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Heteronuclear Multiple Bonding between Heavier Group 14 and 16 Elements. A New Class of Germylated Compounds, the Germanethiocarbamyl and Germaneselenocarbamyl Chlorides $L^2(Cl)GeY$ (Y = S, Se)

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The first monomeric germanethiocarbamyl halides containing a chelating β-diiminate ligand, $L^2(Cl)Ge{=}Y$ (L^2 = PhNC(Me)CHC(Me)NPh; Y = S (**2**), Y = Se (**3**)), have been prepared by the reaction of the corresponding heteroleptic halogermylene $L^2(Cl)Ge$ (**1**) with elemental sulfur or black selenium in refluxing toluene. Single-crystal X-ray structural analyses of **2** and **3** reveal that the germanium centers reside in highly distorted tetrahedral environments in these compounds; short Ge−Y distances (Ge−S = 2.07 Å (**2**); Ge−Se = 2.21 Å (**3**)) are indicative of an unsaturated character of these germanium−chalcogen bonds. Selective reactions between **2** or **3** and MeLi afforded the corresponding alkylated germanechalcogenones $L^2(Me)Ge{=}Y$ (Y = S (**4**), Se (**5**)).

Introduction

The doubly bonded compounds of the heavier group 14 elements >M═M<, >M═C<, >M═Y (M = Si, Ge, Sn, Pb; Y = O, S, Se, N−R) have been long considered to be elusive intermediates, but experimental evidence for the existence of multiply bonded group 14 metal compounds has accumulated in the past few years so that now the stabilization and the chemistry of such species is well documented.[1,2] Several species possessing >M═M< and >M═C< moieties have been isolated recently, but monomeric stable compounds containing a double bond between heavier group 14 and group 16 elements still are much less numerous, particularly in the case of germanium. Only four germanethiones,[3,4e] seven germaneselones,[3b,4] and four germanetellones[3b,4a,5] have been isolated to date as stable species and structurally characterized. These compounds are either thermodynamically stabilized by coordination of Lewis bases to the germanium[3a,b,d,4a−c] (tetra- or pentacoordinate species) or kinetically stabilized using bulky protecting groups on the germanium[3c,4d,e,5] (tricoordinate species). The intrinsic character of the double bond in the thermodynamically stabilized compounds depends on the nature of the Lewis base. The species >M═Y have been obtained by different methods of synthesis. Retrocycloaddition of 1,2,3,4-trithiagermolanes,[6] reaction of divalent germanium compounds with episulfides,[3c,4b] and desulfurization of 1,2,3,4,5-tetrathiagermolanes[3c,4d,e] are the three synthetic approches to the kinetically stabilized $Ar^1Ar^2Ge{=}Y$ species. The tetra- and pentacoordinate germanechalcogenones were prepared by direct reaction of the corresponding germylene with the elemental chalcogen.[3a,b,4a,c] To our knowledge, no halogenated and also no nitrogen-, phosphorus-, oxygen-, or sulfur-substituted germanechalcogenones $\Sigma(X)Ge{=}Y$ (X = Cl, Br, I; Σ = NR_2, PR_2, OR, SR) have been described to date, probably because only a few monosubstituted halogermylenes have been characterized until now, since such $\Sigma(X)Ge$ species undergo typical reactions in which Σ and X are redistributed if the coordination site involved in the first step of this exchange reaction is not blocked by another ligand. We

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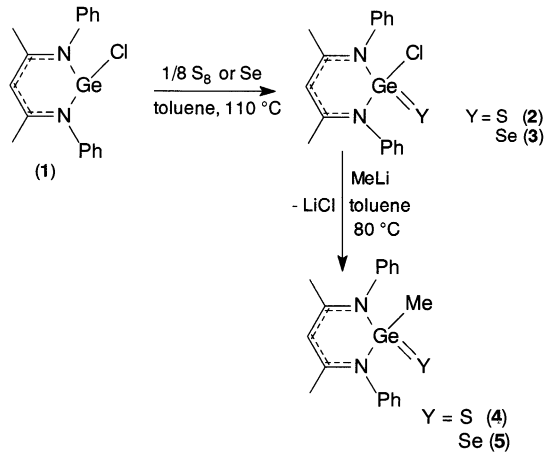
Scheme 1



