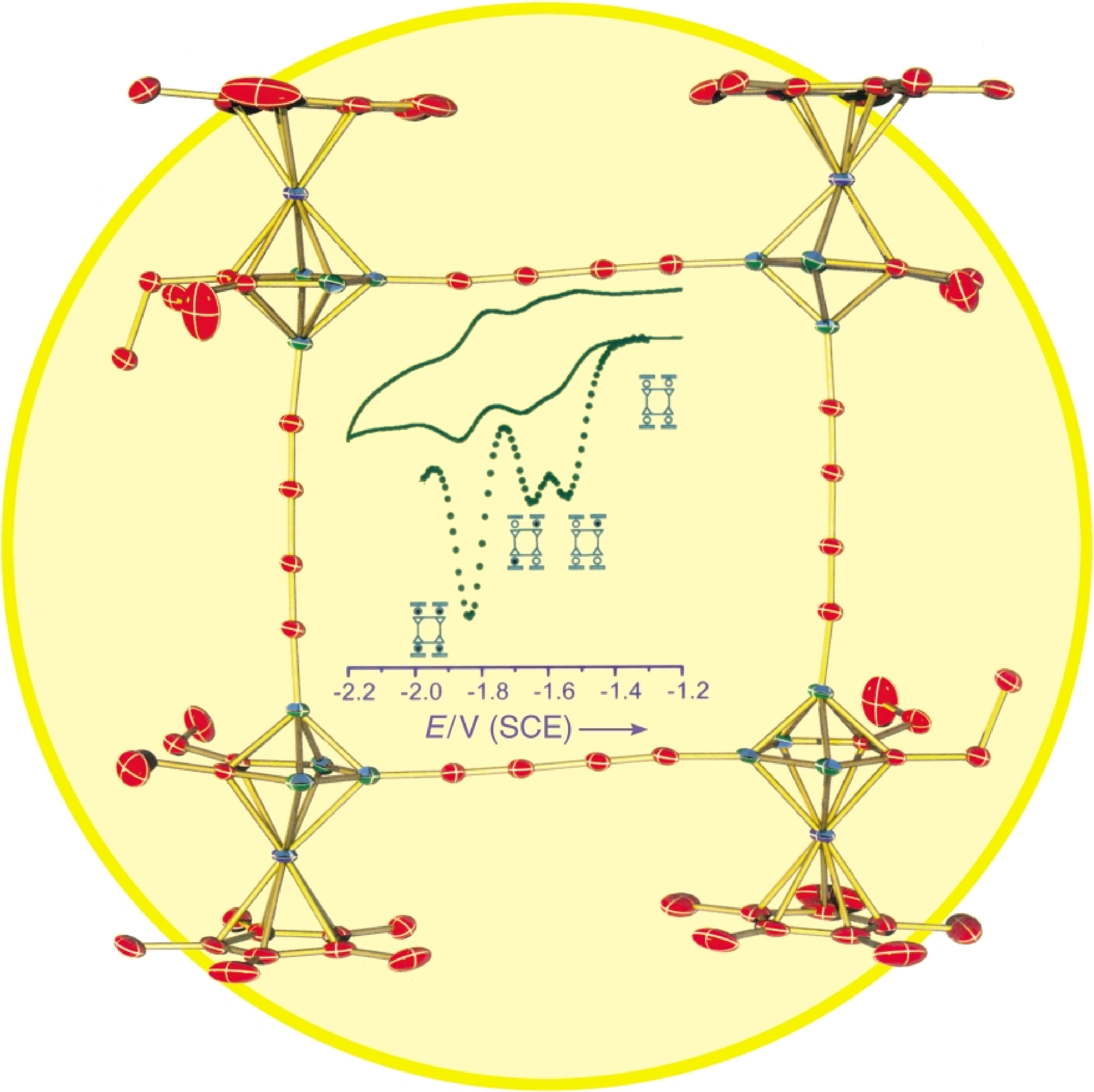
Zuschriften



Ausgehend von Cobaltacarboran-Monomeren wurden planare achteckige Makrocyclen aufgebaut, die luftstabil und stufenweise reduzierbar sind. Gemäß Cyclo- und Square-Wave-Voltammogrammen sind die Elektronen im Ring delokalisiert. Dies und mehr erfahren Sie in der Zuschrift von R. N. Grimes et al. auf den folgenden Seiten.

