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Preparation of Mono- and Bis(germyl)nitrilimines from Germylenes and Stannyl Diazo Derivatives

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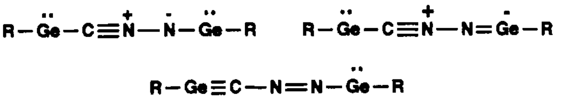
Summary: (Silyl)(germyl)- and bis(germyl)nitrilimines **2** *and* **5** *are obtained by adding [bis(trimethylsilyl)-methyl](pentamethylcyclopentadienyl)germylene (*1*) to (triisopropylsilyl)(trimethylstannyl)diazomethane and bis(trimethylstannyl)diazomethane, respectively; the reaction mechanism is discussed.*

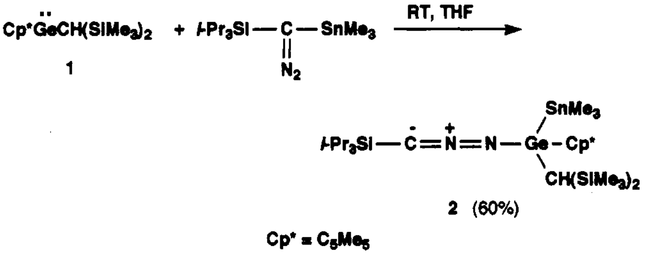
In the last few years, we have shown that, using the right set of substituents, nitrilimines can exist as stable compounds at room temperature.[1] Nitrilimines have a bent allenic structure,[2] except those possessing substituents with accessible vacant orbitals. In the latter case, nitrilimines have a propargylic type structure,[3,4] and the interaction of the CNN skeleton with the heteroatom substituents induces a shortening of the heteroatom–nitrogen or heteroatom–carbon bond lengths compared to classical single bonds; the *N*-phosphonio-[3a] and *C*-borylnitrilimines[3b] are typical examples. Therefore, it was tempting to prepare nitrilimines featuring germanediyl moieties, in order to study the multiple-bond character of the nitrogen- or/and carbon–germanium bond (Chart 1). Stannyl diazo derivatives react with a variety of electrophiles, leading to nitrilimines.[2b,5] On the other hand, pentamethylcyclopentadienyl (Cp*) substituted germylenes are known to undergo nucleophilic substitutions.[6] Here we report the surprising results observed in the reaction of [bis(trimethylsilyl)methyl](pentamethylcyclopentadienyl)germylene (**1**)[6a] with (triisopropylsilyl)(trimethylstannyl)diazomethane[5] and bis(trimethylstannyl)diazomethane.[7]

(Triisopropylsilyl)(trimethylstannyl)diazomethane reacted at room temperature in a THF solution with 1 equiv of **1**, leading, after workup, to a pale yellow oil identified as a nitrilimine[8] on the basis of ^{14}N NMR (δ −183 (C*N*N))[9] and ^{13}C NMR (δ 49.85 (*C*NN)) data and the strong and broad absorption in the IR spectrum at 2076 cm^{-1}.

Chart 1



Scheme 1



Surprisingly, NMR data also revealed the presence of a trimethylstannyl group (^{1}H NMR δ 0.48 ($J_{^{117}\mathrm{SnH}}$ = 47.2 Hz, $J_{^{119}\mathrm{SnH}}$ = 49.2 Hz, 9 H); ^{13}C NMR δ −4.28 ($J_{^{117}\mathrm{SnH}}$ = 244.2 Hz, $J_{^{119}\mathrm{SnH}}$ = 255.6 Hz); ^{119}Sn NMR δ −77.88) and also a fluxional Cp* substituent (^{1}H NMR δ 1.85 (15 H);

