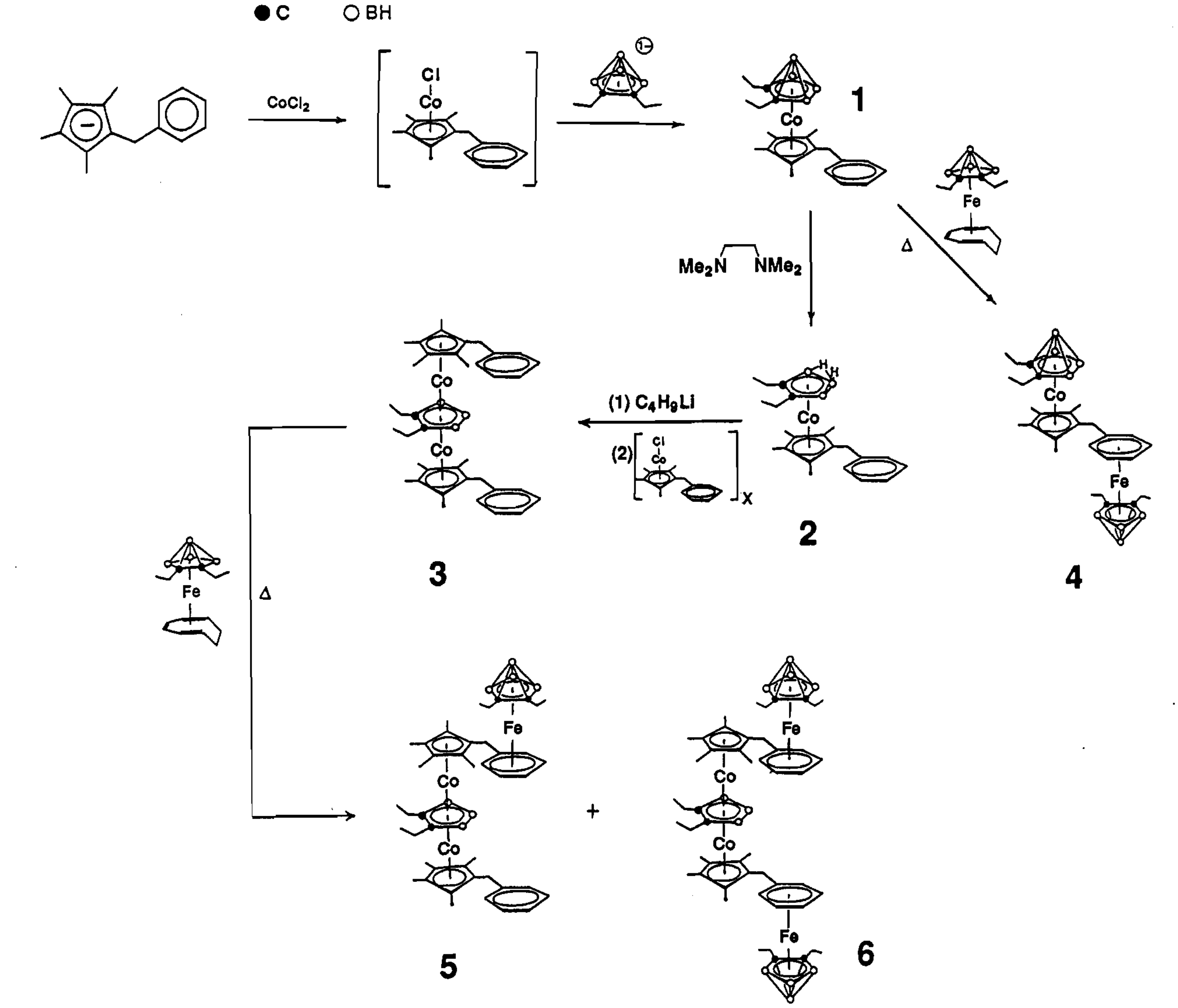
(8) (a) $(Me_2C_2B_4H_4)CoCp$: Weiss, R.; Bryan, R. F. *Acta Crystallogr.* **1977**, *B33*, 589. (b) *nido*-(5-$B_9H_{12}OC_4H_8$)-1,2,3-Co($Me_2C_2B_3H_5$): Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1928. (c) *nido,closo*-($Me_2C_2B_3H_5$)Co($Me_2C_2B_4H_3C_5H_4CoCp$): Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 1447. (d) *nido*-1,2,3-$(CO)_3FeC_2B_3H_7$: Brennan, J. P.; Grimes, R. N.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1973**, *12*, 2266. (e) (Fulvalene)-$Co_2(Et_2C_2B_4H_4)_2$: see ref 4b. Dicobalt–C_2B_3 triple-decker complexes: (f) Beer, D. C.; Miller, V. R.; Sneddon, L. G.; Grimes, R. N.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1973**, *95*, 3046. (g) Robinson, W. T.; Grimes, R. N. *Inorg. Chem.* **1975**, *14*, 3056. (h) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 10. Other M–C_2B_3–M' triple-decker complexes (M, M' = Co, Ru): see refs 4a,b.