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Cobaltacarborane Nanostructures

Metallacarborane-Based Nanostructures: A Carbon-Wired Planar Octagon[**]

Haijun Yao, Michal Sabat, Russell N. Grimes,* Fabrizia Fabrizi de Biani, and Piero Zanello

Stable, covalently bonded metallomacrocycles are currently of considerable interest, in part because of their role, actual and potential, in the development of new molecular materials having tailorable properties.[1] Among the types of target structures attracting attention are highly symmetrical, aesthetically appealing architectures such as molecular squares, rectangles, and boxes,[2] but controlled synthetic routes to metal-containing compounds of this class are relatively rare. Ideally, one looks for metal building-block units that remain intact in a range of environments, suitable organic or inorganic linkers, and efficient methods for assembling these parts into desired target molecules. Since the first of these often presents a challenge, metallacarboranes are obvious candidates for such application because of their synthetic versatility and well-developed derivative chemistry.[3] In recent publications from this laboratory, methods for the regiospecific functionalization of seven-vertex MC_2B_4 metallacarboranes and their linkage through alkynyl, arenyl, and other organic groups have been described.[4] This has allowed the construction of polymetallacarborane molecular architectures that take advantage of special attributes, such as orthogonal substitution at apex and equatorial boron vertices in seven-vertex pentagonal bipyramidal clusters.[4b] Here we report the stepwise assembly of a tetranuclear species that contains four identical cobaltacarborane clusters and features a planar octagonal (tetratruncated square) $\{C_{16}B_8\}$ macrocycle.

Scheme 1 shows the synthesis of the bifunctional 5-iodo-7-trimethylsilyl cobaltacarborane **4** in two steps from either the *closo*-cobaltacarboranes **1a** and **1b** or the *nido*-cobaltacarborane **2**. Desilylation of **4** gave the ethynyl derivative **5** which, in turn, was dimerized through either of two routes, as shown, to give the 5,5′-bis(trimethylsilyl) complex **8**. Treatment of **8** with fluoride ions yielded the 5,5′-diethynyl complex **9**, which was dimerized by treatment with copper acetate and copper(I) chloride to afford the target compound $[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}5\text{-}C{\equiv}C\text{-}7\text{-}C{\equiv}C)]_4$ (**10**, $Cp^* = \eta^5\text{-}C_5Me_5$) as a red crystalline air-stable solid (Scheme 2). Yields of isolated and chromatographically purified individual compounds in the sequence **1b**→**3**→**4**→**5**→**6**→**8**→**9**→**10** ranged between 78 and 99%.

The octagonal macrocyclic geometry of **10** in solution is supported by its extremely simple ^{11}B, ^{1}H, and ^{13}C NMR spectra, which reveal a 2:1:1 boron pattern, just two alkynyl carbon signals, and unique C–ethyl and CoCp* environments. An X-ray crystallographic study[5] of **10** (Figure 1) conducted on crystals grown from a pyridine solution established that the 24-atom ring formed by the four {–C≡C–C≡C–} and four carborane {–B–B–} linkages is essentially planar. The complex is centrosymmetric and crystallizes with two molecules of pyridine per molecule of **10**. Molecules in the crystal form discrete, well-separated layers (approximate interlayer distance of 10 Å), within each of which the $\{C_{16}B_8\}$ rings are nearly coplanar (Figure 2). The bond lengths and angles (Figure 1) are within normal ranges and the {B–C–C–C–C–B} edge lengths are 6.82 Å. The square defined by the centroids of the four $\{C_2B_3\}$ carborane rings is approximately 9.4 Å in length along each edge, and the diagonally measured distance across the molecule is approximately 24 Å.

