

Wired Multidecker Sandwich Assemblies. Stepwise Construction of a Hexanuclear Benzene-Centered Tris(alkynyl triple-decker) Complex¹

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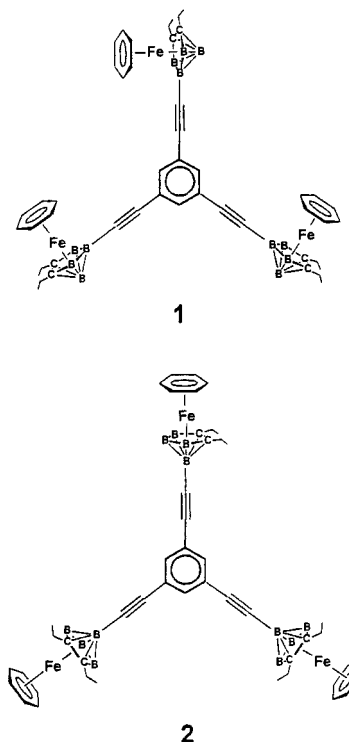
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Summary: A complex containing three multidecker sandwich units anchored to a central benzene ring, 1,3,5-[Cp*Co(2,3-Et₂C₂B₃H₂-5-C≡C)CoCp*]₃C₆H₃ (**8**), has been synthesized via two different routes starting with the monomeric precursors *closo*-Cp*Co(Et₂C₂B₄H₃-5-I) or *nido*-Cp*Co(Et₂C₂B₃H₄-5-I), requiring four steps in each case. In both methods, the ethynyl-substituted species *nido*-Cp*Co(Et₂C₂B₃H₄-5-C≡CH) was generated and treated with 1,3,5-triiodobenzene to give [*nido*-Cp*Co(2,3-Et₂C₂B₃H₅-5-C≡C)]₃C₆H₃, which was bridge-deprotonated and reacted with (Cp*CoCl)₂ in THF solution to afford the target compound **8**, which was characterized from multinuclear NMR, IR, UV–visible, and mass spectra, electrochemical data, and an X-ray diffraction study.

Multinuclear metal coordination compounds featuring highly symmetric, enforced geometries such as squares, triangles, rectangles, or rigid rods, and the development of viable methods for synthesizing them, are the focus of much current activity in organometallic chemistry.² Most such molecules are stable entities held together by strong covalent bonds and are of interest in respect to their electronic, optical, magnetic, catalytic, or other properties, and as building blocks for constructing nanostructured materials. In view of the high thermal, oxidative, and electrochemical stability that are characteristic of small metallocarborane clusters,³ we have been exploring their use as synthons for oligomers and polymers of specified design that would have tunable electronic properties. Recently, our group in collaboration with W. Siebert⁴ reported the first examples of benzene-anchored, multinuclear tris- and tetra(metalcarborane) complexes. In these systems, MC₂B₄ clusters (M = Co or Fe) are directly bound to a common benzene ring. Subsequently, this concept has been extended to include benzene-anchored tris(alkynylferrocenyl) complexes such as **1** and **2** in which seven-vertex MC₂B₄ clusters are linked to the central C₆ ring via –C≡C– units attached to equatorial or apex boron atoms.⁵

We were intrigued by the possibility that this architectural motif might be adapted to multidecker sandwich chemistry, allowing several such sandwiches to be connected via a central benzene ring that could serve as a conduit for electronic communication between multiple metal centers. Since it has long been known that triple-deckers incorporating Co^{III}C₂B₃Co^{III} seven-vertex clusters⁶ can be oxidized or reduced to highly



electron-delocalized Co^{III}–Co^{IV} or Co^{III}–Co^{II} mixed valence species,⁷ we envisioned that a symmetric 1,3,5-trialkynylbenzene-anchored “triple-triple-decker” array containing six identical metal centers might, under appropriate redox action, yield a hexanuclear mixed-

