2116 *Organometallics* **1997,** *16,* 2116−2120

Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanium(II): A Base-Stabilized Germylene and the Corresponding Germanethione, Germaneselenone, and Germanetellurone

Günter Ossig, Anton Meller,* Christiane Brönneke, Olaf Müller,
Martina Schäfer, and Regine Herbst-Irmer

Institut für Anorganische Chemie der Universität Göttingen,
Tammannstrasse 4, D-37077 Göttingen, Germany

Received December 23, 1996[⊗]

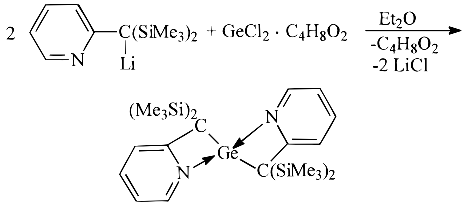
Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanium(II) (**1**) reacts with elemental chalcogens (sulfur, selenium, tellurium) to give the corresponding thione (**2**), selenone (**3**), and tellurone (**4**) at room temperature. At elevated temperatures, the dihydropyridinato compounds **5** and **6** are formed by a 1,3-trimethylsilyl shift from one of the methyl bridges to the sulfur and selenium atoms in **2** and **3**, respectively. The compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, ^{77}Se, ^{125}Te), MS (EI), and elemental analysis. X-ray crystal structure determinations are presented for **1**, **3**, **4**, and **5**.

Introduction

While bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]tin(II) has been described (including X-ray characterization),[1] the preparation of the corresponding germanium compound has been attempted apparently without success.[2] A few monomeric stable germanethiones, -selenones, and -tellurones have been prepared since 1989, when the first base-stabilized germathione was described by Veith et al.[3,4] The germanium in this compound is tetracoordinated by three nitrogen atoms and the double-bonded sulfur. Organometallic germanethiones and -selenones containing a tricoordinate germanium atom were prepared by Okazaki et al.[5−7] using 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl and 2,4,6-triisopropylphenyl substituents on germanium. Recently, the octamethyldibenzotetraaza[14]annulene dianion was employed in preparing a base-stabilized germylene,[8,9] and the corresponding thione, selenone, and tellurone with pentacoordination by four N and X (X = S, Se, Te) were obtained. Preliminary data (^{1}H, ^{13}C NMR, MS) were reported[10] for $(ArO)_2Ge{=}S$ ($ArO = 2,4,6\text{-}(Me_2NCH_2)_3C_6H_2O$) without specification of the coordination number. The tetra- and pentacoordinated germachalcogenones were prepared by the reactions of corresponding germylenes and elemental chalcogens[3,8] (in the case of tellurium with the addition of PMe_3).[8] The three-coordinate thiones[5] and selenones,[6] however, were obtained by elimination of sulfur or selenium, respectively, from the corresponding 1,2,3,4,5-tetrachalcogenagermolanes with the aid of triphenylphosphane. For a recent review, see ref 11.

Results and Discussion

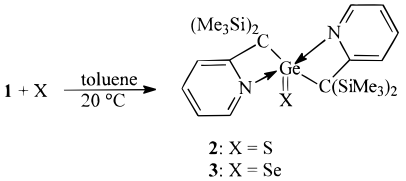
Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanium(II) (**1**) was prepared by reaction of lithiated 2-[bis(trimethylsilyl)methyl]pyridine and $GeCl_2$−dioxane in ether at −78 °C (eq 1). The structure of the product was determined by an X-ray diffraction study.



1

(1)

Compound **1** reacts with elemental sulfur, selenium, and tellurium in toluene to give the corresponding thione, selenone, and tellurone, respectively, in high yield (eq 2).



(2)

2: X = S
3: X = Se
4: X = Te

The synthesis of **4** must be performed under the exclusion of light. If the reactions leading to **2** and **3**

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

[1] Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H., *J. Chem. Soc., Chem. Commun.* **1988**, 336.

[2] Jolly, B. S.; Lappert, M. F.; Engelhardt, L. M.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2653.

[3] Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1989**, *101*, 1287; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237.

[4] Veith, M.; Detemple, A.; Huch, V. *Chem. Ber.* **1991**, *124*, 1135.

[5] Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855.

[6] Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem.* **1994**, *106*, 2418; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339.

[7] Tokitoh, N.; Matsuhashi, Y.; Shibata, K.; Matsumoto, T.; Suzuki, H.; Saito, M.; Manmaru, K.; Okazaki, R. *Main Group Met. Chem.* **1994**, *17*, 55.

[8] Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351.

[9] Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1996**, 1669.

[10] Barrau, J.; Rima, G.; El Amzaoui, T. *Inorg. Chim. Acta* **1996**, *241*, 9.

