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Synthesis of Chalcogeno[3-(pyrid-2-yl)-1-azaallyl]germanium Complexes

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The reaction of [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] (**1**) and [Ge{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] (**2**) with stoichiometric amounts of elemental chalcogens in toluene affords [Ge(E){C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] [E = S (**3**), Se (**4**)] and [Ge(E){N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] [E = S (**5**), Se (**6**)], respectively. Compounds **3**–**6** were characterized by X-ray analysis.

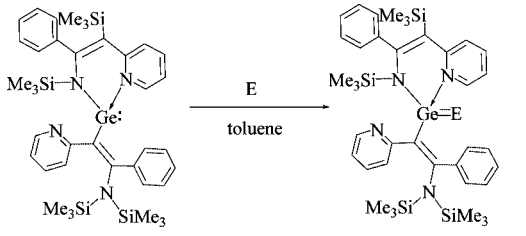
Introduction

Compounds containing a double bond between group 14 and 16 elements are considered to be unstable due to the weak pπ–pπ bonding.[1] Nevertheless, stable chalcogenogermane and -stannane (>M=E) (M = Ge, Sn; E = S, Se, Te) complexes have been isolated in the past few years.[2] These compounds are either base-stabilized or stabilized by sterically bulky protecting group. For example, [{η^4-Me_8taa}M=E] (M = Ge, Sn; E = S, Se; η^4-Me_8taa = octamethyldibenzotetraaza[14]annulene),[3] [(Tbt)(Tip)Ge=E] {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl; E = S, Se, Te},[4] and [R^N_2M=E] [R^N = CPh($SiMe_3$)C_5H_4N-2; M = Ge; E = S, Se, Te; R^N = CH($SiMe_3$)C_9H_6N-8; M = Sn; E = S, Se, Te][5] have been reported. In contrast, chalcogeno group 14 metal halide complexes [RM(E)X] are rare, and to date only the complexes [{HC(CMeNAr)$_2$}Ge(E)X] (Ar = 2,6-*i*$Pr_2C_6H_3$, Ph; E = S, Se; X = F, Cl) have been prepared and structurally characterized.[6]

Recently, we have reported the synthesis of [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] and [Ge{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] from the reaction of $GeCl_2$·dioxane with the [3-(pyrid-2-yl)-1-azaallyl]lithium complex [Li{N($SiMe_3$)C(Ph)C(R)(C_5H_4N-2)}]$_2$.[7] Herein, we report the synthesis of chalcogenogermanium complexes from the direct reaction of these complexes with elemental chalcogens.

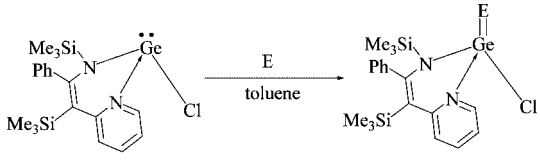
Results and Discussion

The reaction of [Ge{C(C_5H_4N-2)C(Ph)N($SiMe_3$)$_2$}{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}] (**1**) with a stoichiometric amount of elemental chalcogen in toluene afforded the thermally stable germanethione **3** and -selone **4** (Scheme 1). Similarly, treatment of [Ge{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] (**2**) with an equimolar amount of elemental chalcogen in toluene gave the thermally stable complexes [Ge(E){N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] [E = S (**5**), Se (**6**)] (Scheme 2).



1 E = S (**3**), Se (**4**)

Scheme 1.



2 E = S (**5**), Se (**6**)

Scheme 2.

Compounds **3**–**6** are yellow, crystalline solids that are soluble in Et_2O, toluene, and THF and sparingly soluble in hydrocarbon solvents. The ^{13}C NMR spectra of **3** and **4** display three sharp singlets assignable to the three types of $SiMe_3$ groups, consistent with the solid-state structure. The ^{1}H and ^{13}C NMR spectra of **5** and **6** show a similar pattern and display one set of signals due to the 3-(pyrid-2-yl)-1-azaallyl ligand.

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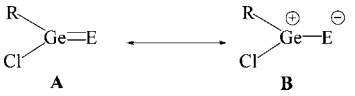
The ^{77}Se NMR spectrum of **4** displays a singlet at δ = –28.63 ppm, whereas the ^{77}Se NMR spectrum of **6** displays a singlet at δ = –266.21 ppm, which is similar to that found for [{HC(CMeNAr)$_2$}Ge(Se)Cl] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$; δ = –228 ppm). The values for **4** and **6** lie between those of [Ge{(NSiMe$_3$)$_2$}$_2$(μ-Se)]$_2$ (δ = –476.0 ppm)[8] and [(Tbt)(Tip)Ge=Se] (δ = 940 ppm).[4b] We suggest that **4** and **6** exist as intermediates between the resonance forms **A** and **B** in solution (Scheme 3).



