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Benzene-Centered Tri- and Tetrametallacarborane Sandwich Complexes[**]

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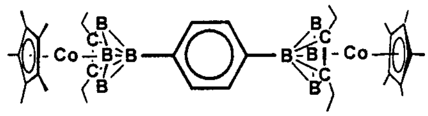
The special steric and electronic properties of polyhedral borane and carborane clusters—notably their three-dimensional geometry and electron delocalization (aromatic character)—are being employed to advantage in the construction of novel molecular architectures for use in a variety of projected applications in materials synthesis, microelectronics, optics, and medicine.[1] In recent work some remarkable compound types have been produced in which boron clusters serve as scaffolds or templates for attachment of organic moieties; examples include $(1,7\text{-}C_2B_{10}H_{10})_nHg_n$ "anti-crowns" ($n = 3$, 4),[1d, 2] peralkylated carboranes that mimic spherical hydrocarbons, [3] and benzene-*m*-carboranyl macrocycles.[4]

This paradigm can be reversed: Hydrocarbons may serve as frameworks for attachment of multiple boron clusters. If an aromatic system such as benzene is employed as a linchpin connecting several metallaboron units, one might prepare polynuclear, electron-delocalized, mixed-valence systems that are not only interesting from a fundamental perspective, but may also have practical potential as precursors or models for new kinds of electronically tailorable organometallic compounds. Although 1,3,5-tris(carboranyl)benzene derivatives incorporating icosahedral 1,2- or 1,12-C_2B_{10} polyhedra have been reported,[5] no corresponding metallaborane or metallacarborane species (i.e., having metal atoms in the polyhedral framework) have been described; to our knowledge, the closest known metal system is the dimetallic 1,4-bis-(7-cobaltacarboranyl)benzene complex **1** (B = BH, B), which was recently prepared in one of our laboratories.[6] In contrast, a number of benzene-centered trinuclear organometallic compounds of the type 1,3,5-$C_6H_3(XML_n)_3$ have been synthesized,[7] in which transition metals M are linked to benzene through groups X (e.g. alkynyl). Here we report the designed synthesis of the first metallacarborane systems of this class.



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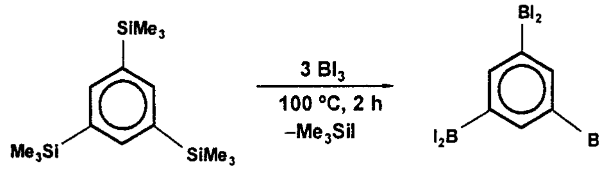
The approach utilized boron-recapping ("recapitation") of *nido*-$[1,2,3\text{-}Cp^*Co(2,3\text{-}Et_2C_2B_3H_3)]^{2-}$ ($Cp^* = C_5Me_5$), a method recently developed in our groups for preparing mono- or dimetallic species bearing substituents at the apex [B(7)] boron atom.[6, 8] In the present work, we required a suitable trifunctional benzene derivative as a precursor to the desired metal complexes. Accordingly, 1,3,5-tris(diiodoboryl)benzene (**3**), previously prepared but not isolated,[9] was generated from the corresponding tris(trimethylsilyl)benzene as shown in Scheme 1 and isolated in 30 % yield as a colorless, air-sensitive solid. Treatment of $Li_2[Cp^*Co(2,3\text{-}Et_2C_2B_3H_3)]$ (**4**) with one-third molar equivalent of **3** in toluene at 0 °C gave the target compound $[\{Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)\}_3C_6H_3]$ (**5**) as a moderately air-stable yellow complex in 46 % yield (Scheme 2).



2 **3**

Scheme 1. Synthesis of **3**.

Characterization of **5** by multinuclear NMR and IR spectroscopy as well as mass spectrometry supports the trigonally symmetric geometry shown (the rotamer depicted is arbitrary), and the solid-state structure has been confirmed by X-ray crystallography (Figure 1).[10] With the exception of the benzene ring (see the figure caption), the bond lengths and angles are normal, and the metal atoms and apical boron atoms are coplanar with the benzene ring. A notable feature of the ^1H NMR spectrum of **5** is the strong upfield shift of the aromatic benzene resonances ($\delta = 5.92$ in $CDCl_3$ versus 7.51 for benzene itself), reflecting the electron-donating character of the carborane ligand (for comparison, the corresponding

