

Article

Isolation of a Cyclic (Alkyl)(amino)germylene

 Liliang Wang ¹, Yi Shan Lim ¹, Yongxin Li ², Rakesh Ganguly ² and Rei Kinjo ^{1,*}
¹ Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Nanyang Link 21, Singapore 637371, Singapore; lwang018@e.ntu.edu.sg (L.W.); limy0252@e.ntu.edu.sg (Y.S.L.)

² NTU-CBC Crystallography Facility, Nanyang Technological University Nanyang Link 21, Singapore 637371, Singapore; yongxin@ntu.edu.sg (Y.L.); rganguly@ntu.edu.sg (R.G.)

* Correspondence: rkinjo@ntu.edu.sg; Tel./Fax: +65-6592-2625

Academic Editor: Mitsuo Kira

Received: 7 July 2016; Accepted: 26 July 2016; Published: 29 July 2016

Abstract: A 1,4-addition of a dichlorogermylene dioxane complex with α,β -unsaturated imine **1** gave a dichlorogermane derivative **2** bearing a GeC_3N five-membered ring skeleton. By reducing **2** with KC_8 , cyclic (alkyl)(amino)germylene **3** was synthesized and fully characterized. Germylene **3** readily reacted with TEMPO, N_2O and S_8 , producing the 1:2 adduct **4**, the oxo-bridged dimer **5** and the sulfido-bridged dimer **6**, respectively.

Keywords: germylene; low-valent germanium; sulfur; TEMPO; nitrous oxide

1. Introduction

Since the seminal work by Harris and Lappert, who discovered stable organogermynes in the 1970s [1–3], a plethora of studies on the synthesis and reactivity of isolable germynes have been reported [4–9]. Among them, the most extensive investigation has been on *N*-heterocyclic germynes such as **I–II** (Figure 1) that are thermodynamically stabilized by incorporation of two N atoms in a position α to the germylene center [10,11]. In recent years, it has been demonstrated that germynes can be widely utilized in a variety of applications, ranging from bond activation to polymer chemistry, in addition to their use as ligands for metal complexes [12–22]. Nevertheless, only a few approaches have been reported thus far to expand the diversity of cyclic germylene frameworks [23–33]. In this respect, Kira and co-workers elegantly developed a cyclic dialkylgermylene (**III**, Figure 1) [34]. We envisioned that by replacing only one of the amino substituents of a classical *N*-heterocyclic germylene such as **I–II** with an alkyl group, the electronic features and steric impact of the Ge center could be finely modulated. Indeed, in carbene chemistry Bertrand and co-workers have successfully synthesized cyclic (alkyl)(amino)carbenes (CAACs) [35–40], and demonstrated that CAACs exhibit both stronger σ -donating and π -accepting characters than classical imidazolin-2-ylidenes, the so-called NHCs. Herein, we reported the preparation, single crystal X-ray diffraction, and computational studies of a cyclic (alkyl)(amino)germylene **IV** (Figure 1).

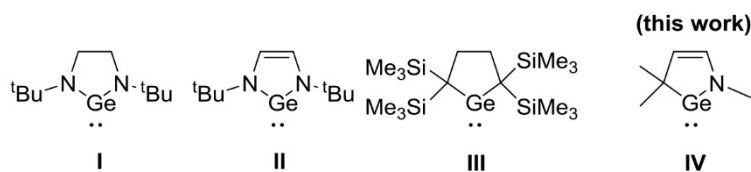


Figure 1. Selected examples of structurally characterized germynes **I–III** featuring five-membered ring skeleton, and this work.

Brief inspection of the molecular orbitals (MOs) of germylenes **A–D** revealed that the HOMO–1 of **A**, **B** and **D** corresponding to the germanium lone pair increases in energy in the order **B** < **A** < **D** (Figure 2). Their HOMOs are mainly centred on the π -system involving the lone pair of the N atoms, and the energies increase in the order **D** < **A** < **B**. In contrast, the Ge lone pair of **C** is found in the HOMO. The energies of the LUMOs, which are predominantly unoccupied p-orbitals on the Ge center for all germylenes **A–D**, decrease in the order **B** > **A** > **D** > **C** from -0.60 eV to -2.71 eV. This short analysis indicates that replacement of a π -electron donating and σ -withdrawing amino group by a σ -donating alkyl group (**D**) enhances the electrophilicity of the germylene center, and concomitantly raises the energy of the orbital involving the lone-pair electrons at the germanium center. Note that due to the presence of only one quaternary carbon atom bonding to the Ge atom, the steric profile at the Ge center in **D** differs from those in **A–C**.

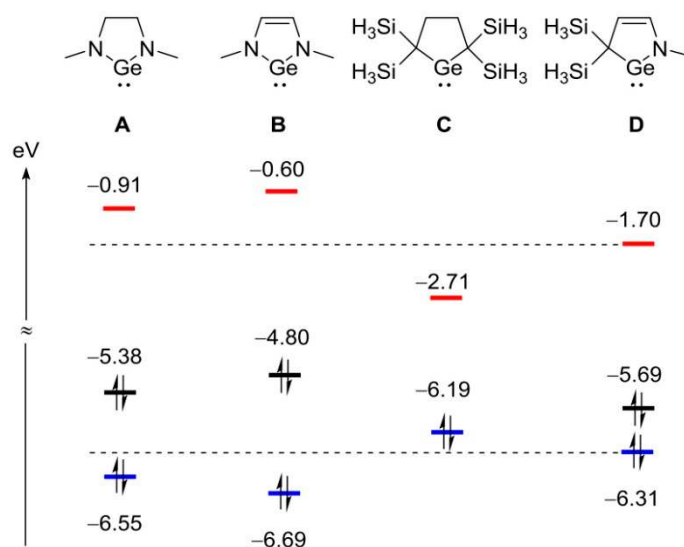
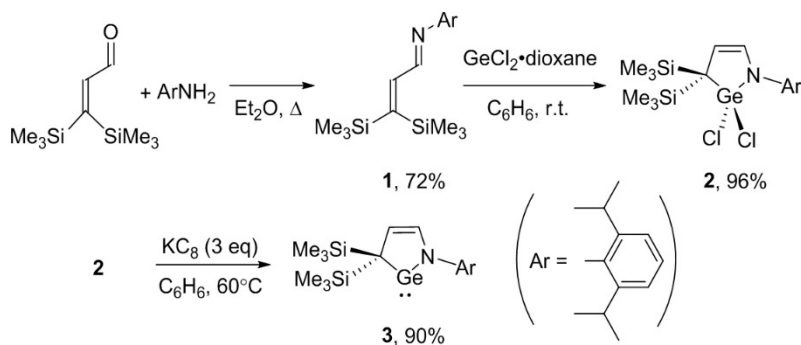


Figure 2. Energy (eV) of frontier orbitals of *N*-heterocyclic germylenes **A**, **B**, cyclic dialkylgermylene **C** and (alkyl)(amino)germylene **D**, calculated at the B3LYP/6-31G(d,p) level of theory.