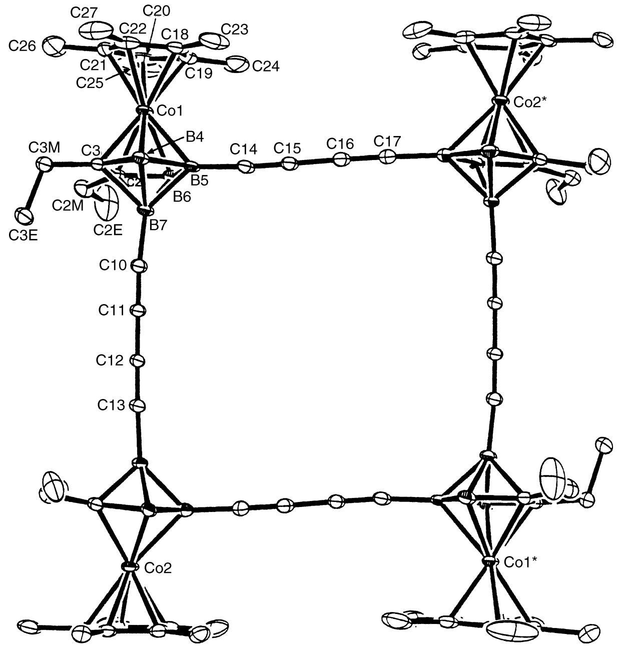

Figure 1. Molecular structure of **10**. Selected bond lengths [Å] and angles [°]: B5-B7 1.760(6), B5-C14 1.517(6), C14-C15 1.209(6), C15-C16 1.379(6), C16-C17, 1.216(6), B7-C10 1.516(5), C10-C11 1.217(5), C11-C12 1.372(5), C12-C13, 1.212(5); B7-B5-C14 137.3(3), B5-C14-C15 171.9(4), C14-C15-C16 177.6(4), C15-C16-C17 177.5(4), B5-B7-C10 136.9(3), B7-C10-C11 174.5(4), C10-C11-C12 178.2(5), C11-C12-C13 179.1(4).

The 24-atom $\{C_{16}B_8\}$ ring in **10** is one of the larger planar molecular macrocycles currently known, and it presents a variety of interesting avenues for exploration of its reactivity and electronic properties. Analysis of **10** by cyclic voltamme-

