Inorganic Chemistry

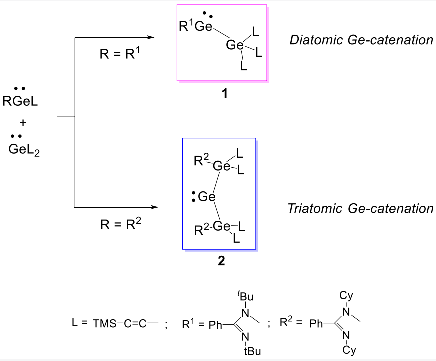
pubs.acs.org/IC Article

Formation of Alkynylgermyl-Substituted Germylenes via a Catenation of Ge Atoms

Chenghuan Liu, Keke Zhu, Weichun Han, Xue Liu, Zheng-Feng Zhang, Ming-Der Su,* Di Wu,* and Yan Li*

Cite This: https://dx.doi.org/10.1021/acs.inorgchem.0c01244

ABSTRACT: Reactions of amidinate-stabilized germylene chlorides $R^1Ge(:)Cl$ (R^1 = $PhC(NtBu)_2$) and $R^2Ge(:)Cl$ (R^2 = $PhC(NCy)_2$, Cy = cyclohexanyl) with trimethylsilylethynyl lithium salt (LLi, L = $-C{\equiv}CTMS$) afforded alkynylgermyl-substituted germylenes $R^1(:)Ge\text{-}GeL_3$ (**1**) and $[R^2GeL_2]_2Ge(:)$ (**2**), respectively. Both of them may undergo the formation of Ge−Ge single bonds with a concomitant 1,2-shift of ethynyl groups. DFT calculations determined the reaction pathways where two possible intermediates $(:)GeL_2$ and $RGe(:)L$ (R = R^1, R^2) are proposed, which were consistent with the trapping reactions of $(:)GeL^2$ toward $I_{Ar}-(:)GeL^2$ (**3**, I_{Ar} = $:C\{N(Ar)CH\}_2$, Ar = 2,6-$iPr_2C_6H_3$). The reaction of **1** with N_3TMS gave a new aminogermylene $R^1(:)Ge-N(TMS)\text{-}GeL_3$ (**4**), indicating a reactive Ge−Ge bond.



■ INTRODUCTION

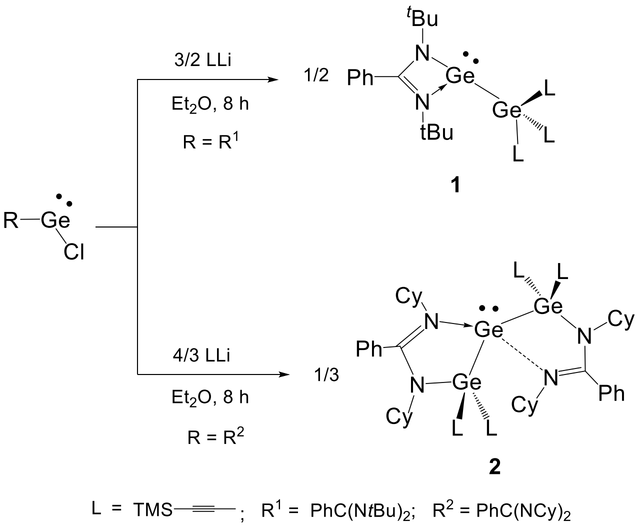
Monomeric germylenes ($R_2Ge(:)$) are reactive organometallic building blocks for germanium-containing compounds with unique electronic structures, owing to the lone pair of electrons and vacant p orbital on the Ge atom.[1] Their synthetic strategies have been extensively documented including the metathesis reactions, the reduction of germanium halide precursors with alkali metals, or the activation of the noninnocent ligand skeletons.[2] Polygermanes $(R_2Ge)_n$ containing catenated Ge atoms are widely explored as optoelectronic materials,[3] which can be considered as the polymeric/oligomeric form of monomeric germylenes. They are mainly synthesized via Wurtz-type coupling reactions, reaction of Grignard reagents with organogermanium halides, Lewis acid-catalyzed rearrangement of oligogermylsilanes, and hydrogermolysis reactions.[4] Several radical-mediated coupling reactions of monomeric germylenes toward digermylenes were also reported.[2c,d,4d] Notably, a polyhalogermane compound $I_{Ar}\text{-}GeCl_2-(:)Ge(GeCl_3)_2$ (I_{Ar} = $:C\{N(Ar)CH\}_2$, Ar = 2,6-$iPr_2C_6H_3$) with a branched Ge_4 core containing Ge centers in formal oxidation states of 0, +2, and +3 was synthesized by Rivard and co-workers via sequential additions of $[(:)GeCl_2]$ units.[5] Synthesis of similar structure $Me_2EtN\text{-}SiCl_2-(:)Si(SiCl_3)_2$ was also achieved through amine-induced disproportionation of Si_2Cl_6 under low temperatures.[6] Theoretical calculations supported both reactions proceeding through a consecutive halide migration to construct a catenated E−E (E = Si, Ge) structure, which paves a way to access novel group 14 heavier analogues of hydrocarbons. Through a surveying of the literature, formation of the polygermanes containing low-valent Ge atoms has not been extensively investigated in recent research.[7,15] In this context, we were intrigued to explore if such Ge catenation can be employed in developing new structures possessing active Ge(II)−C bonds. In this work, we present the syntheses and mechanistic studies of alkynylgermyl-substituted germylenes, which undergo a catenation of Ge atoms.

