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Synthesis and Crystal Structure of a Novel, TMEDA-Stabilized *closo*-Cobalt(II) Carborane: An Intermediate for Anionic, *commo*-Cobalt(III) Carborane Complexes

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Summary: The reaction of closo-exo-5,6-$[(\mu\text{-H})_2\text{Li}(\text{TMEDA})]$*-1-Li(TMEDA)-2,4-*$(\text{SiMe}_3)_2$*-2,4-*$\text{C}_2\text{B}_4\text{H}_4$ *(2) with* CoCl_2 *in a molar ratio of 1:1 in a solvent mixture of dry benzene and n-hexane at 0 °C and then at room temperature produces, in 92% yield, deep green crystals of a paramagnetic, half-sandwich Co(II) carborane, closo-1-(TMEDA)-1-Co-2,4-*$(\text{SiMe}_3)_2$*-2,4-*$\text{C}_2\text{B}_4\text{H}_4$ *(1), which does not undergo disproportionation to give the corresponding Co(III) species and elemental cobalt. Unlike the cases of main-group metallacarboranes, the coordination of the metal in 1 with the Lewis base TMEDA does not produce a distortion of the metallacarborane. Thus, 1 exhibits an almost undistorted "carbons apart" pentagonal-bipyramidal geometry, which was confirmed by a single-crystal X-ray diffraction study.*

The first cobaltacarborane, described by Hawthorne and co-workers almost 30 years ago,[1a] is an anionic complex in which a cobalt center, in the +3 oxidation state, is sandwiched between two dicarbollide ($[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$) ligands to give a *commo* structure. Since then there have been a number of reported *commo*-cobaltacarboranes and mixed Cp/carborane sandwich complexes.[1,2] Essentially all of these complexes contained cobalt in a formal +3 oxidation state. To date, the only known Co(II) carborane complexes are a fused dicobaltacarborane of a C_4B_8 ligand system and several sandwiched species based on tricarbaboranes.[3] Although no half-sandwich Co(II) carborane complexes have been isolated, they are generally believed to be intermediates in the formation of the Co(III) carborane complexes, whose syntheses usually involve CoCl_2 or some other Co(II) compound as synthons. The formation of stable 18-electron species, such as $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}^{\text{III}}]^-$ or $[(\text{C}_2\text{B}_4\text{H}_6)_2\text{Co}^{\text{III}}]^-$, is thought to provide the driving force for the oxidation of the metal.[1a,b,5] We report herein the synthesis and crystal structure of the first *N,N,N′,N′*-tetramethylethylenediamine- (TMEDA-) stabilized, para-

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magnetic cobalt(II) half-sandwich complex, *closo*-1-(TMEDA)-1-Co-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (1).

Since the reaction between the *nido*-[2-(R)-3-(R′)-2,3-$C_2B_4H_5$]$^-$ (R, R′ = Me, Et, *n*-propyl) monoanion and $CoCl_2$ in a molar ratio of 2:1 in tetrahydrofuran (THF) exclusively involves an oxidative insertion of the metal to yield the neutral $(RR'C_2B_4H_4)_2Co^{III}H$ sandwich,[4] and similar reactions with the carborane dianions result in the formation of anionic Co(III) carborane sandwich complexes,[1a,b,5] a new synthetic strategy for the preparation of stable Co(II) carboranes was warranted. As part of this investigation, the monomeric "carbons apart" dilithiacarborane *closo-exo*-5,6-[(μ-H)$_2$Li(TMEDA)]-1-Li(TMEDA)-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (2)[6] was reacted with anhydrous $CoCl_2$ in a molar ratio of 1:1 at 0 °C, and then at room temperature, in a solvent mixture of dry benzene and *n*-hexane to isolate, in 92% yield, a previously unknown "carbons apart" *closo*-cobalt(II) carborane complex, 1, as shown in eq 1.[7] When the reactants were taken in a 2:1 molar ratio, 1 was produced exclusively and all of the unreacted dilithiacarborane precursor 2 was recovered. Under similar reaction conditions, but in the absence of TMEDA, the carborane dianions produced an anionic cobalt(III) carborane complex of the type [(RR′-$C_2B_xH_x)_2Co]^-$ (R, R′ = H, alkyl, aryl, $SiMe_3$; x = 4, 9).[1a,b,5] It is apparent that the base TMEDA imparts considerable stability to the otherwise unstable intermediate 1, allowing its isolation and characterization. Such a phenomenon has recently been observed in the syntheses of *closo*- and *commo*-nickelcarboranes.[6]

