Electronic Supplementary Material (ESI) for Chemical Communications

Elegant Approach to Spacer Arranged Silagermylene and Bis(germylene) Compounds

Sankaranarayana Pillai Sarish, Sakya S. Sen, Herbert W. Roesky,* Ina Objartel, and Dietmar Stalke*

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany.

Content:

S1. Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques or inside a MBraun MB 150-GI glove box maintained at or below 1 ppm of O_2 and H_2O. All solvents were distilled from Na/benzophenone prior to use. The starting materials **1**,[10] **2**,[6] **3**,[11] and **6**[18] are prepared using literature procedures. Other chemicals are purchased commercially and used as received. ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR spectra were recorded on a Bruker Avance DRX instrument and referenced to the $SiMe_4$ in the case of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of 4. A solution of LSiCl (**1**) (0.295 g, 1.00 mmol) in toluene (10 mL) was added to a toluene (10 mL) solution of L^{1}Ge (**3**) (0.489 g, 1.00 mmol) at room temperature under stirring for 12 h. The solvent was removed in vacuum and the residue was dissolved in a mixture of *n*-pentane and toluene, concentrated and stored for crystallization at -32 °C in a freezer for 48 h. Compound **4** was obtained as yellow crystals. Yield (0.688 g, 87.7%); mp. 185-187 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 7.27-7.14, 6.94-6.83 (m, 11H, Ar-*H*); 5.64 (s, 1H, γ-C*H)*, 4.33 (sept, 1H, C*H*$(CH_3)_2$), 4.10 (sept, 1H, C*H*$(CH_3)_2$), 3.68 (sept, 1H, C*H*$(CH_3)_2$), 3.49 (sept, 1H, C*H*$(CH_3)_2$), 2.79 (d, 1H, J = 10.76 Hz, NCC*H*$_2$), 2.39 (d, 1H, J = 10.71 Hz, NCC*H*$_2$), 1.84 (s, 3H, C*H*$_3$), 1.71 (d, 3H, J = 6.73 Hz, CH(C*H*$_3$)$_2$), 1.60 (d, 3H, J = 6.51 Hz, CH(C*H*$_3$)$_2$), 1.57 (d, 3H, J = 6.59 Hz, CH(C*H*$_3$)$_2$), 1.49 (d, 3H, J = 6.83 Hz, CH(C*H*$_3$)$_2$), 1.37 (d, 3H, J = 6.78 Hz, CH(C*H*$_3$)$_2$), 1.36 (d, 3H, J = 6.73 Hz, CH(C*H*$_3$)$_2$), 1.33 (d, 3H, J = 6.93 Hz, CH(C*H*$_3$)$_2$), 1.25 (d, 3H, J = 6.77 Hz, CH(C*H*$_3$)$_2$), 1.03 (s, 9H, C(C*H*$_3$)$_3$), 0.70 (s, 9H, C(C*H*$_3$)$_3$) ppm; ^{13}C NMR (125.77 MHz, C_6D_6): δ 171.8, 162.0, 161.3, 148.0, 146.7, 145.3, 145.0, 140.83, 140.76, 133.9, 130.0, 129.7, 129.5, 128.5, 127.6, 125.5, 125.3, 124.9, 124.0, 102.5, 53.1, 53.0, 41.6, 32.1, 31.2, 29.1, 28.9, 28.8, 28.7, 28.4, 27.9, 27.86, 25.2, 24.8, 24.6,

24.2, 23.6 ppm; ^{29}Si NMR (99.36 MHz, C_6D_6): δ 42.45 ppm. MS (70 eV): *m*/*z* (%): 475.2 (100) $[M\text{-}LSi\text{-}Cl\text{-}Me]^+$, 784.5 (8) $[M]^+$, Anal. calcd. for $C_{44}H_{63}ClGeN_4Si$ (784.18): C, 67.39; H, 8.10; N 7.14. Found: C, 66.41; H, 8.29; N 6.94.

