J|A|C|S
COMMUNICATIONS

Published on Web 06/28/2002

Synthesis and Structures of [{HC(CMeNAr)$_2$}Ge(S)X] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, X = F, Cl, Me): Structurally Characterized Examples with a Formal Double Bond between Group 14 and 16 Elements Bearing a Halide

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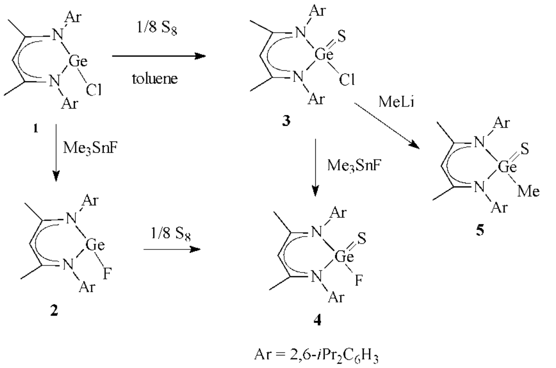
Species containing multiple bonded heavier main group elements are important precursors for a variety of new reactions. Especially of great interest are compounds with halides, where the halides can easily be replaced to synthesize a plethora of new compounds. Over the past few decades, the double bonds 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 the bulky ligands. After that, remarkable progress has been made in the chemistry of multiple bonded compounds of heavier main group elements. In recent years, interest in the chemistry of double bonded species between group 14 and 16 heavier elements M = E (M = Si, Ge, Sn; E = S, Se, Te), analogues of ketone, has remarkably increased.[4] Examples such as Si (E = S),[5] Ge (E = S, Se, Te),[6−12] and Sn (E = S, Se, Te)[13] have been synthesized and structurally characterized. In contrast, the chemistry of compounds involving multiply bonded elements bearing halides was neglected; only one example was recently reported without structural investigation.[14] 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 double bonded heavier main group elements. The preparation of a stable germanium (II) chloride, [{HC(CMeNAr)$_2$}-GeCl] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (**1**)),[15] and its conversion to the structurally characterized germanium (II) hydride and fluoride [{HC(CMeNAr)$_2$}GeF] (**2**)[16] prompted us to study the synthesis of RGe═S(X) compounds. Herein, we report on the synthesis of [{HC(CMeNAr)$_2$}Ge(S)X] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, X = Cl (**3**), F (**4**), Me (**5**)) as well as their solid structures.

Treatment of **1** with elemental sulfur in toluene at ambient temperature for 2 days smoothly afforded [{HC(CMeNAr)$_2$}Ge(S)Cl] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ (**3**)) in excellent yield (0.49 g, 88%) (Scheme 1). Slightly yellow crystals of **3** were obtained from a toluene solution at −32 °C. The fluoro analogue [{HC(CMeNAr)$_2$}-Ge(S)F] (**4**), which is expected to have a different reactivity due to the strong electron-withdrawing property compared to those of other halides, can be generated by two routes: from **3** by the fluorination with Me$_3$SnF or from **2** by the oxidative addition of elemental sulfur (Scheme 1). Both methods yield colorless crystals from toluene solutions. The reactivity of **3** was preliminarily checked by using the smallest alkylation reagent MeLi (Scheme 1). Treatment of **3** with MeLi led to the formation of [{HC(CMeNAr)$_2$}Ge(S)Me] (**5**). The thus-far known structurally characterized double bonded heavier main group elements are bound to bulky ligands. With this reaction a small alkyl group was introduced into such a system for the first time. Compounds **3**, **4**, and **5** were characterized by elemental analysis, EI-MS, ^{1}H, and ^{19}F NMR. All results are in accord with the corresponding formula.[17]

Scheme 1



The solid-state structures of **3**, **4**, and **5** were determined by single-crystal X-ray diffraction. Compound **3** crystallizes in the *P*2$_1$/*c* space group, while **4** and **5** crystallize in the space group *P*2$_1$/*n*.[18] The structures of **3**, **4**, and **5** are shown in Figures 1−3. Selected bond lengths and bond angles are given in the legends. Figures 1−3 show that compounds **3**−**5** are monomeric. The germanium centers adopt four coordinated geometries and reside in a distorted tetrahedral environment.