$$\underset{\mathbf{2}}{5,6\text{-}[(\mu\text{-H})_2\text{Li(TMEDA)}]\text{-1-Li(TMEDA)-2,4-}(\text{SiMe}_3)_2\text{-2,4-C}_2\text{B}_4\text{H}_4} + \text{CoCl}_2 \xrightarrow[\text{benzene}/n\text{-hexane (1:1)}]{\text{(i) 0 °C, 3 h; (ii) 25 °C, 5 h}} 2\text{LiCl} + \text{TMEDA} + \underset{\mathbf{1}}{closo\text{-1-(TMEDA)-1-Co}^{\text{II}}\text{-2,4-}(\text{SiMe}_3)_2\text{-2,4-C}_2\text{B}_4\text{H}_4} \quad (1)$$

The extreme air and moisture sensitivity of 1 made it difficult to obtain accurate microanalytical data, even for the single crystals of 1.[7] Nevertheless, the analytical data obtained,[7] along with the other characterizations (*vide infra*), leave no ambiguity in the identity and structure of 1. The high-resolution peak match and low-resolution fast atom bombardment mass spectrum of 1 exhibited a grouping with the peak match to m/z 391.2351 corresponding to the parent ion, $[^{12}C_{14}{}^{1}H_{38}{}^{14}N_2{}^{10}B_2{}^{11}B_2{}^{28}Si_2{}^{59}Co]^+$.[8] The EPR spectrum of the neutral, deep green cobalt complex 1 at 4 K in frozen toluene shows a well-resolved rhombic EPR signal with components at g_1 = 2.549, g_2 = 2.108, and g_3 = 1.976. The corresponding ^{59}Co coupling constants ($I = {}^7/_2$) are a_1 = 2.9, a_2 = 2.7, and a_3 = 3.5 mT.[9a] While the magnitude of the ^{59}Co hyperfine coupling suggests some covalent bonding between the metal and the carborane ligand, the single rather high component g_1 indicates directed ionic bondings, as in other Co(II) complexes with ethylenediamine ligands.[9b] At room temperature, 1 exhibits an unresolved signal at g = 2.198 with a peak-to-peak line width of 14 mT. The EPR results are consistent with the presence of a low-spin Co(II) (d^7) center in a low-symmetry environment in 1. Due to the paramagnetism of 1, attempts to obtain meaningful NMR data were unsuccessful. Therefore, an X-ray analysis of 1 was carried out.[10]

Figure 1 shows the structure of 1 and also lists some pertinent bond distances and bond angles. Additional crystallographic data, including the atomic coordinates and a more complete listing of bond distances and bond angles, are given in the supplementary material. The figure shows that cobalt is equally bonded to the two nitrogens of a TMEDA molecule and is η^5-bonded to the planar C_2B_3 face of the carborane. The relative orientation of the two ligands is such that the nitrogens of the TMEDA lie in the pseudo mirror plane of the CoC_2B_4 cage (the dihedral angle between this mirror plane and the N(22)–Co–N(21) plane is 4.7°).[11] The Co–C_2B_3 atom distances are all very similar, with the average Co–B(2,4,5) and Co–C(1,3) distances being 2.091 ± 0.004 and 2.13 ± 0.013 Å, respectively, indicating that the cobalt is not slip-distorted. The Co–C bond distances in 1 are slightly greater than the values of 2.119 Å found in (η^5-$C_5H_5)_2Co$[12] and the closest Co–C average distances of 2.03 and 2.01 Å, respectively, reported by Sneddon and co-workers for *commo*-Co^{II}-(1-Co-2-CH_3-2,3,5-$C_3B_7H_9)_2$ and its Me-migrated isomer.[3b] However, the nonplanarity of the C_3B_3 bonding faces in these compounds raises some questions as to whether the