Synthesis of 5. A solution of LGeCl (**2**) (0.340 g, 1.00 mmol) in toluene (10 mL) was added to a toluene (10 mL) solution of L^{1}Ge (**3**) (0.489 g, 1.00 mmol) at room temperature and stirred for 12 h. The solvent was removed in vacuum and the residue was dissolved in a mixture of *n*-pentane and toluene, concentrated and stored for crystallization at -5°C in a freezer for 48 h. Compound **5** was obtained as pale yellow crystals. Yield: (0.742 g, 89.59%); mp. 198-199 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 7.15-7.13, 6.97-6.88 (m, 11H, Ar-*H*); 5.64 (s, 1H, *γ*-C*H)*, 4.34 (sept, 1H, C*H*$(CH_3)_2$), 4.15 (sept, 1H, C*H*$(CH_3)_2$), 3.64 (sept, 1H, C*H*$(CH_3)_2$), 3.48 (sept, 1H, C*H*$(CH_3)_2$), 2.88 (d, 1H, *J* = 8.94 Hz, NCC*H*$_2$), 2.71 (d, 1H, *J* = 8.92 Hz, NCC*H*$_2$), 1.83 (s, 3H, C*H*$_3$), 1.60 (d, 3H, *J* = 6.48 Hz, CH(C*H*$_3)_2$), 1.56 (2d, 6H, *J* = 6.64 Hz, CH(C*H*$_3)_2$), 1.50 (d, 3H, *J* = 6.80 Hz, CH(C*H*$_3)_2$), 1.34 (3d, 9H, *J* = 7.01 Hz, CH(C*H*$_3)_2$), 1.24 (d, 3H, *J* = 6.78 Hz, CH(C*H*$_3)_2$), 0.94 (s, 9H, C(C*H*$_3)_3$), 0.67 (s, 9H, C(C*H*$_3)_3$) ppm. ^{13}C NMR (125.77 MHz, C_6D_6): δ 172.4, 167.1, 161.7, 148.0, 147.1, 145.3, 144.6, 141.0, 140.7, 135.7, 129.7, 128.4, 127.6, 125.6, 125.3, 124.7, 124.0, 101.9, 53.1, 53.0, 46.1, 32.2, 31.5, 29.2, 28.8, 28.7, 28.6, 28.4, 27.9, 27.8, 25.1, 24.8, 24.4, 24.2, 24.1, 23.7 ppm. MS (70 eV): *m*/*z* (%): 475.2 (100) $[M\text{-}LGe\text{-}Cl\text{-}Me]^+$, 830.3(4) $[M]^+$ Anal. calcd. for $C_{44}H_{63}ClGe_2N_4$, (828.73): C, 63.77; H, 7.66; N, 6.76. Found: C, 64.4; H, 8.3; N, 5.7.

Synthesis of 7. A solution of LSiCl (**1**) (0.295 g, 1.00 mmol) in toluene (10 mL) was added to a toluene (10 mL) solution of L^{1}AlMe·thf (**6**) (0.531 g, 1.00 mmol) at room temperature and stirred for 12 h. The solvent was removed in vacuum and the residue was dissolved in a mixture of *n*-pentane and toluene, concentrated and stored for crystallization at -5°C in a freezer for 72 h. Compound **7** was obtained as an off-white solid. Yield: (0.656 g, 86.88%); mp. 116-117 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ 7.27-6.83, 6.94-6.83 (m, 11H, Ar-*H*); 5.71

(s, 1H, γ-C*H*), 4.23 (sept, 1H, C*H*(CH_3)$_2$), 3.99 (sept, 1H, C*H*(CH_3)$_2$), 3.52 (sept, 1H, C*H*(CH_3)$_2$), 3.50 (sept, 1H, C*H*(CH_3)$_2$), 2.46 (d, 2H, J = 3.19 Hz, NCCH_2), 1.82 (s, 3H, CH_3), 1.62 (d, 3H, J = 6.76 Hz, CH(CH_3)$_2$), 1.57 (d, 3H, J = 6.73 Hz, CH(CH_3)$_2$), 1.55 (d, 3H, J = 6.88 Hz, CH(CH_3)$_2$), 1.53 (d, 3H, J = 6.57 Hz, CH(CH_3)$_2$), 1.39 (d, 3H, J = 6.80 Hz, CH(CH_3)$_2$), 1.36 (d, 3H, J = 6.85 Hz, CH(CH_3)$_2$), 1.28 (d, 3H, J = 6.86 Hz, CH(CH_3)$_2$), 1.18 (d, 3H, J = 6.99 Hz, CH(CH_3)$_2$), 0.96 (s, 9H, C(CH_3)$_3$), 0.95 (s, 9H, C(CH_3)$_3$), -0.50 (s, 3H, Al-*Me*) ppm. ^{13}C NMR (125.77 MHz, C_6D_6): δ 177.6, 167.5, 161.1, 146.7, 146.6, 144.5, 144.0, 140.8, 140.5, 134.1, 130.0, 129.7, 129.3, 128.7, 127.2, 125.6, 125.24, 125.20, 124.5, 124.0, 99.8, 53.3, 53.2, 42.2, 31.8, 31.7, 29.1, 28.8, 28.4, 28.2, 28.1, 27.3, 25.7, 25.5, 25.0, 24.8, 24.4, 24.1, 23.6, -10.8 ppm. ^{29}Si NMR (99.36 MHz, C_6D_6): δ 41.16 ppm. MS (70 eV): *m*/*z* (%): 479.2 (100) [M-LSi-Me]$^+$, 753 (20) [M]$^+$. Anal. calcd. for $C_{45}H_{66}AlClN_4Si$, (753.55): C, 71.72; H, 8.83; N, 7.44. Found: C, 70.3; H, 8.2; N, 7.3.