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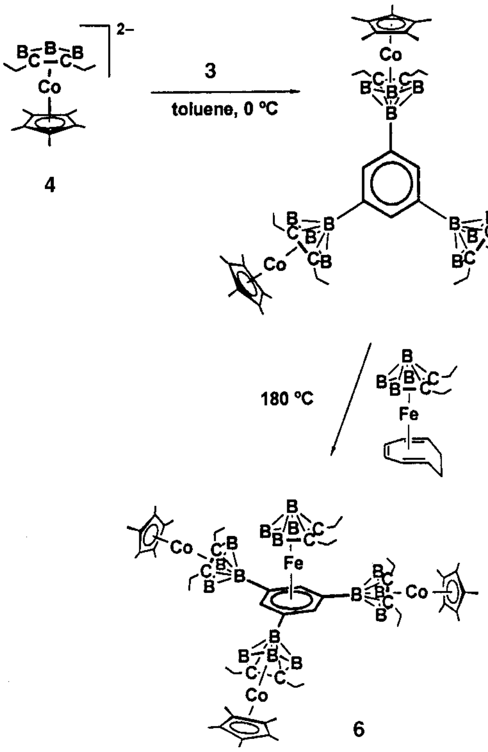


Scheme 2. Synthesis of **5** and **6**. B = BH, B.

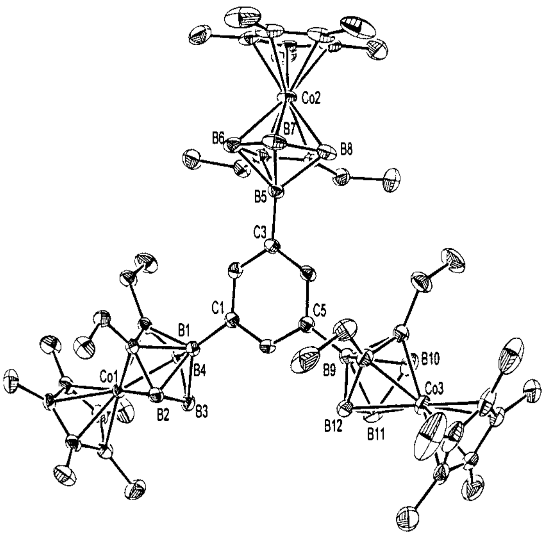


Figure 1. Molecular structure of **5**. The mean benzene ring C–C distance is 1.400 Å (range 1.399–1.402 Å). The mean benzene C-C-C angle centered on C1, C3, and C5 is 117.1°; that centered on C2, C4, and C6 is 122.9°.

signal in **1** appears at $\delta = 6.38$, while those in the monocobalt species [Cp*Co(2,3-$Et_2C_2B_4H_3$-7-C_6H_5)] are found at $\delta = 6.75-7.08$).[6]

A fourth metallacarborane unit was added to **5** by thermal displacement of cyclooctatriene from [(η^6-C_8H_{10})Fe-($Et_2C_2B_4H_4$)][11] to give the heterotetranuclear complex [{Cp*Co($Et_2C_2B_4H_3$-7)}$_3${Fe($Et_2C_2B_4H_4$)}C_6H_3] (**6**, Scheme 2). This species was isolated as a yellow solid in 30 % yield and characterized by spectroscopy and X-ray crystallography (Figure 2).[10]

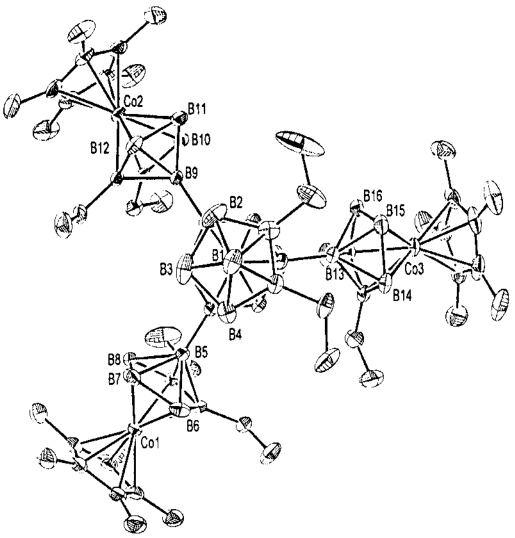
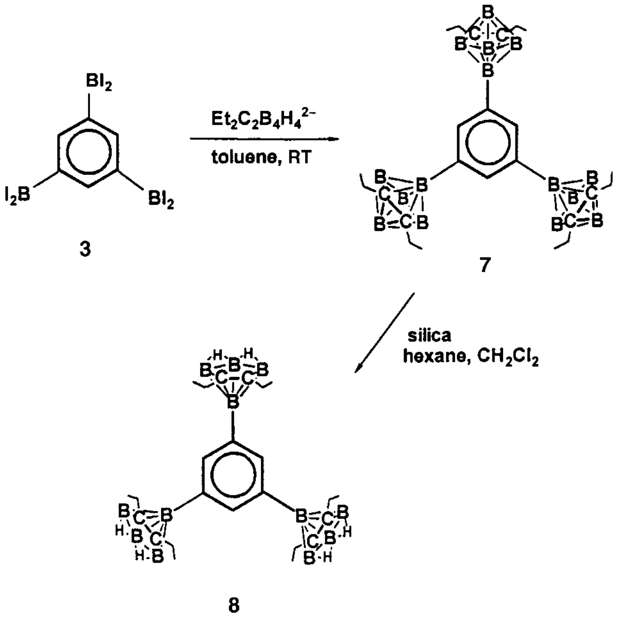


