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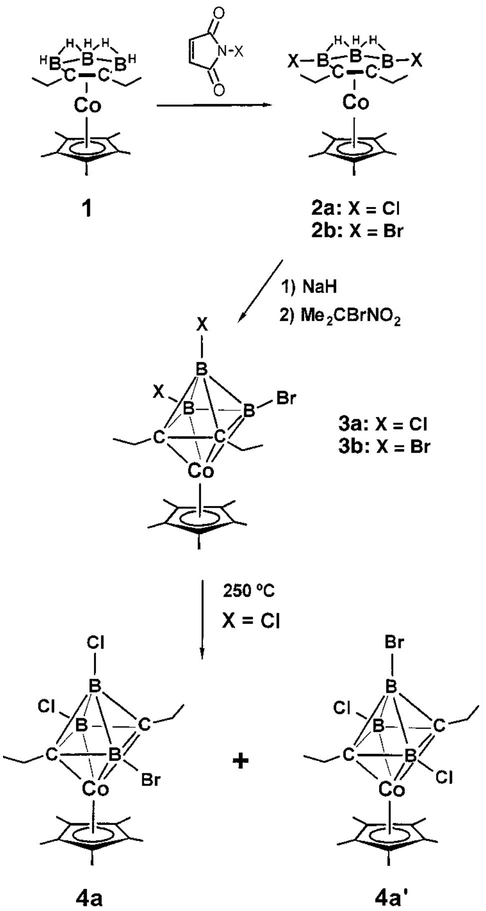
nido ↔ *closo* Interconversion of Six-Vertex Metallacarboranes: Access to CoC_2B_3 and CoC_2B_4 Clusters with Nonadjacent Carbon Atoms**

Hans-Jörg Schanz, Michal Sabat, and
Russell N. Grimes*

Metallacarborane chemistry has been well developed for 12-vertex (icosahedral) and 7-vertex (pentagonal bipyramidal) clusters and, to a lesser extent, for other systems having 8 to 14 vertices.[1] In contrast, little is known of the smallest members of the metallacarborane family, for example, 6-vertex *closo*-MC_2B_3 polyhedra. The first such species were prepared in the 1970s[2, 3] by thermal insertion of metal reagents into *closo*-1,5-$C_2B_3H_5$, a relatively inaccessible small carborane. To date, fewer than half a dozen 6-vertex *closo*-metallacarboranes have been reported,[2–4] and just one crystal structure of a *closo*-MC_2B_3 system is available.[3] In principle, such clusters should be accessible by the oxidation of *nido*-$LMC_2B_3H_5^{2-}$ open-cage dianions having 16 skeletal electrons, generating neutral 14-electron *closo*-$LMC_2B_3H_5$ species as predicted from simple electron-counting arguments (Wade's rules).[5] However, no such conversion has been reported experimentally, and earlier attempts to do this in our laboratory were unsuccessful; our experience has been that oxidants sufficiently strong to remove two electrons tend to degrade the cage structure.

It seemed possible that this problem might be circumvented by modifying the cluster to make it easier to oxidize. Here we report an application of this approach, in which a tribrominated *nido*-1,2,3-MC_2B_3 cage with adjacent carbon atoms undergoes oxidative closure to form the desired *closo* system. This product in turn can be converted into 7-vertex *closo*- and 6-vertex *nido*-metallacarboranes having nonadjacent carbon atoms, families that have heretofore been difficult to access.

Deprotonation of the 4,6-dichloro- or dibromo-*nido*-cobaltacarboranes[6] **2a** or **2b** (Scheme 1) with sodium hydride in THF, followed by addition of 2-bromo-2-nitropropane and



Scheme 1. Synthesis of **3a** and **3b** as well as the thermal rearrangement of **3a** to form a mixture of isomers **4a** and **4a'**.