(9) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

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

(11) (a) Maynard, R. B.; Swisher, R. G.; Grimes, R. N. *Organometallics* **1983**, *2*, 500. (b) Swisher, R. G.; Grimes, R. N. *Organomet. Synth.* **1986**, *3*, 104.

Scheme II



$(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**4**) as a pale orange oil (Scheme II). Analogous treatment of the dicobalt triple-decker **3**, after workup and column chromatography, produced $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (**5**) and a small amount of the tetrametallic complex $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (**6**), both isolated as red oils.

The proposed structures of complexes **4**–**6** are supported by NMR data, in which a particularly notable feature is the upfield shift of the ^1H phenyl resonances upon complexation to an $Fe(Et_2C_2B_4H_4)$ unit; thus, the uncomplexed C_6H_5 proton signals appear in the region of δ 7.0, while those arising from coordinated phenyl rings are seen near δ 5.0.

Regiospecific B(5)-Benzylation of 2 and Synthesis of Iron–Cobalt Polymetallic Complexes. We have demonstrated in recent work[1a,b] that $(ligand)MEt_2C_2B_3H_4^-$ metal sandwich anions react very cleanly with alkyl halides to generate derivatives alkylated at the B(5) (middle boron) position, in high yield with no other detectable isomers. In the present study, we have exploited this reaction in order to attach a second benzyl unit to the cobalt species **2**, thereby augmenting its versatility as a building-block reagent. Accordingly, **2** was deprotonated with butyllithium and the resulting 2^- anion was treated with benzyl bromide, affording the desired species $(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**7**) in good yield as a yellow solid (Scheme III). The characterization of **7** from spectroscopic data was straightforward; a useful feature in the 300-MHz proton NMR spectra of **7** and its metal complexes (vide infra) is the clear distinguishability of the signals arising from the *B*-benzyl and Me_4C_5 benzyl groups. Thus, as is usual in *B*-organo-substituted *nido*-$R_2C_2B_4H_5R'$ derivatives,[12] the resonances of the carborane-attached benzyl methylene protons are notably broadened and shifted upfield compared to those of the cyclopentadienyl-attached benzyl group; identification of the latter resonances in **7** and its derivatives is further aided by their close similarity to the corresponding signals in the spectrum of **2**.

Complex **7**, with two phenyl rings and a C_2B_3 open face, was anticipated to undergo further metal complexation, and its reactivity was examined accordingly, as summarized in Scheme III. The thermolysis of **7** with $(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ gave two isolable products, of which the major one was characterized as $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (**8a**). A smaller quantity of the diiron complex $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (**9**) was also isolated. The proton and boron-11 NMR spectra of the monoiron species **8a** clearly indicate that the ferracarborane unit is coordinated to the benzyl group attached to the C_2B_3 ring. This conclusion is supported by significant shifts in the ^1H phenyl resonances of the carborane-bonded benzyl unit, compared to the uncomplexed species **7**, and also by a similar effect in the ^{11}B spectrum, wherein the unique B(5) signal in **7** is measurably shifted in **8a**; also, in the proton spectrum of **8a**, the resonances of the uncoordinated cyclopentadienyl benzyl group are almost unchanged from those in **7**. Interestingly, the other possible isomer (**8b**), in which the iron is bonded to the cyclopentadienylbenzyl

