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A Base-Stabilized Germylenyl Silaneditelluroate and 1,3-Diaza-2-silaallylgermylene

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Abstract: The trapping of a transient base-stabilized germylenylsilylene by elemental tellurium and arylazide is described. The reaction of the potassium 2-imino-5,6-methylenedioxyphenylgermylidenide [$L_{\text{iminophenyl}}\text{GeK}$] ($L_{\text{iminophenyl}}$ = 2-imino-5,6-methylenedioxyphenyl) with the amidinato chlorosilylene [$L_{\text{amidinate}}\text{SiCl}$] ($L_{\text{amidinate}}$ = $\text{PhC}(\text{N}t\text{Bu})_2$) in THF at -78°C afforded the transient base-stabilized germylenylsilylene [$L_{\text{amidinate}}\text{SiGe}L_{\text{iminophenyl}}$] (**3**). It was unstable in solution, but can be trapped by reacting with elemental tellurium and 2,6-diisopropylphenylazide ArN_3 (Ar = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$) to form the first base-stabilized germylenyl silaneditelluroate [$L_{\text{iminophenyl}}\text{GeTeSi}(=\text{Te})L_{\text{amidinate}}$] (**4**) and 1,3-diaza-2-silaallylgermylene complex [$\{L_{\text{amidinate}}\text{Si}(\text{NAr})_2\text{Ge}L_{\text{iminophenyl}}\}$] (**5**), respectively. In these reactions, elemental tellurium and ArN_3 insert into the $:\text{Si}-\text{Ge}$: bond in **3**, followed by oxidation of the Si center with the substrates to form compounds **4** and **5**, respectively. Compounds **4** and **5** were characterized by X-ray crystallography.

Introduction

Silanylidenide, germylidenide, stannylidenide, and plumblylidenide anions of composition $[\text{RE}^-]$ (E = Si, Ge, Sn, Pb; R = supporting ligands) are low valent group 14 element anionic compounds comprising two lone pairs of electrons on the group 14 elements. They show possible application in the formation of interconnected heterobinuclear σ -bond using salt elimination reaction. The first germylidenide anion $[\text{Ge}\{\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(\text{Ar})\}]^-$ (Ar = 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$) was afforded by the reduction of the β -diketiminato chlorogermylene $[\text{HC}\{\text{C}(\text{Me})\text{N}(\text{Ar})\}_2\text{GeCl}]$ with two equivalents of lithium, whereby a number of steps, including reductive ring contraction reactions, were involved in the synthesis.^[1] Our group then showed that the 2,6-bis(imino)phenyl-stabilized germylidenide,^[2] stannylidenide,^[3] and plumblylidenide anions^[4] $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\text{E}^-]$ (E = Ge, Sn, Pb; R = Ar or $t\text{Bu}$) were isolated by the reduction of the corresponding chlorotetrylene with excess alkali metal. The reaction proceeded through the formation of the group 14 element(I) radical intermediate $[\{2,6-(\text{HCNR})_2\text{C}_6\text{H}_3\}\text{E}^\cdot]$,^[5] which subsequently underwent a further one-electron reduction to form the anions. In addition, the cyclic alkyl(amino) carbene-stabilized silanylidenide anion $[(\text{cAAC})\text{Si}(\text{Tip})]^-$ (cAAC

= $:\text{CC}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_2\text{NAr}$, Tip = 2,4,6-triisopropylphenyl) was afforded by the reduction of the aryltrichlorosilane $[\text{TipSiCl}_3]$ with KC_8 and cyclic alkyl(amino) carbene, where the Si lone pair of electrons in the anion are stabilized by the π -back bonding to the cAAC ligand.^[6]