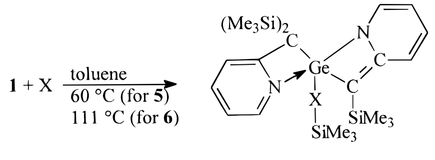
[11] Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1, 3, 4, and 5

Compound **1** (Mean Values with Maximum Deviation)							
Ge(1)−C(1)	2.127(4)	Ge(1)−N(1)	2.273(3)	N(1)−C(6)	1.349(5)	N(1)−C(2)	1.355(5)
C(1)−C(2)	1.502(7)	C(2)−C(3)	1.398(6)	C(3)−C(4)	1.387(5)	C(4)−C(5)	1.380(6)
C(5)−C(6)	1.374(6)						
C(1)[a]−Ge(1)−C(1)	112.5(2)	C(1)[a]−Ge(1)−N(1)	93.9(3)	C(1)−Ge(1)−N(1)	64.8(3)	N(1)[a]−Ge(1)−N(1)	142.4(2)
C(2)−N(1)−Ge(1)	91.0(2)	C(2)−C(1)−Ge(1)	93.0(2)	N(1)−C(2)−C(1)	111.3(3)		
Compound **3**							
Ge(1)−C(13)	2.051(4)	Ge(1)−C(1)	2.055(4)	Ge(1)−N(2)	2.161(3)	Ge(1)−N(1)	2.177(3)
Ge(1)−Se(1)	2.2472(7)	N(1)−C(12)	1.339(4)	N(1)−C(8)	1.354(5)	N(2)−C(24)	1.341(5)
N(2)−C(20)	1.347(5)	C(1)−C(8)	1.504(5)	C(8)−C(9)	1.393(5)	C(9)−C(10)	1.383(6)
C(10)−C(11)	1.372(6)	C(11)−C(12)	1.375(6)	C(13)−C(20)	1.508(5)	C(20)−C(21)	1.396(5)
C(21)−C(22)	1.388(7)	C(22)−C(23)	1.369(8)	C(23)−C(24)	1.373(7)		
C(13)−Ge(1)−C(1)	121.26(15)	C(13)−Ge(1)−N(2)	67.40(13)	C(1)−Ge(1)−N(2)	98.45(13)	C(13)−Ge(1)−N(1)	97.75(13)
C(1)−Ge(1)−N(1)	67.16(13)	N(2)−Ge(1)−N(1)	151.03(11)	C(13)−Ge(1)−Se(1)	119.30(10)	C(1)−Ge(1)−Se(1)	119.43(11)
N(2)−Ge(1)−Se(1)	103.97(8)	N(1)−Ge(1)−Se(1)	105.00(8)	C(8)−N(1)−Ge(1)	90.9(2)	C(20)−N(2)−Ge(1)	91.3(2)
C(8)−C(1)−Ge(1)	91.7(2)	N(1)−C(8)−C(1)	110.0(3)	C(20)−C(13)−Ge(1)	91.2(2)	N(2)−C(20)−C(13)	109.9(3)
Compound **4**							
Ge(1)−C(1)	2.063(2)	Ge(1)−N(1)	2.171(2)	Ge(1)−Te(1)	2.4795(5)	N(1)−C(12)	1.342(3)
N(1)−C(8)	1.351(3)	C(1)−C(8)	1.504(3)	C(8)−C(9)	1.400(3)	C(9)−C(10)	1.392(4)
C(10)−C(11)	1.381(4)	C(11)−C(12)	1.375(4)				
C(1)[b]−Ge(1)−C(1)	120.55(12)	C(1)−Ge(1)−N(1)	67.12(8)	C(1)−Ge(1)−N(1)[b]	98.14(8)	N(1)−Ge(1)−N(1)[b]	151.13(10)
C(1)−Ge(1)−Te(1)	119.73(6)	N(1)−Ge(1)−Te(1)	104.44(5)	C(8)−N(1)−Ge(1)	91.24(13)	C(8)−C(1)−Ge(1)	91.37(13)
C(1)−C(8)−N(1)	110.15(18)						
Compound **5** (Mean Values with Maximum Deviation)							
Ge(1)−C(13)	1.916(3)	Ge(1)−C(1)	2.023(3)	Ge(1)−N(2)	2.095(3)	Ge(1)−S(1)	2.239(1)
Ge(1)−N(1)	2.250(3)	S(1)−Si(4)	2.145(1)	N(1)−C(6)	1.340(4)	N(1)−C(2)	1.343(4)
N(2)−C(18)	1.341(4)	N(2)−C(14)	1.398(4)	C(1)−C(2)	1.506(4)	C(2)−C(3)	1.392(4)
C(3)−C(4)	1.375(5)	C(4)−C(5)	1.374(6)	C(5)−C(6)	1.375(5)	C(13)−C(14)	1.387(4)
C(14)−C(15)	1.434(4)	C(15)−C(16)	1.354(5)	C(16)−C(17)	1.403(5)	C(17)−C(18)	1.363(5)
C(13)−Ge(1)−C(1)	129.7(1)	C(13)−Ge(1)−N(2)	69.6(4)	C(1)−Ge(1)−N(2)	106.1(6)	C(13)−Ge(1)−S(1)	119.0(1)
C(1)−Ge(1)−S(1)	110.76(9)	N(2)−Ge(1)−S(1)	103.2(1)	C(13)−Ge(1)−N(1)	103.0(1)	C(1)−Ge(1)−N(1)	66.6(1)
N(2)−Ge(1)−N(1)	163.4(1)	S(1)−Ge(1)−N(1)	93.3(1)	Si(4)−S(1)−Ge(1)	109.1(1)	C(2)−N(1)−Ge(1)	88.6(2)
C(14)−N(2)−Ge(1)	86.0(2)	C(2)−C(1)−Ge(1)	93.4(2)	N(1)−C(2)−C(1)	111.2(3)	C(14)−C(13)−Ge(1)	93.6(2)
C(13)−C(14)−N(2)	110.8(6)						

