Syntheses, structures and properties of [{HC(CMeNAr)₂}Ge(E)X] (Ar = 2,6-iPr$_2$C$_6$H$_3$; E = S, Se; X = F, Cl)

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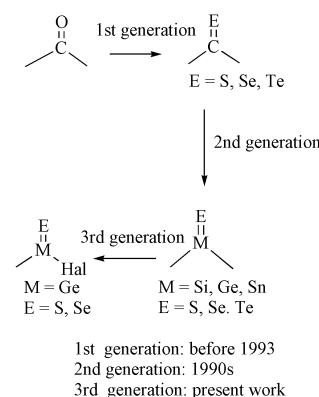
For the first time the structurally characterized heavier chalcogen analogues of alkanoyl halides, [{HC(CMeNAr)₂}Ge(S)X] (Ar = 2,6-iPr$_2$C$_6$H$_3$; X = Cl (**1**), F (**2**)) and [{HC(CMeNAr)₂}Ge(Se)X] (X = Cl (**4**), F (**5**)) have been prepared from the starting material [{HC(CMeNAr)₂}GeCl] (**3**). The nature of the germanium–chalcogen bond is best described as between the two resonance structures, Ge$^+$–E$^-$ ↔ Ge=E. The investigation of the reactivity of the germanium–halogen bond with RLi reagents (R = Me, nBu) led to the formation of [{HC(CMeNAr)₂}Ge(E)R] (E = S, R = Me (**6**); E = Se, R = Me (**7**), nBu (**8**)). The solid-state structures of **1**, **2**, **4**, **5**, **6**, and **8** are reported.

Introduction

Species containing multiple bonded heavier main group elements are important precursors for a variety of new reactions. Especially compounds with halides, where the halides can easily be replaced to synthesize a plethora of new compounds, are of great interest. Over the past few decades, the double bonds between heavier main group elements had been considered to be unstable due to their weak π bonds. However, in 1981, compounds with Si=C,[1] Si=Si,[2] and P=P[3] bonds were prepared by taking advantage of the protection from bulky ligands. After that, remarkable progress has been made in the chemistry of multiple bonded compounds of heavier main group elements. In recent years, the chemistry of formal double bonded species between Group 14 and 16 elements has received much attention, since M=E (M = C, Si, Ge, Sn, Pb; E = O, S, Se, Te) is one of the most important and fundamental functionalities in main group chemistry.[4]

Theoretical calculations show that in the carbon–oxygen double bond (ketone), the σ and π bond energies are almost equal, while in the others (heavier ketone analogues) the σ bond is much greater in energy than the corresponding π bond. Therefore, these heavier ketones are more reactive and hence the formation of one new σ bond on the metal is favorable.[5] Although the chemistry of ketones has long been established, the preparation of heavier congeners of thioketones and selenoketones appeared in the literature in 1980s and in 1993, for telluroketone.[6] Moreover, examples of M=E (M = Si, Ge, Sn; E = S, Sn, Te) were synthesized only after 1989 by taking advantage of the steric bulk of the ligand.[7–9] In contrast, the chemistry of such compounds bearing halides was neglected. We were interested in the preparation of the heavier chalcogen analogues of alkanoyl halide M(Cl)=E as potentially important precursors for the synthesis of compounds containing formal double bonded heavier main group elements (Scheme 1).

In a preliminary communication we reported on the synthesis and structures of [{HC(CMeNAr)₂}Ge(S)X] (Ar = 2,6-iPr$_2$-C$_6$H$_3$; X = Cl (**1**), F (**2**))[10] as the first structurally characterized example with a formal double bond between Group 14 and 16 elements bearing a halide by the reaction of [{HC(CMeNAr)₂}-GeCl] (**3**)[11] with elemental sulfur. In this paper we report the details of the synthesis, structures and some new findings of their properties, along with the selenium analogue [{HC-(CMeNAr)₂}Ge(Se)X] (X = Cl (**4**), F (**5**)), as well as their dehalogenated derivative [{HC(CMeNAr)₂}Ge(E)R] (E = S, Se; R = Me, nBu (**6–8**)).

