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Insertion Reactions of an Aminogermylene and Formation of a Single-Source Precursor for GeTe Thin Films

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Insertion reactions between a liquid germylene **1**, and either a carbodiimide or dialkyl telluride lead to the formation of the group-14-metal(II) guanidinate complex **2** or the stable group-14-metal terminal alkyl tellurolate compound **3**, respectively. The complexes **2** and **3** were structurally elucidated by multinuclear NMR and single-crystal X-ray crystallography. The use of **3** as a single-source precursor (SSP) for the MOCVD of GeTe films was demonstrated.

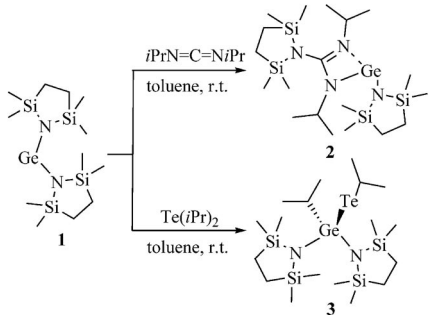
Introduction

Chalcogenide alloy films based on $Ge_2Sb_2Te_5$, GeSb and GeTe have recently been demonstrated as active components in next generation non-volatile phase-change random access memory (PRAM) and may eventually emerge as a direct replacement for dynamic random access memory (DRAM).[1] However, the availability of thermally stable and volatile monomeric germanium(II) compounds suitable for metal-organic chemical vapor deposition (MOCVD) is scarce thus limiting the potential widespread adoption of phase-change memory based on prototype GeTe thin-film materials.[2,3] Another unexplored avenue in the MOCVD of GeTe involves stoichiometric transfer of GeTe from a SSP to a growing GeTe thin film.[4]

Results and Discussion

We report herein on carbodiimide insertion into the Ge^{II}–N bond in diaminogermylene **1**[3e] to give **2**, a rare divalent group-14 guanidinate (Scheme 1).[5] Although the reactivity of group-14 metal(II) amides has been described in the literature,[6] the insertion of carbodiimides into Ge^{II}–N bonds towards divalent group-14 guanidinates such as **2** has, to the best of our knowledge, not been reported before. In a separate reaction the activation of the Te–C bond of diisopropyl telluride by **1** gave complex **3**, the first well-defined, monomeric group-14 tellurolate with a terminal Te–alkyl group (Scheme 1). Reports on M–Te bond formation by reaction of a group-14 metal(II) complex and a dialkyl telluride are unprecedented.[7]

1 [$Ge^{II}(N(Me_2SiCH_2CH_2Me_2Si))_2$]
2 [$Ge^{II}(N(SiMe_2CH_2CH_2Me_2Si))(iPrNCN(SiMe_2CH_2CH_2Me_2Si)NiPr)$]
3 [$Ge^{IV}((N(SiMe_2CH_2CH_2Me_2Si))_2)(iPr)(TeiPr)$]



Scheme 1. Reactions of germylene **1** with *i*PrNCN*i*Pr and Te*i*Pr_2.

Treatment of germylene **1** in toluene with either *i*PrNCN*i*Pr or Te(*i*Pr)$_2$ at room temperature afforded after work-up the colorless crystalline guanidinate compound **2** or the tellurolate compound **3**.[8] The solid-state structures of **2** and **3** were determined by single-crystal X-ray diffraction studies and are illustrated in Figure 1 and Figure 2, respectively.[8] There is a distorted tetrahedral coordination geometry about the Ge^{II} center in compound **2** with the stereoactive lone pair, N1, N2, and N3 occupying the coordination sites. The structure of **3** is also best described as