However, the above anionic compounds are seldom used to undergo salt elimination reaction with group 14 element(II) halides to form low-valent heterobinuclear group 14 element complexes $[\text{RE}-\text{E}'\text{R}']$. It is because the reactive $\text{E}-\text{E}'$ moiety makes such complexes difficult to isolate. Thus far, only a handful of examples were reported, where the sterically hindered germylidenide anions $[\text{Ge}\{\text{C}(\text{R}^1)\text{C}(\text{R}^2)\text{C}(\text{R}^1)\text{N}(\text{Ar})\}]^-$ (R^1 = Me/Ph, R^2 = H/Ph) reacted with the β -diketiminato chlorostannylene and amidinato chlorosilylene to form the corresponding base-stabilized germylenylstannylene and -silylene.^[7] Interestingly, their reactivity was never reported. Considering that low-valent heterobinuclear group 14 element complexes possess exceptional electronic structure, they should be promising building blocks to give rise hitherto unknown compounds. In this paper, we report that a transient base-stabilized germylenylsilylene serves as a synthon in the preparation of a novel germylenyl silaneditelluroate and 1,3-diaza-2-silaallylgermylene complex.

Results and Discussion

The potassium 2-imino-5,6-methylenedioxyphenylgermylidenide [$L_{\text{iminophenyl}}\text{GeK}$] (L = 2-imino-5,6-methylenedioxyphenyl) (**2**) was prepared according to the literature^[2], which was then reacted with the amidinato chlorosilylene^[8] in THF at -78°C (Scheme 1). The reaction mixture immediately changed from dark red to dark blue. It was then warmed to 0°C and stirred for an hour. Volatiles were removed to afford a dark blue solid. Its ^{29}Si NMR spectroscopy in C_6D_6 showed a signal at 70.9 ppm, which is in the downfield region similar to the ^{29}Si NMR signal of the amidinato silicon(II) compound [$L_{\text{amidinate}}\text{Si}$]₂ (76.3 ppm).^[9] This indicates formation of a silicon(II) moiety in the reaction. In addition, the ^1H NMR spectrum of the dark blue solid in C_6D_6 displayed a new set of signals for the iminophenyl and amidinate ligands, where a singlet at 1.08 ppm, two doublets at 1.03 and 1.61 ppm, a septet at 3.12

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ppm, a singlet at 5.71 ppm corresponding to the *t*Bu, *i*Pr and OCH₂O protons, respectively. The ¹H and ²⁹Si NMR signals indicate formation of a base-stabilized germylenylsilylene “L-*iminophenyl*GeSiL_{amidinate}” (**3**) in the reaction (Scheme 1). Compound **3** is a rare example of heterobinuclear group 14 element complex and a valence isomer of elusive germasilyne. However, **3** was highly unstable in solution, which decomposed into the 2-imino-5,6-methylenedioxyphenyl germanium(I), the amidinato silicon(I) and unidentified products at -30 °C within a few hours. Due to its inherent instability in solution, attempts to obtain a suitable single crystal of **3** for X-ray crystallography using a variety of solvents have not been successful. Only fine dark crystalline blue solid was afforded. It seems that **3** is transient in nature. Considering that tetrylenes are capable of activating small molecules,^[10] the existence of **3** in the reaction mixture was evidenced by following trapping reactions with elemental tellurium and arylazide through the oxidation of the Si and Ge centers.

Scheme 1. Synthesis of **3** - **5**.

The transient germylenylsilylene **3** in THF was trapped by adding two equivalents of elemental tellurium to the solution at -78 °C, whereby the reaction mixture immediately changed from dark blue to dark orange (Scheme 1). The reaction mixture was warmed to room temperature and stirred for 16 hours. The ²⁹Si NMR of the reaction mixture showed a singlet at -85.6 ppm, which indicated the formation of a Si=Te bond. Similar upfield signal is found in the dimeric NHC-silicon monotelluride [(L_{Ar})Si=Te]₂ (-107 ppm, L_{Ar} = :C(N(Ar)CH)₂)^[11] and the amidinato silanetellone