1st generation: before 1993
2nd generation: 1990s
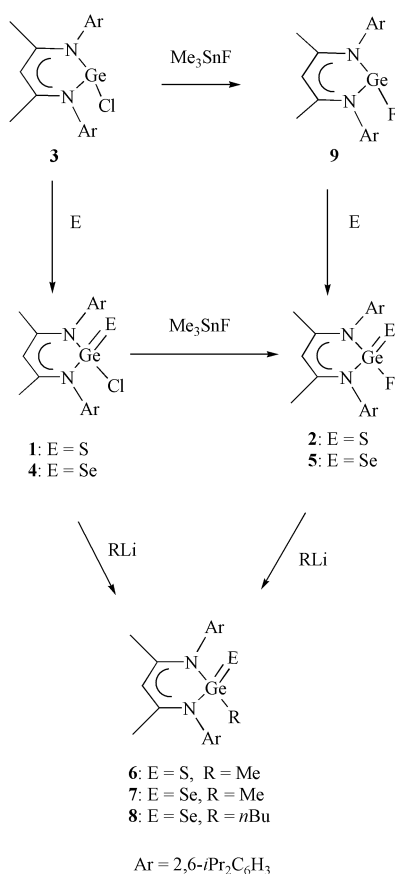3rd generation: present work

Scheme 1

Results and discussion

Syntheses and structures of compounds 1 and 4, the heavier chalcogen analogues of alkanoyl halides

Although chalcogen derivatives of the heavier Group 14 elements are reactive, such species can be stabilized by bulky ligands and are usually prepared by reaction of the divalent Group 14 compounds with elemental chalcogens.[7–9] The successful preparation of the structurally characterized germanium(II) hydride and fluoride [{HC(CMeNAr)₂}GeF] (**9**)[12] from a stable germanium(II) chloride, [{HC(CMeNAr)₂}GeCl] (**3**)[11] prompted us to synthesize [{HC(CMeNAr)₂}GeE(X)] (E = chalcogen, X = halogen). Therefore, compound **3** was treated with elemental sulfur in toluene at ambient temperature for 2 days, and after work up, [{HC(CMeNAr)₂}Ge(S)Cl] (**1**) was obtained in excellent yield (88%) (Scheme 2). With a similar procedure, however, using dichloromethane as a solvent, the selenium analogue [{HC(CMeNAr)₂}Ge(Se)Cl] (**4**) was obtained in 87% yield (Scheme 2).

Compounds **1** and **4** are soluble in toluene, THF, and dichloromethane, but only sparingly soluble in hexane and diethyl ether. They are stable in these solvents or as solids under an inert atmosphere at room temperature, no decomposition was observed under such condition for six months. However, they can be decomposed at temperatures above 225 and 230 °C, respectively.
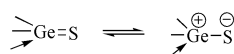
Compounds **1** and **4** were fully characterized by elemental analyses, EI-MS and multinuclear NMR spectroscopy. In the ^{1}H NMR spectra, the resonances of the methyl groups of the

Scheme 2

Fig. 1 Molecular structure of **1** in the crystal (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Ge(1)–Cl(1) 2.195(7), Ge(1)–S(1) 2.053(6), Ge(1)–N(1) 1.881(1), Ge(1)–N(2) 1.910(1); S(1)–Ge(1)–N(1) 118.87(4), S(1)–Ge(1)–N(2) 118.33(4), S(1)–Ge(1)–Cl(1) 116.82(2), N(1)–Ge(1)–N(2) 98.18(6), Cl(1)–Ge(1)–N(1) 99.51(4), Cl(1)–Ge(1)–N(2) 101.54(5).
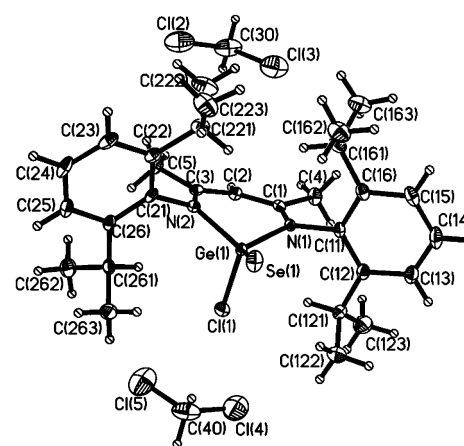
Fig. 2 Molecular structure of **4** in the crystal (50% probability thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ge(1)–Cl(1) 2.164(8), Ge(1)–Se(1) 2.197(6), Ge(1)–N(1) 1.900(2), Ge(1)–N(2) 1.901(2); Se(1)–Ge(1)–N(1) 119.20(6), Se(1)–Ge(1)–N(2) 118.93(6), Se(1)–Ge(1)–Cl(1) 116.99(3), N(1)–Ge(1)–N(2) 97.73(8), Cl(1)–Ge(1)–N(1) 100.04(7), Cl(1)–Ge(1)–N(2) 100.09(6).

aryl substituents could be distinguished due to their different environments (see Experimental section). EI-MS of **1** and **4** both gave the corresponding monomeric molecular ion peak M$^+$. The ^{77}Se NMR spectrum of **4** consists of a singlet resonance at −288 ppm. The elemental analyses are also in accordance with **1** and **4** as formulated.