[a] Symmetry transformations used to generate equivalent atoms: $-x,y,-z+{}^{1}/_{2}$. [b] Symmetry transformations used to generate equivalent atoms: $x-y,-y,-z+{}^{1}/_{3}$.

are carried out at higher temperatures (60 °C for **2**, 111 °C for **3**), one of the trimethylsilyl groups migrates to the chalcogen atom, yielding the dihydropyridinato compounds **5** and **6**, respectively (eq 3). This demonstrates clearly the kinetic stabilization of **2** and **3**, compared to the thermodynamically stable **5** and **6**. The tellurone **4** appears to be stable at its mp of 174 °C in the dark. Heating **4** in refluxing toluene (111 °C) for 4 h led to the formation of a red solution, but **4** could be recovered unchanged from this solution. It appears that **4**, in contrast to **2** and **3**, is thermodynamically stable even at higher temperatures.



(3)

5: X = S **6:** X = Se

We have observed a similar 1,3-trimethylsilyl shift earlier in the attempted preparation of a stannaimine by the reaction of bis[(2-pyridyl)bis(trimethylsilyl)-methyl-*C*,*N*]tin(II)[1] with sterically hindered aryl azides.[12]

The chalcogenones **2**−**4** are not attacked by atmospheric oxygen. With water, hydrolysis occurs, and 2-[bis(trimethylsilyl)methyl]pyridine is formed, together with condensed products containing Ge, O, and the corresponding chalcogen. Products conceivable by the simple addition of 1 equiv of water across the Ge−chalcogen double bond could not be detected.

X-ray structure analyses were performed for **3**−**5**. Compound **4** is the first germatellurone containing a Ge−C bond.[13] For **2**, a possible dimeric structure in solution was excluded by an osmometric molecular weight determination.

Crystal Structures. Selected bond lengths and angles are compiled in Table 1.

Compound **1** crystallizes in the space group *C*2/*c*, with two half molecules with C_2 symmetry in the asymmetric unit. Both molecules show no significant differences. The Ge−N distance (mean value 2.273(3) Å) possesses dative character, while the Ge−C bonds (mean value 2.127(4) Å) are long Ge−C single bonds compared to the value of 1.96 Å calculated by the modified Schomaker−Stevenson equation.[14] The pyridine ring of the 2-methylpyridyl ligand shows typical values for an aromatic system.

Compound **3** crystallizes in the space group $P2_1/c$ with one molecule and two disordered THF groups in the

---

(12) Ossig. G.; Meller, A.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. M. *Chem. Ber.* **1993**, *126*, 2247.

(13) Private communication by a reviewer: Recently, the first base-free germatellurones, i.e., Tbt(R)Ge = Te (tip, R = 2,4,6-triisopropylphenyl; dis, bis(trimethylsilyl)methyl; Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl) have been synthesized, and their structures have been established by X-ray crystallography (*J. Am. Chem. Soc.*, in press). Ge−Te distance: R = Tip, 2.398(1) Å; R = Dis, 2.384(2) Å.

(14) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *128*, 21.