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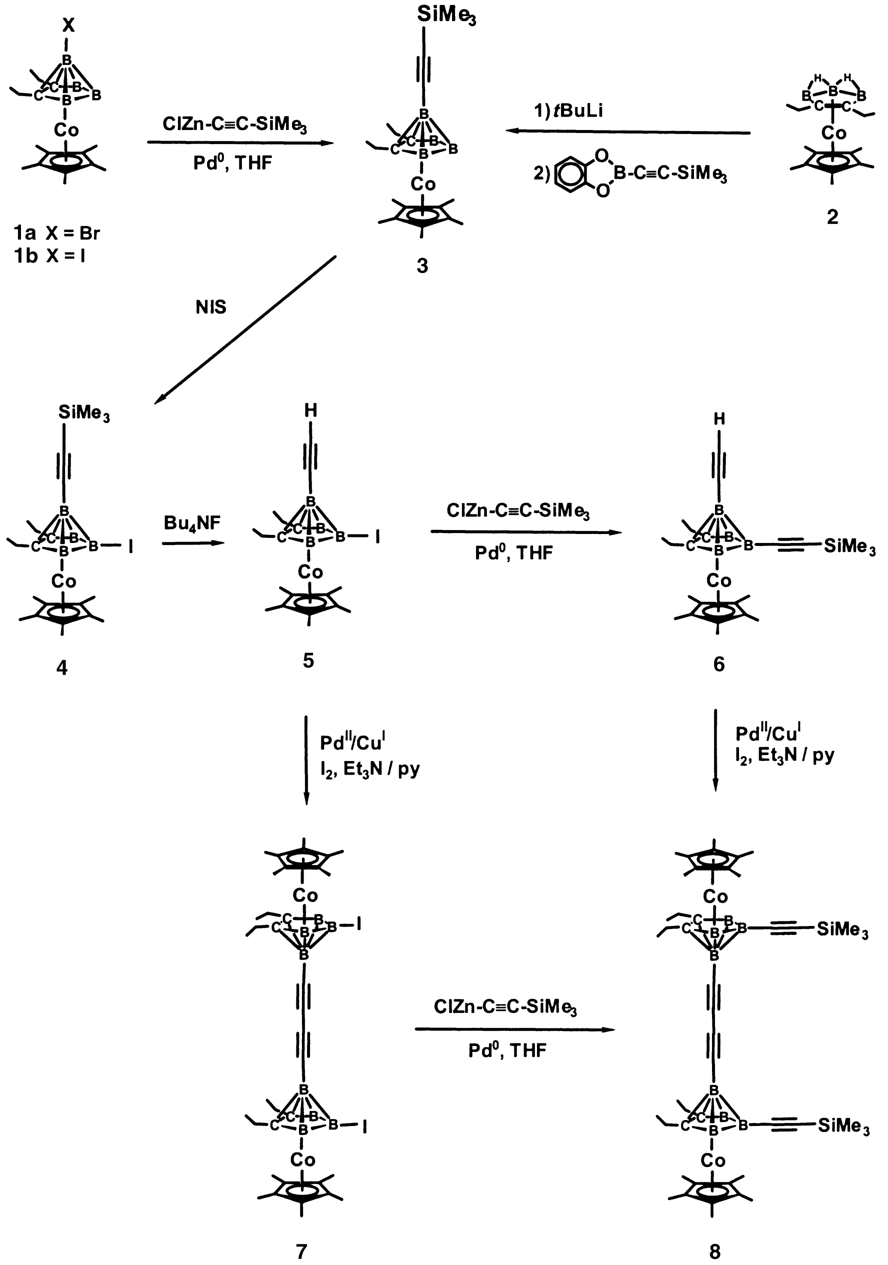
try[6] revealed two separate one-electron reductions followed by a single two-electron reduction (Figure 3), which indicates significant intramolecular electronic communication between the four cobalt centers. A possible pathway for the progressive four-electron addition is suggested in Figure 3. The concomitant entry of the last two electrons is likely because of the charge symmetry that exists following the addition of the first two electrons. Further studies of the electronic and other properties of this and related systems are in progress.

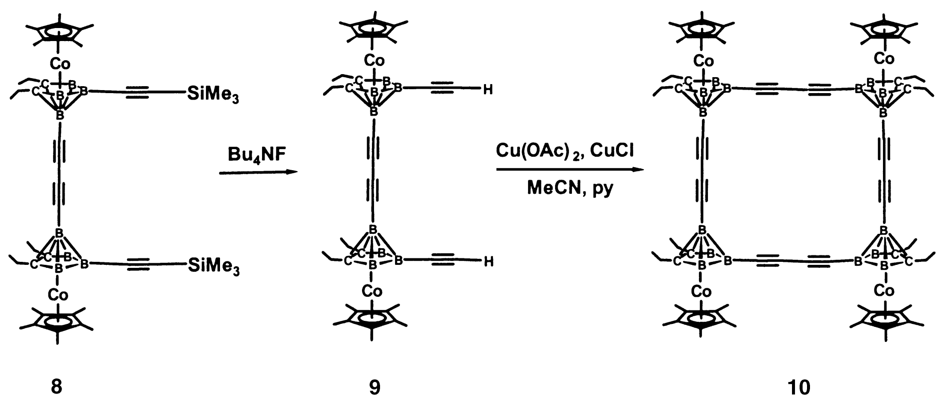


Scheme 1. B = B, BH

Experimental Section

Spectroscopic data for compounds **3**–**9** and details of the alternative preparations of **3** and **8** are available as Supporting Information.