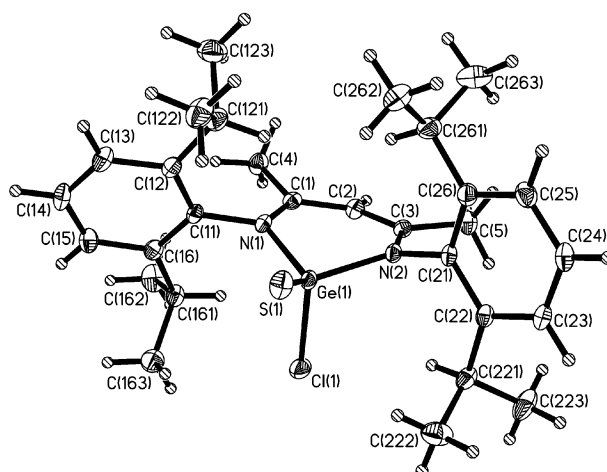One of the interests in **1** and **4** is the nature of the germanium–chalcogen bond. The property of the Ge=E bond in Tbt(Tip)Ge=E (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl; E = S (**10**), Se (**11**)) was studied and showed double bond character.[8g] The germanium–sulfur interaction in those compounds stabilized by intramolecular coordination of a base was described in terms of the resonance structures (Scheme 3) although no direct evidence was given.[8a] In our current work ^{77}Se NMR was applied to obtain more insight into the bonding properties.


Scheme 3

Studies show that the ^{77}Se chemical shift for the Ge–Se single bond in (H$_3$Ge)$_2$Se is −612 ppm (relative to Me$_2$Se).[13] In contrast, the available data for germanium selenones, R$_2$Ge=Se, show resonances at a much lower field (800–1100 ppm).[8f–h] Since the observed chemical shift for **4** is −288 ppm, it appears as though the value is somewhat between that for a single bond and those for double bond systems. This finding suggests that the resonance structure may represent the bonding interaction in **1** and **4**.

In order to obtain more information on the germanium–chalcogen interaction, pale yellow crystals of **1** and **4** were generated from toluene and dichloromethane solution, respectively, at −32 °C and determined by single crystal X-ray diffraction. The structures of **1** and **4** are shown in Figs. 1 and 2 with

selected bond lengths and bond angles in the legends. Figs. 1 and 2 show that compounds **1** and **4** are monomeric. The germanium centers adopt four-coordinated geometries and reside in a distorted tetrahedral environment. The geometries are similar to those compounds containing terminal chalcogenido germanium units.
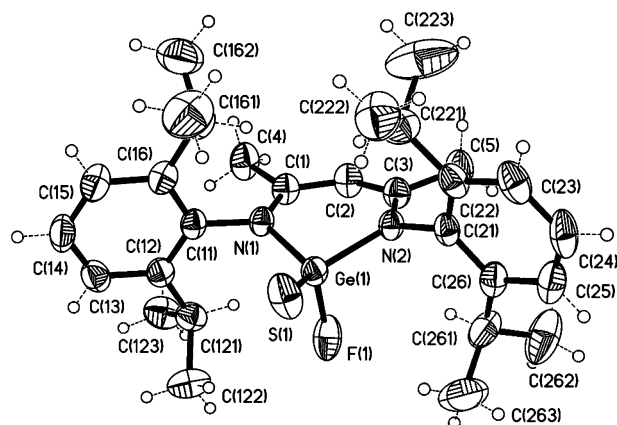
The Ge–S bond length (2.053(6) Å) in **1** which is shorter than the reported Ge–S single bond length (2.239(1) Å),[8f] is in agreement with those (2.063(3) Å[8a] and 2.045(3) Å[8g]) for Ge=S which are stabilized by an intramolecular base. The Ge–Se bond length (2.197(6) Å) in compound **4** is also in the normal range for a Ge=Se double bond (2.180(2)–2.247 Å),[8f,g] and is obviously shorter than the Ge–Se single bond in [Tbt(Mes)-GeSe]$_2$ (Mes = 2,4,6-trimethylphenyl) (2.433(1) Å).[8g] These shorter Ge=E bond lengths in **1** and **4** are indicative for a formal double bond or a Ge–E σ bond with additional significant ionic character. The Ge–Cl bond lengths in **1** (2.195(7) Å) and in **4** (2.164(8) Å) are shorter compared to those in the starting material **3** (2.295(1) Å) due to the higher oxidation state of the metal. It also influences the contact of the germanium atom with the ligand, and therefore, shorter Ge–N bond lengths (1.881(1) and 1.910(1) Å in **1**, 1.900(2) and 1.901(2) Å in **4**) are

observed when compared to those in **3** (1.988(2) and 1.997(3) Å). The N–Ge–N bond angles in **1** (98.18(6)°) and in **4** (97.73(8)°) are larger than that in **3** (90.89(10)°).