■ RESULTS AND DISCUSSION

It is well-known that reactions of germylene chlorides with alkynyllithium salts afford $RGe(:)-C{\equiv}CR'$ (R, R′ = organic groups) as routine substituted products.[2e,8−10] Interestingly, treatment of an amidinate-stabilized germylene $R^1Ge(:)Cl$ (R^1 = $PhC(NtBu)_2$) with the solid of trimethylsilylethynyl lithium salt LLi (prepared in advance, L = $-C{\equiv}CTMS$)[16] in a molar ratio of 1:1 in Et_2O did not give product $R^1Ge(:)L$; instead, a mixture of unreacted $R^1Ge(:)Cl$ and a new compound $R^1(:)Ge\text{-}GeL_3$ (**1**) was obtained, confirmed by the ^1H NMR spectrum. When the reaction molar ratio was changed to 2:3, compound **1** was exclusively isolated as colorless crystals in 51% yield (Scheme 1). Using Et_2O as a solvent is advantageous over THF and toluene since the yields of **1** in the latter two

Received: April 26, 2020

Scheme 1. Syntheses of Compounds 1 and 2



solvents are low. The ^{1}H NMR spectrum of **1** shows the ^{t}Bu-*H* (δ 1.17 ppm) of an amidinate ligand and ethynyl TMS-*Me* (δ 0.08 ppm) resonances. X-ray crystallography of **1** exhibits a tri(TMS)ethynylgermyl-substituted germylene structure (Figure 1). The Ge1 atom is pyramidalized due to the presence of a lone pair ($\sum$°Ge1 = 251.74°). The Ge1−Ge2 bond distance (ca. 2.5068(8) Å) of **1** is slightly longer than ordinary Ge−Ge single bonds (2.41−2.48 Å)[1a,4a] and is comparable to that (2.5439(7) Å) of the alkylgermyl germylene 2,6-Mes$_2$C$_6$H$_3$Ge−Ge^{t}Bu$_3$ (Mes = mesityl).[11] To the best of our knowledge, compound **1** is the first isolated germylene with alkynylgermyl substitutent.

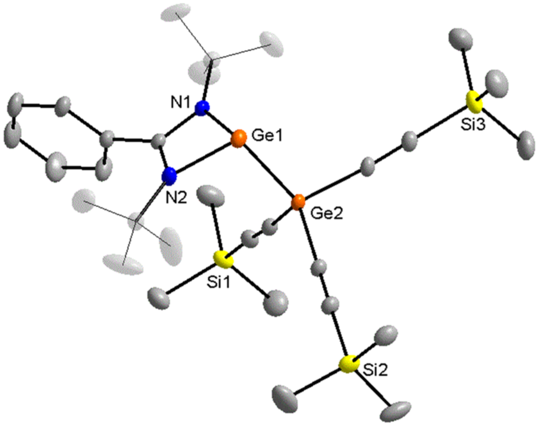


Figure 1. Molecular structure of **1** (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge(1)−Ge(2) 2.5068(8), N(1)−Ge(1) 1.986(3), N(2)−Ge(1) 1.976(3); N(1)−Ge(1)−N(2) 65.38(13), N(1)−Ge(1)−Ge(2) 92.49(9), N(2)−Ge(1)−Ge(2) 93.87(9).