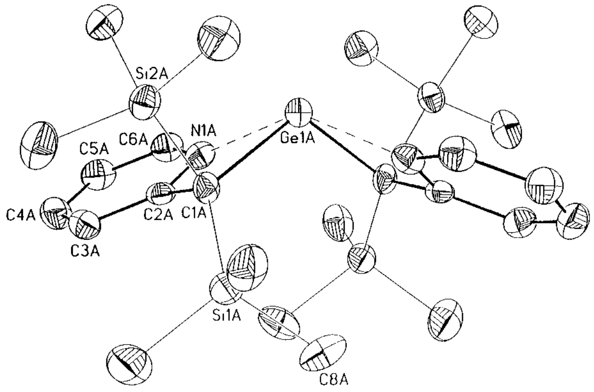


Figure 1. Crystal structure of **1**, with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

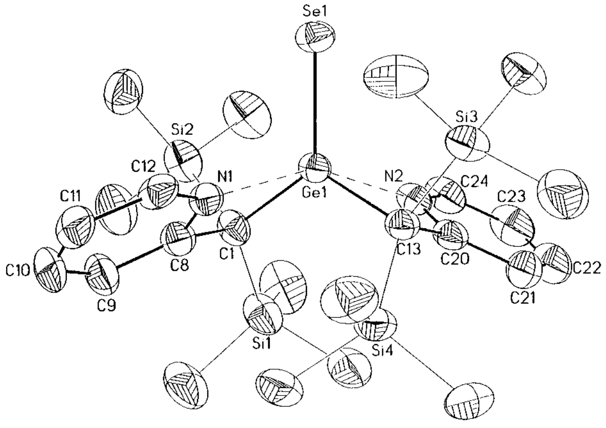


Figure 2. Crystal structure of **3**, with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the two THF molecules have been omitted for clarity.

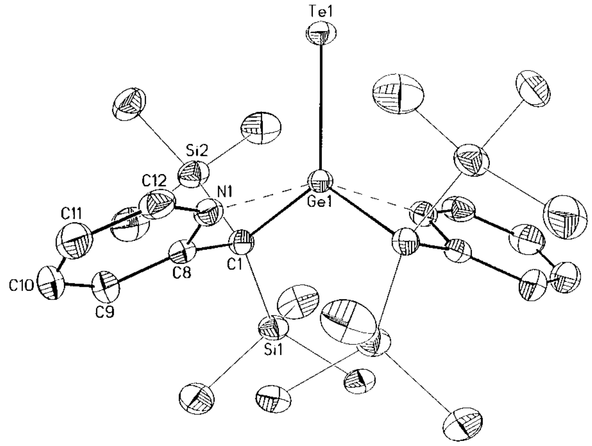


Figure 3. Crystal structure of **4**, with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

asymmetric unit, while **4** crystallizes in space group $P3_2$-21, with half of a molecule with C_2 symmetry in the asymmetric unit. Both structures are isotype, with the only significant difference being in the Ge−element bond. The Ge−Se bond distance (2.247(1) Å) is between those of a single and a double bond. It is in the same range as the magnitude of two of the three known structures of germaneselenones,[8,15] while in the third structure[6] it is nearly (2.180(2) Å) equal to a calculated double bond (2.13 Å).[14] Also, the Ge−Te bond distance (2.480(1) Å) in **4** is between those of a single and a double bond, but it is similar to that of the only yet published germatellurone (2.466(1) Å).[8] In base-free germatellurones, carrying bulky organic substituents[13] (tricoordinate Ge), the X-ray structures show Ge−Te bond lengths of 2.398(1) and 2.384(2) Å, respectively.[13] This is to be expected, considering the decreased coordination on the Ge atom. In comparison to **1**, the Ge−N distances in **3** (mean 2.169(3) Å) and **4** (2.171(2) Å) are shortened by ca. 0.1 Å but are still dative. Also, the Ge−C bonds (mean 2.053(4) Å in **3** and 2.063(2) Å in **4**) are shortened by ca. 0.07 Å. This is caused by the different oxidation state of Ge. The pyridine ring of the 2-methylpyridyl ligand is nearly unchanged.