Figure 2. Molecular structure of **6**. The mean benzene ring C–C distance is 1.422 Å (range 1.421–1.425 Å). The mean benzene C-C-C angle centered on C1, C3, and C5 is 117.4°; that centered on C2, C4, and C6 is 122.6° (the numbering of the benzene ring is analogous to that in **5**, Figure 1).

Tris(diiodoboryl)benzene (**3**) can also serve as a precursor to other trigonally substituted complexes. Scheme 3 shows the preparation of the tris(*nido*-carboranyl)benzene species **8**, a potential building block for metal-connected trigonal sheet polymers. The structure of **8** is assigned from NMR and mass spectra. Full details on this work, including electrochemical and other data bearing on the electronic properties of the polymetallacarborane complexes, will be presented in a later publication.



Scheme 3. Synthesis of **8**. B = BH, B.

Experimental Section

3: BI_3 (3.000 g, 7.66 mmol) and $(Me_3Si)_3C_6H_3$[12] (0.752 g, 2.55 mmol) were heated at 100 °C for 1.5 h, following which the Me_3SiI was removed by vacuum distillation. The solid residue was taken up in pentane (30 mL), and the suspension was cooled to $-78\,^{\circ}C$ and filtered under N_2 to obtain colorless, air-sensitive **3** (0.670 g, 0.77 mmol, 30 %). ^1H NMR (300 MHz, C_6D_6): $\delta = 9.27$ (s, $3\,H_{ar}$); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 152.9$ (C_6H_3), 142.6 (*ipso*-C_6H_3); ^{11}B NMR (115.8 MHz, $CDCl_3$): $\delta = 47.7$ (s); UV/Vis (CH_2Cl_2): λ (rel. intens.) = 229 nm (100); $\varepsilon = 7014\ cm^{-1}M^{-1}$.

5: $[Cp^*Co(Et_2C_2B_3H_5)]$ (200 mg, 0.64 mmol) in toluene (30 mL) at $0\,^{\circ}C$ was treated with 1.6 M *n*-butyllithium (0.8 mL, 1.27 mmol). The solution turned red-orange during warming to room temperature (RT) over a 6 h period. It was cooled to $0\,^{\circ}C$, and **3** (185 mg, 0.21 mmol) was slowly added under nitrogen, causing the solution to become cloudy and turn orange-brown as the flask was warmed to RT. The mixture was stirred for 16 h, after which the toluene was removed in vacuo. The residue was taken up in hexane and washed through silica (3 cm), first with hexane and then with CH_2Cl_2; the hexane wash contained only $[Cp^*Co(Et_2C_2B_3H_5)]$. Column chromatography of the CH_2Cl_2 wash on silica with hexane/CH_2Cl_2 (1/4) afforded **5** as a major yellow band (100 mg, 0.10 mmol, 46 %). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.92$ (s, $3\,H_{ar}$), 2.18 (m, ethyl CH_2), 1.77 (C_5Me_5), 1.27 (t, ethyl CH_3); ^{13}C NMR (75.5 MHz, in C_6D_6): $\delta = 134.8$ (C_6H_3), 94.3 (*ipso*-C_6H_3), 90.4 (C_5Me$_5$), 22.1 (CH_2), 15.1 (ethyl CH_3), 10.1 (C_5*Me*$_5$); ^{11}B NMR (115.8 MHz, C_6D_6): $\delta = 5.0$, 15.0 (B−H coupling not resolved); CI^+-MS: *m*/*z* (%): 1044.7 ([M^+], 100), 721.8 ([$M^+ - Cp^*Co(Et_2C_2B_4H_3)$], 0.9); UV/Vis ($CH_2Cl_2$): λ (rel. intens.) = 229 (41), 304 nm (100); $\varepsilon = 11\,435\ cm^{-1}M^{-1}$.