It is anticipated that the possible generation of (:)GeL (L = −C≡CTMS) moiety in the formation of **1** triggers bonding activations, and we were curious to know if any new reaction arises when the amidinate ligand is varied. Therefore, treatment of R^{2}Ge(:)Cl (R^2 = PhC(NCy)$_2$, Cy = cyclohexanyl) with LLi in a molar ratio of 3:4[12] in Et$_2$O facilely afforded compound [R^{2}GeL$_2$]$_2$Ge(:) (**2**) as colorless crystals in 56% yield (Scheme 1). Product R^{2}Ge(:)-L through simple substitution was not isolated. The ^{1}H NMR spectrum of **2** shows multiple singlets of TMS-*Me* at a range of δ 0.11−0.37 ppm, and ^{29}Si NMR shows four singlets at δ −19.0, −19.4, −19.6, and −20.2 ppm, indicative of different −SiMe$_3$ environments.

In contrast to compound **1**, the molecular structure of **2** shows a Ge−Ge−Ge chain,[14b] which can be considered as a base-stabilized bis(dialkynylgermyl) germylene (Figure 2). The central Ge3 atom adopts significantly pyramidalized geometry ($\sum$°Ge3 = 262.36°) showing the presence of a lone pair. Each Ge1 and Ge2 atom is substituted with two TMS−ethynyl groups. The two Ge−Ge bond distances (2.4310(4) Å and 2.4373(5) Å) fall in the range of a Ge−Ge single bond,[1a,4a] which are obviously shorter than that of **1** (ca. 2.5068(8) Å). The N1 atom shows weak interaction toward the Ge3 center, owing to the much longer Ge3−N1 distance (ca. 2.519 Å) than that of the Ge3−N4 coordinative bond (2.260(2) Å). The Ge$_3$ chain is almost rectangular (Ge1−Ge3−Ge2 angle: 94.728(15)°), which is close to that (Ge−Ge−Ge angle: 90.46(3)°) of the [(:)Ge(GeCl$_3$)$_2$] fragment in the polyhalogermane I$_{Ar}$-GeCl$_2$−(:)Ge(GeCl$_3$)$_2$ (I$_{Ar}$ = :C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[5] while it is more acute than those found in the functionalized Ge$_3$ species (cAAC)Ge(GeR^1)$_2$ (107.65(2)°; cAAC = cyclic alkyl(amino) carbene; R^1 = PhC(N*t*Bu)$_2$)[13] and trigermaallene (RGe)$_2$Ge (122.61(6)°; R = [CC(TMS)$_2$]$_2$).[14a]

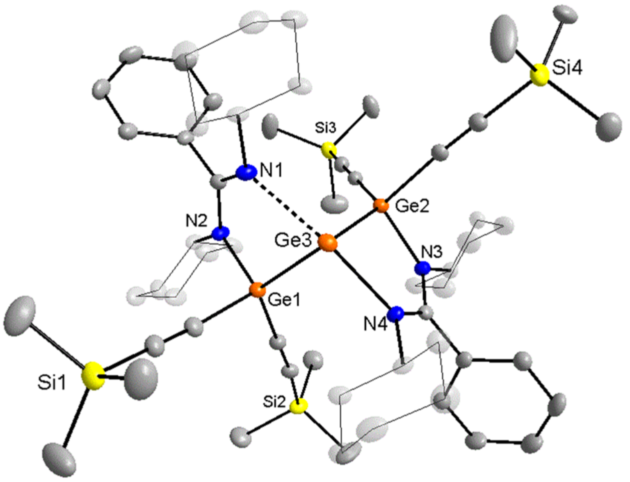


Figure 2. Molecular structure of **2** (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge(1)−Ge(3) 2.4310(4), Ge(2)−Ge(3) 2.4373(5), Ge(1)−N(2) 1.895(2), Ge(2)−N(3) 1.906(2), Ge(3)−N(4) 2.260(2); N(2)−Ge(1)−Ge(3) 107.63(7), N(3)−Ge(2)−Ge(3) 101.38(7), Ge(1)−Ge(3)−N(4) 91.55(6), Ge(2)−Ge(3)−N(4) 76.08(6), Ge(1)−Ge(3)−Ge(2) 94.728(15).