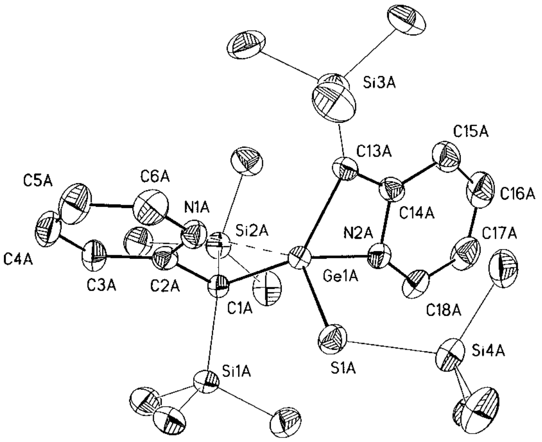


Figure 4. Crystal structure of **5**, with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

The angles of the N_2C_2Ge pyramid are widened compared to those in **1**, because the free electron pair requires more space than the double bond. The geometry around Ge is completely trigonal planar (sum of angles, 360°). The intramolecular coordination of the nitrogen atoms leads to a pseudotrigonal bipyramidal geometry. Therefore, the C−Ge−Se/Te and the C−Ge−C angles are not changed by this coordination, as would be expected with only one additional intramolecular contact, leading to pseudotetrahedral geometry.[3,16]

Compound **5** crystallizes in the space group $P\bar{1}$, with three molecules in the asymmetric unit. The three molecules show only a few significant differences. In one molecule, the Ge(1)−C(13)−Si(3) angle (141.3(2)° in comparison to 132.1(2)° and 130.8(2)°) and the C(14)−C(13)−Si(3) angle (124.6(2)° in comparison to 134.2(2)° and 134.9(2)°) are different. Additionally, the arrangement of the $SiMe_3$ group bond to sulfur is different, caused by the free rotation of the Ge−S single bond. In comparison to structure **1** in the ring Ge(1)−C(1)−C(2)−N(1), only the Ge−C(1) bond (mean 2.023(3) Å) is shortened by 0.1 Å. All other values including the 2-pyridyl ligand are nearly unchanged. In the second ring Ge(1)−C(13)−C(14)−N(2), the situation has changed. C(13) is now planar, and the C(13)−C(14) bond (mean 1.387(4) Å) shows double bond character. The Ge−C(13) bond (mean 1.916(3) Å) is shortened by 0.21 Å. The Ge(1)−N(2) bond (mean 2.095(3) Å) is shortened by 0.18 Å and is now in the range of a single bond. The

---

(15) Sheldrick, W. S.; Schaaf, B. *Z. Naturforsch.* **1994**, *49B*, 655.

(16) Arya, P.; Boyer, J.; Carré, F.; Corriu, R.; Lanneau, G.; Lapasset, J.; Perrot, M.; Priou, C. *Angew. Chem.* **1989**, *101*, 1069; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1016.

Table 2. Crystal Data and Structure Refinement Details for 1, 3, 4, and 5

	1	3	4	5
formula	$C_{24}H_{44}GeN_2Si_4$	$C_{24}H_{44}GeN_2SeSi_4 \cdot 2THF$	$C_{24}H_{44}GeN_2Si_4Te$	$C_{24}H_{44}GeN_2SSi_4$
M_r	545.56	768.73	673.16	577.62
cryst syst	monoclinic	monoclinic	trigonal	triclinic
space group	$C2/c$	$P2_1/c$	$P3_221$	$P\bar{1}$
a (Å)	23.73(2)	12.758(3)	9.558(1)	11.085(2)
b (Å)	18.25(1)	31.399(5)	9.558(1)	15.949(2)
c (Å)	15.952(8)	10.010(2)	30.439(4)	26.910(4))
α (deg)	90	90	90	96.40(1)
β (deg)	120.89(3)	93.20(1)	90	97.28(1)
γ (deg)	90	90	120	90.99(1)
V (Å^3)	5928(6)	4004(1)	2408.2(5)	4687(1)
Z	8	4	3	6
D_x (Mg/m^3)	1.223	1.275	1.393	1.228
μ (mm^{-1})	1.209	1.822	2.008	1.215
F(000)	2320	1616	1026	1836
cryst size (mm)	0.6 × 0.4 × 0.4	0.8 × 0.8 × 0.4	0.4 × 0.3 × 0.2	0.8 × 0.6 × 0.6
2θ range (deg)	8−45	4−52	4−52	7−47
range of hkl	$-25 \leq h \leq 23$	$-15 \leq h \leq 15$	$-11 \leq h \leq 5$	$-12 \leq h \leq 12$
	$-19 \leq k \leq 19$	$0 \leq k \leq 38$	$0 \leq k \leq 11$	$-17 \leq k \leq 17$
	$-3 \leq l \leq 17$	$0 \leq l \leq 12$	$0 \leq l \leq 36$	$-30 \leq l \leq 30$
no. of rflns coll	5058	39735	14464	16489
no. of indep rflns	3939	7304	2939	13787
R(int)	0.0612	0.0278	0.0195	0.0511
T_{max}	0.696	0.694	0.525	0.569
T_{min}	0.679	0.518	0.442	0.518
no. of data	3939	7304	2939	13787
no. of params	294	528	153	901
no. of restraints	0	1088	0	0
S	1.091	1.291	1.135	1.080
R_1 [$I > 2\sigma(I)$]	0.0396	0.0461	0.0162	0.0351
wR_2 (all data)	0.0903	0.0987	0.0380	0.0821
g_1	0.0123	0.0143	0.0118	0.0353
g_2	30.2081	7.7472	1.5165	2.9045
extinction coeff		0.0006(1)	0.0012(1)	
Flack[19] x param			0.007(9)	
largest diff peak	0.339	0.456	0.244	0.543
largest diff hole (e Å^{-3})	−0.532	−0.325	−0.248	−0.326