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(7) A 3.24-mmol (1.50-g) sample of 2 in a 30-mL mixture of dry benzene (50%) and dry *n*-hexane (50%) was allowed to react with 3.24 mmol (0.42 g) of anhydrous $CoCl_2$ *in vacuo* at 0 °C for 3 h and then at 25 °C for 5 h, during which time the solution turned to dark green with the formation of precipitate at the bottom of the flask. At this point, the mixture was filtered through a frit *in vacuo* to collect a dark green filtrate. The solvents and the liberated TMEDA (not measured) were then removed from the filtrate to collect a deep green solid which was then recrystallized *in vacuo* from a solution of benzene (25%) and *n*-hexane (75%) to collect extremely air-sensitive deep green crystals, identified as *closo*-1-(TMEDA)-1-Co-2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$ (1), in 92% yield (1.17 g, 2.98 mmol; mp > 250 °C reasonably soluble in polar and slightly soluble in nonpolar organic solvents). The solid on the frit (not measured), identified by qualitative analysis as LiCl, was discarded. When 5.82 mmol of 2 was reacted with 2.91 mmol of $CoCl_2$, under similar reaction conditions, 2.62 mmol (1.03 g, 90% yield) of 1 was isolated as deep green crystals after recrystallization from a solution of benzene (25%) and *n*-hexane (75%), and nearly all of the unreacted 2 (1.43 g, 3.08 mmol) was recovered. Anal. Calcd for $C_{14}H_{38}N_2B_4Si_2Co$ (1): C, 42.75; H, 9.67; N, 7.12. Found: C, 43.41: H, 8.60; N, 6.16. IR (cm^{-1}, C_6D_6 vs C_6D_6): 3013 (m, s), 2955 (s, s), 2886 (s, s), 2839 (s, s), 2793 (w, s) [ν(CH)], 2492 (vs) [ν(BH)], 1463 (s, s), 1434 (sh), 1405 (w, s) [$\delta(CH)_{asym}$], 1278 (m, s), 1237 (s, s) [$\delta(CH)_{sym}$], 1174 (s, s), 1139 (w, s), 1121 (w, s), 1058 (m, s), 1017 (m, s), 994 (w, s), 948 (m, s), 895 (m, br), 837 (vs, br) [ρ(CH)], 756 (m, s), 681 (m, s), 623 (m, s), 495 (s, s).

(8) Mass spectral determinations were made at the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262).

(9) (a) EPR spectra of 1 were recorded on a Bruker ESP 300 spectrometer in the X band (9.6 GHz). (b) Nishida, Y.; Kida, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 461.

(10) Crystal data: $C_{14}H_{38}B_4N_2Si_2Co$, fw 392.8, deep green plates, monoclinic, $P2_1/n$, a = 8.329(2) Å b = 19.648(6) Å, c = 14.570(4) Å, β = 94.38(2)°, V = 2377(1) Å^3, Z = 4, D_{calcd} = 1.097 g/cm^3, μ = 0.817 mm^{-1}. Of 2898 data collected on a Siemens R3m/V diffractometer (Mo Kα, 2θ = 3.5–42.0°, at −43 °C) 2567 reflections were independent and 1659 were observed ($I > 3.0\sigma(I)$). Data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by heavy-atom methods using SHELXTL-Plus (Sheldrick, G. M. Structure Determination Software Program Package, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). All non-H atoms were refined anisotropically. The slightly disordered C(10), C(23), and C(24) atoms were not constrained during refinement. Cage H atoms were located in difference Fourier maps, and methyl and methylene H atoms were calculated. The final refinement of 1 converged at R = 0.039, R_w = 0.045, and GOF = 1.29 for observed reflections. The maximum and minimum residual electron densities are 0.28 and −0.28 e/Å^3.

(11) The plane is defined as that containing the Co, B(2), and B(6) atoms and the midpoint of the B(4)–B(5) bond. In the discussion of the bonding in 1, this plane is taken as the xz plane, with B(2) being located on the x axis.

(12) Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415.