[L_{amidinate}Si(=Te){N(SiMe₃)₂}] (-47.6 ppm).^[12] In addition, the ¹²⁵Te NMR of the reaction mixture showed two signals at -180 and -738 ppm, which indicate the formation of a bridging -Te- and terminal =Te moiety, respectively. The bridging signal is comparable with the pyridyl-1-azaallyl-stabilized heavier ester analogue of germanium [L_{azaallyl}Ge(=Te)(μ-Te)GeL_{azaallyl}] [L_{azaallyl} = N(SiMe₃)C(Ph)C(SiMe₃)(C₅H₄N-2), -231 ppm],^[13] while the terminal signal is downfield shifted in comparison with [L_{amidinate}Si(=Te){N(SiMe₃)₂}] (-1093 ppm).^[12] Subsequently, the reaction mixture was filtered in the absence of light and the filtrate was concentrated to form the germylenyl silaneditelluroate [L-*iminophenyl*GeTeSi(=Te)L_{amidinate}] (**4**) as a dark orange crystalline solid. Compound **4** is the first low valent heterobinuclear group 14 element analogue of ditelluro-ester. The dark orange crystals are unstable and poorly soluble in most organic solvents. When they dissolved in deuterated organic solvent such as benzene[D₆], acetonitrile[D₃] and THF[D₈], unidentified compounds were observed. The X-ray crystal structure (Figure 1) shows that the Ge1 and Si1 atoms adopt a trigonal pyramidal and tetrahedral geometry, respectively. The sum of bond angles around the Ge1 atom (273.43°) indicates that there is a lone pair of electrons on the Ge1 atom. The Ge1-Te1 bond (2.6604(5) Å) is comparable with the Ge-Te_{bridging} bond (2.632(4), 2.664(4) Å) in the heavier ether analogue of germanium [(L_{azaallyl}Ge)₂Te].^[13] The Si1-Te1 bond (2.4701(13) Å) is comparable with the Si-Te_{bridging} bond in the ditelluradisiletane [(N(Ar)C(H)C(H)N(Ar))Si(μ-Te)]₂ (2.515 Å).^[14] This indicates that the Ge1-Te1 and Si1-Te1 bonds are single bonds. The Si1-Te2 bond (2.3638(12) Å) is shorter than the Si1-Te1 bond, while the former is comparable with the Si-Te_{terminal} bond in the amidinato silanetellone [L_{amidinate}Si(=Te){N(SiMe₃)₂}] (2.3720(15) Å).^[12] This indicates considerable double bond character in the Si1-Te2 bond. On the basis of the X-ray crystal structure of **4**, the transient germylenylsilylene **3** existed in the reaction of the potassium 2-imino-5,6-methylenedioxyphenylgermylidene **2** with the amidinato chlorosilylene. It was reacted with elemental Te, which proceeded through the insertion of elemental Te into the Si-Ge bond in **3** to form a heavier ether analogue intermediate “L-*iminophenyl*Ge-Te-SiL_{amidinate}”, in which the Si center subsequently undergoes an oxidation with elemental Te to form compound **4**. The formation of “L-*iminophenyl*Ge-Te-SiL_{amidinate}” was supported by our recent results, where the reaction of the pyridyl-1-azaallyl germanium(I) [L_{azaallyl}Ge]₂ with elemental Te proceeded through the heavier ether analogue [(L_{azaallyl}Ge)₂Te], which underwent further oxidation to form the heavier ester analogue [L_{azaallyl}Ge(=Te)(μ-Te)GeL_{azaallyl}].^[13]

Figure 1. The X-ray crystal structure of **4** (thermal ellipsoids set at 30% probability). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and

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angles (°): Ge1-N3 2.057(3), Ge1-Te1 2.6604(5), Te1-Si1 2.4701(13), Si1-Te2 2.3638(12), Si1-N1 1.825(4), Si1-N2 1.820(4); N3-Ge1-Te1 99.41(9), C16-Ge1-N3 80.43(15), C16-Ge1-Te1 93.59(12), Ge1-Te1-Si1 92.02(3), Te1-Si1-Te2 117.14(5), Te1-Si1-N1 110.85(12), Te1-Si1-N2 110.35(12), N1-Si1-N2 71.61(16), N1-Si1-Te2 118.94(12), N2-Si1-Te2 119.71(12).

