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Stable Intramolecularly Base-Stabilized Germylene− and Stannylene−Borane Adducts: $M[C_6H_3(NMe_2)_2\text{-}2,6]_2BH_3$ (M = Ge, Sn)

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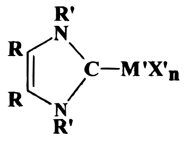
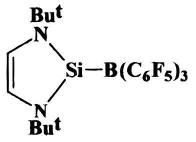
*Summary: The synthesis and characterization of two novel and thermally surprisingly stable main-group-element Lewis acid (BH_3) adducts (**3** and **4**) of a monomeric germylene (**1**) and of a diarylstannylene (**2**) is reported. X-ray crystal structures of the adducts $MAr_2(BH_3)$ reveal a four-coordinated germanium (**3**) but five-coordinated tin (**4**), with regard to the C,N-potentially bidentate chelating ligand $^{-}C_6H_3(NMe_2)_2\text{-}1,2$ and BH_3, respectively.*

There is current interest in the base behavior of monomeric bivalent group 14 metal compounds MX_2 with reference to main-group-element Lewis acids $M'X'_n$. Established compounds are (i) the X-ray-characterized Arduengo-type carbene−$M'X'_n$ adducts **I** ($M'X'_n$ = BH_3 or BF_3 (R = Me; R′ = Me, Et, or Pr^i),[1] AlH_3 (R = H, R′ = $C_6H_2Me_3$-2,4,6),[2] $M'Me_3$ (M′ = Al or Ga, R = H, R′ = Bu^t),[3] or $SiCl_4$, $SiCl_2Me_2$, $SiCl_2Ph_2$, $SnCl_2Ph_2$ or $SnCl_2$ (R = Me; R′ = Me, Et or Pr^i)][4] and (ii) the labile silylene adduct **II** ($t_{1/2}$ ca. 30 days at 20 °C in PhMe), which readily isomerized into the insertion product **III**.[5] A single labile (but X-ray-authenticated) diorganotin(II)−Lewis acid ($SnCl_2$) adduct (**IV**) has been obtained from its acid/base precursors but underwent metathesis in tetrahydrofuran (THF) at 25 °C, yielding the organotin(II) chloride **V**.[6] An early report of $Sn(\eta^5\text{-}C_5H_5)_2{:}BF_3$[7a] proved to have misformulated the compound; it is now established to be the Sn−B-bond-free salt $[Sn(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^5\text{-}C_5H_5)Sn(THF)][BF_4]$.[7b] The cubanes $[M(\mu_3\text{-}NBu^t)]_4$ formed the 1:2 $AlCl_3$ adducts **VI**, which slowly decomposed in solution; X-ray data for the tin compound **VIb** were provided.[8] Not only nucleophilic carbenes[9a] but also silylenes,[9b] germylenes,[10] stannylenes,[10] and plumbylenes MX_2[10] are well-known as ligands in a transition-metal (M′) context, but generally M′ has the possibility of engaging in synergic $d \rightarrow p_\pi$ back-bonding, as in $[Cr(CO)_5\{Sn[CH(SiMe_3)_2]_2\}]$.[11]



I



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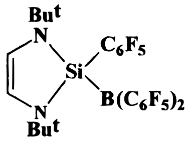

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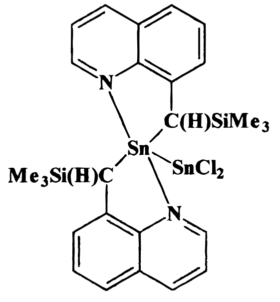

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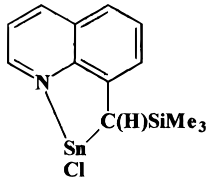
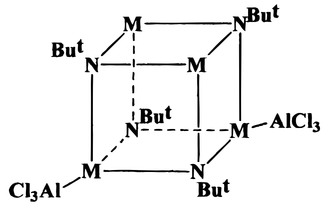
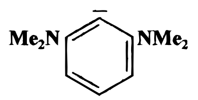


V



VIa M = Ge
VIb M = Sn



VII

We now report the first main-group-element Lewis acid (BH_3; the archetype) adducts of a monomeric intramolecularly base-stabilized germylene and of a diarylstannylene. Treatment of the recently described[12] yellow diarylgermylene GeX_2 (**1**) or -stannylene SnX_2 (**2**) (X^- = **VII**) with a solution of $BH_3(THF)$ in diethyl ether and then successive removal of volatiles *in vacuo* and recrystallization from Et_2O afforded colorless (**3**) or amber (**4**) crystals of $X_2M{:}BH_3$ (M = Ge, **3**; M = Sn, **4**)[13] in good yields (Scheme 1). Each of the compounds **3** and **4** gave satisfactory microanalytical as well as NMR (^1H, ^{11}B, $^{13}C\{^1H\}$, and (for **4**) $^{119}Sn\{^1H\}$), IR, and EI-MS spectra.[14] Compound **3** was thermally stable both in the solid state and in solution, but a solution of the tin analogue **4** slowly deposited tin.