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Scheme 1

B = B, BH

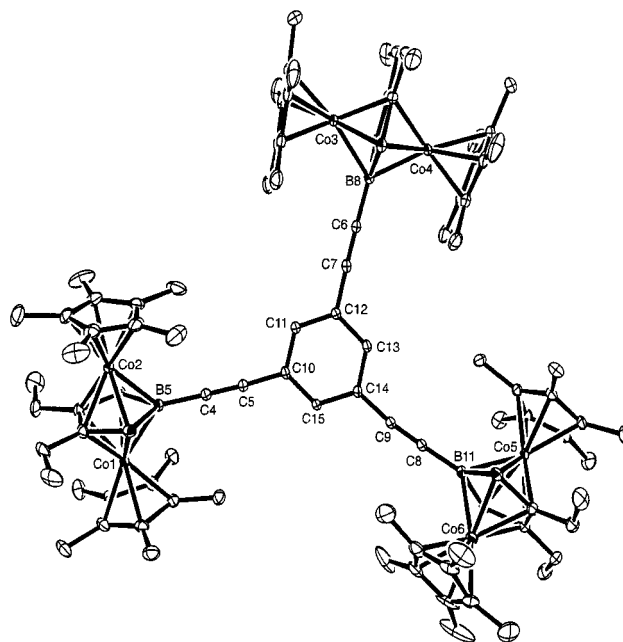
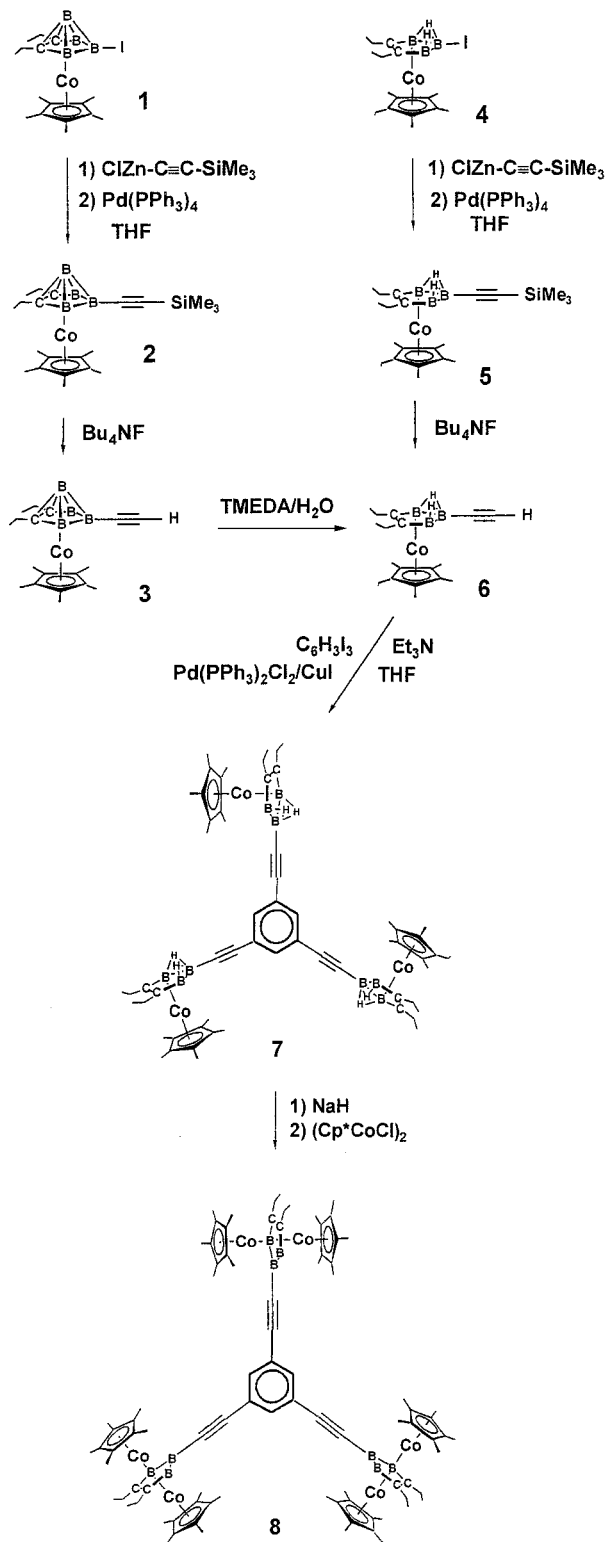