The transient germlyenylsilylene **3** in toluene was further trapped by adding one or two equivalents of 2,6-diisopropylphenylazide (ArN_3) to the solution at -78°C (Scheme 1). Within 5 minutes, effervescence was observed, which indicated elimination of dinitrogen gas from ArN_3 in the reaction. The color gradually changed over the first 10 minutes at -78°C from blue to orange. The reaction mixture was warmed to room temperature and stirred for another 2 hours. It was then filtered and the filtrate was concentrated to afford the amidinate-stabilized 1,3-diaza-2-silaallylgermylene complex $[\{\text{L}_{\text{amidinate}}\text{Si}(\text{NAr})_2\}\text{GeL}_{\text{iminophenyl}}]$ (**5**) as orange crystals (68%). Other silaallyl analogues, namely 1,3-diphospha-2-silaallyl potassium complex $[(\text{THF})\text{K}(18\text{-crown-6})][(\text{TripP})_2\text{SiL}_{\text{amidinate}}]$ ^[15] (Trip = 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$) and germanium(II) siladithiocarboxylate $[\{\text{L}_{\text{amidinate}}\text{Si}(\text{S})_2\}_2\text{Ge}]$ ^[16] were reported. The ^1H NMR spectrum of compound **5** displayed septets at 5.11, 4.23, 4.07, 3.39 and 2.11 ppm for iPr groups and doublets at 5.17 and 5.71 ppm attributable to non-equivalent OCH_2O protons of the 2-imino-5,6-methylenedioxyphenyl ligand. It also showed singlets at 1.06 and 0.80 ppm corresponding to the tBu substituents of the amidinate ligand. The ^{29}Si NMR signal (-75.37 ppm) is downfield shifted in comparison with the silaneimide $[\text{L}_{\text{amidinate}}\text{Si}(=\text{NAr})\text{N}(\text{Ar})\text{L}_{\text{silyl}}]$ (-87.3 ppm, $\text{L}_{\text{silyl}} = \text{Si}(\text{Cl})\{\text{N}(\text{tBu})_2\text{C}(\text{H})\text{Ph}\}$).^[17]

Figure 2. The X-ray crystal structure of **5** with thermal ellipsoids set at 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): N3-Si1 1.6293(14), N2-Si1 1.6750(13), Ge1-N2 2.0133(14), Ge1-N1 2.432(2), N5-Si1 1.8569(13), N4-Si1 1.8435(14), Ge1-C1 2.0192(16), Ge1-N3 2.4005(13), Si1-N4 1.8435(14), Si1-N5 1.8569(13), N3-Si1-N4 133.35(7), N3-Si1-N5 111.81(7), N4-Si1-N5 71.08(6), N3-Si1-N2 102.53(7), N2-Si1-N4 115.02(7), N2-Si1-N5 121.89(6), N2-Ge1-C1 109.07(6).

The X-ray crystal structure of **5** is shown in Figure 2. The silaallyl moiety “ $\text{L}_{\text{amidinate}}\text{Si}(\text{NAr})_2$ ” chelates to the Ge1 atom in an anisobidentate manner (Ge1-N2: 2.0133(14), Ge1-N3: 2.4005(13) Å). The Ge1 atom adopts a distorted seesaw geometry. The N1 and N3 atoms are at the axial positions (N1-Ge1-N3: $172.94(5)^\circ$) and the stereochemically active lone pair of electrons is at the equatorial position. The Ge1-N2 and Ge1-N3 bonds are comparable with those in the bis(amidinato)germylene $[\{\text{MeC}(\text{N}(\text{iPr})_2)_2\text{Ge}\}]$ (1.982(3), 2.300(2) Å),^[18] where the amidinate ligands coordinate to the Ge center in an anisobidentate manner.