Compounds **1** and **2** demonstrate a structural character of double or triple catenation of Ge atoms. Two possible key intermediates RGe(:)L (R = R^1 or R^2) and (:)GeL$_2$ are generated at the beginning of reactions, on the basis of which a formal insertion reaction of Ge(II) atoms into Ge(II)−C$_{sp}$ bonds is then proposed via the formation of Ge−Ge single bonds with concomitant transfer of L groups.[15]

To get a better understanding of the mechanism, DFT calculations were performed at the M06-2X/def2-TZVP//M06-2X/def2-SVP level.[16] As shown in Figure 3, the stoichiometric reactions of RGe(:)Cl (R = R^1 or R^2) with

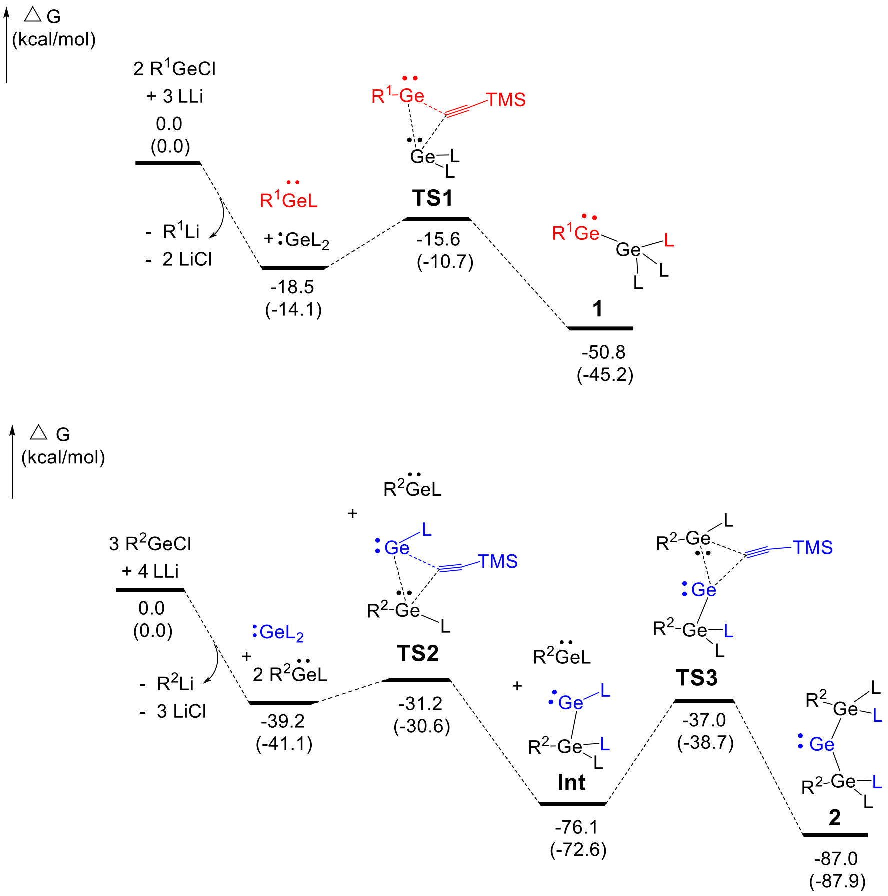
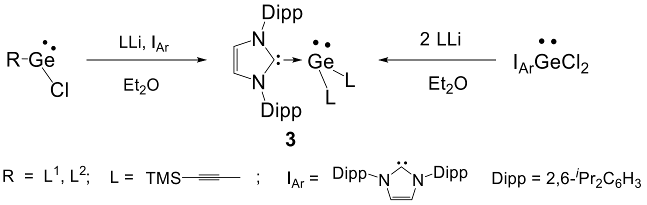


Figure 3. Proposed mechanisms for the formation of **1** and **2**. Free energy data are given in each step at the M06-2X/def2-TZVP/SMD//M06-2X/def2-SVP and M06-2X/def2-SVP (in bracket) levels of theory. (The energy of LiCl is for the gas phase.)