Scheme 3.

The molecular structures, with the atom-numbering schemes, of compounds **3** and **6** are shown in Figures 1 and 2, respectively. Selected bond lengths and angles of complexes **3/4** and **5/6** are listed in Tables 1 and 2, respectively.

Compounds **3** and **4** are isostructural. The germanium center is bonded to an [2-(pyrid-2-yl)ethenyl]amido-*N*,*N*′ chelate and an η^1-alkenyl ligand in a tetrahedral geometry, with the chalcogen atom occupying the axial position. Compounds **5** and **6** are also isostructural, and the geometry around the germanium center is also tetrahedral.

The Ge–S distance of 2.094(8) Å in **3** is similar to that of 2.11 Å in [{η^4-Me$_8$taa}Ge=S][3a] and 2.063(3) Å in [(Tbt)(Tip)Ge=S],[4a] and the Ge–S distance of 2.056(2) Å in **5** is comparable to that of 2.053(6) Å in [{HC(CMeNAr)$_2$}Ge(S)Cl] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).[6a] The Ge–S distances in **3** and **5** are close to the calculated value for a Ge=S bond (2.06 Å).[9] This suggests that the resonance structure **A** contributes more than the resonance **B** (Scheme 3) in compounds **3** and **5**.

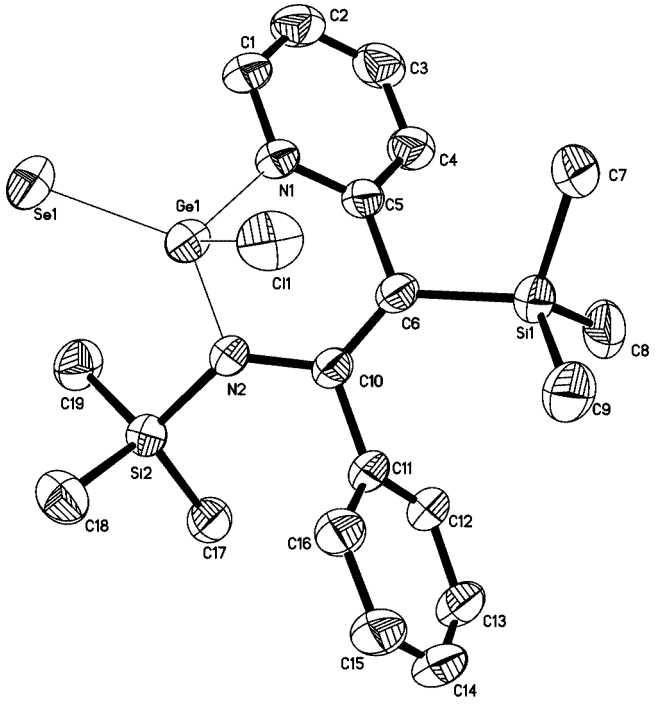


Figure 2. Molecular structure of **6**.

The Ge–Se distance of 2.223(9) Å in **4** is similar to that of 2.247(7) Å in [{C(SiMe$_3$)$_2$C$_5$H$_4$N-2}$_2$Ge=Se][10] and 2.247(1) Å in [{η^4-Me$_8$taa}Ge=Se],[3a] and the Ge–Se distance of 2.191(1) Å in **6** is comparable to that of 2.210(1) Å in [{HC(CMeNPh)$_2$}Ge(Se)Cl].[6b] The Ge–Se bond length in **4** lies between the calculated values for a Ge–Se single (2.39 Å) and double bond (2.19 Å), suggesting that the type of Ge–Se bonding in **4** lies somewhere between the reso-