The Si1 atom adopts a tetrahedral geometry. The Si1-N2 (1.6293(14) Å) and Si1-N3 bonds (1.6750(13) Å) are almost identical. They are intermediate between the Si=N double bond (1.589(5) Å) and Si-N single bond (1.795(4) Å) in the silaneimide $[\text{L}_{\text{amidinate}}\text{Si}(=\text{NAr})\text{N}(\text{Ar})\text{L}_{\text{silyl}}]$.^[17] They are also shorter than the Si-N single bonds in the dimeric silaisonitrile $[\text{Ar}'\text{NSi}]_2$ ($\text{Ar}' = 2,6\text{-bis}(2,4,6\text{-triisopropyl})\text{phenyl}$, 1.755(1) Å).^[19] The results show that the Si-N π bond is delocalized along the N3-Si1-N2 skeleton. Similar to the case of Te, the ArN_3 was inserted into the Si-Ge bond of **3** with the elimination of N_2 to form the imido intermediate $[\text{L}_{\text{iminophenyl}}\text{Ge-N}(\text{Ar})\text{-SiL}_{\text{amidinate}}]$, in which the Si center subsequently undergoes an oxidation with ArN_3 to form compound **5**.

Conclusion

The transient base-stabilized germlyenylsilylene $[\text{L}_{\text{iminophenyl}}\text{GeSiL}_{\text{amidinate}}]$ (**3**) was synthesized by the reaction of the potassium 2-imino-5,6-methylenedioxyphenylgermylidenide $[\text{LGeK}]$ (**1**) with the amidinato chlorosilylene. The existence of **3** in the reaction was evidenced by the subsequent trapping reactions with elemental tellurium and ArN_3 to form the first base-stabilized germlyenyl silaneditealluroate $[\text{L}_{\text{iminophenyl}}\text{GeTeSi}(=\text{Te})\text{L}_{\text{amidinate}}]$ (**4**) and 1,3-diaza-2-silaallylgermylene complex $[\{\text{L}_{\text{amidinate}}\text{Si}(\text{NAr})_2\}\text{GeL}_{\text{iminophenyl}}]$ (**5**). The results show that the transient base-stabilized germlyenylsilylene is a promising building block for the preparation of heterobinuclear group 14 element unknown compounds. Further reactivity of **3** is currently under investigation.

Experimental Section

All manipulations, unless otherwise stated, were carried out by using standard Schlenk and glovebox techniques under an atmosphere of high purity argon. The chemicals were purchased from commercial sources: Sigma-Aldrich, and Alfa Aesar and were used as received. Toluene was dried using a MBraun Solvent Purification System. Benzene[D_6], THF and THF[D_8] were dried and distilled over molten potassium. All NMR spectra were recorded on Bruker Avance 400 or Jeol ECA 400 MHz spectrometers. The NMR spectra were recorded in d-solvents and the chemical shifts are relative to SiMe_4 for ^1H , ^{13}C and ^{29}Si ; Ph_2Te for $^{125}\text{Te}\{^1\text{H}\}$. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of 4. THF (25 mL) was added to a mixture of compound **1** (0.43 g, 1 mmol) and KC_8 (0.47 g, 3.5 mmol) at room temperature and stirred for 1 hour. The excess KC_8 was filtered to generate **2** (Conversion: >99%). A THF solution (10 mL) of the amidinato chlorosilylene (0.29 g, 1 mmol) was added dropwise to **2** at -78°C . The reaction mixture was warmed to 0°C and left to stir for 1 hour at 0°C . Volatiles were removed to afford a dark blue crystalline solid (Conversion: >99 %). The ^1H , ^{13}C and ^{29}Si NMR signals indicate the formation of **3**. ^1H NMR (399.5 MHz, benzene- D_6 , 23.3°C) δ 1.02 (d, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.08 (s, 18H, tBu), 1.61 (d, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.12 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 5.71 (s, 2H, OCH_2O), 6.86 (s, 1H, Ph), 6.88 (s, 1H, Ph), 7.06–7.09 (m, 2H, Ph), 7.20 (br, 3H, Ph), 7.40 (s, 1H, Ph), 7.42 (s, 1H, Ph), 7.55–7.58 (m, 1H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, benzene- D_6 , 25.1°C): δ 17.41, 24.33, 25.57, 28.26, 28.88, 30.78, 31.73, 32.68 ($\text{C}(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)_2$), 52.95 ($\text{C}(\text{CH}_3)_3$), 99.59, 105.93, 123.69, 123.90, 129.01, 129.54, 141.56, 142.89, 143.29, 149.30, 153.27, 155.37, 159.40 (Ar, NCN).