Syntheses and structures of compounds 2 and 5, the fluoro analogues of 1 and 4

We were interested in the synthesis of fluoro analogues of **1** and **4**, which may have different reactivity and structures due to the stronger electron-withdrawing property of fluorine compared to the other halogens. Therefore, [{HC(CMeNAr)$_2$}Ge(E)F] (E = S (**2**), Se (**5**)) was generated by two routes: from **1** and **4** by fluorination with Me$_3$SnF or from **9** by the oxidative addition of elemental chalcogen (Scheme 2). Both methods yield colorless crystals from toluene solutions. The ^{77}Se NMR resonance of **5** at −464 ppm is closer to the chemical shift of compounds containing germanium–selenium single bonds. This indicates the influence of the substituents on the germanium–selenium bond in **5**.

The single crystal X-ray diffraction structures of **2** and **5** were measured and depicted in Figs. 3 and 4 with selected bond lengths and bond angles. Both **2** and **5** are isostructural to the starting materials, with the replacement of chlorine by fluorine. The Ge–E bond lengths in **2** and **5** (2.050(9) and 2.176(7) Å,
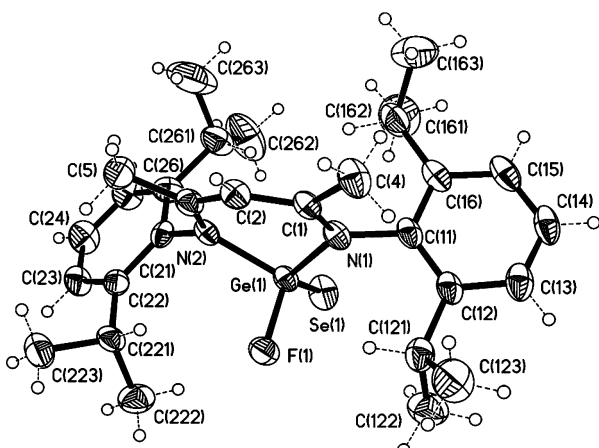
respectively) are slightly shorter compared to the corresponding precursors **1** and **4** (2.053(6) and 2.197(6) Å, respectively) due to the influence of the fluorine. The Ge–F bond lengths in **2** and **5** (1.848(2) and 1.758(3) Å, respectively) are in the expected range (1.781(10)[14] to 1.867(14) Å[15]).

Syntheses and structures of compounds 6–8, the dehalogenated derivatives of 1, 2, 4 and 5

The so far known structurally characterized compounds with formal double bonded heavier main group elements contain bulky ligands. The main interest in compounds **1**, **2**, **4** and **5** is the halogen–germanium bond which can be utilized in metathesis reactions. One routine reaction of such bonds is the treatment with alkylation reagents. Therefore, compounds **1**, **2**, **4** and **5** were treated with RLi (R = Me, nBu) at low temperatures. After work up as described in the Experimental section, crystals of the alkylated compounds [{HC(CMeNAr)$_2$}Ge(E)R] (E = S, R = Me (**6**); E = Se, R = Me (**7**), nBu (**8**)) were obtained in excellent yields (Scheme 2).

Compounds **6–8** were characterized by elemental analysis, EI-MS, ^{1}H, and ^{77}Se NMR spectroscopy. All the EI-MS gave the monomeric molecular ion peak. The other investigations are also clearly in accordance with the corresponding formula. Moreover, the composition was further confirmed by the solid-state structures of **6** and **8** as shown in Figs. 5 and 6. These show that **6** and **8** are monomeric with similar structural features of the precursors. However, Ge–E bond lengths in **6** (2.104(7) Å) and in **8** (2.219(6) Å) are longer than those in the starting materials. As a result, the fluorine compounds have the shortest Ge–E bond lengths within this series due to the strong electron-withdrawing property of the fluorine atom (Ge–S bond length: **2** (2.050(9) Å) < **1** (2.053(6) Å) < **6** (2.104(7) Å); Ge–Se bond length: **5** (2.176(7) Å) < **4** (2.197(6) Å) < **8** (2.219(6) Å)). Consequently this influences the average Ge–N bond length (**2** (1.888 Å) < **1** (1.895 Å) < **6** (1.941 Å); **5** (1.895 Å) < **4** (1.900 Å) < **8** (1.935 Å)).