The Ge−S bond length (2.053(6) Å in **3**, 2.050(9) Å in **4**, and 2.104(7) Å in **5**), which is shorter than the Ge−S single bond length (2.239(1) Å),[11] is in agreement with those (2.063(3) Å[6] and 2.045(3) Å[12]) reported for Ge═S. The Ge−S bond length in **3** (2.053(6) Å) is comparable to that in **4** (2.050(9) Å) but distinctly shorter (0.051 Å) than that of **5** due to the difference of the electron-withdrawing ability among F, Cl, and Me. This property also influences the average Ge−N bond length (**4** (1.888 Å) < **3** (1.895 Å) < **5** (1.941 Å)). The Ge−Cl bond length in **3** (2.195(7) Å) is 0.10 Å shorter than that in the starting material **1** (2.295(1) Å) as expected for the higher oxidation state of the product. The Ge−F bond length in **4** (1.848(2) Å) is in the expected range (1.781(10)[19] to 1.867(14) Å[20]).

The geometries as well as the Ge−S bond length of **3**, **4**, and **5** are very close to those of the compounds containing terminal chalcogenido germanium units.[6,10] The compounds reported are stabilized by intramolecular coordination of a base shown by the resonance structure in Scheme 2.[6] The short Ge−S bond length in compounds **3**, **4**, and **5** is indicative for a double bond or a Ge−S σ bond with an additional percentage of ionic character. The Ge−Cl bond may also influence the Ge−S bond. For discussion of the double bond character, compound [Ge(Cl){C$_6$H$_3$-2,6-Mes$_2$}]$_2$[21] may be used. In this compound, the multiple character of the Ge−Ge

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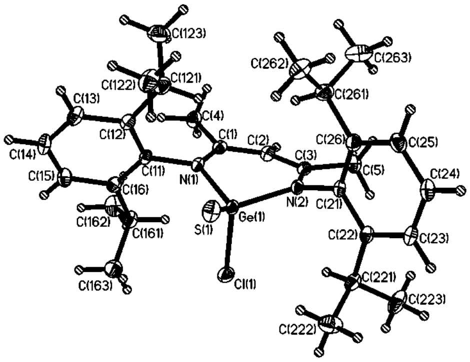


Figure 1. Molecular structure of **3** in the crystal (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Ge(1)−Cl(1) 2.195(7), Ge(1)−S(1) 2.053(6), Ge(1)−N(1) 1.881(1), Ge(1)−N(2) 1.910(1); S(1)−Ge(1)−N(1) 118.87(4), S(1)−Ge(1)−N(2) 118.33(4), S(1)−Ge(1)−Cl(1) 116.82(2), 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).

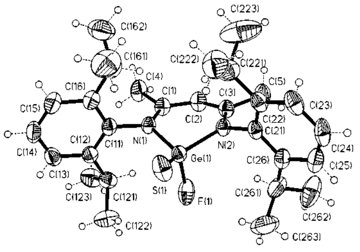


Figure 2. Molecular structure of **4** in the crystal (50% probability thermal ellipsoids). Selected bond lengths and angles (deg): Ge(1)−F(1) 1.848(2), Ge(1)−S(1) 2.050(9), Ge(1)−N(1) 1.892(2), Ge(1)−N(2) 1.884(2); S(1)−Ge(1)−N(1) 120.14(7), S(1)−Ge(1)−N(2) 119.58(7), S(1)−Ge(1)−F(1) 116.57(8), N(1)−Ge(1)−N(2) 97.69(10), F(1)−Ge(1)−N(1) 99.07(9), F(1)−Ge(1)−N(2) 99.61(9).