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$^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, benzene- d_6 , 24.9 °C): 70.9 ppm. Elemental analysis calcd for $\text{C}_{36}\text{H}_{47}\text{GeN}_3\text{O}_2\text{Si}$: C 66.06, H 7.24, N 6.42; found: C 65.57, H 7.18, N 6.49.

The dark blue crystalline solid of **3** was immediately dissolved in THF (35 mL) and was added dropwise to Te (0.26 g, 2 mmol) at -78 °C in the absence of light. The reaction was warmed to room temperature and stirred for another 16 hours. It was monitored by ^{29}Si and ^{125}Te NMR spectroscopy, $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, THF- d_8 , 24.9 °C): δ -85.6 ppm; $^{125}\text{Te}\{^1\text{H}\}$ NMR (79.4 MHz, THF- d_8 , 24.9 °C): δ -738 ppm, -180 ppm. The reaction mixture was filtered and concentrated to afford **4** as orange crystalline solids. M.P. 175 °C (dec.). Elemental analysis calcd for $\text{C}_{36}\text{H}_{47}\text{GeN}_3\text{O}_2\text{SiTe}_2$: C 47.53, H 5.21, N 4.62; found: C 47.17, H 4.86, N 4.28. When the orange crystals dissolved in deuterated organic solvent such as benzene- d_6 , acetonitrile- d_3 and THF- d_8 , unidentified compounds were observed.

Synthesis of **5**. **3** (1 mmol) was prepared as the above procedure. Toluene (30 mL) was added to **3** at -78 °C. A toluene (10 mL) solution of 2,6-diisopropylphenylazide (0.40g, 2 mmol) was added dropwise to the solution of **3** at -78 °C and stirred for one hour. The reaction mixture was warmed to room temperature and stirred for another 2 hours. It was then filtered and concentrated to afford **5** as an orange crystalline solid. Yield: 0.68 g (67%). M.P. 175 °C (dec.). ^1H NMR (399.5 MHz, benzene- d_6 , 24.9 °C): δ 0.56 (d, $^3J_{\text{HH}} = 6.81$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.70 (d, $^3J_{\text{HH}} = 6.81$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.79 (s, 9H, $t\text{Bu}$), 0.80 – 0.86 (m of overlapping d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.06 (s, 9H, $t\text{Bu}$), 1.07 (d overlap with $t\text{Bu}$ signal, 3H, $\text{CH}(\text{CH}_3)_2$), 1.27 – 1.33 (m of overlapping d, 9H, $\text{CH}(\text{CH}_3)_2$), 1.41 – 1.46 (m of overlapping d, 9H, $\text{CH}(\text{CH}_3)_2$), 1.53 (d, $^3J_{\text{HH}} = 6.81$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.85 (s, 3H, CH_3), 2.11 (sept overlap with toluene signal, 1H, $\text{CH}(\text{CH}_3)_2$), 3.39 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.08 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 4.24 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 5.12 (sept, $^3J_{\text{HH}} = 6.81$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 5.17 (d, $^2J_{\text{HH}} = 0.87$ Hz, 1H, OCH_2O), 5.71 (d, $^2J_{\text{HH}} = 0.87$ Hz, 1H, OCH_2O), 6.68 (d, $^3J_{\text{HH}} = 7.92$ Hz, 1H, Ph), 6.74 – 7.01 (m, 6H, Ph), 7.07 – 7.15 (m, 5H, Ph), 7.19 – 7.23 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, benzene- d_6 , 24.9 °C): δ 18.79, 21.11, 23.19, 23.49, 23.66, 24.13, 24.20, 24.71, 25.51, 25.66, 26.04, 26.49, 26.81, 26.94, 27.62, 27.79, 28.12, 28.30, 28.89, 30.63, 30.88 ($\text{C}(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)_2$), 54.09, 55.03 ($\text{C}(\text{CH}_3)_3$), 100.41, 106.34, 116.76, 122.33, 122.60, 122.96, 123.84, 124.11, 124.33, 124.47, 124.82, 125.38, 129.01, 130.09, 137.79, 138.93, 139.99, 140.72, 143.08, 145.08, 145.89, 146.91, 147.27, 147.42, 150.69, 164.86, 178.35 (Ar, NCN). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, benzene- d_6 , 24.9 °C): δ -75.4 ppm. Elemental analysis calcd for $\text{C}_{63.50}\text{H}_{85}\text{GeN}_5\text{O}_2\text{Si}$ ($4.0\text{-}0.5\text{C}_7\text{H}_8$): C 72.56, H 8.15, N 6.66; found: C 72.22, H 8.19, N 6.53.