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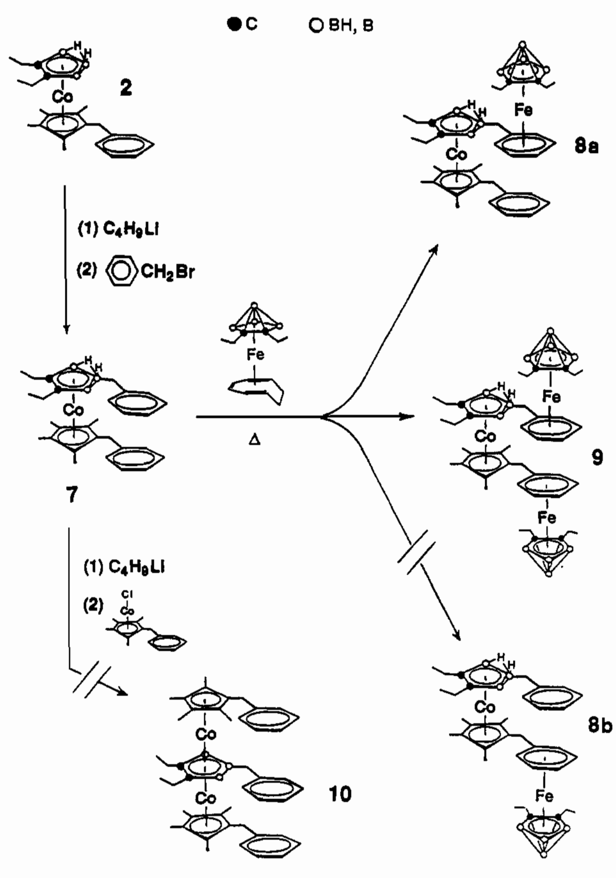
(12) Davis, J. H., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 4213.

Scheme III



ligand, was not isolated and was detected only as a trace (tentatively assigned) in the proton NMR spectrum of **8a**. This represents a clear example of a directive effect, in which the carborane-bonded benzyl is more active toward metal coordination than is the other benzyl. From this observation we infer that the arene portion of the cyclopentadienylbenzyl ligand in **7** is somewhat deactivated by coordination of the adjoining C_5 ring to cobalt, in apparent contrast with the behavior of benzyl units attached to C_2B_4 or C_4B_8 carborane cages (which, for example, readily coordinate to $Cr(CO)_3$[13]). The deactivation in **7** is, however, a relative effect, since coordination of iron to the cyclopentadienylbenzyl unit in **1** (where there is no competing carborane benzyl) does occur to give **4** as described above.

An attempt was made to add a second $Co(Me_4C_5CH_2Ph)$ unit to **7** and thereby construct the triple-decker **10** with three attached benzyl substituents (Scheme III), but deprotonation of **7** followed by treatment with $CoCl_2$ and $Me_4C_5CH_2Ph^-$ failed to generate characterizable products and no evidence of **10** was detected. This result was not unexpected, since we have noted consistently that *nido*-C_2B_3M clusters having an alkyl substituent on the middle boron [B(5)] *do not undergo metal coordination on the open face to form triple-decker sandwiches*,[14] nor do they exhibit oxidative fusion[5] to give $C_4B_6M_2$ cages. In contrast, substitution at the B(4/6) or cage carbon locations does not prevent metalation; for example, *nido*-$[2,3\text{-}R_2C_2B_4H_5\text{-}4\text{-}R']^-$ carborane anions readily form both (carboranyl)Fe(C_8H_{10}) and (carboranyl)Fe complexes, the latter of which fuse on oxidation to give C_4B_8 clusters.[15] This empirical finding suggested that metal complexation on 2,3-C_2B_3 faces proceeds via a metal–B(5) σ-interaction which is blocked when a substituent is present. However, in very recent work we have discovered that electronic effects are also important, in that the presence of electron-withdrawing groups at B(5) actually *enhance* the reactivity of CoC_2B_3 units toward metal coordination.[1c]

Conclusions

In this work, a bicyclic aromatic ligand capable of simultaneous η^5- and η^6-coordination to transition metals was prepared and employed as a bridging unit in the synthesis of bi-, tri-, and tetrametallic cobalt and iron–cobalt carborane sandwich complexes. These syntheses combined procedures that were previously developed in our laboratory for the construction of triple-decker sandwiches and for the preparation of (arene)Fe($R_2C_2B_4H_4$) complexes, thereby further demonstrating the versatility and general applicability of these methods in designed organometallic synthesis. Further extension of these approaches should enable the construction of families of larger heteropolymetallic linked-sandwich complexes in which the metals and certain other features are systematically varied. In turn, such species will be useful in electrochemical, ESR, and other studies of the electronic structures of large electron-delocalized multisandwich systems which are currently in progress.[6d]