2. Results

Our strategy for the synthesis of type-IV germylene is based on oxidative 1,4-addition of germylene with a 1,3-diene [41,42] and subsequent reduction. We envisaged that dichlorogermylene would undergo cyclization with an α,β -unsaturated imine to afford a dichlorogermane precursor featuring a GeC_3N five-membered ring skeleton, which could be reduced to access a type-IV germylene. To bear out this hypothesis, we carried out the reaction of 3,3-bis(trimethylsilyl)-acrylaldehyde and 2,6-diisopropylaniline in Et_2O , from which α,β -unsaturated imine **1** was obtained in 72% yield (Scheme 1). Treatment of a stoichiometric amount of dichlorogermylene dioxane complex with **1** in benzene resulted in a 1,4-addition via a redox reaction between them, which gave the cyclic dichlorogermane derivative **2** in 96% yield. The result represents the first example of a 1,4-addition of Cl_2Ge : to an α,β -unsaturated imine. A mixture of **2** and three equivalents of potassium graphite was heated at 60°C in benzene. After work-up, germylene **3** was isolated as a dark red solid in 90% yield. In the $^1\text{H-NMR}$ spectrum of **3**, a Me_3Si group singlet appears at 0.21 ppm, which is identical to that 0.22 ppm seen for **2**. The $^{13}\text{C-NMR}$ spectrum of **3** displays two peaks at 118.9 and 146.7 ppm for the $\text{C}(\text{sp}^2)\text{-H}$ carbon atoms in the GeNC_3 five-membered ring, which are shifted significantly downfield in comparison to those of **2** (99.0 ppm and 139.1 ppm).



Scheme 1. Synthesis of **2** and **3**.

The solid state molecular structures of compounds **2** and **3** were determined by single crystal X-ray diffraction analysis (Figure 3). Five atoms in the GeNC₃ five-membered ring of **3** are coplanar (the sum of internal pentagon angles = 539.91°), and 2,6-diisopropylphenyl ring at the N1 atom and the GeNC₃ skeleton are nearly perpendicular to each other with the twist angle of 89.86°. The Ge1-N1 bond (1.859(11) Å) and the Ge1-C15 bond (1.998(14) Å) distances are slightly longer than those [Ge1-N1 1.822(2) Å, Ge1-C1 1.959(3) Å] of **2**. The N1-Ge1-C15 bond angle of 86.5(5)° in **3** is more acute than the N1-Ge1-C1 bond angle [94.90(11)°] in **2**, the corresponding N-Ge-N bond angle [84.8(1)°] in **II** [10] as well as the corresponding C-Ge-C bond angle [90.97(9)°] in **III** [34].

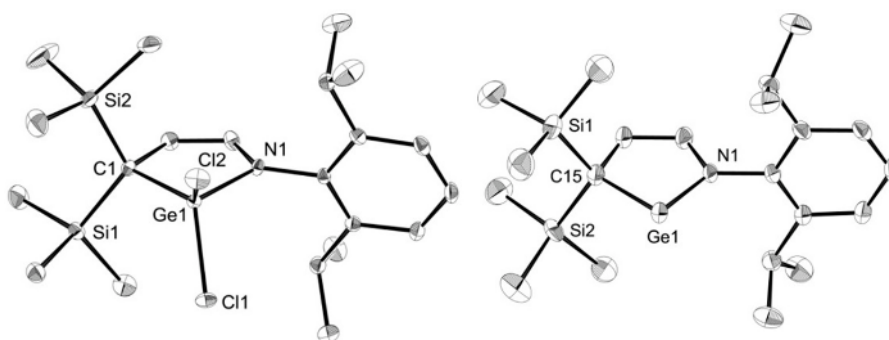


Figure 3. Solid state structures of **2** (left) and **3** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

To gain insight into the electronic features, we carried out quantum chemical calculations on **3**. A lone-pair orbital at the Ge atom was found in the HOMO-1, whereas the HOMO displays a Ge-N π -bonding involving the two C-Si σ -bonds which exhibits anti-bonding conjugation with the π -orbital of the C=C moiety (Figure 4).

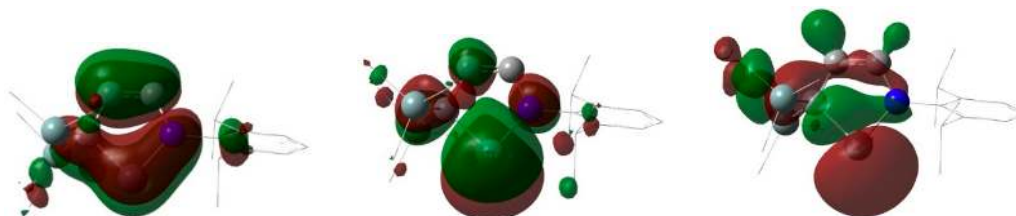
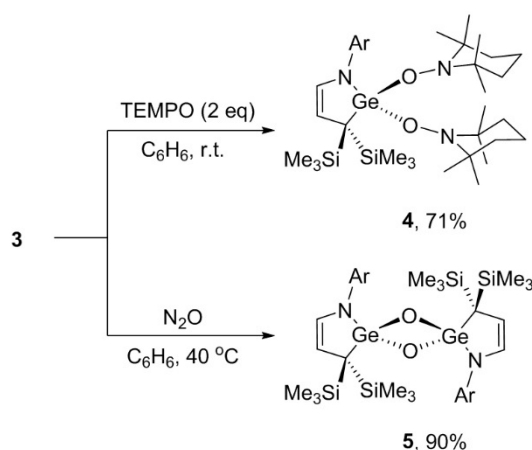


Figure 4. Plots of the HOMO (left), LUMO (middle) and HOMO-1 (right) of **3** calculated at the B3LYP/6-31G(d,p) level of theory (hydrogen atoms are omitted for clarity).