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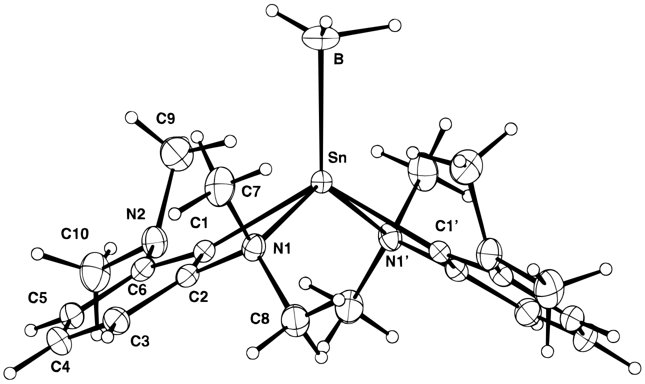


Figure 1. Crystal structure and labeling scheme of **4**. Selected bond lengths and angles are in Table 1; additionally, C(1)−Sn−N(1) = 61.18(10)°, B−Sn−N(1) = 112.86(6)°, C(2)−C(1)−Sn = 100.4(2)°, and C(6)−C(1)−Sn = 141.0(2) °.

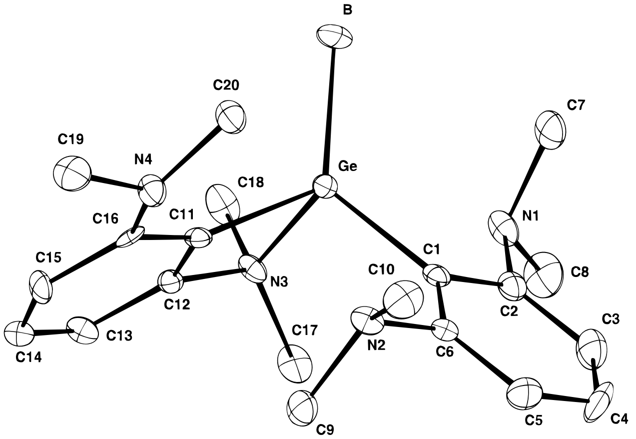
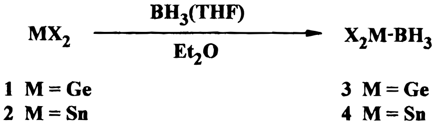
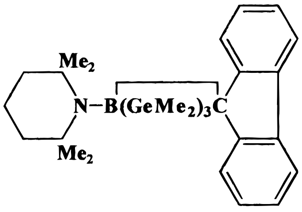


Figure 2. Crystal structure and labeling scheme of **3**. Selected bond lengths and angles are in Table 1.

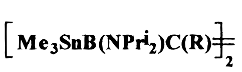
Scheme 1. Synthesis of the Diarylmetallene−BH_3 Adducts 3 and 4 (X^- = VII)



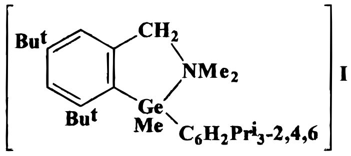
The crystal structures of the borane adducts are illustrated in Figures 1 (**4**) and 2 (**3**).[15] Whereas the crystalline parent base-stabilized germylene (**1**) and stannylene (**2**) are isostructural, both having the metal in a four-coordinate environment (one M−C and one M−N bond from each ligand **VII**),[12,16] the adducts differ in that **3** has four-coordinate germanium (two Ge−C, one Ge−N, and one Ge−B bond), while **4** has five-coordinate Sn (two Sn−C, two Sn−N, and one Sn−B bond). Thus, each aryl ligand **VII** is bound in a *C*,*N*-bidentate chelating fashion in **1**,[12] **2**,[16] and the centrosymmetric **4**; however, in **3** only one of the ligands **VII** adopts this mode, the other being merely C-bonded. Selected comparative geometric parameters for **1**−**4** are given in Table 1; further details for **1**[16] will appear in the full paper. Compounds **3** and **4** have no close analogue in Ge−B or Sn−B chemistry; the M−B bond lengths for the two former species (Table 1) may be compared with the Ge−B length (2.165(10) Å) in **VIII**[17] and the Sn−B lengths in *cis*-**IXa** (2.305−2.323(7) Å) and *trans*-**IXb** (2.286−2.277(17) Å),[18] respectively. The germanium complex **3** may also be compared with salt **X**,[19] noting that BH_3 and CH_3^+ are isoelectronic.