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(8) **2:** Neat (triisopropylsilyl)(trimethylstannyl)diazomethane (0.824 g, 2.3 mmol) was added at room temperature to a THF solution (5 mL) of **1** (0.838 g, 2.3 mmol). After the mixture was stirred for 1.5 h at room temperature, the solvent was removed under vacuum. The pale yellow oily nitrilimine **2** was washed three times with acetonitrile (5 mL) and dried in vacuo (1.00 g, 60% yield): bp 104 °C (5×10^{-2} mmHg); ^{1}H NMR (C_6D_6) δ −0.07, −0.06 (s, 1 H, C*H*SiCH$_3$), 0.13, 0.39 (s, 18 H, SiC*H*$_3$), 0.48 (s, $J_{^{117}\mathrm{SnH}}$ = 47.2 Hz, $J_{^{119}\mathrm{SnH}}$ = 49.2 Hz, 9 H, SnC*H*$_3$), 1.08 (m, 21 H, SiC*H*C*H*$_3$), 1.85 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_6D_6) δ −4.28 (s, $J_{^{117}\mathrm{SnC}}$ = 244.2 Hz, $J_{^{119}\mathrm{SnC}}$ = 255.6 Hz, Sn*C*H$_3$), 3.94, 4.72 (s, Si*C*H$_3$), 12.92 (s, Si*C*HCH$_3$), 13.20 (broad s, Cp*C*H$_3$), 19.21 (s, SiCH*C*H$_3$), 49.85 (s, *C*NN), 135.56 (broad s, Cp), *C*HSiCH$_3$ was not observed, probably hidden by Si*C*H$_3$; ^{14}N NMR (C_6D_6) δ −183 ($\nu_{1/2}$ = 240 Hz, C*N*N); ^{119}Sn NMR (C_6D_6) δ −77.88; ^{29}Si NMR (C_6D_6) δ −0.6, −0.1, 0.9; IR (THF, ν (cm^{-1})) 2076 (CNN). Anal. Calcd for $C_{30}H_{64}GeN_2Si_3Sn$: C, 49.46; H, 8.85; N, 3.84. Found: C, 49.49; H, 8.80; N, 3.79. **5:** The mixture of diastereomeric nitrilimines **5** was obtained as a pale yellow powder from a saturated THF solution at −80 °C (48% yield): ^{1}H NMR (C_6D_6) δ = −0.57, −0.55, −0.47, −0.45 (s, 2 H, C*H*SiCH$_3$), 0.05, 0.12 (s, 18 H, SiC*H*$_3$), 0.37, 0.38 (s, $J_{^{117}\mathrm{SnH}}$ = 46.1 Hz, $J_{^{119}\mathrm{SnH}}$ = 48.2 Hz, 9 H, SnC*H*$_3$), 0.45, 0.52 (s, 18 H, SiC*H*$_3$), 0.63, 0.64 (s, $J_{^{117}\mathrm{SnH}}$ = 46.2 Hz, $J_{^{119}\mathrm{SnH}}$ = 48.1 Hz, 9 H, SnC*H*$_3$), 1.79 (broad s, 15 H, CpC*H*$_3$), 1.90 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_7D_8) δ −5.22 (s, $J_{^{117}\mathrm{SnC}}$ = 250.1 Hz, $J_{^{119}\mathrm{SnC}}$ = 264.6 Hz, Sn*C*H$_3$), −4.28 (s, $J_{^{117}\mathrm{SnC}}$ = 234.8 Hz, $J_{^{119}\mathrm{SnC}}$ = 244.5 Hz, Sn*C*H$_3$), 3.14, 3.44, 3.78, 4.90 (s, Si*C*H$_3$), 12.40 (broad s, Cp*C*H$_3$), 63.71 (s, *C*NN), 135.01 (broad s, Cp), *C*HSiCH$_3$ was not observed, probably hidden by Si*C*H$_3$; ^{14}N NMR (C_7D_8) δ = −173 ($\nu_{1/2}$ = 250 Hz, C*N*N); ^{119}Sn NMR (C_6D_6) δ −83.12, −81.77, −67.09, −66.44; IR (ether, ν (cm^{-1})) 2052 (CNN). Anal. Calcd for $C_{41}H_{86}Ge_2N_2Si_4Sn_2$: C, 44.69; H, 7.87; N, 2.54. Found: C, 44.71; H, 7.79; N, 2.55. Single colorless crystals were grown from a CH_2Cl_2 solution at −30 °C: mp 136 °C. **7:** Carbodiimide **7** was characterized in solution (40% spectroscopic yield): ^{1}H NMR (C_6D_6) δ −0.15 (s, 1 H, C*H*SiCH$_3$), 0.09, 0.36 (s, 18 H, SiC*H*$_3$), 0.42 (s, $J_{^{117}\mathrm{SnH}}$ = 47.7 Hz, $J_{^{119}\mathrm{SnH}}$ = 50.0 Hz, 9 H, SnC*H*$_3$), 1.16 (m, 21 H, SiC*H*C*H*$_3$), 1.82 (broad s, 15 H, CpC*H*$_3$); ^{13}C NMR (C_6D_6) δ −5.94 (s, $J_{^{117}\mathrm{SnC}}$ = 257.1 Hz, $J_{^{119}\mathrm{SnC}}$ = 268.5 Hz, Sn*C*H$_3$) 3.65, 4.33 (s, Si*C*H$_3$), 13.00 (broad s, Cp*C*H$_3$), 13.51 (s, Si*C*HCH$_3$), 18.79 (s, SiCH*C*H$_3$), 126.41 (s, N*C*N), 136.10 (broad s, Cp), *C*HSiCH$_3$ was not observed, probably hidden by Si*C*H$_3$; ^{119}Sn NMR (C_6D_6) δ −64.46; IR (toluene, ν (cm^{-1})) 2162 (CNN); ^{14}N NMR (C_6D_6) δ −365 ($\nu_{1/2}$ = 390 Hz, NCN).

