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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

Introduction

Compounds containing a double bond between group 14 and 16 elements are considered to be unstable due to the weak $p\pi$ - $p\pi$ 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, $[{\eta^4}-$ Me₈taa}M=E] (M = Ge, Sn; E = S, Se; η^4 -Me₈taa = 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^N₂M=E] $[R^{N} = CPh(SiMe_{3})C_{5}H_{4}N-2; M = Ge; E = S, Se, Te; R^{N} =$ CH(SiMe₃)C₉H₆N-8; M = Sn; E = S, Se, Tel^[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 = $2,6-iPr_2C_6H_3$, 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 GeCl₂·dioxane with the [3-(pyrid-2-yl)-1-azaally]]ithium 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 stoichio-

 [a] Department of Chemistry, The Chinese University of Hong Kong,
 Shatin, New Territories, Hong Kong, China E-mail: kevinleung@cuhk.edu.hk (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.

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metric 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).



Scheme 1.



Scheme 2.

Compounds **3–6** are yellow, crystalline solids that are soluble in Et₂O, toluene, and THF and sparingly soluble in hydrocarbon solvents. The ¹³C NMR spectra of **3** and **4** display three sharp singlets assignable to the three types of SiMe₃ groups, consistent with the solid-state structure. The ¹H and ¹³C 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 ⁷⁷Se NMR spectrum of **4** displays a singlet at δ = -28.63 ppm, whereas the ⁷⁷Se 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*Pr₂C₆H₃; δ = -228 ppm). The values for **4** and **6** lie between those of [Ge{(NSiMe₃)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 $[\{\eta^4-Me_8taa\}Ge=S]^{[3a]}$ 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 $[\{HC(CMe-NAr)_2\}Ge(S)Cl]$ (Ar = 2,6-*i*Pr₂C₆H₃).^[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)_2C_5H_4N-2}_2Ge=Se]^[10] and 2.247(1) Å in [{ η^4 -Me_8taa}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.

$[Ge(E){N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}C]$			
	E = S(5)	$\vec{E} = Se(6)$	
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(C₅H₄N-2)C(Ph)N(SiMe₃)₂} {N(SiMe₃)C(Ph)C(SiMe₃)-(C₅H₄N-2)}] [E = S (3), Se (4)] and [Ge(E){N(SiMe₃)C(Ph)-C(SiMe₃)(C₅H₄N-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, CaH₂ (hexane) and/or Na (Et₂O, toluene and THF). Anhydrous S and Se were purchased from Aldrich Chemicals and used without further purification. [Ge{C(C₅H₄N-2)C(Ph)-N(SiMe₃)₂}{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}] (1) and [Ge{N(SiMe₃)C(Ph)C(SiMe₃)-(C₅H₄N-2)}Cl] (2) were prepared according to literature procedures.^[7] The ¹H, ¹³C, and ⁷⁷Se NMR spectra were recorded with Bruker WM-300 or Varian 400 instruments. All spectra were recorded in [D₈]THF, and the chemical shifts are given relative to SiMe₄ (¹H, ¹³C) or Se₂Me₂ (⁷⁷Se).

 $[{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}] C(C_5H_4N-2)C(Ph)N(Si-$ Me₃)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.). C38H54GeN4SSi4 (783.9): calcd. C 58.22, H 6.94, N 7.14; found C 58.12, H 7.03, N 7.29. ¹H NMR (300 MHz, [D₈]THF, 25 °C): $\delta = -0.40$ (s, SiMe₃, 9 H), -0.12 (s, SiMe₃, 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. ¹³C{¹H} NMR (300 MHz, [D₈]THF, 25 °C): δ = 1.76, 2.23, 2.76 (SiMe₃), 94.46 (CSiMe₃), 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 (pyCGe), 164.26, 165.64 (NCPh) ppm.

[{N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2)}{C(C₅H₄N-2)C(Ph)N(Si-Me₃)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.	Crystall	lographic	data	for	compounds	3-6
	~	<u> </u>			1	

	3	4	5	6
Empirical formula	C ₃₈ H ₅₄ GeN ₄ SSi ₄	C ₃₈ H ₅₄ GeN ₄ Si ₄ Se	C ₁₉ H ₂₇ ClGeN ₂ SSi ₂	C ₁₉ H ₂₇ ClGeN ₂ Si ₂ Se
Formula mass	783.86	832.78	479.71	526.61
Color	yellow	yellow	yellow	yellow
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\overline{1}$	$P\overline{1}$	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)
	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)
Ζ	2	2	8	2
$d_{\rm calcd.} [\rm gcm^{-3}]$	1.221	1.283	1.357	1.452
$\mu \text{ [mm^{-1}]}$	0.910	1.697	1.616	2.998
<i>F</i> (000)	828	868	1984	532
Crystal size [mm]	$0.48 \times 0.46 \times 0.38$	$0.30 \times 0.21 \times 0.13$	$0.50 \times 0.40 \times 0.20$	$0.50 \times 0.40 \times 0.30$
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
<i>R</i> 1, <i>wR</i> 2 [$I > 2\sigma(I)$]	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 [eÅ ⁻³]	0.582/-0.703	0.910/-0.610	1.169/-0.582	1.029/-1.399

233–236 °C (dec.). C₃₈H₅₄GeN₄Si₄Se (830.8): calcd. C 54.94, H 6.55, N 6.75; found C 55.07, H 6.63, N 6.94. ¹H NMR (300 MHz, [D₈]THF, 25 °C): δ = -0.30 (s, SiMe₃, 9 H), -0.21 (s, SiMe₃, 9 H), -0.17 (s, SiMe₃, 9 H), 0.00 (s, SiMe₃, 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. ¹³C{¹H} NMR (300 MHz, [D₈]THF, 25 °C): δ = 2.31, 2.77, 2.86 (SiMe₃), 114.60 (*C*SiMe₃), 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 (NCPh) ppm. ⁷⁷Se NMR (400 MHz, [D₈]THF, 25 °C): δ = -28.63 ppm.