The LUMO is mainly the empty p orbital of the Ge center. Natural bond orbital (NBO) analysis gave Wiberg bond index (WBI) values of the Ge-N bond (0.78) and the Ge-C bond (0.73), indicating

single bond nature of these bonds. Natural population analysis (NPA) manifested the second order perturbation energy of $33.97 \text{ kcal}\cdot\text{mol}^{-1}$ for the interaction between a lone-pair on the N atom and formally unoccupied p-orbital of the Ge atom. A UV-vis spectrum of **3** in hexane exhibits a broad peak with λ_{max} at 368 nm, which is due to the HOMO-LUMO transition, responsible for the deep red colour of **3**. Compound **3** is stable at room temperature, both in the solid state and in solutions (benzene and THF), but it rapidly decomposes upon exposure to air, indicating its high reactivity. Then, we turned our interest into the reactivity of **3**. We inferred that the Ge(II) center in **3** would undergo redox reactions with appropriate oxidants [43–45]. Indeed, by analogy to dialkylgermylene **III** [46,47], compound **3** readily reacted with two equivalents of 2,2,6,6-tetramethylpiperidine N-oxide (TEMPO) under ambient conditions, to afford **4** in 71% yield (Scheme 2). We also examined the 1:1 reaction between **3** and TEMPO, which again gave **4**, and unreacted **3** was recovered after the reaction. Kira and co-workers reported that the thermal reaction of the 1:2 **III**·(TEMPO)₂ adduct yielded the corresponding 1,3-digemadioxetane [**III**-O]₂ [46,47]. By contrast, thermolysis of **4** in C₆D₆ led to the formation of a complex mixture. Meanwhile, reaction of **3** and nitrous oxide (N₂O) at 40 °C proceeded smoothly, and the corresponding 1,3-digemadioxetane **5** was obtained as a white solid in 90% yield [48–52]. Notably, Driess et al. reported that six-membered ring *N*-heterocyclic germylene is resistant towards N₂O [53–56], which is in marked contrast to our result. Smooth transfer of an O atom from N₂O to **3** is probably due to the enhanced Lewis acidic nature of the Ge center attributed to the low-lying LUMO, which is in line with our DFT calculation results (Figure 1). Compounds **4** and **5** were fully characterized by standard spectroscopic methods and X-ray diffraction analysis (Figure 5). The Ge-O bond distances (1.814(3) Å and 1.796(3) Å) in **4** are lengthened with respect to the Ge=O double bond distance of 1.6468(5) Å in (Eind)₂Ge=O (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl group) [57], and comparable to those (1.824(2) Å and 1.826(2) Å) in **III**·(TEMPO)₂ [46,47]. Both the Ge-C bond (2.020(4) Å) and Ge-N bond (1.871(3) Å) distances are similar to those of the corresponding bonds in **3**. Compound **5** displays a spiro-structure involving a nearly planar Ge₂O₂ four-membered ring in which two 2,6-diisopropylphenyl groups are located on the opposite side with respect to the Ge₂O₂ plane. The O-Ge-O and Ge-O-Ge bond angles are 86.35(8)° and 93.65(8)°, respectively. The Ge-O bond distances (1.8084(16) Å and 1.8090(17) Å) are almost identical to those (1.821(2) Å and 1.822(2) Å) in [**III**-O]₂ [46,47].



Scheme 2. Reactions of **3** with TEMPO, N₂O.

Successful transfer of oxygen atom from N₂O to **3** prompted us to further investigate the reaction with elemental sulfur. A mixture of **3** and S₈ (1/8 eq) in benzene was stirred at ambient temperature for 1 h. After work-up, sulfido-bridged dimers **6** were obtained as a mixture of two diastereomers in 59% total yield (Scheme 3) [58–60]. Facile oxidation of the Ge center by S₈ supports the electron-donating ability of **3**.

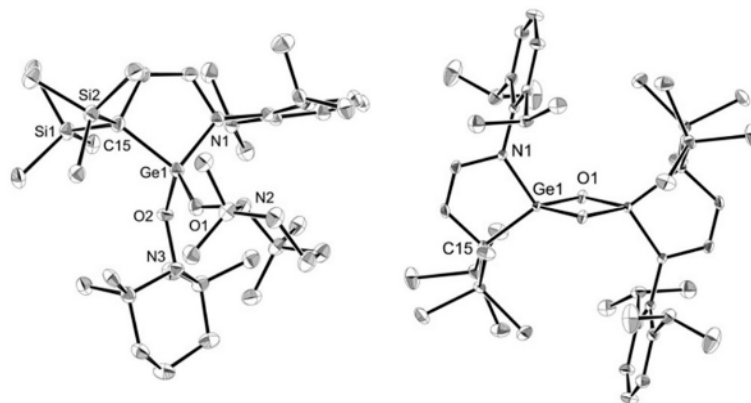
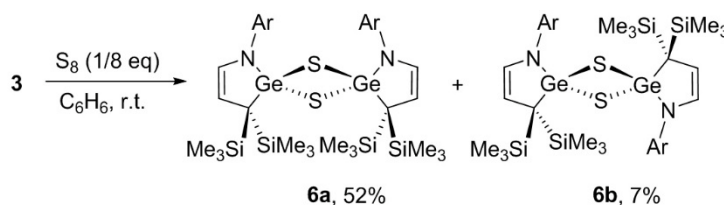


Figure 5. Solid state structures of **4** (left) and **5** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

Interestingly, purification of **6a** and **6b** by column chromatography and subsequent X-ray crystallographic analysis (Figure 6) confirmed that the major product is **6a** bearing two 2,6-diisopropylphenyl groups located on the same side of the Ge_2S_2 plane, which is in sharp contrast to the stereoselective formation of **5** having a similar geometry to **6b**. Both **6a** and **6b** involve a planar Ge_2S_2 four-membered ring. The S-Ge-S and Ge-S-Ge bond angles are $93.47(5)^\circ$ and $86.56(5)^\circ$ for **6a**, and $94.01(12)^\circ$ and $85.99(12)^\circ$ for **6b**, respectively. The Ge-S bond distances (**6a**: 2.2462(13) Å and 2.2406(13) Å, **6b**: 2.231(3) Å and 2.237(3) Å) are in the range reported of Ge-S single bonds (2.17–2.25 Å) [61], and longer than the Ge=S double bond length of 2.049(3) Å in [Tbt(Trip)Ge=S] (Tbt = 2,4,6- $\{(\text{Me}_3\text{Si})_2\text{CH}\}_3\text{C}_6\text{H}_2$, Trip = 2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$) [62]. To investigate the reaction mechanism, we attempted to quench the reaction intermediate employing Lewis bases (pyridine, Me_3N , Ph_3P and Et_3N) and Lewis acids (BPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$) [63–65]. However, none of them afforded any trapped products, and only the formation of **6a** and **6b** were observed.



Scheme 3. Reactions of **3** with S_8 .