have recently reported the syntheses and different aspects of the reactivity of stable divalent species of the type $\Sigma(X)Ge^{II}$ using as Σ monoanionic polydentate ligands such as a phenoxy group bearing in the 2,4,6-positions dimethylamino groups[7] or a β-diiminate.[8] In our previous general report concerning the three-coordinate divalent germanium compounds $L^2(X)Ge$ (L^2 = PhNC(Me)CHC(Me)NPh; X = Cl, I), we also have briefly described the preparation of the corresponding "germanechalcogenones", $L^2(X)Ge{=}Y$, the first examples of formal multiply bonded heavier group 14 elements bearing a halide substituent.[8] Herein we report the full details of the syntheses and the structural characterizations, along with a preliminary assessment of the reactivity, of these "halogenated germanechalcogenones", the first examples[9] of organogermanethiocarbamyl and organogermaneselenocarbamyl halides, compounds of potential interest due to the presence of a halogen substituent on the germanium atom.

Results and Discussion

Stoichiometric amounts of S_8 or black Se were added to saturated solutions of chlorogermylene L^2GeCl (**1**) in toluene (L^2 = PhNC(Me)CHC(Me)NPh) (Scheme 1). The respective mixture was heated at reflux for 3 h and then cooled to room temperature. Yellow diffraction-quality single crystals of $L^2(Cl)Ge{=}S$ (**2**) and $L^2(Cl)Ge{=}Se$ (**3**) grew slowly during this period (yields >80%). Compound **1** does not react with tellurium under these conditions.

Compounds **2** and **3** are stable under an inert atmosphere. Their high melting points (172−173 °C (**2**); 198−199 °C (**3**)) and the presence of the molecular ion peaks in their electronic impact (70 eV) mass spectra are indicative of their thermal stability. Compound **3** is less soluble than **1** and **2** in aromatic and even in polar solvents (**1** already has a very low solubility), preventing an ^{77}Se NMR study. Both compounds were fully characterized by ^1H NMR, EI-MS, and elemental analysis.[8] ^1H NMR spectra of **2** and **3** are quite similar to those of the starting material $L^2Ge(Cl)$, the equivalence of the two methyl and also of the two phenyl groups in the NMR spectra of **2** and **3** indicating the presence of C_s-symmetric species in solution.[8] The solid-state structures of **2** and **3** were determined by single-crystal X-ray diffraction. The molecular structures of compounds **2** and **3** are shown in Figures 1 and 2, respectively. Crystallographic data and processing parameters are given in Table 1.

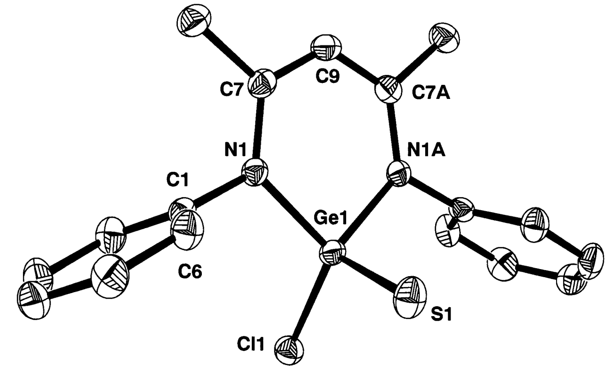


Figure 1. Solid-state structure of **2** (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and bond angles (deg): Ge−S = 2.074(1), GeCl = 2.184(1), Ge−N = 1.882(2), N−C(7) = 1.345(3), C(7)−C(9) = 1.386(3); N−Ge−N = 98.14(12), N−Ge−Cl = 103.03(6), N−Ge−S = 118.17(6), Cl−Ge−S = 113.77(4).

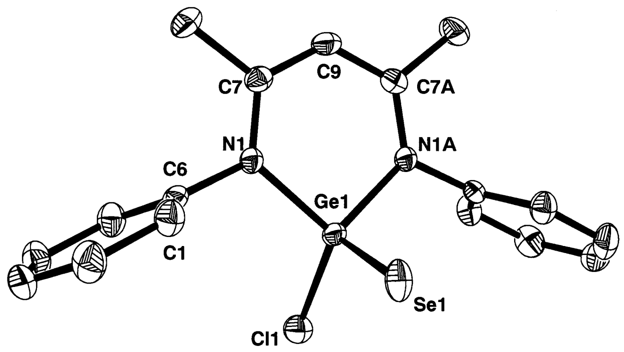


Figure 2. Solid-state structure of **3** (ellipsoids are drawn at the 50% probability level). Selected bond lengths (Å) and bond angles (deg): Ge−Se = 2.210(1), Ge−Cl = 2.215(1), Ge−N = 1.880(3), N−C(7) = 1.343(5), C(7)−C(9) = 1.386(4); N−Ge−N = 98.10(18), N−Ge−Cl = 103.78(10), N−Ge−S = 118.03(9), Cl−Ge−S = 112.88(5).

