Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic temperature factors, and calculated hydrogen atom positions and isotropic thermal parameters (6 pages); a listing of observed and calculated structure factors for **3c** (42 pages). Ordering information is given on any current masthead page.

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Lewis Acidity of Germanium(II) in a η^5-*closo*-Germacarborane: Synthesis and Structure of 1-(2,2′-Bipyridine)-2,3-bis(trimethylsilyl)-2,3-dicarba-1-germa-*closo*-heptaborane(6)

Sir:

Of all the group 14 metallacarboranes, the *closo*-stannacarboranes have been widely explored in terms of their reactivity and bonding.[1–4] This has partly been the result of more structural data being available for these compounds.[2] It has been established that the apical tin atom in the stannacarborane is in its +2 oxidation state and has an unshared pair of electrons.[1c,2b] Despite the presence of this lone pair, there seems to be no tendency to form donor–acceptor complexes with Lewis acids, such as BF_3. On the contrary, the tin atom acts as a Lewis acid site and forms red complexes with tetrahydrofuran, 2,2′-bipyridine, and 2,2′-bipyrimidine.[2,3] Our more recent synthetic and structural studies on the donor–acceptor complexes of the *closo*-stannacarboranes have raised several fundamental questions regarding the bonding of tin to the C_2B_3 face of carboranes.[3] To date, the specific factors influencing the orientation of the base bound to the apical tin and the slippage of this metal in the complex toward the three borons of the C_2B_3 pentagonal face have not been explained theoretically.

During the course of our investigation in this area, we sought to examine the reactivity of the analogous *closo*-1-Ge-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (I)[4] toward Lewis bases. In addition, we also intended to investigate further whether the same factors that determine slippage of the heteroatom and orientation of the base in the *closo*-stannacarboranes could be operative in the donor–acceptor complex with *closo*-germacarborane I, if this complex could be made at all. When a benzene solution of I and 2,2′-bipyridine at 0 °C was stirred in vacuo, a red solution formed immediately indicating that a complexation has occurred between the reactants. This reaction produced in high yield a previously unknown germacarborane complex, which was isolated as an air-sensitive, bright red, crystalline and sublimable solid.[5] The structure of the new germacarborane complex, II, could not be determined from its IR, NMR, and mass spectra[6] as these data are almost identical with those of its precursor I[4] and 2,2′-bipyridine. Furthermore, the structures of both *closo*-Ge^{II}-$(RR'C_2B_9H_9)$ and *closo*-$Ge^{II}(RR'C_2B_4H_4)$ (R, R′ = Me_3Si, Me, or H) systems[1,4,7] have not been reported. Therefore, an X-ray analysis of the red, crystalline solid was undertaken that unambiguously confirmed the solid to be the novel germacarborane complex, 1-$Ge(C_{10}H_8N_2)$-2,3-$(Me_3Si)_2$-2,3-$C_2B_4H_4$ (II) as rep-

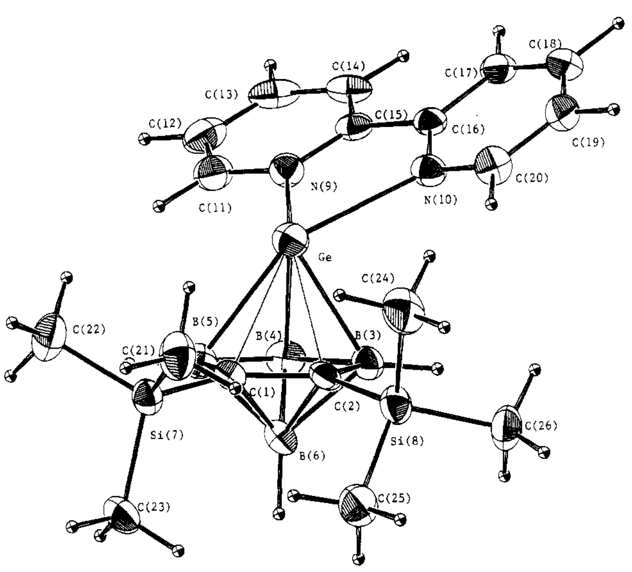

Figure 1. ORTEP view of II showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. Pertinent bonding parameters: Ge–N(9), 2.321 (4) Å; Ge–N(10), 2.474 (4) Å; Ge–B(3), 2.255 (7) Å; Ge–B(4), 2.208 (7) Å; Ge–B(5), 2.371 (7) Å; Ge–C(1), 2.579 (5) Å; Ge–C(2), 2.510 (5) Å.