aromaticity of the pyridine ring of the 2-methylpyridyl ligand is lowered, resulting in alternating bond lengths.

The N_2C_2Ge pyramid changes from structure **3**/**4** to **5**. All angles are widened, while the S−Ge−C1/N1 angles in **5** are smaller than the Se/Te−Ge−C/N angles in **3** and **4**.

Experimental Section

All reactions were performed in an inert atmosphere of dry nitrogen in dry solvents saturated with nitrogen. Melting points were determined in sealed capillaries. Elemental analyses were performed by Mikroanalytisches Labor Beller (Göttingen, Germany). NMR spectra were recorded on Bruker AM-250 or MSL-400 instruments. Heteroelement spectra were recorded in the proton-decoupled mode. Solvents and standards used were as follows: ^{1}H, ^{13}C, ^{29}Si NMR, $CDCl_3$/TMS internal or as individually noted. Mass spectra were obtained on a Varian CH5 instrument and a Finnigan MAT 8230 (EI, 70 eV) spectrometer. 2-[Bis(trimethylsilyl)methyl]-pyridine was prepared according to refs 17 and 18.

Bis[(2-pyridyl)bis(trimethylsilyl)methyl]germanium(II) (1). A solution of BuLi in hexane (27 mL, 40 mmol, 15%) was added dropwise with stirring to 9.5 g (40 mmol) of 2-[bis(trimethylsilyl)methyl]pyridine dissolved in 150 mL of diethyl ether at ambient temperature. Stirring was continued, and after 1 h the solution was heated to reflux for 2 h. The red solution was cooled to −78 °C, and with vigorous stirring 4.6 g (20 mmol) of $GeCl_2$−dioxane (solid) was added in small portions. The reaction mixture was warmed to ambient temperature during 12 h. Volatiles were evaporated under reduced pressure, and 50 mL of hexane was added to the residue. LiCl was filtered, and **1** (orange crystals, 5.8 g, 10.6 mmol, 53% yield) was obtained after 3 days at −25 °C. The mother liquor was decanted, and the crystals were washed with two small portions of cold hexane (−78 °C); mp 129 °C dec. ^{1}H NMR (C_6D_6, TMS ext): δ 0.18 (br, s, 36H, $SiMe_3$), 6.46 (ddd, 2H, $^3J(H^4H^5) = 7.3$ Hz, $^3J(H^5H^6) = 5.3$ Hz, $^4J(H^3H^5) = 1.2$ Hz, 5-H), 6.87 (dt, 2H, $^3J(H^3H^4) = 8.2$ Hz, $^4J(H^3H^5) \approx {}^5J(H^3H^6) = 1.1$ Hz, 3-H), 7.01 (ddd, 2H, $^4J(H^4H^6) = 1.8$ Hz, 4-H), 8.09 (ddd, 2H, $^5J(H^3H^6) = 1$ Hz, 6-H). ^{13}C NMR (C_6D_6, TMS ext): δ 3.2 (br, $SiMe_3$), 36.91 ($C(SiMe_3)_2$), 118.29 (C-5), 124.76 (C-3), 136.27 (C-4), 146.67 (C-6), 171.20 (C-2). ^{29}Si NMR (C_6D_6, TMS ext): δ 2.45 (s). MS (EI; 70 eV): m/z (relative intensity) 546 (11) [M^+], 310 (81) [$M - C_5H_4NC(SiMe_3)_2{}^+$], 206 (100) [$C_5H_4NCSi_2Me_4{}^+$]. Anal. Calcd for $C_{24}H_{44}GeN_2Si_4$ (545.56): C, 52.84; H, 8.13; N, 5.13. Found: C, 52.66; H, 8.08; N, 4.90.