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 having strong parent groups 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. Analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of $Me_4HC_5CH_2Ph$. A solution of benzyllithium was prepared via the procedure of Eisch,[16] as follows. Under an atmosphere of N_2, 7.5 g (0.065 mol) of TMEDA was added to a mixture of 6.0 g (0.065 mol) of toluene and 100 mL of diethyl ether. To this solution was added, *slowly*, 26 mL of 2.5 M n-butyllithium in hexanes, upon which bright yellow needles of $C_6H_5CH_2Li{\cdot}TMEDA$ began to precipitate. The mixture was stirred for an additional 30 min, after which 9.0 g (0.065 mol) of 2,3,4,5-tetramethylcyclopent-2-enone (Aldrich) was added via syringe through a rubber septum; during the addition, the lithium salt gradually dissolved to give a yellow solution. After ca. 1 h, 100 mL of saturated aqueous NH_4Cl was added, the admixed solution was stirred for 30 min, and the aqueous and organic layers were separated. The aqueous layer was washed with two 100-mL portions of CH_2Cl_2, and the organic layers were combined and dried over anhydrous $MgSO_4$. The solution was rotary-evaporated to a dark yellow oil, which was dissolved in ether. The resulting solution was treated with 0.15 g of *p*-toluenesulfonic acid. After 1 h, the ether solution was washed with water, and the organic layer was separated out, dried, and rotary-evaporated to give the benzyltetramethylcyclopentadiene isomer mixture as a dark yellow oil, 12.2 g (0.058 mol, 85% yield). Anal. Calcd for $C_{16}H_{20}$: C, 90.5; H, 9.5. Found: C, 89.9; H, 8.6. Exact mass: calcd for $^{13}C^{12}C_{15}{}^{1}H_{19}{}^{+}$, 212.1521; found, 212.1520.

Synthesis of ($Et_2C_2B_4H_4$)Co($Me_4C_5CH_2Ph$) (1). In an apparatus depicted in Figure 3a of ref 4a, 3.15 g (14.8 mmol) of benzyltetramethylcyclopentadiene from the preceding preparation was placed in the lower side-arm flask (C); at the same time, 1.92 g (14.8 mmol) of $CoCl_2$ was placed in the lower main flask (B), 1.95 g (14.8 mmol) of $Et_2C_2B_4H_6$ in the upper tip-tube, and a 2- to 3-fold excess of NaH powder (washed with hexane to remove oil) in the upper flask (A), and the entire apparatus was evacuated. THF was condensed on top of the hydrocarbon, the $CoCl_2$, and the NaH at liquid-nitrogen temperature, and the liquid-nitrogen baths were removed. To the hydrocarbon solution was added, through the septum, 5.92 mL of 2.5 M *n*-butyllithium in hexanes, producing a deep red solution of the $Me_4C_5CH_2Ph^-$ anion. This solution was added dropwise to the THF/$CoCl_2$ suspension, giving a dark green solution, which was stirred for 1 h, after which the carborane was deprotonated via treatment with NaH as described previously[4a] and added to the green reaction mixture. The color of the solution changed immediately to yellow-brown. The solution was stirred overnight, following which the flask was opened to the air and the THF removed by rotary evaporation. The brown residue was taken up in 1:1 hexane/CH_2Cl_2, and the mixture was suction-filtered through silica gel, yielding an orange-yellow solution. Evaporation of the solvent gave 5.15 g (12.8 mmol, 87%) of orange crystalline **1**. Exact mass: calcd for $^{59}Co^{12}C_{22}{}^{11}B_4{}^{1}H_{33}{}^{+}$, 400.2287; found, 400.2274.

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(13) (a) Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335. (b) Whelan, T.; Spencer, J. T.; Pourian, M. R.; Grimes, R. N. *Inorg. Chem.* **1987**, *26*, 3116.

(14) Davis, J. H., Jr.; Attwood, M. D. Unpublished observations.

(15) Davis, J. H., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 4213.

(16) Eisch, J. J. *Organomet. Synth.* **1981**, *2*, 94.

Synthesis of $(Et_2C_2B_3H_5)Co(Me_4C_5CH_2Ph)$ (2). A 1.0-g (2.5-mmol) sample of **1** was dissolved in 5 mL of TMEDA, and three drops of water were added. The solution was stirred in air at room temperature for 2 h, and the volatiles were removed by rotary-evaporation. The residue was extracted with hexane, and the mixture was suction-filtered through silica to give a yellow solution. Evaporation gave yellow crystals (0.956 g, 2.45 mmol, 98%) of **2**. Exact mass: calcd for $^{59}Co^{12}C_{22}{}^{11}B_3{}^1H_{34}{}^+$, 390.2272; found, 390.2272.