Fig. 3 Molecular structure of **2** in the crystal (50% probability thermal ellipsoids). Selected bond lengths and angles (°): Ge(1)–F(1) 1.848(2), Ge(1)–S(1) 2.050(9), Ge(1)–N(1) 1.892(2), Ge(1)–N(2) 1.884(2); S(1)–Ge(1)–N(1) 120.14(7), S(1)–Ge(1)–N(2) 119.58(7), S(1)–Ge(1)–F(1) 116.57(8), N(1)–Ge(1)–N(2) 97.69(10), F(1) Ge(1)–N(1) 99.07(9), F(1)–Ge(1)–N(2), 99.61(9).
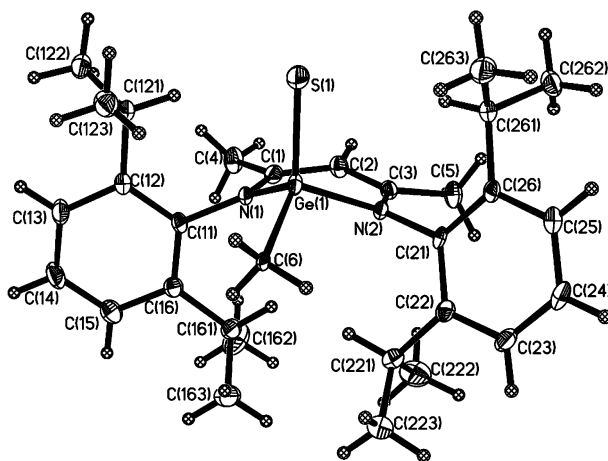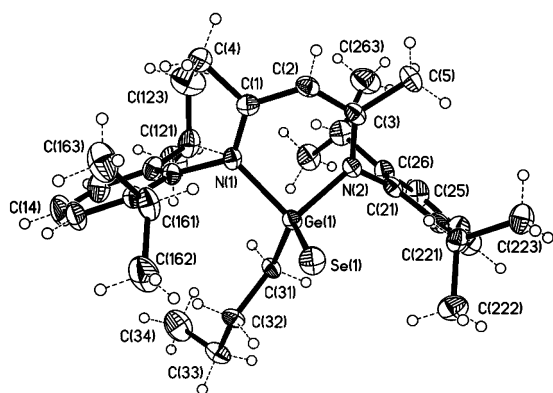

Fig. 5 Molecular structure of **6** in the crystal (50% probability thermal ellipsoids). Selected bond lengths and angles (°): Ge(1)–C(6) 2.009(2), Ge(1)–S(1) 2.104(7), Ge(1)–N(1) 1.930(2), Ge(1)–N(2) 1.952(2); S(1)–Ge(1)–N(1) 111.54(5), S(1)–Ge(1)–N(2) 110.41(5), S(1)–Ge(1)–C(6) 120.25(6), N(1)–Ge(1)–N(2) 94.15(10), C(6)–Ge(1)–N(1) 107.69(8), C(6)–Ge(1)–N(2) 109.66(8).

Fig. 4 Molecular structure of **5** in the crystal (50% probability thermal ellipsoids). Selected bond lengths and angles (°): Ge(1)–F(1) 1.758(3), Ge(1)–Se(1) 2.176(7), Ge(1)–N(1) 1.886(3), Ge(1)–N(2) 1.898(4); Se(1)–Ge(1)–N(1) 120.93(11), Se(1)–Ge(1)–N(2) 121.65(11), Se(1)–Ge(1)–F(1) 116.29(9), N(1)–Ge(1)–N(2) 97.08(16), F(1)–Ge(1)–N(1) 98.72(14), F(1)–Ge(1)–N(2) 97.17(14).

Experimental

General consideration

All manipulations were carried out using standard Schlenk techniques or in a glove box under a nitrogen atmosphere. Toluene was freshly distilled from Na, hexane from K, dichloromethane from CaH$_2$ prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für

Fig. 6 Molecular structure of **8** in the crystal (50% probability thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths and angles (°): Ge(1)–C(31) 1.961(5), Ge(1)–Se(1) 2.219(6), Ge(1)–N(1) 1.941(2), Ge(1)–N(2) 1.930(2); Se(1)–Ge(1)–N(1) 111.55(7), Se(1)–Ge(1)–N(2) 112.08(7), Se(1)–Ge(1)–C(31) 120.95(14), N(1)–Ge(1)–N(2) 94.00(11), C(31)–Ge(1)–N(1) 106.52(17), C(31)–Ge(1)–N(2) 108.29(17).

Anorganische Chemie der Universität Göttingen. A Bruker AM 200 instrument was used to record ^{1}H NMR (200.1 MHz), ^{77}Se NMR (200.1 MHz) and ^{19}F NMR (188.3 MHz) spectra, with reference to TMS, Me$_2$Se, and BF$_3$(OEt$_2$), respectively. Mass spectra were obtained on Finnigan Mat 8230. The compounds [HC(CMeNAr)$_2$GeCl][11] and [HC(CMeNAr)$_2$GeF][10] were prepared by literature procedures. Other chemicals were purchased from Aldrich and used as received.