The X-ray crystallographic analyses confirm that **2** and **3** exist as monomers in the solid state. The two complexes have similar structural features; **2** and **3** show highly distorted tetrahedral geometries around the germanium centers with the dihedral angles between N(1)−Ge(1)−N(1) and Cl(1)−Ge(1)−S(1) being 90° in **2** and **3**. The angles and bond lengths of these compounds are consistent with mirror symmetry of the ligand passing through the germanium, chlorine, carbon C(9), and chalcogen atoms. Therefore, this ligand is sym-

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[9] There had been no example of isolation of a germanechalcogenocarbamyl chloride until we preliminarily reported the syntheses of **2** and **3**[8] and presented their structures (i) at the 6th International Conference on Heteroatom Chemistry, Lodz, Poland, June 22−27, 2001 (P 114) and (ii) at the Xth International Conference on the Coordination and Organometallic Chemistry of Ge, Sn and Pb, Bordeaux, France, July 8−12, 2001 (2P30). During the editing of this paper Roesky et al. described the structures of two sulfur compounds [ArNC(Me)CHC(Me)NAr](X)Ge═S (X = Cl, F), in which Ar is a sterically demanding substituent (Ar = 2,6-$iPr_2C_6H_5$). (Ding, Y.; Ma, Q.; Uson, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G. *J. Am. Chem. Soc.* **2002**, *124*, 8542).

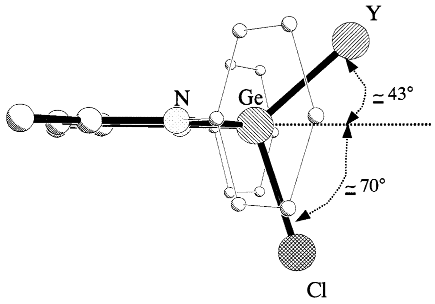


Figure 3. Side view of **2** and **3**.

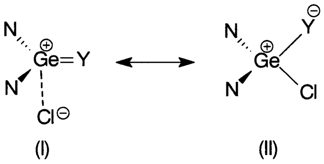
Table 1. Crystal Data and Structure Refinement Details for 2 and 3

	2	3
empirical formula	$C_{18}H_{18}Cl_4GeN_2S$	$C_{18}H_{18}Cl_4GeN_2Se$
fw	508.79	555.69
temp (K)	173(2)	173(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*
a (Å)	14.9919(9)	15.1574(13)
b (Å)	15.4408(9)	15.5540(3)
c (Å)	9.2238(6)	9.1975(8)
V (Å^3)	2135.2(2)	2168.4(3)
Z	4	4
calcd density (Mg/m^3)	1.583	1.702
abs coeff (mm^{-1})	2.038	3.590
F(000)	1024	1096
cryst size (mm^3)	0.2 × 0.3 × 0.4	0.4 × 0.5 × 0.6
θ range for data collecn (deg)	2.57−24.71	2.57−26.41
range of *hkl*	$-17 < h < 15$ $-17 < k < 18$ $-8 < l < 10$	$-18 < h < 18$ $-19 < k < 15$ $-11 < l < 11$
no. of rflns collected	10373	13792
no. of indep rflns	1888 ($R_{int} = 0.0282$)	2317 ($R_{int} = 0.0332$)
abs cor	semiempirical	semiempirical
max/min transmissn	1.000 000/0.773 640	1.000 000/0.599 268
no. of indep data	1888	2317
no. of params	128	134
goodness of fit on F^2	1.043	1.063
R1 ($I > 2\sigma(I)$)	0.0277	0.0385
wR2 (all data)	0.0673	0.1021
largest diff peak, hole (e Å^{-3})	0.869, −0.607	1.631, −1.051

metrically bound to the germanium in **2** and **3**. Contrary to what is observed for $L^2Ge(Cl)$,[10] the five ligand atoms are coplanar, the planarity being confirmed by the fact that the sums of the internal angles for the six-membered L^2Ge ring are exactly equal to 720° in **2** and **3** (Figure 3). The germanium atoms deviate from the ligand plane (N(1A), C(7A), C(7), N(1)) by only 0.044 Å (**2**) and 0.032 Å (**3**), respectively. A more marked puckering is observed in **1**, the corresponding distance of 0.53 Å being more significant in this case.[10]