VIII



IXa R = Et
IXb R = H



X

The nonbonding nitrogen atom of each $^-C_6H_3(NMe_2)_2$-2,6 ligand **VII** is remote from the metal center, *e.g.*, 3.815(2) Å in **4**; *cf.* 3.394(5) and 3.783(5) Å in the free stannylene **2**.[12] The M−C and M−C′ bonds are slightly shorter in the borane adducts **3** and **4** than in the free bases **1** and **2**, consistent with the former being dipolar, $X_2M^+{-}^-BH_3$. Such shortening is even more pronounced

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(13) Preparation of **3** and **4**: a BH_3(THF) solution (2.2 mL of a 1.0 mol L^{-1} solution in THF; 2.25 mmol for **1**, 2.5 mL for **2**) was added to a stirred yellow solution of the germylene **1** (1 g, 2.51 mmol) or stannylene **2** (1 g, 2.25 mmol)[9] in Et_2O (100 mL) at *ca.* 25 °C. The solution slowly became decolorized (for **3**) or slightly darkened (for **4**) and was stirred overnight. Volatiles were removed *in vacuo* to yield solid residues, which were extracted with Et_2O. Filtration to remove a slight cloudiness, concentration of the filtrate *in vacuo*, and cooling to −30 °C afforded colorless crystals of **3** (0.9 g, 95%) or amber-colored crystals of **4** (0.85 g, 82%).

(14) Selected data for **3** and **4** are as follows. NMR spectra at 298 K in C_6D_6 (^1H, ^{13}C) or PhMe + C_6D_6: ^1H NMR, 250.0 MHz; $^{13}C\{^1H\}$ NMR, 62.86 MHz; ^{11}B NMR, 80.21 MHz; $^{119}Sn\{^1H\}$ NMR, 186.36 MHz. **3**: colorless; mp 145−147 °C; ^1H NMR δ 2.61 (s, 24 H, NMe_2), 6.50 (d, 4 H, H-3/5, $^3J(^1H{-}^1H) = 7.9$ Hz), 7.16 (t, 2 H, H-4, $^3J(^1H\text{-}^1H) = 7.9$ Hz); $^{13}C\{^1H\}$ NMR δ 44.5 (NC_2), 110.8, 129.4, 134.8, 156.8 (aromatic C); ^{11}B NMR δ −35.0 (q) ($^1J(^{11}B{-}^1H) = 73$ Hz). EI-MS (70 eV) parent ion at *m*/*z* 414 (7% intensity of the most abundant ion); IR (Nujol) 2235, 2315, 2351, 2389 cm^{-1}. **4**: amber; mp *ca.* 90 °C dec; ^1H NMR δ 2.62 (s, 24 H, NMe_2), 6.49 (d, 4 H, H-3/5, $^3J(^1H{-}^1H) = 7.9$ Hz), 7.16 (t, 2 H, H-4, $^3J(^1H{-}^1H) = 7.9$ Hz); ^{11}B NMR δ −34.3 (broad); $^{119}Sn\{^1H\}$ NMR δ 328. EI-MS (70 eV) parent ion at *m*/*z* 460 (1% intensity of the most abundant ion); IR (Nujol) 2333 cm^{-1} (br).

(15) Crystal data are as follows: **3**: $C_{20}H_{33}BGeN_4$, M_r = 412.9, orthorhombic, space group *Pbca* (No. 61), a = 10.256(2) Å, b = 16.289(5) Å, c = 26.016(10) Å, V = 4346(2) $Å^3$, $F(000)$ = 1744; Z = 8, ρ_{calcd} = 1.26 g/cm^{-3}, μ(Mo Kα) = 14.2 cm^{-1}, specimen 0.3 × 0.1 × 0.1 mm, 3810 reflections collected for $2 < \theta < 25°$, 3810 independent reflections, R1 = 0.075 for 1930 reflections with $I > 2\sigma(I)$, wR2 = 0.183 (for all data), S = 1.007. **4**: $C_{20}H_{33}BN_4Sn$, M_r = 459.0, monoclinic, space group *C*2/c (no. 15), a = 13.154(5) Å, b = 11.373(7) Å, c = 14.832(5) Å, β 98.21(3)°, V = 2196(2) $Å^3$, $F(000)$ = 944; Z = 4, ρ_{calcd} = 1.39 g/cm^{-3}, μ(Mo Kα) = 11.7 cm^{-1}, specimen 0.3 × 0.3 × 0.25 mm, 2022 reflections collected for $2 < \theta < 25°$, 1941 independent reflections, R1 = 0.0257 for 1849 reflections with $I > 2\sigma(I)$, wR2 = 0.0682 (for all data), S = 1.141. For both **3** and **4**: data at T = 173(2) K, Enraf-Nonius CAD-4 diffractometer, absorption correction, structural solution by direct methods, full-matrix least-squares refinement on F^2 using SHELXL-93 with non-H atoms anisotropic.