Synthesis of $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2$ (3). A 250-mL three-necked round-bottom flask (A) containing a stirbar was connected via glass elbow joints to two 100-mL two-necked flasks (B and C), each of which was fitted with a septum cap and stirbar. In flask A was placed 60 mg (0.49 mmol) of $CoCl_2$, 190 mg (0.49 mmol) of **2** was placed in flask B, and 103 mg (0.49 mmol) of benzyltetramethylcyclopentadiene was placed in flask C. Flask A was connected to a vacuum line via its middle neck, and all three flasks were evacuated. THF (ca. 30 mL each) was distilled into the three vessels, and 0.2 mL of 2.5 M *n*-butyllithium in hexane was added to each of flasks B and C; both solutions turned dark red. After 30 min, the hydrocarbon anion solution in flask C was added *dropwise* to the stirred $CoCl_2$ in flask A; the latter solution turned deep green as the addition proceeded. After the reaction mixture was stirred for 1 h, the solution in flask B (containing the deprotonated anion **2**$^-$) was added in one portion. The solution immediately turned a deep burgundy color. After overnight stirring, the solvent was removed to leave a red-brown solid, which was extracted in 50:50 hexane/CH_2Cl_2 and chromatographed on a silica column followed by silica plates (in the same solvent mixture) to give a deep red-brown band. Evaporation of the solvent gave 112 mg (0.17 mmol, 35%) of **3** as a burgundy-colored solid. Exact mass: calcd for $^{59}Co_2{}^{12}C_{38}{}^{11}B_3{}^1H_{51}{}^+$, 658.2934; found, 658.2948.

Synthesis of $(Et_2C_2B_4H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (4). Complex **1** (50 mg, 0.12 mmol) and 80 mg (0.27 mmol) of $(Et_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$[11] were sealed in vacuo into a Carius tube, and the mixture was heated at 200 °C for 4 h. The tube was opened in air, and the contents were extracted with CH_2Cl_2, giving a black solution, which was filtered through silica gel. The yellow filtrate was rotary-evaporated to give a yellow oil, which was thin-layer-chromatographed on silica in 50:50 hexane/CH_2Cl_2, giving two yellow bands. The high R_f band was **1**, 8 mg (0.02 mmol), and the low R_f band was **4**, 20 mg (0.030 mmol, 30%), a pale orange oil. Exact mass: calcd for $^{59}Co^{56}Fe^{12}C_{28}{}^{11}B_8{}^1H_{47}{}^+$, 586.3104; found, 586.3105.

Synthesis of $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe(Et_2C_2B_4H_4)$ (5) and $(Et_2C_2B_3H_3)Co_2(Me_4C_5CH_2Ph)_2Fe_2(Et_2C_2B_4H_4)_2$ (6). Complex **3** (112 mg, 0.170 mmol) and 200 mg (0.68 mmol) of $(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ were sealed in vacuo into a Carius tube, and the mixture was heated at 200 °C for 4 h. The tube was opened in air, and the contents were extracted with CH_2Cl_2, giving a brown solution which was filtered through silica gel. The red filtrate was chromatographed on a preparative-layer silica plate in 50:50 hexane/CH_2Cl_2, giving three red bands. The highest R_f band was recovered **3**, 68 mg (0.10 mmol), the middle band was **5** (15 mg, 0.02 mmol, 26% based on **3** consumed), obtained as a red oil on evaporation of solvent, and the lowest band was **6**, 1 mg (0.001 mmol, 1%), a red oil. Exact mass for **5**: calcd for $^{59}Co_2{}^{56}Fe^{12}C_{44}{}^{11}B_7{}^1H_{65}{}^+$, 844.3751; found, 844.3759. Exact mass for **6**: calcd for $^{59}Co_2{}^{56}Fe_2{}^{12}C_{50}{}^{11}B_{11}{}^1H_{59}{}^+$, 1030.4568; found, 1030.4564.

Synthesis of $(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (7). Compound **2** (237 mg, 0.61 mmol) was dissolved in THF and deprotonated in vacuo by addition of 0.24 mL of 2.5 M *tert*-butyllithium in hexane, giving a dark red solution of the **2**$^-$ anion. To this solution was added 0.80 mL of benzyl bromide, which caused an immediate color change to yellow. Evaporation of the solvent gave a yellow solid, which was extracted in hexane. The mixture was filtered through silica, and the solvent was removed to give 220 mg (0.45 mmol, 74%) of yellow solid **7**. Exact mass for **7**: calcd for $^{59}Co^{12}C_{29}{}^{11}B_3{}^1H_{40}{}^+$, 480.2741; found, 480.2747.