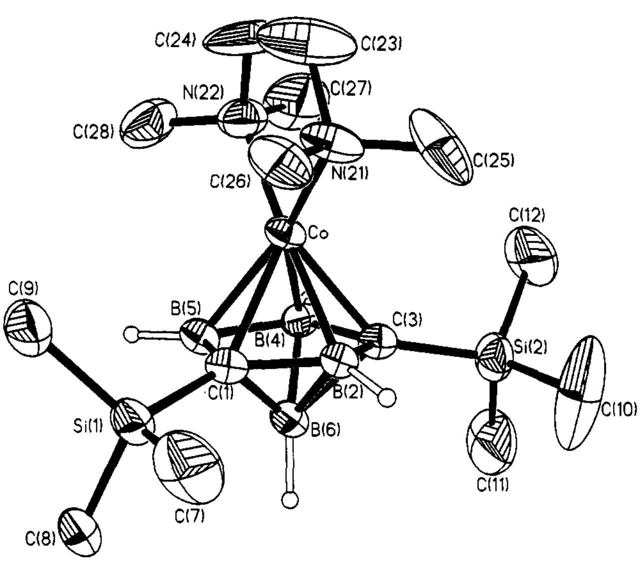

Figure 1. Perspective view of 1 with thermal ellipsoids drawn at the 40% probability level, showing the atom-numbering scheme. The methyl and methylene H atoms are omitted for clarity. Pertinent parameters include (distances in Å and angles in deg) Co–C(1) = 2.124(5), Co–B(2) = 2.087(6), Co–C(3) = 2.150(5), Co–B(4) = 2.092(7), Co–B(5) = 2.093(6), Co–Cnt = 1.626, Co–N(21) = 2.050(4), Co–N(22) = 2.005(5), Cnt–Co–N(21) = 135.2, Cnt–Co–N(22) = 138.8, N(21)–Co–N(22) = 86.0(2).

orbitals used by the carborane to bond to the metal might better be described as σ-type, rather than π-type orbitals. On the other hand, there have been several structurally determined "carbons adjacent" pentagonal-bipyramidal Co(III) carborane complexes. Weiss and Bryan[13] reported bond distances of 2.031, 2.086, and 2.104 Å, respectively, for the Co–C(cage), Co–B(basal), and Co–B(unique) bonds in 1-(η^5-C_5H_5)Co-2,3-$(CH_3)_2$-2,3-$C_2B_4H_4$, while the analogous bond distances of 2.09, 2.12, and 2.16 Å were found by Grimes and co-workers[14] for 1,1-$(Ph_2PCH_2)_2$-1-Cl-2,3-$(C_2H_5)_2$-1,2,3-$CoC_2B_4H_4$. All of these distances are very similar to those found in 1, reflecting a general insensitivity of the metal–carborane bond distances to the charge of the metal; this had also been observed in the *commo*-chromacarboranes.[15]

A preliminary molecular orbital (MO) analysis of 1 shows that the metal bonds to the carborane mainly through the interaction of its $3d_{xz}$ and $3d_{yz}$ orbitals with symmetry-compatible π-type orbitals on the carborane.[11] The electron count in the complex is such that the d^7 electrons will begin to fill a set of three nearly energy-equivalent MO's mainly comprised of the metal's $3d_{z^2}$, $3d_{x^2-y^2}$, and $3d_{xy}$ orbitals, which contribute very little to metal–carborane bonding. The next set of MO's are the antibonding pairs arising from the metal ($3d_{xz}$, $3d_{yz}$)–carborane interactions; the singly occupied MO (SOMO) has metal $3d_{yz}$ character, while the LUMO is localized on the metal in the mirror plane of the complex. Since this latter MO interacts strongly with the filled "lone pair" orbitals of the TMEDA, an orientation of the TMEDA in the mirror plane of 1 would be expected.

The present results, coupled with those of a half-sandwich nickelacarborane,[6] demonstrate the ability of TMEDA to stabilize metallacarboranes that ordinarily would undergo disproportionation reactions, forming the corresponding oxidized species. Studies involving other d-block metals and the C_2B_4 carborane ligands are currently underway in the authors' laboratories.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters, bond distances and bond angles, and H atom coordinates (5 pages). Ordering information is given on any current masthead page.

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