Synthesis of [{HC(CMeNAr)$_2$}Ge(S)Cl] (1)

A solution of **3** (0.53 g, 1.0 mmol) in toluene (20 ml) was added to a stirred suspension of sulfur (0.03 g, 1.0 mmol) in toluene (10 ml). The reaction mixture was stirred at room temperature for 2 d during which time the color changed from yellow to slightly green. Storage of the reaction mixture at −32 °C for 3 d afforded greenish crystals of **1** (yield 0.49 g, 88%). Mp 225 °C (decomp). Anal. Calc. for C$_{29}$H$_{41}$ClGeN$_2$S: C, 62.45; H, 7.41; N, 5.02. Found: C, 62.31; H, 7.44; N, 5.05%. EI-MS: m/z 558 (M$^+$), 543 ([M$^+$ − Me]). ^{1}H NMR (C$_6$D$_6$): δ 0.97 (d, 6 H, CH*Me*$_2$), 1.13 (d, 6 H, CH*Me*$_2$), 1.44–1.51 (t, 18 H, CH*Me*$_2$, β-Me), 3.22–3.39 (sept, 2 H, C*H*Me$_2$), 3.50–3.75 (sept, 2 H, C*H*Me$_2$), 4.96 (s, 1 H, γ-CH), 7.08–7.10 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$).

Synthesis of [{HC(CMeNAr)$_2$}Ge(S)F] (2)

Route (a): A solution of **1** (0.56 g, 1.0 mmol) in dichloromethane (10 ml) was added to a suspension of Me$_3$SnF (0.18 g, 1.0 mmol) in dichloromethane (10 ml). The reaction mixture was stirred for 2 d at room temperature. After removal of all volatiles the residue was extracted with toluene (10 ml). Storage of the extract in a −32 °C freezer for 24 h afforded colorless crystals of **2** (yield 0.53 g, 87%). Mp 247 °C. Anal. Calc. for C$_{29}$H$_{41}$FGeN$_2$S: C, 64.35; H, 7.63; N, 5.18. Found: C, 64.30; H, 7.40; N, 5.12%. EI-MS: m/z 542 (M$^+$), 527 ([M$^+$ − Me]). ^{1}H NMR (C$_6$D$_6$): δ 1.05 (d, 6 H, CH*Me*$_2$), 1.18 (d, 6 H, CH*Me*$_2$), 1.42–1.55 (t, 18 H, β-Me, CH*Me*$_2$), 3.05–3.20 (sept, 2 H, C*H*Me$_2$), 3.40–3.55 (sept, 2 H, C*H*Me$_2$), 4.82 (s, 1 H, γ-CH), 6.95–7.10 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). ^{19}F NMR (C$_6$D$_6$): δ 49.23. Route (b): A solution of **9** (0.51 g, 1.0 mmol) in toluene (10 ml) was added to a suspension of elemental sulfur (0.03 g, 1.0 mmol) in toluene (10 ml). The reaction mixture was stirred for 2 d. After filtration and storage of the filtrate in a −32 °C freezer for 24 h crystals of **2** were afforded in 71% yield.

Synthesis of [{HC(CMeNAr)$_2$}Ge(Se)Cl] (4)

A solution of **3** (0.53 g, 1.0 mmol) in dichloromethane (10 ml) was added to a suspension of elemental selenium (0.08 g, 1.0 mmol) in dichloromethane (10 ml). The reaction mixture was

stirred for 24 h. After filtration a yellow solution was obtained. Concentration (*ca.* 10 ml) and storage of the yellow solution in a −32 °C freezer for 24 h afforded yellow crystals of **4** (yield 0.53 g, 87%). Mp 230 °C (deomp.). Anal. Calc. for C$_{29}$H$_{41}$ClGeN$_2$Se: C, 57.61; H, 6.83; N, 4.63. Found: C, 57.69; H, 6.92; N, 4.70%. EI-MS: m/z 605 (M$^+$), 590 ([M$^+$ − Me]), 526 ([M$^+$ − Se]). ^{1}H NMR (C$_6$D$_6$): δ 0.98 (d, 6 H, CH*Me*$_2$), 1.15 (d, 6 H, CH*Me*$_2$), 1.47 (d, 6 H, CH*Me*$_2$), 1.481 (s, 6 H, β-Me), 1.484 (d, 6 H, CH*Me*$_2$), 3.25–3.32 (sept, 2 H, C*H*Me$_2$), 3.62–3.70 (sept, 2 H, C*H*Me$_2$), 5.00 (s, 1 H, γ-CH), 7.08–7.15 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). ^{77}Se NMR (C$_6$D$_6$): δ −287.90.