Preparation of Compounds 2-4. To a solution of **1** (2.0 g, 3.67 mmol) in 40 mL of toluene at ambient temperature was added an equimolar amount of chalcogen (0.12 g of S_8, 0.29 g of Se, 0.47 g of Te) with stirring. Stirring was continued for 1 h for **2** and **3** or 36 h (under exclusion of light) for **4**. The precipitated products were filtered, washed with 5 mL of toluene, and dried in vacuo. Yields obtained were as follows: **2**, pale yellow solid, 1.77 g (2.98 mmol), 81%; **3**, yellow solid, 1.80 g (2.88 mmol), 79%; and **4**, yellow to orange solid, 1.84 g (2.73 mmol), 75%. The products were recrystallized from THF (crystallization at −25 °C). Overheating of the solution (>40 °C for **2**, >60 °C for **3**) must be avoided, as otherwise a color change from yellow to red occurs, and this is indicate of decomposition. Melting (decomposition) points: **2**, >90 °C; **3**, >110 °C; **4**, 174 °C (red melt), dec in light >90 °C.

Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanethione (2). ^{1}H NMR: δ −0.07 (s, 18H), 0.37 (br, s, 18H), 7.16 (dt), 7.19 (ddd), 7.72 (ddd), 8.26 (ddd), all 2H, coupling

---

(17) Papasergio, R. I.; Raston, C. L.; White, A. H., *J. Chem. Soc., Chem. Commun.* **1983**, 1419.

(18) Izod, K. J.; Thornton, P. *Polyhedron* **1993**, *12*, 1613.

constants correspond to **1**. ^{13}C NMR: δ 3.03, 4.00, 47.23, 120.17, 123.01, 139.13, 144.39, 168.17 (assignments as for **1**). ^{29}Si NMR: δ −3.21, 7.49. MS (EI; 70 eV): *m*/*z* (relative intensity) 578 (35) [M$^+$], 563 (4) [M − Me$^+$], 73 (100) [SiMe$_3^+$]. Molecular mass (osmometric in CH_2Cl_2) found, 490. Anal. Calcd for $C_{24}H_{44}GeN_2SSi_4$ (577.62): C, 49.90; H, 7.68; N, 4.85. Found: C, 50.30; H, 7.45; N, 4.86.

Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]germaneselenone (3). ^{1}H NMR: δ −0.11 (s, 18H), 0.39 (br, s, 18H), 7.11 (dt), 7.18 (ddd), 7.69 (ddd), 8.22 (ddd), all 2H, coupling constants correspond to **1**. ^{13}C NMR (THF-d_8, TMS ext): δ 3.81, 4.50, 46.49, 121.34, 124.38, 140.04, 145.54, 169.15 (assignments as for **1**). ^{29}Si NMR (THF-d_8, TMS ext): δ −3.37, 7.39. ^{77}Se NMR (THF, C_6D_6, SeMe$_2$ ext): δ −97.64. MS (EI; 70 eV): *m*/*z* (relative intensity) 624 (5) [M$^+$], 206 (100) [$C_5H_4NCSi_2Me_4^+$]. Anal. Calcd for $C_{24}H_{44}GeN_2SeSi_4$ (624.52): C, 46.16; H, 7.10; N, 4.49. Found: C, 46.20; H, 7.11; N, 4.47.

Bis[(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]germanetellurone (4). ^{1}H NMR: δ −0.08 (s, 18H), 0.39 (br, s, 18H), 7.11 (dt), 7.23 (ddd), 7.73 (ddd), 8.18 (ddd), all 2H, coupling constants correspond to **1**. ^{13}C NMR: δ 4.17, 4.21 (br), 43.52, 120.52, 123.36, 139.19, 144.25, 168.77 (assignments as for **1**). ^{29}Si NMR: δ −3.11, 7.64. ^{125}Te NMR (THF, C_6D_6, TeMe$_2$ ext): δ −460.93. MS (EI; 70 eV): *m*/*z* (relative intensity) 674 (2) [M$^+$], 601 (1) [M − SiMe$_3^+$], 206 (100) [$C_4H_4NCSi_2Me_4^+$]. Anal. Calcd for $C_{24}H_{44}GeN_2Si_4Te$ (673.16): C, 42.82; H, 6.59; N, 4.16. Found: C, 43.04; H, 6.67; N, 3.85.

Preparation of 5 and 6. If the reactions described for the preparation of **2**−**4** were carried out at 60 °C (for **5**) or 111 °C (for **6**), respectively (heating for 4 h), deep red solutions were formed. Toluene was evaporated in vacuo, and 30 mL of hexane was added to the residue. At −25 °C, **5** crystallized as deep red crystals, mp 131 °C, yield 1.52 g (2.63 mmol), 72%; **6** formed brown-red crystals, mp 135 °C, yield 1.14 g (1.83 mmol), 50%.