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distorted tetrahedral with a Ge^{IV} center surrounded by N1 and N2 from the amide ligands, C1 of the alkyl functionality, and Te1. We interpret this as oxidative addition of an alkyl–Te bond in diisopropyl telluride to **1**, where the migrated *i*Pr group is bonded to Ge through C1 in the thermal ellipsoid plot of **3**. The germanium–amide bond lengths in **2** [Ge1–N3 1.880(2) Å] and **3** [Ge1–N1 1.856(3), Ge1–N2 1.853(3) Å] are consistent with the reported data in N-heterocyclic germylenes [Ge–N1 1.856(1) Å],[3a] Ge[N(SiMe$_3$)$_2$]$_2$ [Ge–N1 1.878(5), Ge–N2 1.873(5) Å][3b] and bis heterocyclic germylenes [Ge–N1 1.856(1) Å],[3a] Ge[N(Si-(2,2,6,6-tetramethylpiperidinato)germanium [Ge–N 1.87(1), Ge–N′ 1.90(1) Å].[3c] The bond lengths between Ge^{II} and the two nitrogen atoms of the guanidinate ligand in **2** [Ge1–N1 2.0133(17), Ge1–N2 2.0328(17) Å] are slightly longer in comparison to the reported values [1.937(5) and 1.970(5) Å in Ge^{II}[Giso-N*i*Pr$_2$]Cl (Giso-N*i*Pr$_2$ = [(2,6-C$_6$H$_3$*i*Pr$_2$N)$_2$ heterocyclic germylenes [Ge–N1 1.856(1) Å],[3a] Ge[N(Si-CN*i*Pr$_2$]$^-$),[5a] 1.993(3) and 2.003(3) Å in [Ge^{II}(Giso-NCy$_2$) heterocyclic germylenes [Ge–N1 1.856(1) Å],[3a] Ge[N(Si-Cl] (Giso-NCy$_2$ = [(2,6-C$_6$H$_3$*i*Pr$_2$N)$_2$CNCy$_2$]$^-$).[5b] The distance between Ge1 and Te1 in **3** of 2.5992(6) Å is very close to the reported values in a tellurium-bridged germanium(IV) compound [Ge(N(SiMe$_3$)$_2$)$_2$(μ-Te)]$_2$ [2.599(2), 2.596(2), 2.595(2) and 2.592(2) Å][7a] and a telluradigermirane [Ar′$_4$Ge$_2$(μ-Te)] [2.597(2) Å, Ar′ = 2,6-diethylphenyl].[7c] In contrast, the Ge1–Te1 bond length is longer than those in [(4-CH$_3$C$_6$H$_4$)(C=O)]TeGePh$_3$ [2.5742(3) Å][7i] and Ge(TePh)$_4$ [2.575(1), 2.578(1), 2.582(1), 2.582(1) Å][7j] when there are aromatic substituents bound to Te. The bond length of Te1–C16 is at the upper end of the range of reported for Te–C(sp^3) distances.[3d]

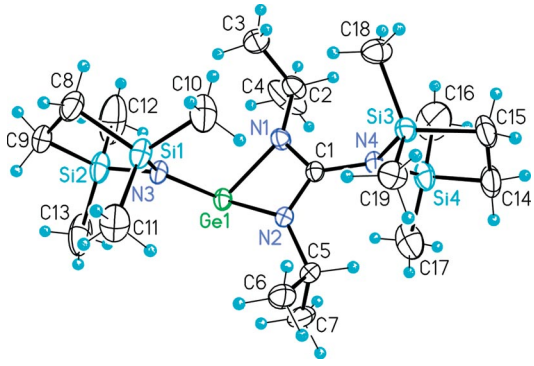

Figure 1. Thermal ellipsoid plot of **2** showing 30% thermal ellipsoids. Selected bond length [Å] and angles [°]: Ge1–N1 2.0133(17), Ge1–N2 2.0328(17), Ge1–N3 1.8796(18), C1–N1 1.321(3), C1–N2 1.344(3), C1–N4 1.401(3), N1–Ge1–N2 64.40(7), N1–Ge1–N3 103.59(8), N2–Ge1–N3 105.71(8).

The monomeric solid-state structure of **3** implies its potential use as the first SSP for MOCVD/ALD of group-14 chalcogenide films. Binary films of GeTe were deposited using precursor **3** and the stoichiometric codeposition of Ge and Te from **3** vs. deposition time (4–16 min) was moni heterocyclic germylenes [Ge–N1 1.856(1) Å],[3a] Ge[N(Si-

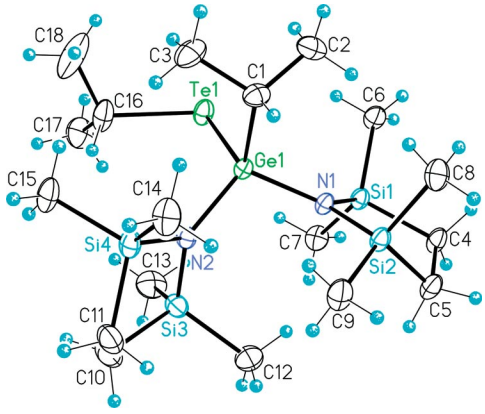

Figure 2. Thermal ellipsoid plot of **3** showing 30% thermal ellipsoids. Selected bond length [Å] and angles [°]: Ge1–N1 1.856(3), Ge1–N2 1.853(3), Ge1–C1 1.985(4), Ge1–Te1 2.5992(6), Te1–C16 2.177(4), N1–Ge1–N2 108.63(7), C1–Ge1–N1 107.38 (16), C1–Ge1–Te1 105.36(12), Te1–Ge1–N2 110.64(10).

tored by wavelength-dispersive X-ray fluorescence (XRF).[8] The XRF data confirmed a 1:1 stoichiometric growth rate for Ge and Te over a wide temperature range (Figure 3). To the best of our knowledge this is the first report confirming the 1:1 transfer of Ge and Te to a growing GeTe film deposited by MOCVD using a SSP.