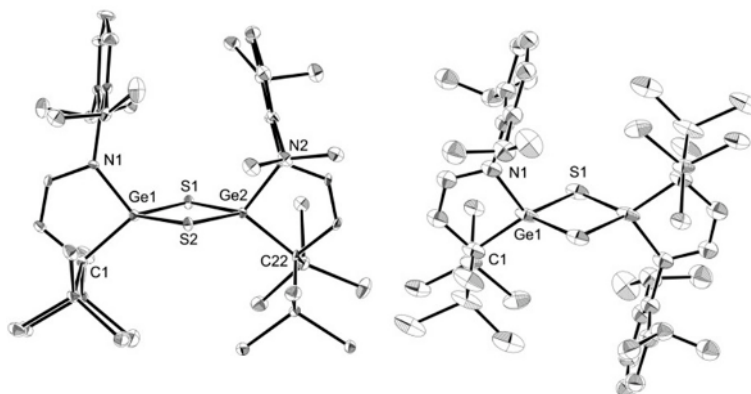


Figure 6. Solid state structures of **6a** (left) and **6b** (right). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

3. Materials and Methods

3.1. General Information

All reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques. Solvents were dried over Na metal, K metal or CaH₂. All the substrates were obtained from commercial sources or synthesized following literature procedures. Analytical thin layer chromatography was performed on trimethylamine-deactivated 0.25 mm silica gel 60-F254 plates (Merck, Darmstadt, Germany). Visualization was carried out with UV light. ¹H (400 MHz), and ¹³C (100 MHz) spectra were obtained with an AVIII 400 MHz BBFO1 spectrometer (Bruker Instruments, Karlsruhe, Germany) at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt system (Stanford Research Systems, Sunnyvale, CA, USA).

¹H-, and ¹³C-NMR spectra of all compounds are provided in Supplementary Material (Figures S1–S16).

3.2. Synthesis of 1

2,6-Diisopropylaniline (55 mmol, 9.75 g) and 3,3-bis(trimethylsilyl)acrylaldehyde [66] (50 mmol, 10.00 g) were mixed in ether (100 mL). After the mixture was refluxed overnight, the product was purified by silica gel column chromatography (petroleum ether/ethyl acetate= 10:1) to afford **1** as a yellow solid (12.9 g, 72%). Mp: 109 °C; ¹H-NMR (CDCl₃) δ 8.13 (d, *J* = 10.1 Hz, 1H, CH), 7.36 (d, *J* = 10.1 Hz, 1H, CH), 7.18–7.07 (m, 3H, Ar-H), 2.91 (dt, *J* = 13.7, 6.9 Hz, 2H, CH), 1.17 (s, 6H, CH₃), 1.15 (s, 6H, CH₃), 0.24 (s, 9H, Si(CH₃)₃), 0.21 (s, 9H, Si(CH₃)₃); ¹³C-NMR (CDCl₃) δ 163.40 (CH), 162.04 (C^q), 151.12 (CH), 148.79 (C^q), 137.23 (C^q), 124.26 (C^q), 122.96 (CH), 27.73 (CH), 23.61 (CH₃), 2.39 (Si(CH₃)₃), 0.05 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₂₁H₃₈NSi₂: 359.2465 [(M + H)]⁺; found: 359.2468.

3.3. Synthesis of 2

Compound **1** (4 mmol, 1.42 g) and dichlorogermadiyl dioxane (4 mmol, 0.93 g) were mixed in benzene (20 mL). The mixture was stirred at room temperature overnight, and then all volatiles were removed under vacuum to afford **2** as a yellow solid (1.93 g, 96%). Mp: 154 °C; ¹H-NMR (C₆D₆) δ 7.15–6.88 (m, 3H, Ar-H), 6.30 (d, *J* = 6.3 Hz, 1H, CH), 4.60 (d, *J* = 6.3 Hz, 1H, CH), 3.48 (dt, *J* = 13.7, 6.9 Hz, 2H, CH), 1.31 (d, *J* = 6.9 Hz, 6H, CH₃), 1.14 (d, *J* = 6.9 Hz, 6H, CH₃), 0.22 (s, 18H, Si(CH₃)₃); ¹³C-NMR (C₆D₆) δ 147.82 (C^q), 139.06 (CH), 137.11 (C^q), 127.91 (CH), 124.04 (CH), 98.98 (CH), 33.96 (C^q), 28.04 (CH), 25.72 (CH₃), 23.06 (CH₃), 0.47 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₂₁H₃₈NSi₂Cl₂Ge: 504.1132 [(M + H)]⁺; found: 504.1156.

3.4. Synthesis of 3

Compound **2** (2 mmol, 1.02 g) and KC₈ (6 mmol, 0.81 g) were mixed in benzene (30 mL). The mixture was stirred at 60 °C for 6 h. After stirring for another 30 min at room temperature, the mixture was filtered and then the solution was concentrated under vacuum which afforded **3** as a dark red solid (0.78 g, 90%). Mp: 95 °C; ¹H-NMR (C₆D₆) δ 7.22 (d, *J* = 4.1 Hz, 1H, CH), 7.22–7.14 (m, 3H, Ar-H), 6.08 (d, *J* = 4.1 Hz, 1H, CH), 3.25 (dt, *J* = 13.8, 6.9 Hz, 2H, CH), 1.21 (d, *J* = 6.9 Hz, 6H, CH₃), 1.17 (d, *J* = 6.9 Hz, 6H, CH₃), 0.21 (s, 18H, Si(CH₃)₃); ¹³C-NMR (C₆D₆) δ 146.70 (CH), 144.51 (C^q), 143.89 (C^q), 126.87 (CH), 123.30 (CH), 118.94 (CH), 27.94 (CH), 24.94 (CH₃), 23.83 (CH₃), 1.78 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₂₁H₃₈NSi₂Ge: 434.1755 [(M + H)]⁺; found: 434.1761.

3.5. Reaction of **3** with TEMPO

TEMPO (0.50 mmol, 78 mg) and **3** (0.23 mmol, 100 mg) were mixed in benzene (2 mL) and stirred for 5 min at room temperature. After the solvent was removed under vacuum, the residue was recrystallized from hexane to afford **4** as colorless crystals (120 mg, 71%). Mp: 195 °C. ¹H-NMR (C₆D₆) δ 7.18 (s, 3H, Ar-H), 6.43 (d, *J* = 6.6 Hz, 1H, CH), 4.66 (d, *J* = 6.6 Hz, 1H, CH), 3.87 (s, 2H, CH), 2.15–0.87 (m, 48H), 0.47 (s, 18H, Si(CH₃)₃); ¹³C-NMR (C₆D₆) δ 147.32 (C^q), 144.21 (C^q), 140.67 (CH), 126.43 (CH), 123.63 (CH), 97.13 (CH), 61.35 (C^q), 61.15 (C^q), 41.85 (CH₃), 41.35 (CH₃), 34.30 (CH₂), 28.10 (CH₂), 26.47 (CH), 21.83 (CH₂), 16.96 (CH₃), 4.16 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₃₉H₇₄N₃O₂Si₂Ge: 746.4531. [(M + H)]⁺; found: 746.4509.