LLi in molar ratios of 2:3 and 3:4 give two intermediates, RGe(:)L and (:)GeL$_2$, in an equivalent molar ratio by eliminating LiCl and LLi, which is energetically favored by 18.5 and 39.2 kcal/mol, respectively. For the former case, R^{1}Ge(:)L interacts readily (2.9 kcal/mol) with (:)GeL$_2$ via a transition state of **TS1**, where the Ge−C$_{sp}$ bond of R^{1}Ge(:)L is weakened and a Ge$_2$C three-membered ring is built in a concerted manner. Then, formation of a Ge−Ge bond occurs with an intermolecular transfer of the L group from R^{1}Ge(:)L to (:)GeL$_2$ leading to product **1**, showing energetic preference by 35.2 kcal/mol. In contrast, a different formation route is shown in the case of compound **2** (Figure 3). The interaction between R^{2}Ge(:)L and (:)GeL$_2$ forms a Ge$_2$C three-membered ring (**TS2**), where the Ge−C$_{sp}$ bond cleavage of (:)GeL$_2$ instead of R^{2}Ge(:)L happens. A subsequent migration of the L group as well as the formation of a Ge−Ge bond lead to intermediate R^{2}GeL$_2$−(:)GeL (**Int**) with a substantial total free energy change of 44.9 kcal/mol (calculated by considering one remaining R^{2}Ge(:)L molecule). Furthermore, the **Int** reacts with another molecule of R^{2}Ge(:)L in solution through similar concerted Ge$_2$C three-membered ring (**TS3**) by conquering a barrier of 39.1 kcal/mol to obtain product **2**. Due to the large excess energy of 76.1 kcal/mol obtained by the decay from reactants (3RGe(:)Cl + 4LLi) to **Int** (with one R^{2}Ge(:)L molecule), the above energy barrier can be easily surmounted. Theoretical results estimated that the relative energy of the final product **2** is −87.0 kcal/mol, with respect to the corresponding reactants (3RGe(:)Cl + 4LLi). Accordingly, the present theoretical findings suggest that both reactions given in Figure 3 can readily proceed since all the relative energies of the critical points (such as **TS1**, **1**, and **TS2**, **Int**, **TS3**, **2**) are calculated to be lower than those of their corresponding reactants.[17] Such germylene formation is rare, which is comparable to the reported carbene-supported (GeCl$_2$)$_x$ oligomers via formal Ge(II) insertion into the Ge(II)−Cl bonds.[5]

Numerous attempts to isolate intermediates RGe(:)L (R = R^1, R^2) were not successful. But the existence of key intermediate (:)GeL$_2$ can be evidenced by the reactions of RGe(:)Cl (R = R^1 and R^2) with LLi in the presence of N-heterocyclic carbene I$_{Ar}$ (:C{N(Ar)CH}$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) as a trapping reagent (Scheme 2). Dialkynylgermylene compound I$_{Ar}$−(:)GeL$_2$ (**3**) was successfully isolated as colorless plates from both reactions, yielding 31% and 34%, respectively. A similar (:)Ge(C≡CPh)$_2$ species was postulated as intermediate in the formation of lithium germinate [{(PhC≡C)$_3$Ge}$_3$GeLi(Et$_2$O)$_3$].[9] Compound **3** can be

Scheme 2. Trapping Reactions of (:)GeL$_2$ Intermediate and the Alternative Synthesis of Compound 3

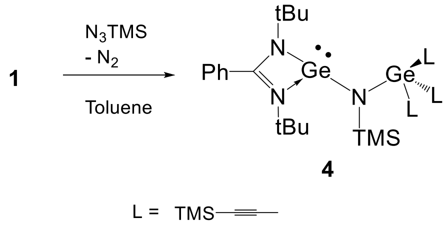


https://dx.doi.org/10.1021/acs.inorgchem.0c01244

alternatively synthesized by stoichiometric reaction of I_{Ar}−(:)$GeCl_2$ and LLi in 75% yield.[16] The X-ray structure of **3** shows two types of configurations in one asymmetric unit (Figure S1 in Supporting Information), where the (:)GeL_2 moiety in one molecule is distorted probably due to the crystal packing effect.[18]

To investigate the reactivity of the newly synthesized germylenes, compound **1** was treated with organic azide N_3TMS in a molar ratio of 1:1 in toluene. Compound R^1(:)Ge−N(TMS)−GeL_3 (**4**) was smoothly afforded as colorless crystals in 90% yield (Scheme 3). The X-ray crystallography of **4** clearly shows an aminogermylene structure (Figure 4), where the Ge1 atom adopts pyramidalized geometry (∑°Ge1 = 275.70°) indicating the presence of a lone pair. The formation of **4** may undergo a possible germanimine[19] R^1Ge(═NTMS)−GeL_3, accompanied by a migration of the −GeL_3 group from the $Ge_{Ge=N}$ atom to the $N_{Ge=N}$ atom, showing a reactive Ge−Ge bond in compound **1**.[19] This reaction mode contrasts markedly with the ubiquitous formation of stable Ge═N species or azagermanes containing Ge_2N, GeN_4, and Ge_2N_2 rings.[20] A similar reaction was not reported in the alkylgermyl germylene 2,6-$Mes_2C_6H_3$Ge−Ge*t*Bu_3 (Mes = mesityl) system with the strong electron-donating −Ge*t*Bu_3 substituent.[11] The related reaction of compound **2** with N_3TMS shows the formation of a product mixture containing unknown species transpired, which is still under investigation now.