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(5) A benzene (10 mL) solution of $Ge^{II}(Me_3Si)_2C_2B_4H_4$ (I) (0.62 g, 2.13 mmol) was added to a benzene (10 mL) solution of freshly sublimed anhydrous 2,2′-bipyridine, $C_{10}H_8N_2$ (0.33 g, 2.13 mmol) in vacuo, and the resulting red solution was constantly stirred for 4 h at 0 °C. After removal of C_6H_6 at 0 °C via vacuum distillation for 4 h, the reaction flask was attached to a detachable high-vacuum U-trap, and the flask was heated gently to 50 °C to sublime the unreacted 2,2′-bipyridine (0.11 g; 0.71 mmol) out of the flask into the U-trap. With identical sublimation procedures and times as described for stannacarborane–2,2′-bipyridine complexes,[2b–d] at the sublimation temperature of 90 °C, compound II (0.46 g, 1.03 mmol; 73% yield based on $C_{10}H_8N_2$ consumed) was collected in one of the detachable U-traps held at 0 °C as a bright red crystalline solid. This solid (m.p. 88 °C) is highly soluble in both polar and nonpolar organic solvents.

(6) IR ($CDCl_3$ vs $CDCl_3$; cm^{-1}): 3050 (m, s), 2920 (s, br), 2860 (w) [ν(C–H)]; 2580 (s) [ν(B–H);] 1880 (m, br), 1620 (m, s), 1555 (s), 1450 (m), 1415 (w, br), 1250 (w, br), 1145 (m, s), 1085 (m, s), 1065 (w), 1035 (m, br), 990 (m), 960 (w), 930 (w), 820 (vs, br), 750 (vs, br), 670 (m), 650 (w), 610 (m), 390 (m). FT NMR Data: ^1H NMR (C_6D_6, relative to external Me_4Si) δ 8.63 [d, 2 H, bpy ring, $J(^1H-^1H) = 4.3$ Hz], 8.56 [d, 2 H, bpy ring, $J(^1H-^1H) = 4.9$ Hz], 7.27 [t, 2 H, bpy ring, $J(^1H-^1H) = 7.2$ Hz], 6.76 [t, 2 H, bpy ring, $J(^1H-^1H) = 6.2$ Hz], 3.92 [q (br), 3 H, basal H_t, $^1J(^1H-^{11}B) = 137$ Hz], 1.64 [q (br), 1 H, apical H_t, $^1J(^1H-^{11}B) = 164$ Hz], 0.38 [s, 18 H, $(CH_3)_3Si$]; ^{11}B NMR (C_6D_6, relative to external $BF_3 \cdot OEt_2$) δ 23.14 [d, 3 B, basal BH, $^1J(^{11}B-^1H) = 137$ Hz], –5.30 [d, 1 B, apical BH, $^1J(^{11}B-^1H) = 164$ Hz]; ^{13}C NMR (C_6D_6, relative to external Me_4Si) δ 156.02 [s, 2,2′-C, bpy ring], 148.86 [d, bpy ring, $^1J(^{13}C-^1H) = 178$ Hz], 136.20 [d, bpy ring, $^1J(^{13}C-^1H) = 162$ Hz], 123.27 [d, bpy ring, $^1J(^{13}C-^1H) = 164$ Hz], 120.77 [d, bpy ring, $^1J(^{13}C-^1H) = 167$ Hz], 132.88 [s (br), cage carbon], 1.35 [q, $(CH_3)_3Si$, $^1J(^{13}C-^1H) = 119$ Hz]; ^{29}Si NMR (C_6D_6, relative to external Me_4Si) δ–1.30 [m, $Si(CH_3)_3$, $^2J(^{29}Si-^1H) = 6.4$ Hz]; Mass Spectrum: The electron-impact (EI) mass spectrum of II does not exhibit the parent ion. However, both the bipyridine ion fragment with 100% relative intensity and the germacarborane precursor ion (I) were present in the EI mass spectrum.

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resented in its ORTEP drawing in Figure 1.[8]

The X-ray crystal structure of II reveals that the Ge^{II} atom is displaced substantially from the centroidal position above the C_2B_3 face of the carborane cage. This displacement apparently causes the Ge–C distances [2.579 (5) and 2.510 (5) Å] to be longer than the Ge–B distances [2.255 (7), 2.208 (7), and 2.371 (7) Å]. The most significant feature in the structure of II is the orientation (B–Ge–N bond angle of 84–105°) of the Lewis base, 2,2′-bipyridine, bound to the apical Ge^{II}. In addition, the base is tilted more toward the B(3) and B(4) atoms than in the corresponding stannacarborane complex and is not directly opposite the cage carbons. Consequently, B(5)–Ge and Ge–N(10) distances are somewhat longer than the other similar bond distances in II. It is interesting to point out that the Lewis base in the structures of stannacarborane–2,2′-bipyridine complexes is directly opposite the cage carbons making rather severe bond angles (85–92°) with cage ligand which is a common structural feature in these donor-acceptor complexes.[2b–d] Despite the asymmetry found in II, the donor–acceptor bonds between $Ge_{(cage)}$ and nitrogens of the 2,2′-bipyridine confirm the Lewis acidity of the Ge(II) in *closo*-germacarboranes.