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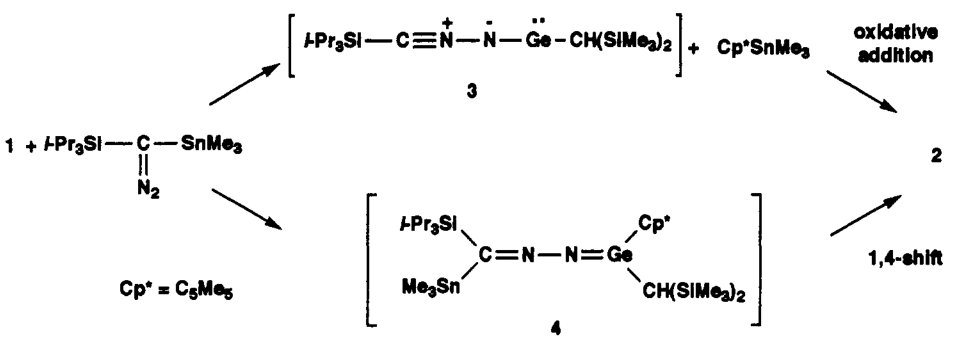
Scheme 2



^{13}C NMR δ 135.56 (C_5Me_5)). On the basis of these spectroscopic data, it was clear that the product obtained was the nitrilimine 2 (60% yield), featuring a tetracoordinated germanium atom (Scheme 1).

A nucleophilic substitution of the germylene leading to the desired nitrilimine 3 and Cp*$SnMe_3$, followed by oxidative addition[10] of Cp*$SnMe_3$ to the germylene center of 3, could rationalize the formation of compound 2. However, all attempts to trap the supposed intermediate 3, with an excess of classical germylene reagents such as 2,3-dimethylbutadiene or even Cp$SnMe_3$, failed. Thus, it is more likely that the mechanism involves a Staudinger–Meyer type intermediate 4,[11] which undergoes a subsequent 1,4-migration of the trimethylstannyl group. The migrating ability of the Me_3Sn group,[12] as well as the reluctance of germanium to form π double bonds,[13] probably explains this unprecedented rearrangement (Scheme 2).

Although these results showed that *N*-germanediylnitrilimines of type 3 are not accessible by this route, the question arose as to whether a *C*-germanediylnitrilimine could be formed. Since the tin–carbon bond of transient *C*-stannylnitrilimines is extremely reactive,[5] we then performed the reaction of bis(trimethylstannyl)diazomethane with 2 equiv of 1. A 1/1 mixture of two bis(germyl)nitrilimine diastereoisomers 5 was obtained 48% total yield.[8] The spectroscopic data for the CNN skeleton are quite comparable to those for nitrilimine 2, and the NMR data show the presence of two different trimethylstannyl (^{13}C NMR δ -5.22 ($J_{^{117}SnC}$ = 250.1 Hz, $J_{^{119}SnC}$ = 264.6 Hz), -4.28 ($J_{^{117}SnC}$ = 234.8 Hz, $J_{^{119}SnC}$ = 244.5 Hz); ^{119}Sn NMR δ -83.12, -81.77, -67.09, -66.44) and two inequivalent fluxional Cp* groups (^{1}H NMR δ 1.79 (15 H), 190 (15 H)). The structure of 5 was clearly established by a single-crystal X-ray diffraction study.[14] The molecular structure is shown in Figure 1, and the pertinent metric parameters are listed in the caption. The nitrilimine skeleton is almost linear (C(1)–N(1)–N(2) = 174.2(11)°); the C(1)–N(1) (1.183(17) Å) and the N(1)–N(2) (1.264(16) Å) bond lengths are comparable with those of allenic type nitrilimines.[2] The steric hindrance around the germanium atom is noteworthy; in fact, we are at the upper limit, since no reaction occurs between germanediyl 1 and bis(triphenylstannyl)diazomethane or between (pentamethylcyclopentadienyl)(2,4,6-tri-*tert*-butylphenyl)germylene[6a] and bis(trimethylstannyl)diazomethane, even at elevated temperature.