Scheme 3. Synthesis of Compound 4



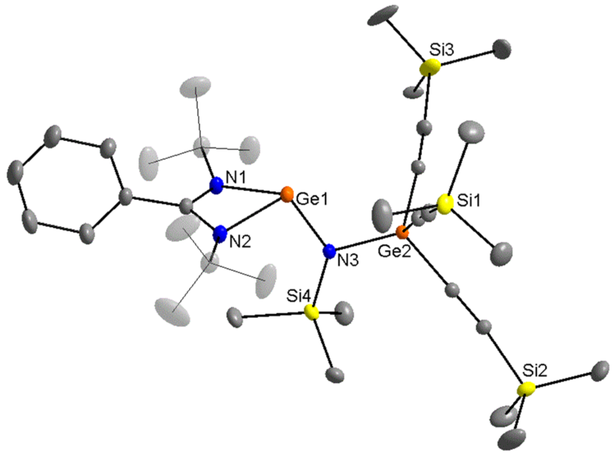


Figure 4. Molecular structure of **4** (H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): N(1)−Ge(1) 2.011(3), N(2)−Ge(1) 2.020(3), N(3)−Ge(1) 1.913(2), N(3)−Si(4) 1.738(3), N(3)−Ge(2) 1.818(2); N(1)−Ge(1)−N(3) 106.30(11), N(2)−Ge(1)−N(3) 104.96(11), N(2)−Ge(1)−N(3) 64.443(11), Ge(1)−N(3)−Ge(2) 106.45(11), Ge(1)−N(3)−Si(4) 133.77(13), Ge(2)−N(3)−Si(4) 119.78(13).

■ CONCLUSION

In summary, alkynylgermyl-substituted germylenes **1** and **2** were synthesized by reactions of amidinate-stabilized germylene chlorides RGe(:)Cl (R = R^1, R^2) with TMS−C≡CLi salt, which may undergo the formation of Ge−Ge single bonds with concomitant 1,2-shifts of ethynyl groups. The mechanisms were supported by DFT calculations and the capture reactions of the key intermediate (:)GeL_2. The amidinate scaffolds may have an important influence upon dictating the Ge catenation style. It is assumed that the Cy group has less steric hindrance than *t*Bu, which could facilitate the addition of another Ge unit in **2**. Compound **1** exhibits unique reactivity toward N_3TMS to form an aminogermylene **4**, which was rarely reported in the reaction modes of germylenes with organic azides. Exploration of other catenated Ge species containing the Ge−C_{sp} bond and relevant reactivity studies toward small molecules are currently under way.

■ EXPERIMENTAL SECTION

All manipulations were carried out under a dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. Organic solvents Et_2O, THF, toluene, and *n*-hexane were dried by refluxing with Na/K under N_2 prior to use. R^1GeCl (R^1 = PhC(N*t*Bu)$_2$),[2c] I_{Ar} (:C{N(Ar)CH}$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$),[21] and $I_{Ar}GeCl_2$[22] were synthesized according to the literature. TMSC≡CH (LH, L = TMSC≡C−) and N_3TMS were dried by CaH_2 prior to use. R^2GeCl (R^2 = PhC(NCy)$_2$, Cy = cyclohexanyl) was prepared in the same manner as R^1GeCl and was used directly. LLi (L = TMSC≡C−) was prepared in advance by the treatment of LH with *n*-BuLi (1.05 equiv) in *n*-hexane at room temperature, which was used directly as white powder.[23] ^{1}H NMR spectra were recorded on a Bruker Avance II 400 spectrometer, and ^{13}C{^{1}H} and ^{29}Si spectra were recorded on a Bruker Avance II 500 spectrometer. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from TCI and J&K Chemical Co.

Synthesis of 1. At −78 °C, Et_2O (25 mL) was added to a mixture of R^1GeCl (0.68 g, 2.0 mmol) and LLi (0.33 g, 3.0 mmol). The mixture was allowed to warm to room temperature and stirred overnight. The suspension was filtered and the filtrate was dried under a vacuum to give an oily solid. The residue was extracted with *n*-hexane (ca. 5 mL), and colorless crystals of **1** were grown at 0 °C. Yield: 0.34 g (51% based on R^1GeCl). mp: 143 °C (dec.). Elemental analysis calcd (%) for $C_{30}H_{50}Ge_2N_2Si_3$ (668.26, the solvent *n*-hexane was removed after drying the crystals): C, 53.92; H, 7.54; N, 4.19. Anal. found: C, 53.60; H, 7.42; N, 3.89. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.93 (m, 1H, Ph*H*), 7.13−6.95 (m, 4H, Ph*H*), 1.17 (s, 18H, *t*Bu*H*), 0.08 (s, 27H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 298 K, ppm): δ = 165.1(Ph*C*N_2), 135.2, 131.6, 129.4, 127.7, (Ph*C*) 114.1(≡*C*Si), 110.6(Ge*C*≡), 53.1(*C*Me_3), 31.4(C*Me*$_3$), 0.4(Si*Me*$_3$). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K, ppm): δ −19.9.