Figure 1. ORTEP drawing of **8** with 30% thermal ellipsoids. Selected bond distances (Å): C(4)–B(5) 1.522, C(6)–B(8) 1.518, C(8)–B(11) 1.523, C(4)–C(5) 1.205, C(6)–C(7) 1.210, C(8)–C(9) 1.222, C(5)–C(10) 1.437, C(7)–C(12) 1.442, C(9)–C(14) 1.426, C(10)–C(11) 1.394, C(11)–C(12) 1.391, C(12)–C(13) 1.390, C(13)–C(14) 1.400, C(14)–C(15) 1.398, C(15)–C(10) 1.402. Selected angles (deg): B(5)–C(4)–C(5) 178.7, C(4)–C(5)–C(10) 175.1, B(8)–C(6)–C(7) 178.7, C(6)–C(7)–C(12) 178.3, B(11)–C(8)–C(9) 177.3, C(8)–C(9)–C(14) 171.2, C(10)–C(11)–C(12) 121.0, C(11)–C(12)–C(13) 119.1, C(12)–C(13)–C(14) 121.3, C(13)–C(14)–C(15) 118.9, C(14)–C(15)–C(10) 120.4, C(15)–C(10)–C(11) 119.3.

5-I) (**1**) or *nido*-Cp*Co(Et₂C₂B₃H₄-5-I) (**4**), the latter route involving a previously known⁹ complex, **5**, obtained here via a different route. While both approaches gave satisfactory results, the overall yield of **6** from starting materials was 85% from **1** vs 56% from **4**. The palladium-mediated reaction of **6** with 1,3,5-triodobenzene gave the 1,3,5-tris(*nido*-cobaltacarboranylethynyl)benzene complex **7**, isolated as an orange-yellow solid in 87% yield. Bridge-deprotonation of the open C₂B₃ faces in **7** with NaH, followed by capping with Cp*Co²⁺ units, afforded the target compound 1,3,5-[Cp*Co(2,3-Et₂C₂B₃H₂-5-C≡C)CoCp*]₃C₆H₃ (**8**) as a dark red air-stable solid in 69% yield.^{10,11}

The trigonally symmetrical benzene-centered tris(triple-decker) structure of **8** (Figure 1) was established from multinuclear NMR, IR, and mass spectra and an X-ray diffraction study.^{12–14} The bond lengths and angles in the individual cobaltacarborane sandwich units are closely similar to those previously observed in triple-decker^{6,15} and higher multidecker¹⁶ complexes containing seven-vertex CoC₂B₃Co clusters. In the crystal, the three C₂B₃ ring planes are tilted out of the plane of the benzene ring with dihedral angles of 67°, 85°, and 65°, respectively, resulting in a triclinic unit cell.

In solution, we assume free rotation of the sandwich units around their respective B–C≡C–C axes connect-

valence system. We now report the synthesis, isolation, and characterization of the first complex of this structural type.

Scheme 1 shows two alternative sequences by which the key B(5)-ethynyl *nido*-cobaltacarborane synthon **6** was prepared,⁸ starting from *closo*-Cp*Co(Et₂C₂B₄H₃-

(8) Full details of the synthesis and characterization of compounds **2**, **3**, **5**, **6**, and **7** are available as Supporting Information.