[Ge(S){N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-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. C₁₉H₂₇ClGeN₂SSi₂ (479.7): calcd. C 47.63, H 5.68, N 5.85; found C 47.36, H 5.10, N 5.85. ¹H NMR (300 MHz, [D₈]THF, 25 °C): δ = -0.14 (s, SiMe₃, 9 H), 0.00 (s, SiMe₃, 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. ¹³C{¹H} NMR (300 MHz, [D₈]THF, 25 °C): δ = 1.80, 3.11 (SiMe₃), 116.01 (*C*SiMe₃), 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.

 $[Ge(Se){N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N-2)}C]$ (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 CH₂Cl₂ and concentrated to yield yellow crystals of **5**. Yield: 0.35 g (60%); m.p. 198–200 °C. C₁₉H₂₇ClGeN₂Si₂Se•1/2CH₂Cl₂ (569.1): calcd. C 41.15, H 4.96, N 4.96; found C 41.41, H 5.17, N 5.17. ¹H NMR (300 MHz, [D₈]THF, 25 °C): δ = -0.15 (s, SiMe₃, 9 H), -0.01 (s, SiMe₃, 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. ¹³C{¹H} NMR (300 MHz, [D₈]THF, 25 °C): δ = 1.74, 3.47 (SiMe₃), 116.47 (*C*SiMe₃), 122.70, 127.50, 128.63, 129.52, 131.48, 132.19, 142.73, 144.83, 157.28 (Ph and py), 164.65 (NCPh) ppm. ⁷⁷Se NMR (400 MHz, [D₈]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 ($\lambda = 0.71073$ Å) from a rotatinganode 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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FULL PAPER

- [1] J. Barrau, J. Escudié, J. Satgé, J. Chem. Rev. 1990, 90, 283.
- [2] For selected reviews and examples of chalcogenones, see: a)
 P. P. Power, Chem. Rev. 1999, 99, 3463; b) N. Tokitoh, R. Okazaki, Adv. Organomet. Chem. 2001, 47, 121; c) R. Okazaki, N. Tokitoh, Acc. Chem. Res. 2000, 33, 625; d) M. Veith, S. Becker, V. Huch, Angew. Chem. Int. Ed. Engl. 1989, 28, 1237; e) S. R. Foley, C. Bensimon, D. S. Richeson, J. Am. Chem. Soc. 1997, 119, 10359; f) T. Matsumoto, N. Tokitoh, R. Okazaki, J. Am. Chem. Soc. 1999, 121, 8811; g) N. Tokitoh, M. Saito, R. Okazaki, J. Am. Chem. Soc. 1993, 115, 2065; h) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, Organometallics 1993, 12, 2573.
- [3] a) M. C. Kuchta, G. Parkin, J. Chem. Soc., Chem. Commun.
 1994, 1351; b) M. C. Kuchta, G. Parkin, J. Am. Chem. Soc.
 1994, 116, 8372.
- [4] a) N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, J. Am. Chem. Soc. 1993, 115, 8855; b) T. Matsumoto, N. Tokitoh, R. Okazaki, Angew. Chem. Int. Ed. Engl. 1994, 33, 2316; c) N. Tokitoh, T. Matsumoto, R. Okazaki, J. Am. Chem. Soc. 1997, 119, 2337.
- [5] a) W.-P. Leung, W.-H. Kwok, Z.-Y. Zhou, T. C. W. Mak, Organometallics 2000, 19, 296; b) W.-P. Leung, W.-H. Kwok,

L. T. C. Law, Z.-Y. Zhou, T. C. W. Mak, Chem. Commun. 1996, 505.

- [6] a) Y. Ding, Q. Ma, H. W. Roesky, I. Usón, M. Noltemeyer, H. G. Schmidt, *Dalton Trans.* 2003, 1094; b) Y. Ding, Q. Ma, I. Usón, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *J. Am. Chem. Soc.* 2002, 124, 8542; c) I. Saur, G. Rima, H. Gornitzka, K. Miqueu, J. Barrau, *Organometallics* 2003, 22, 1106.
- [7] W.-P. Leung, C.-W. So, Y.-S. Wu, H.-W. Li, *Eur. J. Inorg. Chem.* 2005, 3, 513.
- [8] P. B. Hitchcock, E. Jang, M. F. Lappert, J. Chem. Soc., Dalton Trans. 1995, 3179.
- [9] L. Pauling *The Nature of The Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., **1960**, p. 224.
- [10] G. Ossig, A. Meller, C. Brönneke, O. Müller, M. Schäfer, R. Herbst-Irmer, Organometallics 1997, 16, 2116.
- G. M. Sheldrick, in Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases (Eds.: G. M. Sheldrick, C. Kruger, R. Goddard), Oxford University Press, New York, 1985, p. 175.

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