Synthesis of 2. At−78 °C, Et_2O (25 mL) was added to a mixture of R^2GeCl (0.59 g, 1.5 mmol) and LLi (0.22 g, 2.0 mmol). The mixture was allowed to warm to room temperature and stirred overnight. The suspension was filtered, and the filtrate was dried under a vacuum to give an oily solid. The residue was extracted with *n*-hexane (ca. 5 mL), and colorless crystals of **2** were grown at room temperature. Yield: 0.33 g (56% based on R^2GeCl). mp: 130 °C (dec.). Elemental analysis calcd (%) for $C_{58}H_{90}Ge_3N_4Si_4$ (1173.62): C, 59.36; H, 7.73; N, 4.77. Anal. found: C, 59.52; H, 7.18; N, 4.56. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 7.75 (m, 1H, Ph*H*), 7.38−6.85 (m, 4H, Ph*H*), 3.31−0.72 (m, 44H, Cy*H*), 0.37−0.11 (m, 36H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 298 K, ppm): δ 167.8 (Ph*C*N_2), 137.0, 135.4, 126.5, 125.6 (Ph*C*), 118.3, 116.7 (≡*C*Si), 115.1, 111.0 (Ge*C*≡), 66.0, 60.9, 60.4, 54.3, 36.6, 36.5, 35.1, 33.8, 33.6, 27.1, 26.7, 26.5, 26.2, 25.9, 25.8, 25.3 (Cy*C*), 1.5, 1.1, 0.4, 0.0 (Si*Me*$_3$). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K, ppm): δ −19.0, −19.4, −19.6, −20.2 (*Si*Me_3).

*Trapping Reactions of GeL$_2$ toward I$_{Ar}$GeL$_2$ (**3**).* (A) At room temperature, Et$_2$O (30 mL) was added to a mixture of R^{1}GeCl (0.34 g, 1.0 mmol), LLi (0.11 g, 1.0 mmol), and I$_{Ar}$ (0.39 g, 1.0 mmol). The mixture was allowed to warm to room temperature and stirred overnight. The suspension was filtered, and the filtrate was dried under a vacuum to give an oily solid. Colorless plates of **3** were grown slowly from a mixture of THF/*n*-hexane solvents at room temperature. Yield: 0.20 g (31%). (B) At room temperature, Et$_2$O (30 mL) was added to a mixture of R^{2}GeCl (0.39 g, 1.0 mmol), LLi (0.11 g, 1.0 mmol), and I$_{Ar}$ (0.39 g, 1.0 mmol). The mixture was allowed to warm to room temperature and stirred overnight. The suspension was filtered, and the filtrate was dried under a vacuum to give an oily solid. Colorless plates of **3** were grown slowly from a mixture of THF/*n*-hexane solvents at room temperature. Yield: 0.22g (34%).

Alternative Synthesis of 3. At room temperature, Et$_2$O (30 mL) was added to a mixture of I$_{Ar}$GeCl$_2$(0.53 g, 1.0 mmol) and LLi (0.21 g, 2.0 mmol). The mixture was allowed to warm to room temperature and was stirred overnight. The suspension was filtered, and the filtrate was concentrated under a vacuum to give colorless crystals of **3**. Yield: 0.49 g (75%). mp: 154 °C (dec.). Elemental analysis calcd (%) for $C_{37}H_{54}GeN_2Si_2$ (655.66): C, 67.78; H, 8.30; N, 4.27. Anal. found: C, 67.52; H, 8.13; N, 4.06. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K, ppm): δ 7.18−6.90 (m, 6H, Ph*H*), 6.25 (s, 2H, C*H*), 2.70 (sept, 4H, $^3J_{HH}$ = 8.0 Hz, C*H*Me$_2$), 1.42 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH*Me*$_2$), 0.95 (d, 12H, $^3J_{HH}$ = 8.0 Hz, CH*Me*$_2$), 0.00 (s, 18H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K, ppm): δ 174.7 (NCN), 145.0, 133.6, 130.0, 126.9 (Ph*C*), 123.4 (≡*C*Si), 113.0 (Ge*C*≡), 28.2 (*C*HMe$_2$), 24.3, 22.8 (CH*Me*$_2$), 0.0 (Si*Me*$_3$). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 298 K, ppm): δ −24.0 (*Si*Me$_3$).