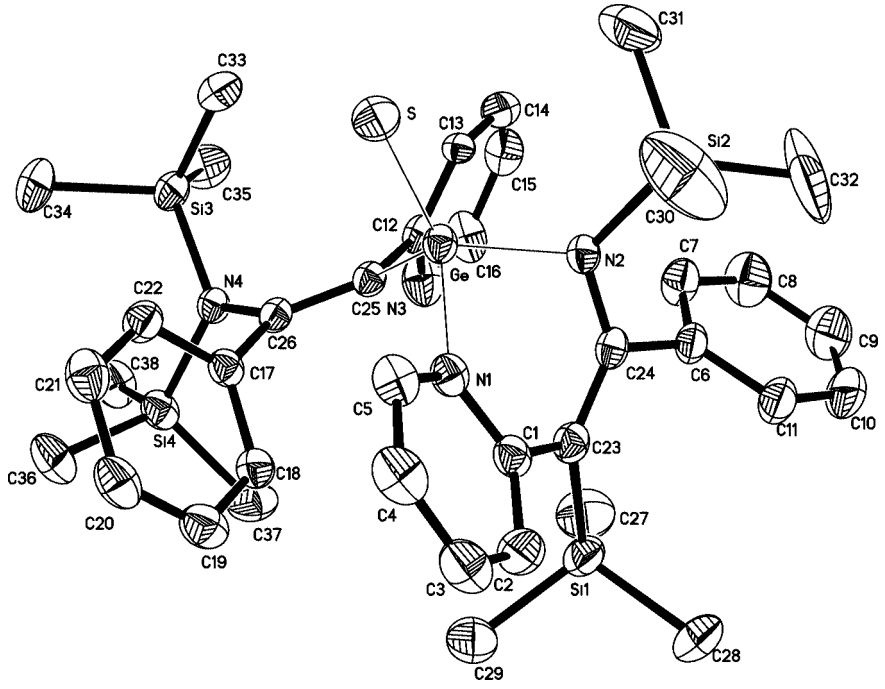


Figure 1. Molecular structure of **3**.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3** and **4**.

	3		
Ge–S	2.094(8)	Ge–N(2)	1.878(17)
Ge–N(1)	1.999(17)	Ge–C(25)	1.969(19)
C(25)–C(26)	1.349(3)	N(4)–C(26)	1.435(2)
N(4)–Si(4)	1.768(18)	Si(3)–N(4)	1.764(18)
C(12)–C(25)	1.482(3)	C(17)–C(26)	1.498(3)
N(1)–C(1)	1.357(3)	C(1)–C(23)	1.466(3)
C(23)–C(24)	1.382(3)	N(2)–C(24)	1.388(3)
Si(1)–C(23)	1.902(2)	Si(2)–N(2)	1.778(7)
N(2)–Ge–C(25)	108.4(8)	N(2)–Ge–N(1)	89.0(7)
C(25)–Ge–N(1)	109.1(8)	N(2)–Ge–S	121.2(6)
C(25)–Ge–S	117.8(6)	N(1)–Ge–S	106.9(6)
C(1)–N(1)–Ge	118.8(1)	N(1)–C(1)–C(23)	121.2(2)
C(24)–C(23)–C(1)	124.3(2)	N(4)–C(26)–C(17)	114.3(2)
C(25)–C(26)–N(4)	124.3(2)	C(26)–N(4)–Si(3)	119.0(2)
	4		
Ge–Se	2.223(9)	Ge–N(2)	1.873(3)
Ge–N(1)	1.996(3)	Ge–C(23)	1.976(4)
N(2)–C(26)	1.402(6)	C(25)–C(26)	1.399(6)
C(5)–C(25)	1.465(7)	N(1)–C(5)	1.365(6)
C(18)–C(23)	1.502(5)	C(23)–C(24)	1.345(5)
C(12)–C(24)	1.490(6)	N(4)–C(24)	1.441(4)
Si(2)–N(4)	1.757(4)	Si(1)–N(4)	1.767(3)
Si(3)–N(2)	1.762(4)	Si(4)–C(25)	1.894(5)
C(6)–C(26)	1.490(6)		
N(2)–Ge–C(23)	109.7(2)	N(2)–Ge–N(1)	88.9(1)
C(23)–Ge–N(1)	109.0 (2)	N(2)–Ge–Se	120.6(1)
C(23)–Ge–Se	116.6(1)	N(1)–Ge–Se	108.0(1)
C(18)–C(23)–Ge	111.4(3)	C(24)–C(23)–C(18)	124.1(3)
C(23)–C(24)–C(12)	120.5(3)	N(4)–C(24)–C(12)	114.9(3)
C(24)–N(4)–Si(1)	118.3(3)	Si(2)–N(4)–Si(1)	122.1(2)
C(24)–C(23)–Ge	122.3(3)	C(26)–N(2)–Ge	113.3(3)
C(26)–N(2)–Si(3)	122.8(2)	Si(3)–N(2)–Ge	121.8(2)
C(25)–C(26)–C(6)	118.5(4)	C(25)–C(26)–N(2)	125.2(4)
C(26)–C(25)–C(5)	117.6(4)	N(1)–C(5)–C(25)	120.6(4)

Table 2. Selected bond lengths [Å] and angles [°] for compounds **5** and **6**.