S2. Crystallographic details for compounds 4 and 5

A shock cooled crystal was selected and mounted under nitrogen atmosphere using the X-TEMP2.[S1] The data sets were collected on an INCOATEC Microfocus with mirror optics instrument equipped with a Bruker Apex II detector (Mo Kα radiation, λ = 0.71073 Å, 100K).[S2] The integration was performed with SAINT V7.68A[S3], which was followed by an empirical absorption correction with SADABS 2008/1.[S4] The structures were solved by direct methods (SHELXS)[S5] and refined against F^2 using the full-matrix least-squares methods with SHELXL.[S6] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model except H16A, H16B, and H18 in **4** which was found and refined freely.

Table 1. X-ray data for compound **4** and **5**

	4	**5**
empirical formula	$C_{44}H_{63}ClGeN_4Si$	$C_{44}H_{63}ClGe_2N_4$
CCDC number	819683	819684

formula weight	784.11	828.61
T(K)	99(2)	100(2)
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.1815(10)	13.207(2)
b (Å)	22.4798(17)	22.515(3)
c (Å)	15.2220(11)	15.273(2)
β (°)	106.3880(10)	106.601(2)
V, (Å^3)	4327.3(6)	4352.4(11)
Z	4	4
ρ_{calc} (Mg m^{-3})	1.204	1.265
μ (mm^{-1})	0.831	1.476
F(000)	1672	1744
reflections collected	96322	90869
data/restraints/parameters	9189 / 0 / 487	7962 / 0 / 475
GooF	1.047	1.038
$R1$, $wR2$[$I > 2\sigma(I)$][a]	0.0318, 0.0673	0.0325, 0.0642
$R1$, $wR2$ (all data)	0.0453, 0.0722	0.0459, 0.0690
largest diff peak, hole (e Å^{-3})	0.571, -0.313	0.710, -0.474

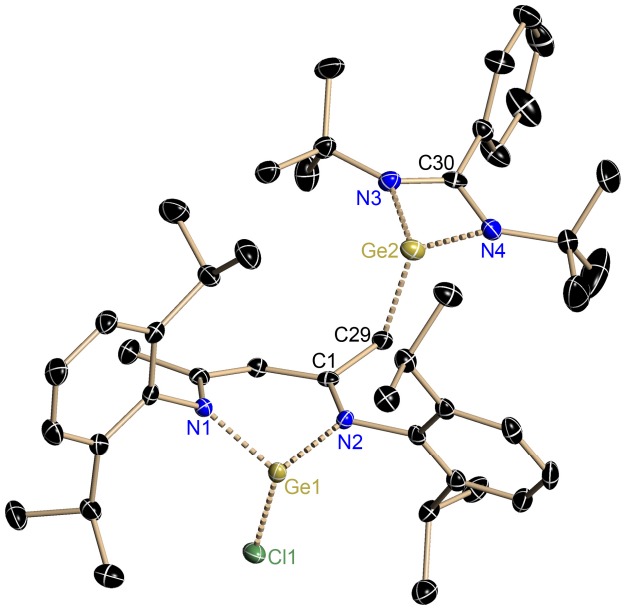

Fig. 2 Molecular structure of **5**. The anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity.

S3. References

(S1). (a) T. Kottke and D. Stalke, *J. Appl. Crystallogr.* **1993** *26*, 615-619. (b) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171-178.

(S2). T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr*. **2009**, *42*, 885-891.

(S3). Bruker *SAINT v7.68A*, WI, USA, Madison, **2009**.

(S4). G. M. Sheldrick, *SADABS 2008/1*, Göttingen, **2008**.

(S5). G. M. Sheldrick, *SHELXS* in *SHELXTL v2008/4*, WI, USA, Madison, **2008**.

(S5). G. M. Sheldrick, *SHELXS* in *SHELXTL v2008/4*, WI, USA, Madison, **2008**.