(*SPY*-5-13)-[(Trimethylsilyl)thio][(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]{2-[(trimethylsilyl)methylene]-1,2-dihydropyridinato(2−)-*C,N*}germanium(IV) (5). ^{1}H NMR (C_6D_6, TMS ext): δ 0.291, 0.293, 0.35, 0.56 (4s, 9H each, SiMe$_3$), 5.53, 6.21, 6.33, 6.58, 6.73, 6.85, 7.20, 8.03 (8m, 1H each, C_5H_4N). ^{13}C NMR (C_6D_6, TMS ext): δ 2.10, 2.30, 2.79, 3.90 (all SiMe$_3$), 46.74 (*C*(SiMe$_3$)$_2$), 83.46 (C═*C*SiMe$_3$), 102.37, 113.83, 119.88, 122.39, 137.10, 138.22, 143.12, 145.54, 166.30, 169.27 (C_5H_4N). ^{29}Si NMR (C_6D_6, TMS ext): δ −14.97 (SiC═C), 2.21, 3.40 (C(SiMe$_3$)$_2$), 15.59 (S − SiMe$_3$). MS (EI; 70 eV): *m*/*z* (relative intensity): 578 (43) [M$^+$], 73 (100) [SiMe$_3^+$]. Anal. Calcd for $C_{24}H_{44}GeN_2SSi_4$ (577.62): C, 49.90; H, 7.68; N, 4.85. Found: C, 49.80; H, 7.73; N, 4.87.

(*SPY*-5-13)-[(Trimethylsilyl)seleno][(2-pyridyl)bis(trimethylsilyl)methyl-*C,N*]{(trimethylsilyl)methylene]-1,2-dihydropyridinato(2−)-*C′,N*}germanium(IV) (6). ^{1}H NMR: δ 0.02, 0.23, 0.24, 0.47 (4s, 9H each, SiMe$_3$), 5.44, 5.95, 6.61, 6.99, 7.07, 7.13, 7.70, 8.22 (8m, 1H each, C_5H_4N). ^{13}C NMR: δ 1.84, 1.88, 2.67, 3.74 (SiMe$_3$), 46.54 (*C*(SiMe$_3$)$_2$), 84.76 (*C*═CSiMe$_3$), 101.25, 113.30, 119.93, 122.31, 136.24, 138.29, 142.90, 145.36, 165.96, 168.01 (C_5H_4N). ^{29}Si NMR: δ −15.03 (C═CSiMe$_3$), 2.48, 3.40 (C(SiMe$_3$)), 13.65 (^1J(SeSi) = 112 Hz (Se − SiMe$_3$). ^{77}Se NMR (CDCl$_3$, SeMe$_2$ ext): δ −210.9. MS (EI; 70 eV): *m*/*z* (relative intensity) 624 (8) [M$^+$], 206 (100) [$C_5H_4NCSi_2Me_4^+$]. Anal. Calcd for $C_{24}H_{44}GeN_2SeSi_4$ (624.52): C, 46.16; H, 7.10; N, 4.49. Found: C, 46.06; H, 7.00; N, 4.48.

X-ray Structure Determinations for 1, 3, 4, and 5. Data of **3** and **4** were collected at −80 °C on a Stoe-Siemens-Huber diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å) using a SMART-CCD area detector. For the integration of intensities, the program SAINT[20] was used. Data of **1** and **5** were collected at −120 and −80 °C, respectively, on a Stoe-Siemens AED diffractometer with monochromated Mo Kα radiation. A semiempirical absorption correction was employed for all structures. All structures were solved by direct methods using SHELXS-90.[21] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms, the riding model was used. The structures were refined against F^2 with a weigthing scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$, with $P = (F_o^2 + 2F_c^2)/3$, using SHELXL-96.[22] The *R* values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$. Figures 1−4 (hydrogen atoms omitted) show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 2.

In structure **1**, the hydrogen atoms of C(8A) show two different rotameric conformations with occupancies of 0.57: 0.43. The two THF molecules in **3** are disordered over two (occupancies 0.52:0.48) and three positions (0.35:0.40:0.25), respectively. They were refined with distance restraints and restraints for the anisotropic displacement parameters.

Acknowledgment. Support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank Markus Teichert for assistance with X-ray structure calculations.

Supporting Information Available: For **1**, **3**, **4**, and **5**, tables of data collection parameters, displacement parameters, non-hydrogen atomic coordinates, bond distances and angles, and hydrogen coordinates and *U* values (31 pages). Ordering information is given on any current masthead page.

OM961087T

---

(19) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(20) SAINT, program for reduction and integration of diffraction data, V. 4.050, Siemens, 1996.

(21) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(22) Sheldrick, G. M. SHELXL-96, program for crystal structure refinement; University of Göttingen, Germany, 1996.