3: $Me_3SiC{\equiv}CH$ (570 mg, 5.73 mmol) in THF (20 mL) was added to *n*BuLi (1.51 M in hexane, 3.8 mL, 5.73 mmol) at 0 °C. After stirring for 30 min, anhydrous $ZnCl_2$ (781 mg, 5.73 mmol) in THF (20 mL) was added at 0 °C, and the mixture was then stirred at room temperature for 2 h. [Cp*Co(2,3-$Et_2C_2B_4H_3$-7-I)] (**1b**, 860 mg, 1.91 mmol) and [Pd(PPh_3)$_4$] (110 mg, 0.10 mmol) were then added. The mixture was refluxed for 4.5 days, after which time the solvent was removed in vacuo and the residue was purified by flash chromatography through 5 cm of silica gel in 1:1 hexane/CH_2Cl_2 to give one orange band. Removal of the solvent gave 755 mg (94 %) of an orange-red product. Compound **3** was also prepared in moderately lower yields by a similar procedure from [Cp*Co(2,3-$Et_2C_2B_4H_3$-7-Br)] (**1a**), or by the insertion of $C_6H_4O_2BC{\equiv}CSi(CH_3)_3$ into the *nido*-[Cp*Co(2,3-$Et_2C_2B_3H_3$)]$^{2-}$ ion derived from **2**.



Scheme 2. B = B, BH

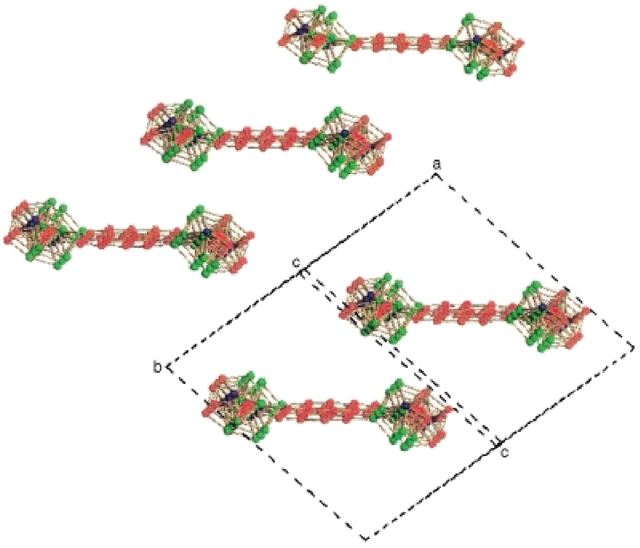


Figure 2. Unit cell packing diagram for **10** showing a view parallel to the *c* axis.

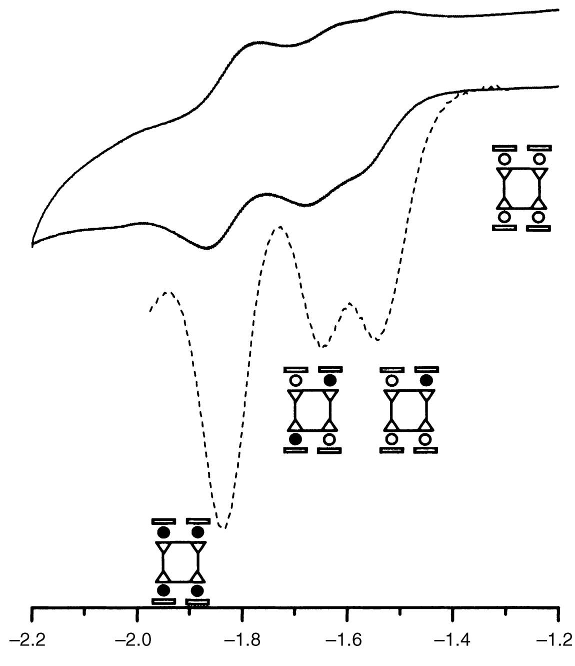


Figure 3. Cyclic (——) and Osteryoung square-wave (–•–•) voltammograms recorded at a gold electrode in a solution of **10** in THF (0.2×10^{-3} mol dm^{-3}) versus a saturated calomel electrode; Bu$_4$NPF$_6$ supporting electrolyte (0.2 mol dm^{-3}). Scan rates: (——) 0.2 V s^{-1}; (–•–•) 0.1 V s^{-1}.