6: Compound **5** (20 mg, 0.020 mmol) and $[(\eta^6\text{-}C_8H_{10})Fe(Et_2C_2B_4H_4)]$ (56 mg, 0.19 mmol) were heated in a Pyrex tube at $185\,^{\circ}C$ for 20 min, after which the black solid was taken up in CH_2Cl_2 and washed through silica (3 cm), first with CH_2Cl_2 and then with ethyl acetate; the CH_2Cl_2 wash contained only unchanged starting materials. The ethyl acetate wash was purified by chromatography on a TLC plate with hexane/ethyl acetate (3/1), affording a major yellow band that was characterized as **6** (7 mg, 30 %). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (s, $3\,H_{ar}$), 2.44 (m, ethyl CH_2) 2.22 (m, ethyl CH_2), 2.07 (m, ethyl CH_2) 1.78 (C_5Me_5), 1.19 (t, ethyl CH_3), 1.07 (t, ethyl CH_3); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 93.8$ (*ipso*-C_6H_3), 90.6 (C_5Me$_5$), 87.6 (C_6H_3), 25.5 (CH_2), 22.4 (CH_2), 15.7 (ethyl CH_3), 15.3 (ethyl CH_3), 9.9 (C_5*Me*$_5$); ^{11}B NMR (115.8 MHz, C_6D_6): $\delta = 3.8$ (B−H coupling not resolved); CI^+-MS: *m*/*z* (%): 1229.9 ([M^+], 100), 1044.6 ([$M^+ - Fe(Et_2C_2B_4H_4)$], 7); UV/Vis (CH_2Cl_2): λ (rel. intens.) = 230 (57), 296 nm (100); $\varepsilon = 91\,138\ cm^{-1}M^{-1}$.

8: 2,3-$Et_2C_2B_4H_6$ (118 mg, 0.9 mmol) in absolute diethyl ether (30 mL) at $-78\,^{\circ}C$ was treated with 1.6 M *n*-butyllithium (1.1 mL, 1.8 mmol). The solution was stirred for 4 h at RT. The Et_2O was removed, the residue taken up in absolute toluene (30 mL), and the mixture cooled to $-14\,^{\circ}C$. Compound **3** (260 mg, 0.3 mmol) was slowly added under nitrogen while warming up to RT The resulting solution became cloudy. The mixture was stirred for 16 h, after which the toluene was removed in vacuo. The residue was taken up in hexane and washed through silica (3 cm), first with hexane and then with CH_2Cl_2. The complete wash was purified by chromatography on a TLC plate with CH_2Cl_2/hexane (1/4), affording a colorless band that was characterized as **8** in low yield. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.51$ (s, $3\,H_{ar}$), ethyl proton resonances from **8** and unchanged $Et_2C_2B_4H_6$; CI^+-MS: *m*/*z* (%): 468.4 ([M^+], 100)

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[10] Crystal structure determinations: Data were collected on a Bruker AXS SMART 1000 diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, ω scans), at 173 K, up to $\theta_{max} = 26.4°$. Structures were solved with direct methods and refined by least-squares against F^2 (SHELXTL V5.10); non-hydrogen atoms were anisotropic, and hydrogen atoms were located and refined isotropically. **5** ($C_{61}H_{95}B_{12}Co_3$, crystal contains one toluene molecule per complex): $M_r = 1134.9$, orthorhombic, space group *Pbca*, $a = 14.6958(3)$, $b = 24.7128(5)$, $c = 34.4880(8)$ Å, $V = 12525.2(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.204\ g\,cm^{-3}$. Of 81 401 measured reflections, 12 821 were independent ($R_{int} = 0.071$), 1033 parameters, $R1 = 0.041$ (for reflections with $I > 2\sigma(I)$), $wR2 = 0.111$ (for all reflections), max./min. residual electron density $0.72/-0.51\ e\,Å^{-3}$. **6** ($C_{63}H_{104}B_{16}FeCo_3$, crystal contains 0.5 benzene molecules per complex): $M_r = 1267.1$, triclinic, space group $P\bar{1}$, $a = 11.1196(3)$, $b = 13.9542(4)$, $c = 23.2691(6)$ Å, $\alpha = 85.959(2)°$, $\beta = 79.768(2)°$, $\gamma = 77.633(2)°$, $V = 3468.7(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.213\ g\,cm^{-3}$. Of 46 579 measured reflections, 16 911 were independent ($R_{int} = 0.037$), 1153 parameters, $R1 = 0.036$ (for reflections with $I > 2\sigma(I)$), $wR2 = 0.096$ (for all reflections), max./min. residual electron density $0.61/-0.38\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147113 (**5**) and CCDC-147114 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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