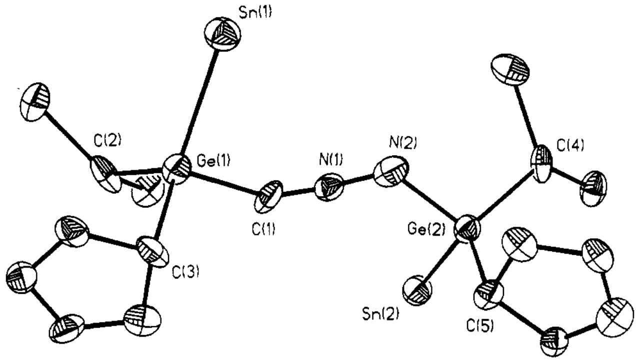
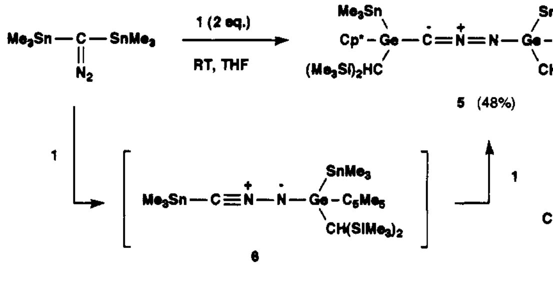


Figure 1. ORTEP drawing of 5. Hydrogen atoms and methyl groups are omitted for clarity. Bond lengths (Å): Ge(1)–C(2) = 1.984(11), Ge(1)–Sn(1) = 2.648(2), Ge(1)–C(3) = 2.056(11), Ge(1)–C(1) = 1.935(13), C(1)–N(1) = 1.183(17), N(1)–N(2) = 1.264(16), N(2)–Ge(2) = 1.883(11), Ge(2)–Sn(2) = 2.652(2), Ge(2)–C(4) = 1.969(11), Ge(2)–C(5) = 2.056(10). Bond angles (deg): Sn(1)–Ge(1)–C(1) = 94.9(4), Sn(1)–Ge(1)–C(2) = 118.8(3), Sn(1)–Ge(1)–C(3) = 118.0(3), Ge(1)–C(1)–N(1) = 150.1(11), C(1)–N(1)–N(2) = 174.2(11), N(1)–N(2)–Ge(2) = 129.9(8), Sn(2)–Ge(2)–N(2) = 100.9(3), Sn(2)–Ge(2)–C(4) = 117.5(3), Sn(2)–Ge(2)–C(5) = 114.8(3).

Scheme 3



Since all attempts to trap a possible transient *C*-germanediylnitrilimine failed, it is postulated that the mechanism involves the formation of the *C*-stannylnitrilimine 6, which undergoes an insertion reaction of a second molecule of 1 into the carbon–tin bond.

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(14) Crystal data for compound 5: $C_{41}H_{86}Ge_2N_2Si_4Sn_2$, fw 1102.0, monoclinic, space group $P2_1/c$, a = 9.463(4) Å, b = 19.041(5) Å, c = 29.840(9) Å, β = 94.74(3)°, V = 5359(3) Å^3, Z = 4, d_{calc} = 1.37 g/cm^3, μ(Mo Kα) = 2.136 mm^{-1}. Data reflections were collected by a Syntex P2$_1$ diffractometer in the 2θ range 3–50°; T = 173 K. The structure was solved by direct methods and refined to R = 0.069 and R_w = 0.050 with 4844 reflections having $F > 4.0\sigma(F)$ (460 variables).

Under irradiation, (silyl)(germyl)nitrilimine 2 undergoes the classical rearrangement[1,15] into its carbodiimide isomer $i\text{-}Pr_3SiN{=}C{=}NGeCp^*(SnMe_3)[(CHSiMe_3)_2]$ (7).[8] However, in contrast to all known allenic type nitrilimines, these first fourth-row-element-substituted nitrilimines 2 and 5 do not react as 1,3-dipoles, probably because of the excessive steric hindrance.

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Supplementary Material Available: Tables giving crystal data and conditions and parameters for the data collection and refinement, atomic coordinates and isotropic thermal parameters for all atoms, anisotropic thermal parameters for the nonhydrogen atoms, and bond distances and angles and a figure showing additional atom labeling for compound 5 (11 pages). Ordering information is given on any current masthead page.

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