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[*] Prof. Dr. R. N. Grimes, Dr. H.-J. Schanz, Dr. M. Sabat
Department of Chemistry
University of Virginia
Charlottesville, VA 22901 (USA)
Fax: (+1) 804-924-3710
E-mail: rng@virginia.edu

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purification of the product by column chromatography on silica in air, afforded orange crystals of **3a** or **3b** (Cp* = C_5Me_5). Characterization of these two products by ^1H, ^{11}B, and ^{13}C NMR spectroscopy and mass spectrometry, and an X-ray crystal structure determination on **3b**,[7] established the octahedral cluster geometry shown in Figure 1. The $C(2)-C(3)$ interaction is significantly longer than the skeletal C–C bonds in 7-vertex MC_2B_4 and $M_2C_2B_3$ *closo* clusters,[1] but is comparable to the corresponding distance in the 6-vertex carborane $1,2\text{-}C_2B_4H_6$ (1.535 Å) as determined from gas-phase electron diffraction.[8] In $1,2\text{-}(Me_3Si)_2C_2B_4H_4$ the C–C bond is somewhat longer (1.59(4) Å from X-ray crystallography), with the lengthening attributed to the $SiMe_3$ groups.[9]

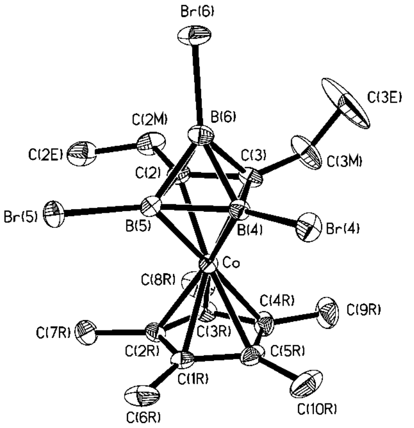


Figure 1. Molecular structure of **3b**. Selected distances [Å] and angles [°]: C(2)–C(3) 1.502(6), Co–C_5 ring 1.660(2), Co–C_2B_2 ring 1.605(2); B(5)-C(2)-C(3) 94.0(3), C(2)-C(3)-B(4) 94.9(3), C(3)-B(4)-B(5) 86.4(3), C(2)-B(5)-B(4) 84.7(3).

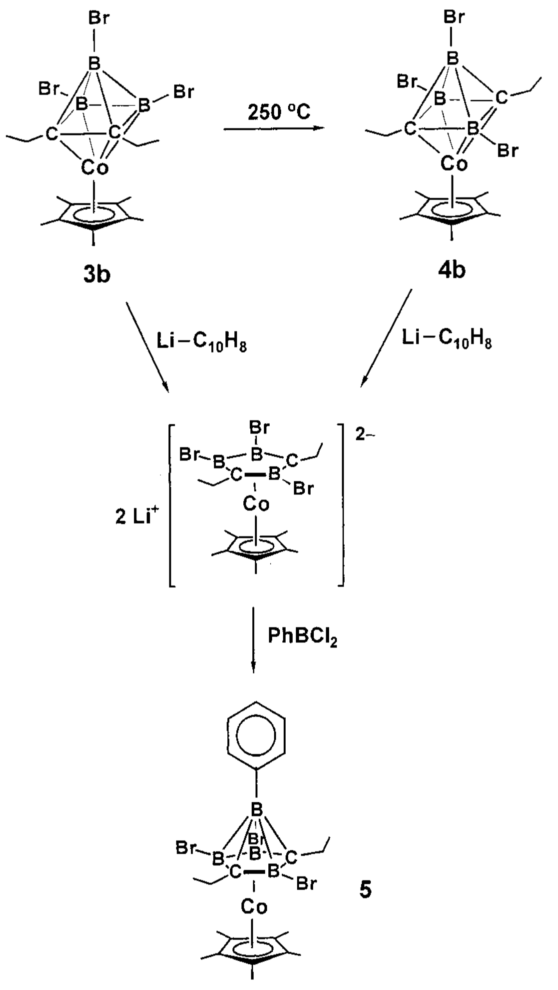
closo-[1,2,3-Cp*Co($Et_2C_2B_3$-4,6-Cl_2-5-Br)] **3a**