Due to the change of the germanium environment (tricoordinate in **1**, tetracoordinate in **2** and **3**), the Ge−N distances in **2** and **3** (1.88 Å) are shorter by 0.08 Å than those of the corresponding bond lengths of L^2-Ge(Cl). For the same reason the Ge−Cl distances in **2** (2.18 Å) and **3** (2.22 Å) are shorter than in **1** (2.34 Å). The Ge−Y bond distances in **2** and **3** (Ge−S = 2.07 Å (**2**), Ge−Se = 2.21 Å (**3**)) are more consistent with a double than a single covalent bond, since calculations concerning $H_2Ge{=}Y$ have predicted 2.04 Å for Ge=S and 2.17 Å for Ge=Se,[5a] whereas typical Ge−Y single-bond distances are ∼2.26 Å (Y = S) and ∼2.39 Å (Y = Se), respectively.[3b] In fact, the Ge=Y bond lengths in **2** and **3** are slightly longer than those observed in the only kinetically stabilized germanechalcogenones known to date, $Ar^1Ar^2Ge{=}Y$ (Ar^1 = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl, Ar^2 = 2,4,6-triisopropylphenyl, Y = S (2.05 Å),[3c] Se (2.18 Å);[4d] Ar^2 = bis(trimethylsilyl)methyl, Y = Se (2.17 Å)[4e]). These distances can be compared to those observed for the tetra- or pentacoordinate base-stabilized compounds L^nGeY and L_2GeY (Y = S, L^n = η^3-[(μ-Bu^{t}N)$_2$(SiMeNBu^t)$_2$] (2.06 Å),[3a] η^4-[Me$_8$taa] (2.11 Å);[3b] Y = Se, L = η^2-[(2-C$_5$H$_4$N)(Me$_3$Si)$_2$C] (2.25 Å),[4a] η^2-[(C$_6$H$_{11}$)NC(^{t}Bu)N(C$_6$H$_{11}$)] (2.20 Å),[4b] η^2-[2-(C$_5$H$_4$N)-(Me$_3$Si)(Ph)C] (2.43 Å)[4c]). In fact, in these two compounds the geometries around the Ge centers are between distorted tetrahedrons and trigonal pyramids since, as shown in Figure 3, the chalcogens deviate by about 43° from the N(1)−Ge−N(1) planes and the Cl centers by about 70°. Thus, these data suggest that the germanium−chalcogen bonds in **2** and **3** can be considered as intermediate between those of the structures containing formal group 16−group 14 element double bonds (I) and those of the ylide forms presented (II), considering that an amino group is a better nucleophile than a chloride ion, in Scheme 2.

Scheme 2



The heteroleptic germanethiocarbamyl and germaneselenocarbamyl chlorides are of interest, since the presence of a halogen on the germanium atom offers numerous possibilities for the synthesis of new and unusual germylated species. The reactions of **2** and **3** with methyllithium are illustrative. We observed selective alkylation of germanium to give the germanechalcogenones $L^2(Me)Ge{=}Y$ (Y = S (**4**), Se (**5**)).

Conclusion

We have shown that β-diketiminato ligands are well-suited for preparing germanechalcogenocarbamyl chlorides, $L^2(Cl)Ge{=}Y$, underlining the influence of the stabilizing ligand on the magnitude of the Ge=Y interaction. The β-diiminate ligand PhNC(Me)CHC(Me)-NPh by its nucleophilicity and its structure appears to permit to the germanium−chalcogen bond to obtain double-bond character. It should be possible to modulate this property by designing β-diketiminato ligands with different electronic and steric properties. These mixed-ligand species, $L^2(Cl)Ge{=}Y$, are of interest as possible precursors of various unusual low-coordinate germanium species.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk and high-vacuum-line techniques. Solvents were distilled from conventional drying agents

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and degassed twice prior to use.[11] The ^{1}H and ^{13}C NMR were recorded on Bruker AC-80 and AC-200 spectrometers. All spectra were recorded in C_6D_6, and the chemical shifts δ are relative to $SiMe_4$. Mass spectra were recorded on a Nermag R10-10H or a Hewlett-Packard 5989 instrument operating in the electron impact mode at 70 eV, and samples were contained in glass capillaries under argon. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR instrument. Irradiations were carried out at 25 °C by using a low-pressure mercury immersion lamp in a quartz tube. Melting points were taken on a Leitz Biomed hot-plate microscope apparatus. Elemental analyses (C, H, N) were performed at the Microanalysis Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse.