3.6. Reaction of **3** with N₂O

Nitrous oxide (0.23 mmol, 10 mg) was condensed at liquid nitrogen in a benzene solution of **3** (0.23 mmol, 100 mg). The reaction mixture was heated at 40 °C and stirred for 1 h. After the solvent was removed under vacuum, recrystallization of the residue from benzene afforded **5** as colorless crystals (93 mg, 90%). Mp: 278 °C (dec). ¹H-NMR (C₆D₆) δ 7.19 (m, 2H, Ar-H), 7.15–7.11 (m, 4H, Ar-H), 6.34 (d, *J* = 6.3 Hz, 2H, CH), 4.65 (d, *J* = 6.3 Hz, 2H, CH), 3.50 (dt, *J* = 13.6, 6.8 Hz, 4H, CH), 1.42 (d, *J* = 6.8 Hz, 12H, CH₃), 1.21 (d, *J* = 6.8 Hz, 12H, CH₃), 0.05 (s, 36H, Si(CH₃)₃); ¹³C-NMR (C₆D₆) δ 147.81 (C^q), 141.12 (CH), 140.44 (C^q), 123.91 (CH), 120.00 (CH), 97.48 (CH), 28.23 (CH), 26.01 (CH₃), 22.70 (CH₃), 0.25 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₄₂H₇₅N₂O₂Si₄Ge₂: 899.3329. [(M+H)]⁺; found: 899.3361.

3.7. Reaction of **3** with S₈

Sulfur (0.03 mmol, 7.4 mg) and **3** (0.23 mmol, 100 mg) were mixed in benzene (2 mL) and the mixture was stirred at room temperature for 1 h. After the solvent was removed under vacuum, the product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford colorless crystals of **6a** (56 mg, 52%) and **6b** (7.5 mg, 7%).

6a: Mp: 230 °C (dec); ¹H-NMR (CDCl₃) δ 7.10 (t, *J* = 7.7 Hz, 2H, Ar-H), 6.89 (d, *J* = 7.7 Hz, 4H, Ar-H), 6.19 (d, *J* = 6.1 Hz, 2H, CH), 4.75 (d, *J* = 6.1 Hz, 2H, CH), 3.00 (dt, *J* = 13.6, 6.8 Hz, 4H, CH), 0.96 (d, *J* = 6.9 Hz, 12H, CH₃), 0.93 (d, *J* = 6.7 Hz, 12H, CH₃), 0.27 (s, 36H, Si(CH₃)₃); ¹³C-NMR (CDCl₃) δ 146.96 (C^q), 140.92 (CH), 139.61 (C^q), 126.38 (CH), 123.58 (CH), 98.98 (CH), 28.18 (CH), 26.00 (CH₃), 22.91 (CH₃), 1.05 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₄₂H₇₅N₂S₂Si₄Ge₂: 931.2872. [(M + H)]⁺; found: 931.2892.

6b: Mp: 237 °C (dec); ¹H-NMR (CDCl₃) δ 7.18 (m, 6H, Ar-H), 6.32 (d, *J* = 6.0 Hz, 2H, CH), 4.68 (d, *J* = 6.0 Hz, 2H, CH), 3.24 (dt, *J* = 13.5, 6.8 Hz, 4H, CH), 1.32 (d, *J* = 6.8 Hz, 12H, CH₃), 1.04 (d, *J* = 6.8 Hz, 12H, CH₃), −0.01 (s, 36H, Si(CH₃)₃); ¹³C-NMR (CDCl₃) δ 147.88 (C^q), 140.31 (CH), 139.73 (C^q), 126.90 (CH), 123.67 (CH), 98.65 (CH), 28.55 (CH), 26.56 (CH₃), 22.27 (CH₃), 0.61 (Si(CH₃)₃); HRMS (ESI): *m/z* calcd for C₄₂H₇₅N₂S₂Si₄Ge₂: 931.2872. [(M + H)]⁺; found: 931.2898.

3.8. X-ray Crystallography

X-ray data collection and structural refinement. Intensity data for compounds **1–5**, and **6a,b** was collected using a Bruker APEX II diffractometer. The crystals were measured at 103(2) K. The structure was solved by direct phase determination (SHELX-2013) and refined for all data by full-matrix least-squares methods on F² [67,68]. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC; 1447574, 1447575, 1447576, 1447577, 1447578, 1447579 and 1491124 contains 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.

3.9. Theoretical Study

Gaussian 09 was used for all density functional theory (DFT) calculations [69]. Geometry optimization and frequency calculations for **A**, **B**, **C** and **D** were performed at the B3LYP/6-31G(d,p) level of theory. Geometry optimization, frequency calculations, natural bond orbital (NBO) analysis of compound **3** were performed at the B3LYP/6-31G(d,p) level of theory.

4. Conclusions

In conclusion, we have developed a direct approach for the synthesis of a dichlorogermanium derivative **2** featuring a five-membered GeNC₃ ring through simple 1,4-addition of dichloro-germylene dioxane complex with α,β -unsaturated imine **1**. Subsequent reduction of **2** with KC₈ gave cyclic (alkyl)(amino)germylene (CAAGe) **3** possessing the low-lying LUMO, as supported by DFT calculations. Compound **3** readily reacted with TEMPO and N₂O. The former afforded 1:2 adduct **4** whereas the latter yielded the oxo-bridged dimer **5** stereoselectively. In contrast, oxidation of **3** with S₈ led to the formation of the sulfido-bridged dimers **6** as a mixture of two diastereomers involving Ge₂S₂ four-membered ring framework. Development of the silicon analogue of compound **3** is currently under investigation in our laboratory.

Supplementary Materials: Supplementary materials can be accessed at: <http://www.mdpi.com/1420-3049/21/8/990/s1>.

Acknowledgments: We are grateful to the Nanyang Technological University (NTU) and the Ministry of Education, Singapore (MOE2013-T2-1-005) for financial supports.