The structural similarities of the closo and commo complexes formed by the *nido*-carborane anions $[C_2B_9H_{11}]^{2-}$ and $[C_2B_4H_6]^{2-}$ with group 13 and 14 elements strongly suggest that the two carboranes are using very similar orbitals in bonding to the heteroatom. This similarity is indicated by an inspection of the nondegenerate a′ orbital[9] of the $[C_2B_9H_{11}]^{2-}$ and the 4S orbital[10] of *closo*-1-Me-$GaC_2B_4H_6$.[11] Each of these orbitals possesses a nodal plane between the carbons and their adjacent borons in the open pentagonal face of the carborane, and electron density is greater on the boron opposite the carbons.[9,10] In these cases, it seems that the filled frontier orbitals of the carborane dianions are such that they are localized toward the boron atoms in the C_2B_3 face, and the center of this face may not offer the strongest σ interactions with an electrophile. A slippage of the group 13 or 14 heteroatom toward the borons would thus tend to stabilize the complex. It seems therefore that σ interactions in II between the germanium atom and the carborane would be favored by a slippage of the germanium atom away from centroidal position. On the other hand, some π interactions favor a more centroidal location of the apical germanium atom. From the orientation of the 2,2′-bipyridine molecule, it is likely that the coordinating lone pairs on the nitrogens are interacting with the Ge orbitals that were originally involved in π-bonding. As germanium–carborane σ-bonding becomes a predominant interaction, the germacarborane complex is more stabilized by a larger shift of Ge away from the central position. Thus, it may well be that as the Ge–N interaction increases, further slippage of the germanium from the centroidal position will be observed. A number of reported metallacarborane structures show diverse degrees of slippage of the metal atom relative to the bonded cage.[9,11,12] Since the 2,2′-bipyridine nitrogens are equivalent and the *closo*-germacarborane, presumably, has a plane of symmetry bisecting the C–C cage bond and passing through the opposite boron in the C_2B_3 face, the tilt of the 2,2′-bipyridine in II cannot be explained at this time.

Studies of the reactivity of *closo*-germacarboranes and *closo*-silacarboranes of the type 1-M-2-(Me_3Si)-3-(R)-2,3-$C_2B_4H_4$ (M = Ge, Si; R = Me_3Si, Me, H) toward a variety of monodentate, bidentate, and tetradentate Lewis bases and the structural consequences in the resulting complexes are currently under way in this laboratory.

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Supplementary Material Available: Tables of positional parameters (Table I), bond distances and angles (Table II), and thermal parameters (Table III) (6 pages); a listing of observed and calculated structure factors (Table IV) (10 pages). Ordering information is given on any current masthead page.

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(8) Crystal and experimental data for II: $C_{18}H_{30}B_4N_2Si_2Ge$, mol wt 446.46, monoclinic $P2_1/n$, $a = 7.102$ (5) Å, $b = 34.61$ (2) Å, $c = 9.774$ (4) Å, $\beta = 102.55$ (4)°, $V = 2345$ (2) Å^3, $T = 295$ K, $Z = 4$, $d_{calcd} = 1.26$ g cm^{-3}, μ(Mo Kα) = 13.94 cm^{-1}. Data were collected on a Syntex $P2_1$ diffractometer with a crystal coated with an epoxy resin. A total of 2209 independent reflections was measured in the range $3 < 2\theta < 40°$ ($\theta/2\theta$ scan type, graphite-monochromatized Mo Kα radiation). The data were corrected for decay (ca 2%) and *Lp* effects but not for absorption. Only the 1793 observed reflections with $I > 3\sigma(I)$ were used subsequently. The structure was solved by direct methods (Sheldrick, G. M. "SHELX86, Programs for Structure Solution") and subsequent difference Fourier methods. All non-H atoms were refined anisotropically. All H atoms were located and included in the refinement with isotropic temperature factors. Final full-matrix least-square refinement (Sheldrick, G. M. SHELX76, Programs for Structure Refinement) converged to $R = 0.040$ and $R_w = 0.038$. The function minimized was $\sum w(|F_o|-|F_c|)^2$, the weight used being $w^{-1} = \sigma F^2 + 0.000065F^2$, $(\Delta/\sigma)_{max} = 0.53$ and $\Delta\rho_{max} = 0.28$ e/Å^3. Scattering factors for C, H, B, N, and Si were calculated from the data stored in SHELX76. Scattering factors and $\Delta f'$ and $\Delta f''$ for Ge were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, U.K., 1974; Vol. IV.

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