closo-[1,2,3-Cp*Co($Et_2C_2B_3Br_3$)] **3b**

Thermal rearrangement of cluster **3a** in vacuo at 250 °C effected separation of the skeletal carbon atoms, yielding a mixture of isomers **4a** and **4a′** (50% yield, Scheme 1). In the case of **3b**, a single product **4b** was formed in 94% yield (Scheme 2). The isomers **4a** and **4a′** were not separated, but the nonadjacent-carbon *closo*-[1,2,4-Cp*CoC_2B_3] cage structure shown is supported by spectroscopic data and by analogy with **4b**. These cluster interconversions—the first to be demonstrated in 6-vertex metallacarborane systems—are reminiscent of the thermal rearrangement of $1,2\text{-}C_2B_4H_6$ to $1,6\text{-}C_2B_4H_6$ at 250 °C.[10]

closo-1,2,4-[Cp*Co($Et_2C_2B_3Br_3$)] **4b**

Cage opening of the *closo* cluster **3b** with lithium–naphthalene in THF gave a presumed *nido*-cobaltacarborane dianion (not isolated), which underwent boron insertion with phenyldichloroborane to form bright yellow crystalline **5**, which was isolated in 35% yield (Scheme 2); the same compound was also generated in lower yield from the nonadjacent-carbon isomer **4b** by an analogous procedure. The structure of **5** (Figure 2), was confirmed from multinuclear NMR spectroscopy, mass spectrometry, and X-ray crystallography.[7]



Scheme 2. Reactivity of cluster **3b**.

closo-[1,2,4-Cp*Co($Et_2C_2B_4$-3,5,6-Br_3-7-Ph)] **5**

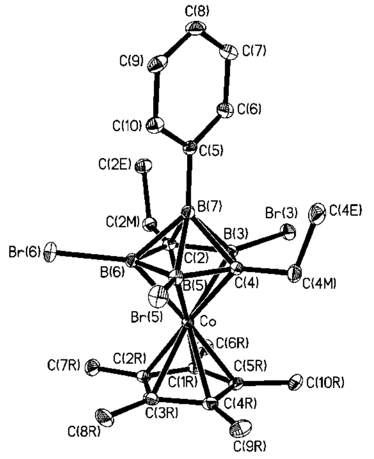


Figure 2. Molecular structure of **5**. Selected distances [Å]: C(2)–B(3) 1.551(3), B(3)–C(4) 1.556(3), C(4)–B(5) 1.542(3), B(5)–B(6) 1.658(4), B(6)–C(2) 1.548(3), Co–C_5 ring 1.641(1), Co–C_2B_3 ring 1.581(1).

Three processes that are fundamental to the synthesis of large carboranes[1]—oxidative cage closure, reductive cage opening, and thermal rearrangement—have been applied here for the first time to 6-vertex metallacarboranes, allowing rational syntheses of new clusters. The results demonstrate the practical synthetic applicability of skeletal electron-counting considerations to these smallest members of the metallacarborane family.

Experimental Section

3a: NaH (30 mg, 1.3 mmol) was added to a solution of **2a**[6] (96 mg, 0.25 mmol) in absolute THF (15 mL), and the mixture was stirred at RT for 15 min. Addition of 2-bromo-2-nitropropane (400 mg, 2.50 mmol) produced an instant color change from orange to green. After 2–3 h the color returned to orange-red. The reaction mixture was stirred for another 10 h and then opened to the air, and water (0.2 mL) was added to remove residual NaH. Volatile material was removed under reduced pressure, and the residue was suspended in CH_2Cl_2 (3 mL) and filtered through 5 cm of silica gel. An orange-red band was eluted with hexanes/CH_2Cl_2 (1/1) to yield 68 mg of crude material after removal all volatile components. Pure **3a** was obtained by thin-layer chromatography (TLC) on silica gel (20 cm) with hexanes to give an intense yellow band ($R_f = 0.40$) that was eluted with CH_2Cl_2. Volatile components were then removed to afford 35 mg (33 %) of **3a**. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.88$ (m, 4H, CH_2 (Et)), 1.84 (s, 15H, C_5Me_5), 1.14 (t), 1.13 (t, 6H, CH_3 (Et)); ^{11}B NMR (96.4 MHz, 25 °C, $CDCl_3$): $\delta = 15.0$, 9.1 (B4, B5), 6.3 (B6); ^{13}C NMR (75.5 MHz, 25 °C, $CDCl_3$): $\delta = 92.4$ (C_5Me$_5$), 19.7, 19.3 (CH_2 (Et)), 12.0, 11.8 (CH_3 (Et)), 9.1 (C$_5$*Me*$_5$) (cage C not observed); CI$^+$-MS: *m/z* (%): 461.3 (100) [M^+].

