

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)diazomethane⁵ 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 nitrilimine⁸ on the basis of ¹⁴N NMR (δ -183 (CNN))⁹ and ¹³C NMR (δ 49.85 (CNN)) data and the strong and broad absorption in the IR spectrum at 2076 cm⁻¹.

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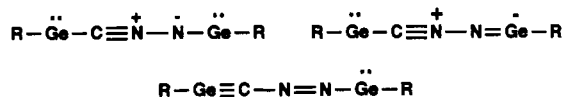
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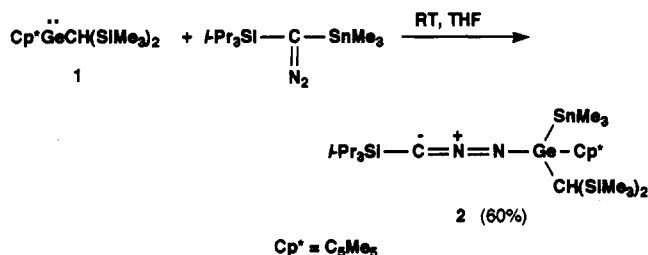
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Chart 1



Scheme 1



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

(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); ¹H NMR (C_6D_6) δ -0.07, -0.06 (s, 1 H, CHSiCH₃), 0.13, 0.39 (s, 18 H, SiCH₃), 0.48 (s, $J_{117\text{SnH}} = 47.2$ Hz, $J_{119\text{SnH}} = 49.2$ Hz, 9 H, SnCH₃), 1.08 (m, 21 H, SiCHCH₃), 1.85 (broad s, 15 H, CpCH₃); ¹³C NMR (C_6D_6) δ -4.28 (s, $J_{117\text{SnC}} = 244.2$ Hz, $J_{119\text{SnC}} = 255.6$ Hz, SnCH₃), 3.94, 4.72 (s, SiCH₃), 12.92 (s, SiCHCH₃), 13.20 (broad s, CpCH₃), 19.21 (s, SiCHCH₃), 49.85 (s, CNN), 135.56 (broad s, Cp), CHSiCH₃ was not observed, probably hidden by SiCH₃; ¹⁴N NMR (C_6D_6) δ -183 ($\nu_{1/2} = 240$ Hz, CNN); ¹¹⁹Sn NMR (C_6D_6) δ -77.88; ²⁹Si NMR (C_6D_6) δ -0.6, -0.1, 0.9; IR (THF, ν (cm⁻¹)) 2076 (CNN). Anal. Calcd for C₃₀H₆₄GeN₂Si₃Sn: 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): ¹H NMR (C_6D_6) δ -0.57, -0.55, -0.47, -0.45 (s, 2 H, CHSiCH₃), 0.05, 0.12 (s, 18 H, SiCH₃), 0.37, 0.38 (s, $J_{117\text{SnH}} = 46.1$ Hz, $J_{119\text{SnH}} = 48.2$ Hz, 9 H, SnCH₃), 0.45, 0.52 (s, 18 H, SiCH₃), 0.63, 0.64 (s, $J_{117\text{SnC}} = 46.2$ Hz, $J_{119\text{SnC}} = 48.1$ Hz, 9 H, SnCH₃), 1.79 (broad s, 15 H, CpCH₃), 1.90 (broad s, 15 H, CpCH₃); ¹³C NMR (C_7D_8) δ -5.22 (s, $J_{117\text{SnC}} = 250.1$ Hz, $J_{119\text{SnC}} = 264.6$ Hz, SnCH₃), -4.28 (s, $J_{117\text{SnC}} = 234.8$ Hz, $J_{119\text{SnC}} = 244.5$ Hz, SnCH₃), 3.14, 3.44, 3.78, 4.90 (s, SiCH₃), 12.40 (broad s, CpCH₃), 63.71 (s, CNN), 135.01 (broad s, Cp), CHSiCH₃ was not observed, probably hidden by SiCH₃; ¹⁴N NMR (C_7D_8) δ -173 ($\nu_{1/2} = 250$ Hz, CNN); ¹¹⁹Sn NMR (C_6D_6) δ -83.12, -81.77, -67.09, -66.44; IR (ether, ν (cm⁻¹)) 2052 (CNN). Anal. Calcd for C₄₁H₈₆GeN₂Si₄Sn₂: 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 CH₂Cl₂ solution at -30 °C: mp 136 °C. **7**: Carbodiimide **7** was characterized in solution (40% spectroscopic yield): ¹H NMR (C_6D_6) δ -0.15 (s, 1 H, CHSiCH₃), 0.09, 0.36 (s, 18 H, SiCH₃), 0.42 (s, $J_{117\text{SnH}} = 47.7$ Hz, $J_{119\text{SnH}} = 50.0$ Hz, 9 H, SnCH₃), 1.16 (m, 21 H, SiCHCH₃), 1.82 (broad s, 15 H, CpCH₃); ¹³C NMR (C_6D_6) δ -5.94 (s, $J_{117\text{SnC}} = 257.1$ Hz, $J_{119\text{SnC}} = 268.5$ Hz, SnCH₃), 3.65, 4.33 (s, SiCH₃), 13.00 (broad s, CpCH₃), 13.51 (s, SiCHCH₃), 18.79 (s, SiCHCH₃), 126.41 (s, NCN), 136.10 (broad s, Cp), CHSiCH₃ was not observed, probably hidden by SiCH₃; ¹¹⁹Sn NMR (C_6D_6) δ -64.46; IR (toluene, ν (cm⁻¹)) 2162 (CNN); ¹⁴N NMR (C_6D_6) δ -365 ($\nu_{1/2} = 390$ Hz, NCN).

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