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Table 1. Selected Geometric Parameters for Crystalline 1−4

	compd			
param	**1**[16]	**2**[12]	**3**	**4**[a]
M−C, M−C′/Å	2.014(8), 2.024(7)	2.212(5), 2.216(5)	1.962(8), 1.959(8)	2.170(3), 2.170(3)
M−N, M−N′/Å	2.394(6), 2.722(6)	2.607(5), 2.669(5)	2.110(6)	2.456(2), 2.456(2)
M−B/Å			2.041(11)	2.262(5)
C−M−C′/deg	105.1(3)	105.6(2)	112.7(3)	118.98(13)
C−M−B, C′−M−B/deg			125.7(3), 117.2(4)	120.51(7), 120.51(7)
Σ/deg[b]			355.6	360

[a] Centrosymmetric. [b] Sum of the angles C−M−C′, C−M−B, and C′−M−B.

for the M−N and M−N′ bonds. The atom M is the centroid of a near-equilateral (more closely for **4** than **3**) $\overline{\mathrm{CBC'}}$ triangle; *cf.* ΣM in Table 1; the C−M−C′ angles are wider than in the parent base **1** or **2**. The dihedral angles in **4** between the SnCBC′ plane and each plane containing Sn and the C_6N_2 skeleton of a ligand **VII** is 78.04(8)°. The five-coordinate Sn atom may be described as being in a trigonal-bipyramidal environment with the N and N′ atoms occupying *trans*-apical sites. To enable optimal M−N bonding to be achieved, both C−M bonds in **4** are tilted toward the coordinating N atoms (C(6)−C(1)−Sn = 141.0(2)°, C(2)−C(1)−Sn = 100.4(2)°), but only one in **3** (114.6(6), 96.1(5)°) and hence are strongly (**4**) or less strongly (**3**) divergent from sp^2 values; this is illustrated in Figure 2 for **3**.

At 298 K the ^1H and $^{13}C\{^1H\}$ NMR solution spectra of **3** and **4** each showed singlet NMe_2 signals,[14] indicating that (as in **1** and **2**[12]) there is a rapid exchange involving $2\text{-}Me_2N{-}M \leftrightarrow 6\text{-}Me_2N{-}M$ groups. The $^{119}Sn\{^1H\}$ signal at δ 328 in **4** was at lower frequency than in the free base **2** (δ 442).[12] The ^{11}B signals showed well-resolved proton coupling for **3** but not for **4**, perhaps because of ^{14}N coupling. The ^{11}B chemical shifts of δ −35 (**3**) or δ −34 (**4**) are similar to those in **I** ($M'X'_n = BH_3$; δ (−35)[1] or in the ylides $Me_3PCH_2BH_3$ and **I** ($M'X_n = CH_2BH_3$)[1] as are the $^1J(^{11}B{-}^1H)$ values of 73 Hz in **3** and 86 Hz in **I** ($M'X'_n = BH_3$).[1] They may also be compared with the $\delta[^{11}B]$ values of a variety of other Lewis-base−borane adducts, e.g. $Me_2O{-}BH_3$ (δ 2.5), $Me_3N{-}BH_3$ (δ −8.3), $Me_2S{-}BH_3$ (δ −20.1), or $Me_3P{-}BH_3$ (δ −36.8).[20]

The germylene **1** and stannylene **2** have been shown to form quite strong bonds to BH_3, as is also evident from the fact that their preparation involved displacement of THF from BH_3(THF). The choice of the ligand **VII** in MX_2 ($X^- = {}^-C_6H_3(NMe_2)_2$-2,6, **VII**) was crucial, since we found that under conditions similar to those used for the synthesis of **3** and **4** (Scheme 1), $Sn[CH(SiMe_3)_2]_2$ was unreactive toward BH_3(THF), while $Sn[N(SiMe_3)_2]_2$ was slowly reduced to elemental tin. The results here presented demonstrate that the germylene **1**, stannylene **2**, and ligand **VII** have a significant potential use as new versatile ligands.

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Supporting Information Available: Tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates for **3** and **4** (13 pages). Ordering information is given on any current masthead page.

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