	[Ge(E){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl]	
	E = S (**5**)	E = Se (**6**)
Ge(1)–E(1)	2.056(2)	2.191(1)
Ge(1)–Cl(1)	2.180(2)	2.179(2)
Ge(1)–N(2)	1.840(4)	1.823(5)
N(2)–C(10)	1.392(6)	1.410(7)
C(6)–C(10)	1.388(7)	1.362(7)
C(5)–C(6)	1.475(8)	1.465(7)
C(5)–N(1)	1.345(7)	1.357(8)
N(1)–Ge(1)	1.952(5)	1.947(5)
N(1)–Ge(1)–N(2)	94.0(2)	94.5(2)
E(1)–Ge(1)–Cl(1)	116.1(8)	116.1(8)
N(2)–Ge(1)–E(1)	124.5(1)	125.8(1)
N(2)–Ge(1)–Cl(1)	103.5(2)	103.1(2)
Ge(1)–N(2)–C(10)	113.3(3)	112.9(3)
N(2)–C(10)–C(6)	124.5(5)	124.2(5)
C(10)–C(6)–C(5)	120.0(5)	120.1(5)
C(5)–N(1)–Ge(1)	119.0(4)	117.9(3)
N(1)–Ge(1)–Cl(1)	99.2(2)	99.7(2)
N(1)–Ge(1)–E(1)	114.9(2)	112.9(1)

nance structures **A** and **B**. The short Ge–Se distance in **6** indicates a double bond between germanium and selenium in the solid state.

The Ge–Cl distances of 2.180(2) Å in **5** and 2.179(2) Å in **6** are shorter than that of 2.283(9) Å in **2**. Similarly, the Ge–N$_{amide}$ distances [1.878(17) (**3**), 1.873(3) (**4**), 1.840(4) (**5**), 1.823(5) Å (**6**)] are shorter than those in the corresponding parent complexes [1.942(17) (**1**), 1.920(2) Å (**2**)].[7] This is because the germanium center in **3**–**6** has a higher oxidation state.

Conclusions

A series of chalcogeno[2-(pyrid-2-yl)-1-azaallyl]germanium complexes has been synthesized, namely [Ge(E)-{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}{N(SiMe$_3$)C(Ph)C(SiMe$_3$)-(C$_5$H$_4$N-2)}] [E = S (**3**), Se (**4**)] and [Ge(E){N(SiMe$_3$)C(Ph)-C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] [E = S (**5**), Se (**6**)]. The Ge–E bond lengths in compounds **3**–**6** are indicative of a formal double bond or a Ge–E σ-bond with significant ionic character.[6a,6b]

Experimental Section

General Remarks: All manipulations were carried out under dinitrogen by standard Schlenk techniques. Solvents were dried with, and distilled from, CaH_2 (hexane) and/or Na (Et_2O, toluene and THF). Anhydrous S and Se were purchased from Aldrich Chemicals and used without further purification. [Ge{C(C$_5$H$_4$N-2)C(Ph)-N(SiMe$_3$)$_2$}{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (**1**) and [Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)-(C$_5$H$_4$N-2)}Cl] (**2**) were prepared according to literature procedures.[7] The ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded with Bruker WM-300 or Varian 400 instruments. All spectra were recorded in [D$_8$]THF, and the chemical shifts are given relative to SiMe$_4$ (^{1}H, ^{13}C) or Se$_2$Me$_2$ (^{77}Se).