Synthesis of [{HC(CMeNAr)$_2$}Ge(Se)F] (5)

Both procedures for **5** are similar to those for **2**. Colorless crystals of **5** were obtained. Mp 266 °C. Anal. Calc. for C$_{29}$H$_{41}$FGeN$_2$Se: C, 59.22; H, 7.03; N, 4.76. Found: C, 59.15; H, 7.15; N, 4.55%. EI-MS: m/z 589 (M$^+$), 574 ([M$^+$ − Me]). ^{1}H NMR (C$_6$D$_6$): δ 1.04 (d, 6 H, CH(C*H*$_3$)$_2$), 1.18 (d, 6 H, CH(C*H*$_3$)$_2$), 1.42–1.55 (t, 18 H, β-Me, CH(C*H*$_3$)$_2$), 3.05–3.20 (m, 2 H, C*H*(CH$_3$)$_2$), 3.40–3.60 (m, 2 H, C*H*(CH$_3$)$_2$), 4.89 (s, 1 H, γ-CH), 7.02–7.10 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). ^{19}F NMR (C$_6$D$_6$): δ 54.2. ^{77}Se NMR (C$_6$D$_6$): δ −465.1.

Synthesis of [{HC(CMeNAr)$_2$}Ge(S)Me] (6)

Route (a): A solution of MeLi (0.65 ml, 1.6 M in ether) was added to a solution of **1** (0.56 g, 1.0 mmol) in toluene (20 ml) at −42 °C. The reaction mixture was allowed to warm to room temperature and was stirred for another 2 h. After filtration and the addition of hexane (10 ml) to the filtrate, standing of the solution at room temperature for 2 d afforded yellow crystals of **6** (yield 0.38 g, 71%). Mp 192 °C. Anal. Calc. for C$_{30}$H$_{44}$GeN$_2$S: C, 67.06; H, 8.25; N, 5.21. Found: C, 67.03; H, 8.34; N, 4.86%. EI-MS: m/z 538 (M$^+$), 523 ([M$^+$ − Me]). ^{1}H NMR (C$_6$D$_6$): δ 0.76 (s, 3 H, GeMe), 1.01 (d, 6 H, CH*Me*$_2$), 1.11 (d, 6 H, CH*Me*$_2$), 1.19 (d, 6 H, CH*Me*$_2$), 1.47 (s, 6 H, β-Me), 1.64 (d, 6 H, CH*Me*$_2$), 2.95–3.05 (sept, 2 H, C*H*Me$_2$), 4.00–4.15 (sept, 2 H, C*H*Me$_2$), 4.84 (s, 1 H, γ-CH), 6.95–7.15 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). Route (b): The procedure is the same as that of route (a) except **2** was used as starting material.

Synthesis of [{HC(CMeNAr)$_2$}Ge(Se)Me] (7)

7 can be prepared from **4** and **5**, respectively. The procedure is similar to that for **6**. Mp 210–213 °C (decomp.). Anal. Calc. for C$_{30}$H$_{44}$GeN$_2$Se (584.22): C, 61.67; H, 7.58; N, 4.79. Found: C, 61.5; H, 7.5; N, 4.8. EI-MS: m/z 584 (M$^+$), 569 ([M$^+$ − Me]), 506 ([M$^+$ − Se]). ^{1}H NMR (C$_6$D$_6$): δ 1.06 (d, 6 H, CH(C*H*$_3$)$_2$), 1.09 (d, 6 H, CH(C*H*$_3$)$_2$), 1.10 (s, 3 H, GeMe), 1.25 (d, 6 H, CH(C*H*$_3$)$_2$), 1.46 (s, 6 H, β-CH$_3$), 1.63 (d, 6 H, CH(C*H*$_3$)$_2$), 2.92–3.02 (m, 2 H, C*H*(CH$_3$)$_2$), 3.80–3.90 (m, 2 H, C*H*(CH$_3$)$_2$), 4.81 (s, 1 H, γ-CH), 7.01–7.15 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). ^{77}Se NMR (C$_6$D$_6$): δ −349.

Synthesis of [{HC(CMeNAr)$_2$}Ge(Se)nBu] (8)

The procedure is the same like that for **7** except nBuLi was used as the alkylation reagent. Mp 165–168 °C. Anal. Calc. for C$_{33}$H$_{50}$GeN$_2$Se (626.20): C, 63.28; H, 8.05; N, 4.47. Found: C, 63.3; H, 8.1; N, 4.5%. EI-MS: m/z 526 (M$^+$), 491 ([M$^+$ − Se − nBu]). ^{1}H NMR (toluene-d_8): δ 0.55 (m, 3 H, (CH$_2$)$_3$C*H*$_3$), 0.80–1.10 (m, 6 H, (C*H*$_2$)$_3$CH$_3$), 0.87 (d, 6 H, CH(C*H*$_3$)$_2$), 1.01 (d, 6 H, CH(C*H*$_3$)$_2$), 1.31 (d, 6 H, CH(C*H*$_3$)$_2$), 1.53 (s, 6 H, β-CH$_3$), 1.61 (d, 6 H, CH(C*H*$_3$)$_2$), 3.20–3.30 (m, 2 H, C*H*(CH$_3$)$_2$), 4.30–4.40 (m, 2 H, C*H*(CH$_3$)$_2$), 4.93 (s, 1 H, γ-CH), 7.01–7.10 (m, 6 H, 2,6-iPr$_2$C$_6$*H*$_3$). ^{77}Se NMR (toluene-d_8): δ −297.