Synthesis of $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)$ (8) and $(Et_2C_2B_4H_4)Fe(5\text{-}PhCH_2Et_2C_2B_3H_4)Co(Me_4C_5CH_2Ph)Fe(Et_2C_2B_4H_4)$ (9). In a procedure analogous to that employed in the preparation of **5** and **6**, 100 mg (0.209 mmol) of **7** and 300 mg (1.03 mmol) of $(R_2C_2B_4H_4)Fe(\eta^6\text{-}C_8H_{10})$ were sealed in vacuo into a Carius tube and the mixture was heated at 200 °C for 2 h. After cooling, the tube was opened and the contents were dissolved in 2:1 *n*-hexane/CH_2Cl_2. The solution was chromatographed on a silica gel column, giving four bands, of which the first two were unreacted **7** and the iron reagent. Band 3 was isolated as **8a**, a yellow oil (41 mg, 0.062 mmol, 30%), while band 4 was isolated as **9**, also a yellow oil (20 mg, 0.012 mmol, 11%). Exact mass for **8a**: calcd for $^{59}Co^{56}Fe^{12}C_{35}{}^{11}B_7{}^1H_{52}{}^+$, 666.3401; found, 664.3433. The composition of **9** was established via analysis of its unit-resolution mass spectral profile, which closely matches the calculated intensity pattern based on natural isotope abundances, supported by proton NMR and boron-11 NMR data.

Attempted Synthesis of $(Et_2C_2B_3H_2\text{-}5\text{-}CH_2Ph)Co_2(Me_4C_5CH_2Ph)_2$ (10). In an evacuated apparatus similar to that employed in the preparation of **3** from **2**, a solution of the $Me_4C_5CH_2Ph^-$ anion (prepared as above from 28 mg (0.013 mmol) of benzyltetramethylcyclopentadiene and an equimolar quantity of butyllithium in hexane) was slowly added to a solution of 0.13 mmol of $CoCl_2$ in THF in the lower flask. The solution was stirred for 20 min. In the upper flask, a solution of 63 mg (0.13 mmol) of **7** in THF was deprotonated with 0.013 mmol of butyllithium in hexane, and the dark orange solution was stirred for 20 min. This solution was then added through a filter, in vacuo, to the solution of the chloro(benzyltetramethylcyclopentadienyl)cobalt intermediate in the lower flask. The reaction mixture turned dark brown and was stirred for 16 h at room temperature with no further color changes. Following removal of the solvent in a rotary evaporator, the brown residue was extracted in 50:50 hexane/CH_2Cl_2 solution, and the resulting solution was placed on a silica column. Only bands identified as starting materials were obtained, and further careful chromatography of these bands gave no evidence of the desired **10**.

Acknowledgment. We thank Dr. Mike Kinter for the high-resolution mass spectra and Kevin Chase for 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.

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Synthesis of the PPh_4^+ and NEt_4^+ Salts of $M(SePh)_4^{2-}$ (M = Mn, Fe, Co, Ni) and the Structure of $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$

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Received December 28, 1990

The syntheses of the PPh_4^+ and NEt_4^+ salts of the $M(SePh)_4^{2-}$ (M = Mn, Fe, Co, Ni) anions by reaction of the metal chlorides with LiSePh in the presence of the cations are described. $[NEt_4]_2[Fe(SePh)_4]\cdot MeCN$ crystallizes with four formula units in the orthorhombic space group D_2^4-$P2_12_12_1$ in a cell of dimensions a = 14.787 (1) Å, b = 16.485 (1) Å, and c = 18.273 (2) Å. Four benzeneselenol ligands provide slightly distorted tetrahedral coordination about the Fe^{II} center. The Fe–Se distances average 2.460 (12) Å; the Se–C distances average 1.907 (8) Å. The Se–Fe–Se angles range from 103.6 (1) to 114.9 (1)°. UV–vis and ^1H NMR data for the PPh_4^+ and NEt_4^+ salts of $M(SePh)_4^{2-}$ (M = Mn, Fe, Co, Ni) are assigned and discussed.

Introduction

Interest in metal coordination in metalloenzymes prompted the synthesis and characterization of $M(SPh)_4^{2-}$ complexes (M = Mn, Fe, Co, Ni, Zn, Cd).[1-3] These simple metal thiolates are useful precursors for soluble metal sulfides[4,5] and mixed-metal sulfides.[6] The number of stucturally characterized soluble metal sulfides

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0020-1669/91/1330-1770$02.50/0