3b: The procedure for the synthesis of **3a** was followed using **2b** (142 mg, 0.30 mmol) in absolute THF (20 mL) and 2-bromo-2-nitropropane (470 mg, 2.93 mmol), yielding 96 mg of crude material, which on TLC purification gave 81 mg (49 %)of air-stable **3b** (m.p. 215–220 °C). Cooling of a saturated solution in hexanes at −20 °C gave suitable crystals for X-ray diffraction. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): $\delta = 1.90$ (m, 4H, CH_2 (Et)), 1.83 (s, 15H, C_5Me_5), 1.15 (t, 6H, CH_3 (Et)); ^{11}B NMR (96.4 MHz, 25 °C, $CDCl_3$): $\delta = 10.8$ (2B), 2.6 (1B); ^{13}C NMR (75.5 MHz, 25 °C, $CDCl_3$): $\delta = 92.6$ (C_5Me$_5$), 63.7 (br s, cage C), 20.2 (CH_2 (Et)), 11.8 (CH_3 (Et)), 9.1 (C$_5$*Me*$_5$); CI$^+$-MS: *m/z* (%): 549.6 (65) [M^+], 275.3 (100) [$M^+ -$ Cp*Co − Br].

4a and **4a′**: Compound **3a** (20 mg, 0.044 mmol) was heated to 250 °C in vacuo in a Pyrex tube for 18 h and then opened to the air at RT. The product was dissolved in CH_2Cl_2 (2 mL) and filtered through 5 cm of silica gel in hexanes/CH_2Cl_2 (1/1), eluting a strong yellow band. Removal of volatile components gave a 3:2 orange-red solid mixture of air-stable **4a** and **4a′**, which was further purified by TLC (silica gel, hexanes, intense orange-yellow band $R_f = 0.40$) to give 10 mg (50 %) of product. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): $\delta = 1.80$ (s, 2 equiv), 1.79 (s, 3 equiv, 15H, C_5Me_5), 1.58 (m, 4H, CH_2 (Et)), 1.00 (m, 6H, CH_3 (Et)); ^{13}C NMR (75.5 MHz, 25 °C, $CDCl_3$): $\delta = 92.1$ (C_5Me$_5$), 65.1 (cage C), 19.5 (CH_2 (Et)), 13.0 (CH_3 (Et)), 9.0 (C$_5$*Me*$_5$); CI$^+$-MS: *m/z* (%): 461.3 (100) [M^+].

4b: Treatment of **3b** (78 mg, 0.14 mmol) as in the synthesis of **4a** and **4a′**, with elution of the product with hexanes/CH_2Cl_2 (1/1), gave an intense yellow band from which volatile components were removed to afford pure orange-red solid **4b** (73 mg, 94 %; m.p. 215–220 °C). While solid **4b** is air-stable, solutions in chlorinated solvents turn dark green after several days, indicating decomposition. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): $\delta = 1.78$ (s, 15H, C_5Me_5), 1.60 (q, 4H, CH_2 (Et)), 1.01 (t, 6H, CH_3 (Et)); ^{11}B NMR (96.4 MHz, 25 °C, $CDCl_3$): $\delta = 7.6$ (B6), 2.6 (B3, B5); ^{13}C NMR (75.5 MHz, 25 °C, $CDCl_3$): $\delta = 92.2$ (C_5Me$_5$), 83.7 (br s, cage-C), 19.9 (CH_2 (Et)), 12.9 (CH_3 (Et)), 9.0 (C$_5$*Me*$_5$); CI$^+$-MS: *m/z* (%): 549.3 (30) [M^+], 275.1 (100) [$M^+ -$ Cp*Co − Br].