X-Ray crystallography

Single crystals of **1**, **2**, **4**, **5**, **6** and **8** were taken from the flask under nitrogen gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether. Diffraction data were collected

Table 1 Crystallographic data for compounds **1**, **2**, **4**, **5**, **6** and **8**

Complex	1	2	4	5	6	8
Formula	$C_{29}H_{41}ClGeN_2S$	$C_{29}H_{41}FGeN_2S\cdot$ C_7H_8	$C_{29}H_{41}ClGeN_2Se\cdot$ $2CH_2Cl_2$	$C_{29}H_{41}FGeN_2Se$	$C_{30}H_{44}GeN_2S$	$C_{35}H_{54}GeN_2Se$
M_w	557.74	633.42	774.49	588.19	537.32	654.35
Color	Pale yellow	Colorless	Pale yellow	Colorless	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
$a/Å$	16.880(3)	13.467(2)	13.176(3)	21.096(4)	12.663(3)	16.714(3)
$b/Å$	13.044(3)	16.804(3)	15.269(3)	13.380(1)	19.441(4)	10.213(2)
$c/Å$	13.801(3)	15.668(3)	18.045(4)	21.605(4)	13.350(3)	18.801(4)
$\alpha/°$	90	90	90	90	90	90
$\beta/°$	108.57(3)	92.783(16)	91.44(3)	101.514(13)	117.49(3)	90.00(3)
$\gamma/°$	90	90	90	90	90	90
$V/Å^3$	2880.5(10)	3541.5(11)	3629.2(13)	5975.9(16)	2915.4(10)	3170.1(11)
Z	4	4	4	8	4	4
$D_c/\text{g cm}^{-3}$	1.286	1.188	1.417	1.308	1.224	1.371
μ/mm^{-1}	1.248	0.945	2.238	2.268	1.142	2.141
$F(000)$	1176	1344	1584	2432	1144	1376
Crystal size/mm	$0.25 \times 0.13 \times 0.130$	$1.00 \times 0.40 \times 0.40$	$0.50 \times 0.50 \times 0.20$	$0.80 \times 0.60 \times 0.60$	$0.50 \times 0.10 \times 0.10$	$1.00 \times 0.60 \times 0.40$
2θ range/°	4.026–55.64	7.30–50.26	4.62–55.10	7.06–45.06	5.42–55.34	7.10–50.02
Index range	$-22 \le h \le 22$	$-16 \le h \le 16$	$-17 \le h \le 17$	$-22 \le h \le 22$	$-9 \le h \le 16$	$-19 \le h \le 19$
	$-17 \le k \le 15$	$-8 \le k \le 20$	$-14 \le k \le 19$	$-9 \le k \le 14$	$-25 \le k \le 25$	$-7 \le k \le 12$
	$-17 \le l \le 18$	$-18 \le l \le 18$	$-23 \le l \le 23$	$-17 \le l \le 23$	$-17 \le l \le 17$	$-14 \le l \le 22$
No.of reflns. collected	42179	9893	40850	8225	32774	5791
No. of indep. reflns. (R_{int})	6747 (0.0457)	6266 (0.0300)	8346 (0.0522)	7806 (0.0925)	6754 (0.0412)	5569 (0.0568)
$R, wR2$ ($I > 2\sigma(I)$)	0.0312, 0.0699	0.0469, 0.1239	0.0365, 0.0834	0.0440, 0.1075	0.0373, 0.0975	0.0430, 0.1029
$R, wR2$ (all data)	0.0369, 0.0721	0.0551, 0.1318	0.0553, 0.0929	0.0565, 0.1182	0.0448, 0.1032	0.0523, 0.1091
Goodness of fit, F^2	1.092	1.024	1.052	1.059	1.080	1.110
Data/restraints/ params.	6747/120/317	6266/0/381	8346/120/371	7806/0/633	6745/120/314	5569/315/350
Largest diff. peak, hole/e $Å^3$	0.355, -0.448	0.821, -0.736	0.609, -1.073	0.827, -0.593	0.953, -1.063	0.575, -1.603

on a Stoe–Siemens–Huber four-circle diffractometer coupled to a Siemens CCD area detector at 200(2) K with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXL-97.[16] All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms were included in the refinement in geometrically ideal positions. Crystallographic data are given in Table 1.

CCDC reference numbers 191193–191195, 192394, 192395 and 198629.

See http://www.rsc.org/suppdata/dt/b2/b211617k/ for crystallographic data in CIF or other electronic format.

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