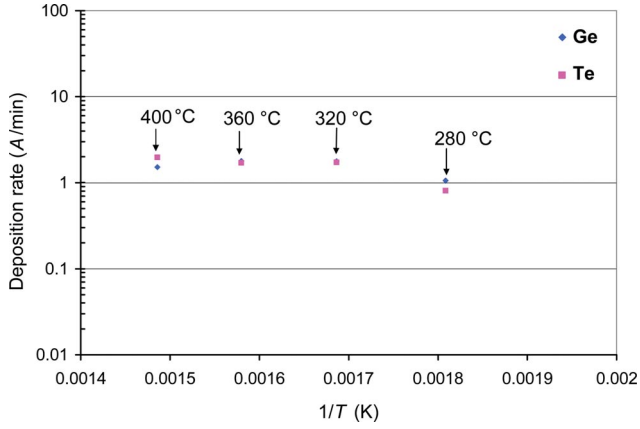

Figure 3. An Arrhenius plot showing GeTe film growth rate (log scale) as a function of the inverse substrate temperature for precursor **3** in NH_3.

Conclusions

The reactions depicted in Scheme 1 are believed to be the first of a series of transformations involving germylenes with carbodiimides and group-16 alkyl compounds. Compound **3** was shown to function as a novel SSP in the MOCVD of GeTe films providing efficient delivery and enabling superior control of the film composition in an MOCVD process.[9] In addition, compounds based on **3** may provide important starting materials for transition-metal chalcogen clusters and nanoparticles of intriguing optical and electronic properties.[10]

Experimental Section

2: *N*,*N*′-Diisopropylcarbodiimide (0.39 g, 3.09 mmol) was slowly added to a solution of **1** (1.2 g, 3.08 mmol) in toluene (10 mL) at room temperature and stirred overnight. The solvent was removed under reduced pressure to afford **2** as a pale yellow solid (1.4 g, 2.72 mmol, 88%). ^{1}H NMR (300 MHz, [D$_8$]toluene, 21 °C): δ = 0.08 (br. s, 6 H, NSiCH_3), 0.22 (br. s, 6 H, NSiCH_3), 0.46 (s, 12 H, GeNSiCH_3), 0.65 (br. m, 2 H, NSiCH_2), 0.71 (br. m, 2 H, NSiCH_2), 0.92 (s, 4 H, GeNSiCH_2), 1.25–1.27 (m, 12 H, NCH(CH_3)$_2$), 3.71 (sept, 2 H, NCH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]toluene, 21 °C): δ = 0.6 and 1.5 (NSiCH$_3$), 3.6 (GeNSiCH_3), 8.0 and 9.2 (NSiCH$_2$), 10.9 (GeNSiCH$_2$), 25.8 and 28.8 (NCH(CH$_3$)$_2$), 45.8 (NCH(CH$_3$)$_2$), 157.2 (C(NCH(CH$_3$)$_2$)$_2$) ppm. $C_{19}H_{46}GeN_4Si_4$ (515.55): calcd. C 44.26, H 8.99, N 10.87; found C 44.32, H 9.02, N 10.88. M.p. 100.7 °C. X-ray quality single-crystals were grown from a saturated diethyl ether/pentane (1:1 volume ratio) solution at –35 °C.

3: Te*i*Pr$_2$ (0.53 g, 2.47 mmol) was slowly added to a solution of **1** (1.1 g, 2.47 mmol) in toluene (10 mL) at room temperature forming a colorless/pale yellow solution and stirred overnight. The solvent was removed in vacuo to afford **3** as a brown solid (1.2 g, 1.99 mmol, 81%). ^{1}H NMR (300 MHz, [D$_8$]toluene, 21 °C): δ = 0.35 (s, 12 H, NSiCH_3), 0.40 (s, 12 H, NSiCH_3), 0.81 (ov, m, 8 H,NSiCH_2), 1.19 (d, 6 H, CH(CH_3)$_2$), 1.62 (d, 6 H, CH(CH_3)$_2$), 1.62 (sept, 1 H, CH(CH$_3$)$_2$), 3.35 (sept, 1 H, TeCH(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]toluene, 21 °C): δ = 4.0 and 4.3 (NSiCH$_3$), 10.2 (TeCH(CH$_3$)$_2$), 10.4 (NSiCH$_2$), 20.0 (GeCH-(CH$_3$)$_2$), 27.1 (GeCH(CH$_3$)$_2$), 30.4 (TeCH(CH$_3$)$_2$) ppm. $C_{18}H_{46}GeN_2Si_4Te$ (603.12): calcd. C 35.85, H 7.69, N 4.64; found C 35.87, H 7.82, N 4.66. M.p. 72.1 °C. X-ray quality single-crystals were grown from a saturated diethyl ether/pentane (1:1 volume ratio) solution at –35 °C.

Supporting Information (see also the footnote on the first page of this article): The synthesis and characterization of complex **1**, the crystal structure of its starting material lithium (2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentanide)·thf and all the thermal data of **1**, **2** and **3**.

CCDC-701973 [for lithium (2,2,5,5-tetramethyl-2,5-disila-1-azacyclopentadienide)·thf], -701974 (for **2**) and -701975 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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