[{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}Ge=S] (3): A solution of **1** (0.73 g, 0.97 mmol) in toluene (30 mL) was added slowly to a suspension of sulfur (0.03 g, 0.97 mmol) in toluene (25 mL) at 0 °C. The yellow mixture was warmed to room temperature and stirred at room temperature for 16 h. The precipitate was filtered and the filtrate was concentrated to yield yellow crystals of **3**. Yield: 0.23 g (30%); m.p. 222–226 °C (dec.). C$_{38}$H$_{54}$GeN$_4$SSi$_4$ (783.9): calcd. C 58.22, H 6.94, N 7.14; found C 58.12, H 7.03, N 7.29. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = –0.40 (s, SiMe$_3$, 9 H), –0.12 (s, SiMe$_3$, 9 H), –0.06 (s, SiMe$_3$, 9 H), –0.03 (s, SiMe$_3$, 9 H), 6.70 (t, J = 6.5 Hz, py, 1 H), 7.21–7.32 (m, Ph, 5 H), 7.34–7.37 (m, py, 1 H), 7.40–7.47 (m, Ph, 5 H), 7.61–7.65 (m, py, 1 H), 7.77–7.79 (m, py, 1 H), 8.35 (d, J = 5.7 Hz, py, 1 H), 8.47 (d, J = 4.5 Hz, py, 1 H), 8.53 (d, J = 4.8 Hz, py, 1 H), 8.78 (d, J = 6 Hz, py, 1 H) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 1.76, 2.23, 2.76 (SiMe$_3$), 94.46 (*C*SiMe$_3$), 111.70, 119.02, 125.05, 128.49, 130.81, 132.08, 133.10, 134.44, 137.29, 140.76, 143.45, 145.18, 146.21, 147.81, 151.83, 157.03, 160.04, 162.42 (Ph and py), 163.95 (py*C*Ge), 164.26, 165.64 (N*C*Ph) ppm.

[{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}{C(C$_5$H$_4$N-2)C(Ph)N(SiMe$_3$)$_2$}Ge=Se] (4): A solution of **1** (0.75 g, 1.00 mmol) in toluene (15 mL) was added to a stirred suspension of selenium powder (0.08 g, 1.00 mmol) in toluene (15 mL) at 0 °C. The resultant yellowish-orange solution was warmed to room temperature and stirred for 18 h. Unreacted selenium powder was removed by filtration. The filtrate was concentrated and stored at –30 °C. Compound **4** was obtained as yellow crystals. Yield: 0.50 g (60%); m.p.

Table 3. Crystallographic data for compounds **3**–**6**.

	3	**4**	**5**	**6**
Empirical formula	$C_{38}H_{54}GeN_4SSi_4$	$C_{38}H_{54}GeN_4Si_4Se$	$C_{19}H_{27}ClGeN_2SSi_2$	$C_{19}H_{27}ClGeN_2Si_2Se$
Formula mass	783.86	832.78	479.71	526.61
Color	yellow	yellow	yellow	yellow
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a [Å]	11.290(2)	11.380(2)	33.234(3)	6.7285(13)
b [Å]	12.724(3)	12.722(3)	6.5646(3)	11.154(2)
c [Å]	15.977(3)	16.049(3)	21.5209(3)	16.577(3)
α [°]	77.49(3)	77.12(3)	90	86.17(3)
β [°]	89.89(3)	89.53(3)	90.750(2)	88.45(3)
γ [°]	72.51(3)	72.42(3)	90	76.08(3)
V [Å^3]	2132.1(7)	2154.9(7)	4694.8(6)	1204.8(4)
Z	2	2	8	2
$d_{calcd.}$ [g cm^{-3}]	1.221	1.283	1.357	1.452
μ [mm^{-1}]	0.910	1.697	1.616	2.998
$F(000)$	828	868	1984	532
Crystal size [mm]	0.48 × 0.46 × 0.38	0.30 × 0.21 × 0.13	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.30
2θ range [°]	2.13–24.99	1.73–25.00	1.23–28.72	1.23–25.60
Index range	$-13 \le h \le 12$	$-13 \le h \le 13$	$-38 \le h \le 44$	$-7 \le h \le 7$
	$-15 \le k \le 0$	$-14 \le k \le 15$	$-8 \le k \le 8$	$-13 \le k \le 0$
	$-18 \le l \le 18$	$0 \le l \le 19$	$-27 \le l \le 29$	$-20 \le l \le 19$
No. of reflections collected	7488	4741	16056	3778
No. of independent reflections	5814	3833	6019	3778
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0496, 0.1366	0.0771, 0.1983	0.0668, 0.1534	0.0722, 0.1955
$R1$, $wR2$ (all data)	0.0739, 0.1495	0.0972, 0.2149	0.1606, 0.2041	0.0771, 0.2043
Goodness of fit (F^2)	1.025	1.067	0.949	1.082
No. of data/restraints/parameters	7488/0/434	4741/0/447	6019/0/235	3778/0/235
Largest difference peaks [e Å^{-3}]	0.582/–0.703	0.910/–0.610	1.169/–0.582	1.029/–1.399