Author Contributions: L.W. and R.K. conceived and designed the experiments; L.W. and Y.S.L. performed the experiments; Y.L. and R.G. analyzed the X-ray data; L.W. and R.K. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gynane, M.J.S.; Harris, D.H.; Lappert, M.F.; Power, P.P.; Riviere, P.; Riviere-Baudet, M. Subvalent group 4B metal alkyls and amides. Part 5. The synthesis and physical properties of thermally stable amides of germanium(II), tin(II), and lead(II). *J. Chem. Soc. Dalton Trans.* **1977**, 2004–2009. [[CrossRef](#)]
2. Davidson, P.J.; Harris, D.H.; Lappert, M.F. Subvalent group 4B metal alkyls and amides. Part I. The synthesis and physical properties of kinetically stable bis[bis(trimethylsilyl)methyl]-germanium(II), -tin(II), and -lead(II). *J. Chem. Soc. Dalton Trans.* **1976**, 2268–2274. [[CrossRef](#)]
3. Harris, D.H.; Lappert, M.F. Monomeric, volatile bivalent amides of group IV_B elements, M(NR¹₂)₂ and M(NR¹R²)₂ (M = Ge, Sn, or Pb; R¹ = Me₃Si, R² = Me₃C). *J. Chem. Soc. Chem. Commun.* **1974**, 895–896. [[CrossRef](#)]
4. Asay, M.; Jones, C.; Driess, M. N-Heterocyclic carbene analogues with low-valent group 13 and group 14 elements: Syntheses, structures, and reactivities of a new generation of multitolerant ligands. *Chem. Rev.* **2011**, *111*, 354–396. [[CrossRef](#)] [[PubMed](#)]
5. Fischer, R.C.; Power, P.P. π -Bonding and the lone pair effect in multiple bonds involving heavier main group elements: Developments in the new millennium. *Chem. Rev.* **2010**, *110*, 3877–3923. [[CrossRef](#)] [[PubMed](#)]
6. Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Stable heavier carbene analogues. *Chem. Rev.* **2009**, *109*, 3479–3511. [[CrossRef](#)] [[PubMed](#)]
7. Nagendran, S.; Roesky, H.W. The chemistry of aluminum(I), silicon(II), and germanium(II). *Organometallics* **2008**, *27*, 457–492. [[CrossRef](#)]
8. Zabula, A.V.; Hahn, F.E. Mono- and bidentate benzannulated N-heterocyclic germylenes, stannylenes and plumblylenes. *Eur. J. Inorg. Chem.* **2008**, *2008*, 5165–5179. [[CrossRef](#)]
9. Lappert, M.; Protchenko, A.; Power, P.; Seeber, A. Subvalent amides of silicon and the group 14 metals. In *Metal Amide Chemistry*; John Wiley & Sons, Ltd.: Chichester, UK, 2008; pp. 263–326.
10. Herrmann, W.A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. Stable cyclic germanediyls (“cyclogermylenes”): Synthesis, structure, metal complexes, and thermolyses. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1485–1488. [[CrossRef](#)]

11. West, R.; Moser, D.F.; Guzei, I.A.; Lee, G.-H.; Naka, A.; Li, W.; Zabula, A.; Bukalov, S.; Leites, L. The surprising reactions of 1,3-di-tert-butyl-2,2-dichloro-1,3-diaza-2-germa-4-cyclopentene. *Organometallics* **2006**, *25*, 2709–2711. [[CrossRef](#)]
12. Gallego, D.; Brück, A.; Irran, E.; Meier, F.; Kaupp, M.; Driess, M.; Hartwig, J.F. From bis(silylene) and bis(germylene) pincer-type nickel(II) complexes to isolable intermediates of the nickel-catalyzed sonogashira cross-coupling reaction. *J. Am. Chem. Soc.* **2013**, *135*, 15617–15626. [[CrossRef](#)] [[PubMed](#)]
13. Jana, A.; Objartel, I.; Roesky, H.W.; Stalke, D. Cleavage of a N–H bond of ammonia at room temperature by a germylene. *Inorg. Chem.* **2009**, *48*, 798–800. [[CrossRef](#)] [[PubMed](#)]
14. Kobayashi, S.; Iwata, S.; Hiraishi, M. Novel 2:1 periodic copolymers from cyclic germylenes and p-benzoquinone derivatives. *J. Am. Chem. Soc.* **1994**, *116*, 6047–6048. [[CrossRef](#)]
15. Shoda, S.-I.; Iwata, S.; Kim, H.J.; Hiraishi, M.; Kobayashi, S. Poly(germanium thiolate): A new class of organometallic polymers having a germanium-sulfur bond in the main chain. *Macromol. Chem. Phys.* **1996**, *197*, 2437–2445. [[CrossRef](#)]
16. Shoda, S.-i.; Iwata, S.; Yajima, K.; Yagi, K.; Ohnishi, Y.; Kobayashi, S. Synthesis of germanium enolate polymers from germylene monomers. *Tetrahedron* **1997**, *53*, 15281–15295. [[CrossRef](#)]
17. Al-Rafia, S.M.I.; Malcolm, A.C.; Liew, S.K.; Ferguson, M.J.; Rivard, E. Stabilization of the heavy methylene analogues, GeH₂ and SnH₂, within the coordination sphere of a transition metal. *J. Am. Chem. Soc.* **2011**, *133*, 777–779. [[CrossRef](#)] [[PubMed](#)]
18. Hashimoto, H.; Tsubota, T.; Fukuda, T.; Tobita, H. Synthesis and structure of a hydrido(hydrogermylene) tungsten complex and its reactions with nitriles and ketones. *Chem. Lett.* **2009**, *38*, 1196–1197. [[CrossRef](#)]
19. Hlina, J.; Baumgartner, J.; Marschner, C.; Zark, P.; Müller, T. Coordination chemistry of disilylated germylenes with group 4 metallocenes. *Organometallics* **2013**, *32*, 3300–3308. [[CrossRef](#)] [[PubMed](#)]
20. Brück, A.; Gallego, D.; Wang, W.; Irran, E.; Driess, M.; Hartwig, J.F. Pushing the σ -donor strength in iridium pincer complexes: Bis(silylene) and bis(germylene) ligands are stronger donors than bis(phosphorus(III)) ligands. *Angew. Chem. Int. Ed.* **2012**, *51*, 11478–11482. [[CrossRef](#)] [[PubMed](#)]
21. Lappert, M.F.; Rowe, R.S. The role of group 14 element carbene analogues in transition metal chemistry. *Coord. Chem. Rev.* **1990**, *100*, 267–292. [[CrossRef](#)]
22. Petz, W. Transition-Metal complexes with derivatives of divalent silicon, germanium, tin, and lead as ligands. *Chem. Rev.* **1986**, *86*, 1019–1047. [[CrossRef](#)]
23. Li, Y.; Mondal, K.C.; Stollberg, P.; Zhu, H.; Roesky, H.W.; Herbst-Irmer, R.; Stalke, D.; Fliegl, H. Unusual formation of a N-heterocyclic germylene via homolytic cleavage of a C–C bond. *Chem. Commun.* **2014**, *50*, 3356–3358. [[CrossRef](#)] [[PubMed](#)]
24. Baker, R.J.; Jones, C.; Mills, D.P.; Pierce, G.A.; Waugh, M. Investigations into the preparation of groups 13–15 N-heterocyclic carbene analogues. *Inorg. Chim. Acta* **2008**, *361*, 427–435. [[CrossRef](#)]
25. Heinicke, J.; Oprea, A.; Kindermann, M.K.; Karpati, T.; Nyulászi, L.; Veszprémi, T. Unsymmetrical carbene homologues: Isolable pyrido[b]-1,3,2 λ^2 -diazasilole, -germole and -stannole and quantum-chemical comparison with unstable pyrido[c] isomers. *Chem. Eur. J.* **1998**, *4*, 541–545. [[CrossRef](#)]
26. Tomasik, A.C.; Hill, N.J.; West, R. Synthesis and characterization of three new thermally stable N-heterocyclic germylenes. *J. Organomet. Chem.* **2009**, *694*, 2122–2125. [[CrossRef](#)]
27. Fedushkin, I.L.; Skatova, A.A.; Chudakova, V.A.; Khvoinova, N.M.; Baurin, A.Y.; Dechert, S.; Hummert, M.; Schumann, H. Stable germylenes derived from 1,2-bis(arylimino)acenaphthenes. *Organometallics* **2004**, *23*, 3714–3718. [[CrossRef](#)]
28. Ullah, F.; Oprea, A.I.; Kindermann, M.K.; Bajor, G.; Veszprémi, T.; Heinicke, J. Homologues of N-heterocyclic carbenes: Detection and electronic structure of N-bridgehead pyrido[a]-annelated 1,3,2-diazagermol-2-ylidenes. *J. Organomet. Chem.* **2009**, *694*, 397–403. [[CrossRef](#)]
29. Huang, M.; Kireenko, M.M.; Zaitsev, K.V.; Oprunenko, Y.F.; Churakov, A.V.; Howard, J.A.K.; Lermontova, E.K.; Sorokin, D.; Linder, T.; Sundermeyer, J.; et al. Stabilized germylenes based on diethylenetriamines and related diamines: Synthesis, structures, and chemical properties. *Eur. J. Inorg. Chem.* **2012**, *2012*, 3712–3724. [[CrossRef](#)]
30. Karwasara, S.; Yadav, D.; Jha, C.K.; Rajaraman, G.; Nagendran, S. Single-Step conversion of silathiogermylene to germaacid anhydrides: Unusual reactivity. *Chem. Commun.* **2015**, *51*, 4310–4313. [[CrossRef](#)] [[PubMed](#)]
31. Okazaki, R.; Tokitoh, N. Heavy ketones, the heavier element congeners of a ketone. *Acc. Chem. Res.* **2000**, *33*, 625–630. [[CrossRef](#)] [[PubMed](#)]

32. Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, T.C.W. Synthesis of a germanium analogue of a dithiocarboxylic acid anhydride from the Ge(I) pyridyl-1-azaallyl dimer. *Chem. Commun.* **2009**, 6822–6824. [[CrossRef](#)] [[PubMed](#)]
33. Ding, Y.; Ma, Q.; Usón, I.; Roesky, H.W.; Noltemeyer, M.; Schmidt, H.-G. Synthesis and structures of $[\{HC(CMeNAr)_2\}Ge(S)X]$ (Ar = 2,6-*i*Pr₂C₆H₃, X = F, Cl, Me): Structurally characterized examples with a formal double bond between group 14 and 16 elements bearing a halide. *J. Am. Chem. Soc.* **2002**, *124*, 8542–8543. [[CrossRef](#)] [[PubMed](#)]
34. Kira, M.; Ishida, S.; Iwamoto, T.; Ichinohe, M.; Kabuto, C.; Ignatovich, L.; Sakurai, H. Synthesis and structure of a stable cyclic dialkylgermylene. *Chem. Lett.* **1999**, *28*, 263–264. [[CrossRef](#)]
35. Martin, D.; Soleilhavoup, M.; Bertrand, G. Stable singlet carbenes as mimics for transition metal centers. *Chem. Sci.* **2011**, *2*, 389–399. [[CrossRef](#)] [[PubMed](#)]
36. Martin, C.D.; Soleilhavoup, M.; Bertrand, G. Carbene-Stabilized main group radicals and radical ions. *Chem. Sci.* **2013**, *4*, 3020–3030. [[CrossRef](#)] [[PubMed](#)]
37. Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): Stable carbenes on the rise. *Acc. Chem. Res.* **2015**, *48*, 256–266. [[CrossRef](#)] [[PubMed](#)]
38. Melaimi, M.; Soleilhavoup, M.; Bertrand, G. Stable cyclic carbenes and related species beyond diaminocarbenes. *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849. [[CrossRef](#)] [[PubMed](#)]
39. Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. A brief survey of our contribution to stable carbene chemistry. *Organometallics* **2011**, *30*, 5304–5313. [[CrossRef](#)] [[PubMed](#)]
40. Roy, S.; Mondal, K.C.; Roesky, H.W. Cyclic alkyl(amino) carbene stabilized complexes with low coordinate metals of enduring nature. *Acc. Chem. Res.* **2016**, *49*, 357–369. [[CrossRef](#)] [[PubMed](#)]
41. Al-Rafia, S.M.I.; Momeni, M.R.; McDonald, R.; Ferguson, M.J.; Brown, A.; Rivard, E. Controlled growth of dichlorogermanium oligomers from lewis basic hosts. *Angew. Chem. Int. Ed.* **2013**, *52*, 6390–6395. [[CrossRef](#)] [[PubMed](#)]
42. Tokitoh, N.; Manmaru, K.; Okazaki, R. Synthesis and crystal structure of the first base-free diarylgermylene-transition metal mononuclear complexes. *Organometallics* **1994**, *13*, 167–171. [[CrossRef](#)]
43. Naka, A.; Hill, N.J.; West, R. Free radical reactions of stable silylenes and germylenes. *Organometallics* **2004**, *23*, 6330–6332. [[CrossRef](#)]
44. Tokitoh, N.; Matsumoto, T.; Okazaki, R. Formation and reactions of the first diarylgermanone stable in solution. *Chem. Lett.* **1995**, *24*, 1087–1088. [[CrossRef](#)]
45. Jutzi, P.; Schmidt, H.; Neumann, B.; Stammer, H.-G. Bis(2,4,6-tri-*tert*-butylphenyl)germylene reinvestigated: Crystal structure, lewis acid catalyzed C–H insertion, and oxidation to an unstable germanone. *Organometallics* **1996**, *15*, 741–746. [[CrossRef](#)]
46. Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. Diverse reactions of nitroxide-radical adducts of silylene, germylene, and stannylene. *J. Organomet. Chem.* **2004**, *689*, 1337–1341. [[CrossRef](#)]
47. Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. Addition of stable nitroxide radical to stable divalent compounds of heavier group 14 elements. *J. Am. Chem. Soc.* **2003**, *125*, 9300–9301. [[CrossRef](#)] [[PubMed](#)]
48. Spikes, G.H.; Peng, Y.; Fettingner, J.C.; Steiner, J.; Power, P.P. Different reactivity of the heavier group 14 element alkyne analogues Ar'MMAR' (M = Ge, Sn; Ar' = C₆H₃₋₂,6(C₆H₃₋₂,6-Prⁱ)₂) with R₂NO. *Chem. Commun.* **2005**, 6041–6043. [[CrossRef](#)] [[PubMed](#)]
49. Ramaker, G.; Schäfer, A.; Saak, W.; Weidenbruch, M. One-Pot synthesis of a tetragermabutadiene and its reactions with oxygen and sulfur. *Organometallics* **2003**, *22*, 1302–1304. [[CrossRef](#)]
50. Ellis, D.; Hitchcock, P.B.; Lappert, M.F. Preparation and X-ray structure of $[Ge\{N(SiMe_3)_2\}_2(\mu-O)]_2$, a rare 1,3-cyclodigermoxane. *J. Chem. Soc. Dalton Trans.* **1992**, 3397–3398. [[CrossRef](#)]
51. Masamune, S.; Batcheller, S.A.; Park, J.; Davis, W.M.; Yamashita, O.; Ohta, Y.; Kabe, Y. Oxygenation of digermene derivatives. *J. Am. Chem. Soc.* **1989**, *111*, 1888–1889. [[CrossRef](#)]
52. Jana, A.; Roesky, H.W.; Schulzke, C. Reactivity of germanium(II) hydride with nitrous oxide, trimethylsilyl azide, ketones, and alkynes and the reaction of a methyl analogue with trimethylsilyl diazomethane. *Dalton Trans.* **2010**, *39*, 132–138. [[CrossRef](#)] [[PubMed](#)]
53. Yao, S.; Xiong, Y.; Driess, M. From NHC→germylenes to stable NHC→germanone complexes. *Chem. Commun.* **2009**, 6466–6468. [[CrossRef](#)] [[PubMed](#)]

