

Synthesis of a germanium analogue of a dithiocarboxylic acid anhydride from the Ge(I) pyridyl-1-azaallyl dimer

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Supplementary Material

Experimental Section

General procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from CaCl₂ (CH₂Cl₂) and/or Na (Et₂O, toluene and THF). Compound **1** [Ge{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Cl] was prepared according to the literature procedures.¹ Lithium metals and anhydrous sulfur powder were purchased from Aldrich Chemical Co. and used without further purification. The ¹H and ¹³C NMR spectra were recorded on Brüker WM-300 or Varian 400 spectrometers. The NMR spectra were recorded in THF-*d*₈ or benzene-*d*₆ and the chemical shifts δ are relative to SiMe₄.

Synthesis of Compound 2. A solution of [Ge{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}Cl] (**1**) (0.81g, 1.82 mmol) in THF (25 ml) was added slowly to a stirring suspension of lithium powder (0.013g, 1.87 mmol) in THF (30 ml) at -90 °C. The resultant dark green mixture was warmed to ambient temperature and stirred for 12 h. The solution was filtered and the volatiles were removed under reduced pressure. The black green residue was extracted with Et₂O. After filtration, concentration of filtrate and storage at 0 °C afforded dark green crystals. Yield: 0.16g (21%). Mp: 226-230 °C. Anal. Found: C 54.79, H 7.16, N 7.06. Calcd for C₃₈H₅₄Ge₂N₄Si₄: C 55.31, H 6.60, N 6.79. ¹H NMR (benzene-*d*₆): δ = 0.24 (s, 9H, SiMe₃), 0.26 (s, 9H, SiMe₃), 6.06-6.12 (m, 1H, 5-py), 7.17-7.39 (m, 5H, Ph), 7.41-7.45 (m, 1H, 3-py), 7.78-7.82 (m, 1H, 4-py), 8.09-8.11 (d, 1H, 6-py). ¹³C{¹H} NMR (benzene-*d*₆): δ = 2.63, 3.74 (SiMe₃), 114.215 (CSiMe₃), 124.65, 130.01, 138.08, 142.23, 143.54, 145.94, 147.97, 156.45, 159.53 (Ph and Py), 164.60 (NCPH).

Synthesis of Compound 4. A solution of [{[N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)]Ge₂}]

(**2**) (1.65g, 2.00 mmol) in toluene (25 ml) was added slowly to a stirring suspension of sulfur powder (0.115g, 3.59 mmol) in toluene (15 ml) at 0 °C. The resultant yellowish-orange solution was warmed to room temperature and stirred for another 18h. The volatiles were then removed under reduced pressure and extracted with CH₂Cl₂ (20 ml). The extract was then added with 2 ml of toluene. Concentration of the extract afforded yellow crystals. Yield: 0.59g (32%). Mp: 273-278 °C. Anal. Found: C 50.05, H 6.11, N 6.42. Calcd for C₃₈H₅₄Ge₂N₄S₃Si₄: C 49.53, H 5.91, N 6.08. ¹H NMR (THF-*d*₈): δ = -0.01 (s, 9H, SiMe₃), 0.16 (s, 9H, SiMe₃), 6.60-6.64 (t, 1H, 5-py), 7.02-7.28 (m, 5H, Ph), 7.36-7.40 (d, 1H, 3-py), 7.50-7.52 (t, 1H, 4-py), 7.81-7.83 (d, 1H, 6-py). ¹³C{¹H} NMR (THF-*d*₈): δ = 2.63, 3.31 (SiMe₃), 118.66 (CSiMe₃), 125.18, 128.08, 129.56, 131.50, 136.63, 137.37, 144.60, 146.18, 147.16 (Ph and Py), 159.18 (NCPh).

X-ray crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2** and **4** were collected on a Rigaku R-Axis II imaging plate using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a rotating-anode generator operating at 50kV and 90mA. Crystal data are summarized in Table 1. The structures were solved by direct phase determination using the computer program SHELXTL-PC¹ on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations.

Table 1. Crystallographic Data for Compound **2** and **4**

	2	4
Formula	C ₃₈ H ₅₄ Ge ₂ N ₄ Si ₄	C ₃₈ H ₅₄ Ge ₂ N ₄ S ₃ Si ₄
Fw	824.39	920.57
Color	Dark Green	Yellow
cryst syst	Monoclinic	Orthorhombic
space group	P2 ₁	Pna2 ₁
<i>a</i> (Å)	13.346(3)	24.360(6)
<i>b</i> (Å)	11.006(3)	11.062(3)
<i>c</i> (Å)	15.589(4)	17.424(5)
<i>α</i> (deg)	90	90
<i>β</i> (deg)	108.301(4)	90
<i>γ</i> (deg)	90	90
<i>V</i> (Å ³)	2173.8(9)	4695(2)
<i>Z</i>	2	4
<i>d</i> _{calcd} (g cm ⁻³)	1.259	1.302
<i>μ</i> (mm ⁻¹)	1.523	1.546
<i>F</i> (000)	860	1912
cryst size (mm)	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.20
2 <i>θ</i> range (deg)	1.61 to 25.00	1.67 to 28.07
index range	-15 ≤ <i>h</i> ≤ 15, -13 ≤ <i>k</i> ≤ 13, -18 ≤ <i>l</i> ≤ 13	-32 ≤ <i>h</i> ≤ 32, -14 ≤ <i>k</i> ≤ 7, -23 ≤ <i>l</i> ≤ 22
no. of rflns collected	11671	30667
no. of indep rflns	7263	11252
R1, wR2 (<i>I</i> > 2(<i>σ</i>))	0.0397, 0.0913	0.0694, 0.1370
R1, wR2 (all data)	0.0516, 0.0984	0.2263, 0.1943
goodness of fit, <i>F</i> ²	0.967	0.928
no. of data/restraints/params	7263 / 1 / 433	11252 / 1 / 461
largest diff peaks, eÅ ⁻³	0.597 to -0.281	0.602 to -1.095

References

- 1 Leung, W. -P.; So, C. -W.; Wu, Y. S.; Li, H. -W.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2005**, 513.
- 2 Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds; Oxford University Press: New York, 1985; p 175.