(9) Malaba, D.; Sabat, M.; Grimes, R. N., *Eur. J. Inorg. Chem.* **2001**, 2557.

ing them to the benzene ring, and the very high (idealized D_{3h} point group) symmetry of the molecule is reflected in the single ^1H NMR resonances observed for the Cp^* , ethyl CH_3 , ethyl CH_2 , and C_6H_3 protons; the presence of only two ^{11}B NMR signals in a 1:2 ratio, arising from the B(5) and B(4,6) boron atoms in the three equivalent carborane rings; and the ^{13}C NMR spectrum, which is consistent with the structure. The

(10) To an 84 mg (0.077 mmol) sample of **7** in 8 mL of THF was added 11 mg of NaH (0.46 mmol) at room temperature. This solution was stirred for 1 h, 53 mg (0.12 mmol) of $(\text{Cp}^*\text{CoCl})_2^{11}$ in 5 mL of THF was added, and the mixture was stirred overnight, after which the solvent was removed in vacuo. The red-brown residue was washed through 3 cm of alumina with dichloromethane, and the crude material was chromatographed on alumina TLC in 1:1 hexane–dichloromethane to afford **8** as an air-stable dark red solid (88 mg, 0.053 mmol, 69% yield). Crystals of **8** suitable for X-ray diffraction were grown from a chloroform–ethyl alcohol solution at 0 °C. ^1H NMR (300 MHz, 25 °C, CDCl_3): δ 1.57 (t, 6H, $J = 7.2$ Hz, ethyl CH_3), 1.67 (s, 30H, C_5Me_5), 2.53–2.60 (q, 4H, $J = 7.5$ Hz, ethyl CH_2), 7.61 (s, 3H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 25 °C, CDCl_3): δ 9.4 (C_5Me_5), 15.6 (ethyl CH_3), 23.9 (ethyl CH_2), 87.6 (C_5Me_5), 88.1 (C_2B_4), 122.8 (BC=C), 127.1 (C_6H_4), 129.1 (C_6H_4). ^{11}B NMR (96.4 MHz, 25 °C, CDCl_3): δ 8.6 (BH, 2B, unresolved), 41.5 (s, 1B). IR (KBr pellet, cm^{-1}): ν 2974.2 (m), 2903.7 (vs), 2471.7 (s, B–H), 2131.7(w, C=C), 1569.7 (m), 1560.2 (m), 1458.6 (m), 1457.0 (m), 1379.4 (s), 1212.3 (w), 1079.5 (w), 1025.7 (m), 960.3 (w), 803.5 (s). UV–vis (CH_2Cl_2): 243 (100%), 276 (68), 345 (98), 428 (31), 528 (8), 753 (10). ϵ_{max} 74, 074 $\text{cm}^{-1} \text{M}^{-1}$. CI^+ -mass: m/z (%) 1662.7 ($[\text{M}]^+$, 100). In lieu of satisfactory combustion analyses (a recurring problem in some large metallocarboranes), the purity of **8** was established from clean multinuclear NMR spectra (see Supporting Information).