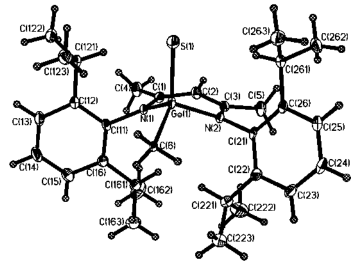
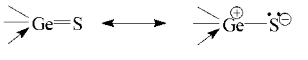


Figure 3. Molecular structure of **5** in the crystal (50% probability thermal ellipsoids). Selected bond lengths and angles (deg): Ge(1)−C(6) 2.009(2), Ge(1)−S(1) 2.104(7), Ge(1)−N(1) 1.930(2), Ge(1)−N(2) 1.952(2); S(1)−Ge(1)−N(1) 111.54(5), S(1)−Ge(1)−N(2) 110.41(5), S(1)−Ge(1)−C(6) 120.25(6), N(1)−Ge(1)−N(2) 94.15(10), C(6)−Ge(1)−N(1) 107.69(8), C(6)−Ge(1)−N(2) 109.66(8).

Scheme 2



bond is open to debate because of the significantly longer Ge−Ge bond length compared to those of other digermenes.

In summary, compounds **3** and **4** are the structurally characterized examples with a formal double bond between group 14 and 16 elements bearing a halide. The chemistry without degradation of the Ge═S bond is shown by the metathesis reaction of **3** to **4** and **5**.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Dedicated to Professor R. Usón.

Supporting Information Available: The detailed synthetic procedures, analytical and spectral characterization data (PDF). X-ray crystallographic files (CIF) for **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The physical data of **3**, **4**, and **5** are given in the Supporting Information.

(18) The structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement in geometrically ideal positions. (a) Crystallographic data for **3**: $C_{29}H_{41}ClGeN_2S$, $M_r = 557.74$, crystal size: $0.25 \times 0.13 \times 0.13$ mm^3, monoclinic, space group $P2_1/c$, $a = 16.880(3)$ Å, $b = 13.044(3)$ Å, $c = 13.801(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.57(3)°$, $V = 2880.5(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.286$ Mgm^{-3}, $F(000) = 1176$, $T = 133(2)$ K, μ (Mo Kα) = 1.248 mm^{-1}, $2.01° \leq \theta \leq 27.82°$; of the 42179 reflections collected, 6747($R_{int} = 0.0457$) were independent. The R values are R1 = 0.0312 ($I > 2\sigma(I)$) and wR2 = 0.0721 (all data); max/min residual electron density: 0.355/−0.448 e Å^{-3}. (b) Crystallographic data for **4**: $C_{36}H_{49}FGeN_2S$ incl.toluene, $M_r = 633.42$, crystal size: $1.00 \times 0.40 \times 0.40$ mm^3, monoclinic, space group $P2_1/n$, $a = 13.467(2)$ Å, $b = 16.804(3)$ Å, $c = 15.668(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 92.783(16)°$, $V = 3541.5(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.188$ Mgm^{-3}, $F(000) = 1344$, $T = 200(2)$ K, μ (Mo Kα) = 0.945 mm^{-1}, $3.65° \leq \theta \leq 25.13°$; of the 9893 reflections collected, 6266 ($R_{int} = 0.0300$) were independent. The R values are R1 = 0.0467 ($I > 2\sigma(I)$) and wR2 = 0.1318 (all data); max/min residual electron density: 0.821/−0.736 eÅ^{-3}. (c) Crystallographic data for **5**: $C_{30}H_{44}GeN_2S$, $M_r = 537.32$, crystal size: $0.50 \times 0.13 \times 0.13$ mm^3, monoclinic, space group $P2_1/n$, $a = 12.663(3)$ Å, $b = 19.441(4)$ Å, $c = 13.350(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 117.49°$, $V = 2915.4(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.224$ Mgm^{-3}, $F(000) = 1144$, $T = 133(2)$ K, μ (Mo Kα) = 1.142 mm^{-1}, $2.71 \leq \theta \leq 27.67°$; of the 32774 reflections collected, 6745 ($R_{int} = 0.0412$) were independent. The R values are R1 = 0.0373 ($I > 2\sigma(I)$) and wR2 = 0.1032 (all data); max./min. residual electron density: 0.953/−1.063 eÅ^{-3}.

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JA017645Z