X-ray Data Collection and Structural Refinement. Intensity data for compounds **4** and **5** were collected by using a Bruker APEX II diffractometer. Reflections were measured at 100(2) K. The structures were solved by direct-phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 . All nonhydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. CCDC-2008664 (**4**) and -2008665 (**5**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data of **4**: $\text{C}_{36}\text{H}_{47}\text{GeN}_3\text{O}_2\text{SiTe}_2$; $M = 909.64$; orthorhombic $P 2_1 2_1 2_1$; $a = 11.7824(3)$, $b = 16.6918(3)$, $c = 19.1208(4)$ Å; $\alpha = \beta = \gamma = 90^\circ$; $V = 3760.48(14)$ Å 3 ; $Z = 4$; $d_{\text{calcd}} = 1.607$ g cm $^{-3}$; $\mu = 2.402$ mm $^{-1}$; $F(000) = 1800$; $-19 \leq h \leq 19$, $-20 \leq k \leq 27$, $-31 \leq l \leq 23$; 45926 reflections collected; $R1 = 0.0464$, $wR2 = 0.0611$ ($I > 2\sigma(I)$); $R1 = 0.0812$, $wR2 = 0.0715$ (all data).

Crystallographic data of **5**: $\text{C}_{63.50}\text{H}_{85}\text{GeN}_5\text{O}_2\text{Si}$; $M = 1051.04$; triclinic $P - 1$; $a = 12.0310(4)$, $b = 12.9024(4)$, $c = 21.3468(7)$ Å; $\alpha = 76.2660(10)^\circ$, $\beta = 81.5820(10)^\circ$, $\gamma = 62.9540(10)^\circ$; $V = 2864.05(16)$ Å 3 ; $Z = 2$; $d_{\text{calcd}} = 1.219$ g

cm $^{-3}$; $\mu = 0.603$ mm $^{-1}$; $F(000) = 1126$; $-19 \leq h \leq 19$, $-20 \leq k \leq 20$, $-34 \leq l \leq 33$; 63449 reflections collected; $R1 = 0.0546$, $wR2 = 0.1220$ ($I > 2\sigma(I)$); $R1 = 0.0936$, $wR2 = 0.1400$ (all data).

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Keywords: silylene • germylene • tellurium • azide • heterobinuclear

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Entry for the Table of Contents

Group 14 Compounds

The transient base-stabilized germylenesilylene **1** was trapped by elemental tellurium and 2,6-diisopropylphenylazide to form the first germylenyl silaneditelluroate **2** and 1,3-diaza-2-silaallylgermylene complex **3**.