X-ray Crystal Structure Determination of Compounds 2 and 3. Suitable yellow (**2**) and yellowish green (**3**) crystals for X-ray diffraction experiments were obtained at low temperature (−20 °C) by cooling concentrated chloroform solutions of **2** and **3**.

Crystal data for **2** and **3** are presented in Table 1. All data were collected at low temperatures on a Bruker-AXS CCD 1000 diffractometer with Mo Kα (λ = 0.710 73 Å). The structures were solved by direct methods by means of SHELXS-97[12] and refined with all data on F^2 by means of SHELXL-97.[13] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Full details of the crystallographic analysis of **2** and **3** are given in the Supporting Information.

L^2(Cl)Ge═S (2). A solution of L^2(Cl)Ge (0.29 g, 0.81 mmol) in toluene (10 mL) was added to a suspension of elemental sulfur (0.026 g, 0.81 mmol) in toluene (5 mL). The reaction mixture was heated at reflux for 3 h, during which time the reaction mixture became red. After removal of all volatiles the residue was washed with pentane and the product **2** was obtained as a green powder (0.23 g, 80%). Mp: 172−173 °C. ^{1}H NMR: δ (ppm) 1.38 (s, 6H, Me), 4.66 (s, 1H, CH), 7.00−7.10 (m, 10H, Ph). EI-MS: *m*/*z* 390 ($M^{•+}$). Anal. Calcd for $C_{17}H_{17}N_2ClSGe$ (M_r = 389.454): C, 52.43; H, 4.39; N, 7.19. Found: C, 52.98; H, 4.68; N, 6.86.

L^2(Cl)Ge═Se (3). Using the same experimental procedure as for the synthesis of **2**, the reaction of L^2(Cl)Ge (0.25 g, 0.69 mmol) with elemental selenium (0.054 g, 0.69 mmol) gave **3** as a yellowish orange solid (0.25 g, 86%). Mp: 198−199 °C. ^{1}H NMR: δ (ppm) 1.34 (s, 6H, Me), 4.67 (s, 1H, CH), 7.10−7.18 (m, 10H, Ph). EI-MS: *m*/*z* 436 ($M^{•+}$). Anal. Calcd for $C_{17}H_{17}N_2ClSeGe$ (M_r = 436.344): C, 46.79; H, 3.92; N, 6.42. Found: C, 46.12; H, 3.48; N, 6.81.

L^2(Me)Ge═S (4). A solution of MeLi (1.6 M in ether, 0.4 mL, 0.64 mmol) was added to a stirred solution of L^2Ge(Cl)S (0.25 g, 0.64 mmol) in toluene (20 mL) at 80 °C. The reaction mixture was stirred for 3 h. After filtration, the solvent was removed under vacuum, and **3** was obtained as a yellow solid (0.1 g, 42%). Mp: 158−160 °C dec. ^{1}H NMR: δ (ppm) 0.84 (s, 3H, Me), 2.01 (s, 6H, Me), 4.82 (s, 1H, CH), 7.30−7.43 (m, 10H, Ph). ^{13}C NMR: δ (ppm) 11.23 (Me), 20.60 (Me), 98.22 (CH), 125.07 (*m* aryl C), 126.21 (*p* aryl C), 128.38 (*o*-aryl C), 140.82 (C−N), 167.58 (C_{ipso}). EI-MS: *m*/*z* 370 ($M^{•+}$). Anal. Calcd for $C_{18}H_{20}N_2SGe$ (M_r = 369.038): C, 58.58; H, 5.46; N, 7.59. Found: C, 58.47; H, 5.31; N, 7.32.

L^2(Me)Ge═Se (5). The same procedure as for **4** was used for **5** (0.08 g, 30%). Mp: 140−142 °C dec. ^{1}H NMR: δ (ppm) 1.01 (s, 3H, Me), 1.98 (s, 6H, Me), 4.80 (s, 1H, CH), 7.28−7.41 (m, 10H, Ph). ^{13}C NMR: δ (ppm) 11.19 (Me), 20.40 (Me), 98.12 (CH), 124.81 (*m* aryl C), 126.12 (*p* aryl C), 127.75 (*o* aryl C), 140.32 (C−N), 167.21 (C_{ipso}). EI-MS: *m*/*z* 416 ($M^{•+}$). Anal. Calcd for $C_{18}H_{20}N_2SeGe$ (M_r = 415.928): C, 51.98; H, 4.85; N, 6.74. Found: C, 51.63; H, 4.78; N, 6.82.

Supporting Information Available: Tables giving X-ray crystallographic data and figures giving additional ORTEP views of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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