4: *N*-iodosuccinimide (203 mg, 0.90 mmol) in CH$_2$Cl$_2$ (15 mL) was added dropwise to **3** (345 mg, 0.82 mmol) in dry CH$_2$Cl$_2$ (15 mL) at 0 °C. The mixture was stirred at that temperature for 1 h, followed by 1 h at room temperature, after which time the solvent was removed and the residue taken up in hexane. Purification by flash chromatography in hexane (to remove iodine) after washing with CH$_2$Cl$_2$ led to one orange band. Removal of the solvent gave orange-red **4** (445 mg, 99 %).

5: Compound **4** (445 mg, 0.816 mmol) was treated with a solution of Bu$_4$NF (1.0 M, 0.82 mL, 0.82 mmol) in dry THF (20 mL) for 40 min at 0 °C, after which the THF was removed and the residue was purified by flash chromatography in CH$_2$Cl$_2$ to give one orange band. Removal of the solvent gave red-orange solid **5** (370 mg, 96 %).

6: Me$_3$SiC≡CH (157 mg, 1.6 mmol) was deprotonated in THF (8 mL) by the addition of *n*BuLi (1.51 mmol in hexane) at 0 °C. After stirring for 30 min, anhydrous ZnCl$_2$ (204.5 mg, 1.5 mmol) in THF (6 ml) was added at 0 °C, and the mixture was stirred at room temperature for 2 h, after which time compound **5** (237 mg, 0.5 mmol) and [Pd(PPh$_3$)$_4$] (29 mg, 0.025 mmol) were added. The mixture was refluxed for 3.5 days, then the solvent was removed in vacuo and the residue purified by flash chromatography in 1:1 hexane/CH$_2$Cl$_2$ to give one orange band. Removal of the solvent gave orange-red **6** (185 mg, 83 %).

8: Compound **6** (166 mg, 0.374 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (7 mg, 0.01 mmol), CuI (4 mg, 0.02 mmol), I$_2$ (50 mg, 0.2 mmol), pyridine (8 mL), and Et$_3$N (3 mL) were combined, and the mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and the residue was purified by flash chromatography through 5 cm of silica gel in 1:1 hexane/CH$_2$Cl$_2$ to give one orange band. Removal of solvent gave orange solid **8** (130 mg, 78 %).

9: Compound **8** (100 mg, 0.113 mmol) was desilylated with Bu$_4$NF (1.0 M, 0.23 mL, 0.23 mmol) in dry THF (15 mL). The mixture was stirred at 0 °C for 1 h, then the solvent was removed, and the residue purified by flash chromatography in CH$_2$Cl$_2$ to give one orange band. Removal of solvent gave orange solid **9** (71 mg, 85 %).