5: Lithium–naphthalene in THF (0.1 mL, 1 M) was added dropwise to **4b** (20 mg, 0.036 mmol) in diethyl ether (10 mL) at RT until no instant decolorization of the intensely colored solution of $LiC_{10}H_8$ occurred. The solvent was removed in vacuo and the residue was dissolved in toluene (10 mL). Phenyldichloroborane (10 mg, 0.063 mmol) was added and the reaction mixture was stirred for 12 h at RT. Following removal of solvent, the residue was taken up in CH_2Cl_2 (2 mL) and the suspension was filtered through 5 cm of silica gel, eluting the crude product with hexanes/CH_2Cl_2 (1/1). Elution of **5** in hexanes followed by CH_2Cl_2 through 20 cm of silica gel afforded a bright yellow band ($R_f = 0.35$), which upon removal of solvent gave yellow solid air-stable **5** (8 mg, 35 %; m.p. 199–202 °C). The identical procedure using **3b** as starting material (20 mg, 0.036 mmol) afforded 4 mg (17 %) of pure **5**. Slow evaporation of a saturated solution in hexanes at RT gave suitable crystals for X-ray diffraction. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): $\delta = 7.28$ (d, 2H), 7.15 (t, 1H), 7.06 (t, 2H, C_6H_5), 2.38 (m, 2H), 2.09 (m, 2H, CH_2 (Et)), 1.78 (s, 15H, C_5Me_5), 0.68 (t, 6H, CH_3 (Et)); ^{11}B NMR (96.4 MHz, 50 °C, [D$_6$]acetone): $\delta = 9.6$ (br s, B5, B6), 7.1, 6.8 (br s, B3, B7); ^{13}C NMR (75.5 MHz, 25 °C, $CDCl_3$): $\delta = 133.6$, 128.3, 126.9 (C_6H_5, *ipso*-C not found), 93.1 (C_5Me$_5$), 22.6 (CH_2 (Et)), 13.2 (CH_3 (Et)), 8.5 (C$_5$*Me*$_5$) (cage C not found); CI$^+$-MS: *m/z* (%): 637.1 (80), 638.9 (70) [M^+], 560.0 (80), 559.1 (100), 558.1 (70), 557.1 (50) [$M^+ - C_6H_5$] and [$M^+ -$ Br].

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[7] Crystal structure determinations: Data were collected on a Bruker SMART APEX CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, ω scans) at 153 K. For each structure, a total of 1321 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s per frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm, and the structures were solved and refined using the Bruker SHEXTL software package. **3b** ($C_{16}H_{25}B_3Br_3Co$): $M_r = 548.45$, monoclinic, space group $P2_1/c$, $a = 8.5481(4)$, $b = 14.1576(6)$, $c = 17.6004(8)$ Å, $\beta = 102.659(1)°$, $V = 2078.23(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.753$ g cm^{-3}. Of 16311 measured reflections, 5723 were independent ($R_{int} = 0.031$), 214 parameters, $R1 = 0.041$ (for reflections with $I > 2\sigma(I)$), $wR2 = 0.116$ (for all reflections), max./min. residual electron density 1.413/−1.142 e Å^{-3}. Hydrogen atoms, except for those of the C(3M)−C(3E) ethyl group, were fixed in the calculated positions. **5** ($C_{22}H_{30}B_4Br_3Co$): $M_r = 636.36$, monoclinic, space group $P2_1/c$, $a = 9.2268$ (5), $b = 31.709$ (2), $c = 9.3033$ (5) Å, $\beta = 113.963(1)°$, $V = 2487.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.699$ g cm^{-3}. Of 18623 measured reflections, 6165 were independent ($R_{int} = 0.027$), 391 parameters, $R1 = 0.025$ (for reflections with $I > 2\sigma(I)$), $wR2 = 0.061$ (for all reflections), max./min. residual electron density 0.485/−0.738 e Å^{-3}. All hydrogen atoms were found in the difference Fourier maps and were refined with isotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159114 (**3b**) and -159115 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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