233–236 °C (dec.). $C_{38}H_{54}GeN_4Si_4Se$ (830.8): calcd. C 54.94, H 6.55, N 6.75; found C 55.07, H 6.63, N 6.94. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = –0.30 (s, SiMe$_3$, 9 H), –0.21 (s, SiMe$_3$, 9 H), –0.17 (s, SiMe$_3$, 9 H), 0.00 (s, SiMe$_3$, 9 H), 6.87–6.90 (m, py, 1 H), 6.91–6.94 (m, py, 1 H), 7.05–7.14 (m, Ph, 5 H), 7.16–7.18 (m, py, 1 H), 7.25–7.27 (m, py, 1 H), 7.33–7.38 (m, Ph, 5 H), 7.48–7.52 (m, py, 1 H), 7.67 (t, J = 6.9 Hz, py, 1 H), 7.98 (d, J = 4.8 Hz, py, 1 H), 8.27 (d, J = 3.9 Hz, py, 1 H) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 2.31, 2.77, 2.86 (SiMe$_3$), 114.60 (*C*SiMe$_3$), 118.94, 119.46, 124.54, 124.69, 127.60, 127.95, 128.33, 129.08, 130.99, 131.59, 135.63, 137.93, 144.30, 145.67, 147.59, 148.31, 150.69, 153.95 (Ph and py), 156.32 (py*C*Ge), 167.06, 171.49 (N*C*Ph) ppm. ^{77}Se NMR (400 MHz, [D$_8$]THF, 25 °C): δ = –28.63 ppm.

[Ge(S){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (5): A solution of **2** (0.48 g, 1.07 mmol) in toluene (15 mL) was added to a stirred suspension of sulfur powder (0.035 g, 1.09 mmol) in toluene (15 mL) at 0 °C. The resultant yellowish-orange solution was warmed to room temperature and stirred for 18 h. The precipitate was filtered and the filtrate was concentrated to yield yellow crystals of **5**. Yield: 0.28 g (54%); m.p. 250–252 °C. $C_{19}H_{27}ClGeN_2SSi_2$ (479.7): calcd. C 47.63, H 5.68, N 5.85; found C 47.36, H 5.10, N 5.85. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = –0.14 (s, SiMe$_3$, 9 H), 0.00 (s, SiMe$_3$, 9 H), 7.42–7.49 (m, 1 H, 5-py), 7.49–7.69 (m, 5 H, Ph), 7.75–7.78 (m, 1 H, 3-py), 8.25–8.26 (m, 1 H, 4-py), 9.26–9.28 (m, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 1.80, 3.11 (SiMe$_3$), 116.01 (*C*SiMe$_3$), 123.73, 128.65, 129.46, 131.48, 131.89, 132.14, 142.11, 144.80, 157.63 (Ph and py), 164.83 (N*C*Ph) ppm.

[Ge(Se){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (6): A solution of **2** (0.50 g, 1.12 mmol) in toluene (15 mL) was added to a stirred suspension of selenium powder (0.089 g, 1.13 mmol) in toluene (15 mL) at 0 °C. The resultant yellowish-orange solution was warmed to room temperature and stirred for 18 h. The precipitate was filtered and the filtrate was added to 5 mL of CH_2Cl_2 and concentrated to yield yellow crystals of **5**. Yield: 0.35 g (60%); m.p. 198–200 °C. $C_{19}H_{27}ClGeN_2Si_2Se\bullet1/2CH_2Cl_2$ (569.1): calcd. C 41.15, H 4.96, N 4.96; found C 41.41, H 5.17, N 5.17. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = –0.15 (s, SiMe$_3$, 9 H), –0.01 (s, SiMe$_3$, 9 H), 7.42–7.52 (m, 1 H, 5-py), 7.58–7.72 (m, 5 H, Ph), 7.75–7.77 (m, 1 H, 3-py), 8.24–8.25 (m, 1 H, 4-py), 9.34–9.36 (m, 1 H, 6-py) ppm. ^{13}C{^{1}H} NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 1.74, 3.47 (SiMe$_3$), 116.47 (*C*SiMe$_3$), 122.70, 127.50, 128.63, 129.52, 131.48, 132.19, 142.73, 144.83, 157.28 (Ph and py), 164.65 (N*C*Ph) ppm. ^{77}Se NMR (400 MHz, [D$_8$]THF, 25 °C): δ = –266.21 ppm.

X-ray Crystallographic Study: Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **3**–**6** were collected with a Rigaku R-AXIS II imaging plate using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **3**–**6** are summarized in Table 3. The structures were solved by direct phase determination using the computer program SHELXTL-PC[11] with 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. CCDC-292827 (**3**), -292825 (**4**) -292826 (**5**), and -292824 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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