54. Yao, S.; Xiong, Y.; Wang, W.; Driess, M. Synthesis, structure, and reactivity of a pyridine-stabilized germanone. *Chem. Eur. J.* **2011**, *17*, 4890–4895. [[CrossRef](#)] [[PubMed](#)]
55. Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. A heterofulvene-like germylene with a betain reactivity. *Angew. Chem. Int. Ed.* **2006**, *45*, 4349–4352. [[CrossRef](#)] [[PubMed](#)]
56. Wang, W.; Inoue, S.; Enthaler, S.; Driess, M. Bis(silylenyl)- and bis(germylenyl)-substituted ferrocenes: Synthesis, structure, and catalytic applications of bidentate silicon(II)–cobalt complexes. *Angew. Chem. Int. Ed.* **2012**, *51*, 6167–6171. [[CrossRef](#)] [[PubMed](#)]
57. Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. A stable germanone as the first isolated heavy ketone with a terminal oxygen atom. *Nat. Chem.* **2012**, *4*, 361–365. [[CrossRef](#)] [[PubMed](#)]
58. Liew, S.K.; Al-Rafia, S.M.I.; Goettel, J.T.; Lummis, P.A.; McDonald, S.M.; Miedema, L.J.; Ferguson, M.J.; McDonald, R.; Rivard, E. Expanding the steric coverage offered by bis(amidosilyl) chelates: Isolation of low-coordinate n-heterocyclic germylene complexes. *Inorg. Chem.* **2012**, *51*, 5471–5480. [[CrossRef](#)] [[PubMed](#)]
59. Al-Rafia, S.M.I.; Lummis, P.A.; Ferguson, M.J.; McDonald, R.; Rivard, E. Low-Coordinate germylene and stannylene heterocycles featuring sterically tunable bis(amido)silyl ligands. *Inorg. Chem.* **2010**, *49*, 9709–9717. [[CrossRef](#)] [[PubMed](#)]
60. Bazinet, P.; Yap, G.P.A.; Richeson, D.S. Synthesis and properties of a germanium(II) metalloheterocycle derived from 1,8-di(isopropylamino)naphthalene. A novel ligand leading to formation of $\text{Ni}\{\text{Ge}[(i\text{PrN})_2\text{C}_{10}\text{H}_6]\}_4$. *J. Am. Chem. Soc.* **2001**, *123*, 11162–11167. [[CrossRef](#)] [[PubMed](#)]
61. Matsumoto, T.; Tokitoh, N.; Okazaki, R. The first kinetically stabilized germanethiones and germaneselonones: Syntheses, structures, and reactivities. *J. Am. Chem. Soc.* **1999**, *121*, 8811–8824. [[CrossRef](#)]
62. Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. Synthesis and crystal structure of the first stable diarylgermanethione. *J. Am. Chem. Soc.* **1993**, *115*, 8855–8856. [[CrossRef](#)]
63. Xiong, Y.; Yao, S.; Karni, M.; Kostenko, A.; Burchert, A.; Apeloig, Y.; Driess, M. Heavier congeners of CO and CO₂ as ligands: From zero-valent germanium ('germylone') to isolable monomeric GeX and GeX₂ complexes (X = S, Se, Te). *Chem. Sci.* **2016**, *7*, 5462–5469. [[CrossRef](#)]
64. Sinhababu, S.; Yadav, D.; Karwasara, S.; Sharma, M.K.; Mukherjee, G.; Rajaraman, G.; Nagendran, S. The preparation of complexes of germanone from a germanium μ -oxo dimer. *Angew. Chem. Int. Ed.* **2016**, *55*, 7742–7746. [[CrossRef](#)] [[PubMed](#)]
65. Xiong, Y.; Yao, S.; Driess, M. Chemical tricks to stabilize silanones and their heavier homologues with E=O bonds (E = Si–Pb): From elusive species to isolable building blocks. *Angew. Chem. Int. Ed.* **2013**, *52*, 4302–4311. [[CrossRef](#)] [[PubMed](#)]
66. Yan, L.; Sun, X.; Li, H.; Song, Z.; Liu, Z. Geminal bis(silyl) enal: A versatile scaffold for stereoselective synthesizing C³,O¹-disilylated allylic alcohols based upon anion relay chemistry. *Org. Lett.* **2013**, *15*, 1104–1107. [[CrossRef](#)] [[PubMed](#)]
67. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]
68. SHELX-2013. Available online: <http://shelx.uni-ac.gwdg.de/SHELX/index.php> (accessed on 15 July 2014).
69. *Gaussian 09*, Revision B.01; Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al.; Gaussian, Inc.: Wallingford, CT, USA, 2010.

Sample Availability: Samples of the compounds are not available from the authors.



© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).