10: Compound **9** (22 mg, 0.03 mmol) in pyridine (10 ml) was added to a mixture of Cu(OAc)$_2$ (54 mg, 0.3 mmol) and CuCl (30 mg, 0.3 mmol) in CH$_3$CN (10 mL), and the mixture was stirred at 60 °C for 17 h. The mixture was allowed to cool down, and water (30 mL) was added. The resulting precipitate was filtered off, washed with water, and dried in vacuo. The residue was crystallized from pyridine, 1,2-dichloroethane, and ethanol at 0 °C to give red crystals (18 mg, 82 %). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.26$ (t, 6H, $J = 7.5$ Hz, ethyl CH$_3$), 1.77 (s, 15H, C$_5$Me$_5$), 2.17 and 2.35 ppm (sextet, 4H, $J = 7.5$ Hz, ethyl CH$_2$); ^{13}C NMR (75.5 MHz, pyridine-d_5): $\delta = 9.5$ (C$_5$Me$_5$), 14.9 (ethyl CH$_3$), 22.0 (ethyl CH$_2$), 75.6 (BC≡C−C≡CB), 91.9 (C$_5$Me$_5$), 95.2 (C$_2$B$_4$), 97.2 ppm (BC≡C−C≡CB); ^{11}B NMR (96.4 MHz, pyridine-d_5): $\delta = -4.5$ (s, 1B), 4.5 (2B, BH unresolved), 8.9 ppm (s, 1B). IR (KBr pellet): $\tilde{\nu} = 2972.7$ (s), 2932.8 (m), 2913.0 (m), 2871.6 (w), 2545.2 (s, B−H), 2168.0 (w, C≡C), 2090.8 (m, C≡C), 1471.9 (m), 1456.7 (m), 1383.9 (vs), 1155.7 (w), 1114.9 (m), 1055.9 (m), 1028.6 (m), 804.9 (s), 633.7 (w) cm^{-1}. UV/Vis (CH$_2$Cl$_2$, nm (%)): 323 (100), 231 (67), 464 (4) $\varepsilon_{\max} = 67170$ cm^{-1}M^{-1}. Positive-mode CI-MS: m/z (%) = 1479.9 ([M^+], 100).

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[5] Crystal structure determination of **10**: Data were collected on a Bruker SMART APEX CCD diffractometer ($\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation, $\lambda = 0.71073$ Å, ω scans) at 153 K. 1800 frames were collected up to $2\theta = 65°$. Intensities were corrected for absorption applying the SADABS program.[7] The structure was solved by direct methods using the Bruker SHELXTL software.[8] Full-matrix least-squares refinement on F^2 was applied. All non-hydrogen atoms, except those on one of the pyridine solvent molecules, were refined with anisotropic thermal displacement parameters. The hydrogen atoms attached to boron were found in difference Fourier maps and were refined with isotropic thermal displacement parameters. All remaining hydrogen atoms of the complex molecule, as well as those of the pyridine ring C1S–N5S were fixed in calculated positions. Difference Fourier maps indicated the presence of three pyridine solvent molecules; since high values of the thermal displacement parameters for one pyridine suggested that the site was only partially occupied, its atoms were assigned population parameters of 0.5. A third pyridine was found disordered between two sites related by a center of symmetry. The atoms of this molecule were refined with isotropic thermal displacement parameters and occupancies of 0.5. The final difference map showed the presence of a residual peak with the height of $1.29\ \mathrm{e\,Å^{-3}}$, located in the vicinity of a pyridine ring. $\mathrm{C_{90}H_{118}B_{16}Co_4N_2}$, $M_\mathrm{W} = 1636.54$, triclinic, space group $P\bar{1}$, $a = 11.8321(7)$, $b = 15.0873(8)$, $c = 15.2047(8)$ Å, $\alpha = 85.300(2)$, $\beta = 70.754(2)$, $\gamma = 89.068\ (1)°$, $V = 2553.8(2)\ \mathrm{Å^3}$, $Z = 1$, $\rho_\mathrm{calcd} = 1.064\ \mathrm{g\,cm^{-3}}$. Of 35421 measured reflections, 18073 were independent ($R_\mathrm{int} = 0.053$), 609 parameters, $R1 = 0.089$ (for reflections with $I > 2\sigma(I)$), $wR2 = 0.2506$ (for all reflections). CCDC-194783 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[6] The electrochemical materials, apparatus, and procedures are described elsewhere: see F. Fabrizi de Biani, M. Fontani, E. Ruiz, P. Zanello, J. M. Russell, R. N. Grimes, *Organometallics* **2002**, *21*, 4129. THF was refluxed from metallic sodium under an inert atmosphere. All potential values are referred to the saturated calomel electrode (SCE). Under the experimental conditions used, the one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.54$ V.

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