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(12) Crystal data for **8**· CHCl_3 : crystal dimensions 0.24 × 0.11 × 0.09 mm; triclinic space group $P1$ (No.2); $a = 10.9779(5)$ Å, $b = 17.3161(8)$ Å, $c = 24.4229(11)$ Å, $\alpha = 93.718(1)^\circ$, $\beta = 92.478(1)^\circ$, $\gamma = 91.923(1)^\circ$; $V = 4625.5(4)$ Å³; $Z = 2$; $d_{\text{calcd}} = 1.279$ Mg/m³; Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073$ Å; $T = -120$ °C; $2\theta_{\text{max}} = 65^\circ$; 63 949 reflections were collected applying ω scans on a Bruker SMART APEX CCD diffractometer, of which 32 717 with $I > 2\sigma(I)$ were used in the structure determination and refinement ($R_{\text{int}} = 0.036$). The intensities were corrected for absorption using the Bruker SADABS¹³ program with the transmission factors ranging 0.59–0.80. The structure was solved by direct methods with the Bruker SHELXTL¹⁴ program. Full-matrix least-squares refinement on $|F|^2$ yielded the final R1 of 0.0579 and wR2 of 0.1716. All hydrogen atoms were located in difference Fourier maps. The hydrogen atoms of the central phenyl ring and those attached to the boron atoms were refined with isotropic displacement parameters. The remaining hydrogen atoms were included without refinement. The difference map showed the highest peak of 2.06 $e/\text{Å}^3$ in the vicinity of the disordered CHCl_3 solvent molecule. Crystallographic data for this structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 185704. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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CI mass spectrum of **8** shows a strong parent peak at 1662.7, and the complex appears stable to air indefinitely, both as a solid and in solution. The UV–visible spectrum in CH_2Cl_2 shows maxima at 243 nm (100%, $\epsilon = 74\,074 \text{ cm}^{-1} \text{M}^{-1}$), 276 (68), 345 (98), and several smaller bands, with the very high molar absorptivity consistent with charge-transfer transitions. Cyclic voltammetric measurements on **8** reveal strong communication (ca. 1.2 V) between the two Co centers within each sandwich unit and weak interaction (ca. 90 mV) between the triple-decker units.¹⁷ A comparative study of the electrochemistry of **8** and related polynuclear cobaltacarborane sandwich complexes is in progress and will be reported in full subsequently.¹⁸

This work demonstrates the utility of the tris(*nido*-cobaltacarboranylalkynyl)benzene complex **7** as a synthon for multinuclear systems via bridge deprotonation and metal complexation of its open C_2B_3 faces. Current synthetic objectives in our laboratory include the extension of this approach to heteropolynuclear systems (e.g., Co_xM_y , M = Fe, Ni, Ru, Rh) and the construction of extended three-dimensional networks of benzene-anchored multidecker sandwich units.

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Supporting Information Available: Details on synthesis and spectroscopic characterization of compounds **2**, **3**, **5**, **6**, and **7**, and on the X-ray structure determination of **8**; tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, calculated mean planes for **8**, and ^1H and ^{13}C NMR spectra of **8** with full assignments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) Cyclic voltammetric responses for **8** recorded at a platinum electrode [E^0 (V vs SCE); peak separations in mV, scan rate 0.2 V s^{-1}] in THF with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ supporting electrolyte: $\text{Co}_3^{\text{IV}}\text{Co}_3^{\text{III}}/\text{Co}_3^{\text{III}}\text{Co}_3^{\text{III}}$, +0.32 ($\Delta E = 120$); $\text{Co}_3^{\text{III}}\text{Co}_3^{\text{III}}/\text{Co}_3^{\text{III}}\text{Co}_3^{\text{II}}$, -1.82 ($\Delta E = 70$); $\text{Co}_3^{\text{III}}\text{Co}_3^{\text{II}}/\text{Co}_3^{\text{II}}\text{Co}_3^{\text{II}}$, -2.8. In CH_2Cl_2 with 0.1 M $[\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ supporting electrolyte: $\text{Co}_3^{\text{IV}}\text{Co}_3^{\text{IV}}/\text{Co}_3^{\text{IV}}\text{Co}_3^{\text{III}}$, +1.4; $\text{Co}_3^{\text{IV}}\text{Co}_3^{\text{III}}/\text{Co}_3^{\text{III}}\text{Co}_3^{\text{III}}$, 0.17 ($\Delta E = 230$). Square wave measurements on the $\text{Co}_3^{\text{IV}}\text{Co}_3^{\text{III}}/\text{Co}_3^{\text{III}}\text{Co}_3^{\text{III}}$ signal show three peaks at +0.26, +0.18, and +0.09 V. We thank Dr. F. Fabrizi de Biani and Prof. P. Zanollo of the University of Siena, Italy, for providing these data.

(18) Zanollo, P.; Fabrizi de Biani, F.; Russell, J. M.; Grimes, R. N. To be published.