Synthesis of 4. At room temperature, N$_3$TMS (0.15 mL, 1.0 mmol) was added to the solution of **1** (0.67 g, 1.0 mmol) in toluene (25 mL). The mixture was stirred overnight. The insoluble materials were removed by filtration, and the filtrate was dried under a vacuum to give a gray oil. The oil was extracted with *n*-hexane (8 mL), and the extract was kept at 0 °C for 12 h to give colorless crystals of **4**. Yield: 0.68 g (90%). mp: 146 °C (dec.). Elemental analysis calcd (%) for $C_{33}H_{59}Ge_2N_3Si_4$ (755.46): C, 52.47; H, 7.87; N, 5.56. Anal. found: C, 52.98; H, 7.34; N, 5.85. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K, ppm): δ 8.01 (m, 1H, Ph*H*), 7.33 (m, 1H, Ph*H*), 7.08−6.83 (m, 3H, Ph*H*), 1.32 (s, 6H, *t*Bu*H*), 1.22 (s, 12H, *t*Bu*H*), 0.83 (s, 3H, NSi*Me*$_3$), 0.78 (s, 6H, NSi*Me*$_3$), 0.11 (s, 9H, CSi*Me*$_3$), 0.08 (s, 18H, CSi*Me*$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K, ppm): δ 165.0 (Ph*C*N$_2$), 136.7, 130.0, 128.1, 127.9 (Ph*C*), 114.3, 113.8 (≡*C*Si), 112.1, 110.2 (Ge*C*≡), 54.3 (*C*Me$_3$), 32.9, 32.6 (C*Me*$_3$), 5.8, 5.5 (NSi*Me*$_3$), 0.1, 0.0 (CSi*Me*$_3$). ^{29}Si{^{1}H} NMR (99 MHz, C$_6$D$_6$, 298 K, ppm): δ 10.22 (N*Si*Me$_3$), −18.5 (C*Si*Me$_3$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01244.

Details of Experimental Section, X-ray crystallography, theoretical calculations, and collected NMR spectra of compounds **1**−**4** (PDF)

Accession Codes

CCDC 1974194−1974197 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Yan Li − *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*; orcid.org/0000-0001-7703-6560; Email: yli@hznu.edu.cn

Ming-Der Su − *Department of Applied Chemistry, National Chiayi University, Chiayi 60004, Taiwan; Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan*; orcid.org/0000-0002-5847-4271; Email: midesu@mail.ncyu.edu.tw

Di Wu − *College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 311121, China*; Email: wudi@hznu.edu.cn

Authors

Chenghuan Liu − *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*

Keke Zhu − *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*

Weichun Han − *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*

Xue Liu − *Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China*

Zheng-Feng Zhang − *Department of Applied Chemistry, National Chiayi University, Chiayi 60004, Taiwan*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.inorgchem.0c01244

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is funded by the NSF of China (No. 21801055), Zhejiang Provincial Natural Science Foundation (No. LY20B020009 and LQ20B010007). Y.L. acknowledges the support from the open fund of State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University (No. 201916). Z.-F.Z. and M.-D.S. are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time, and the Ministry of Science and Technology, Taiwan for the financial support. We thank greatly Dr. Xuqiong Xiao for the X-ray crystallographic assistance.

■ REFERENCES

(1) (a) Baines, K. M.; Stibbs, W. G. The molecular structure of organogermanium compounds. *Coord. Chem. Rev.* **1995**, *145*, 157−200. (b) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Stable heavier carbene analogues. *Chem. Rev.* **2009**, *109*, 3479−3511. (c) 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 multitalented ligands. *Chem. Rev.* **2011**, *111*, 354−396.

(2) Examples: (a) 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. (b) Arii, H.; Amari, T.; Kobayashi, J.; Mochida, K.; Kawashima, T. Low-coordinate germanium(II) centers within distorted axially chiral seven-membered chelates: stereo- and enantioselective cycloadditions. *Angew. Chem., Int. Ed.* **2012**, *51*, 6738−6741. (c) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. RGe(I)Ge(I)R compound (R = PhC(N*t*Bu)$_2$) with

a Ge-Ge single bond and a comparison with the Gauche conformation of hydrazine. *Organometallics* **2008**, *27*, 5459−5463. (d) Wang, X.; Liu, J.; Yu, J.; Hou, L.; Sun, W.; Wang, Y.; Chen, S.; Li, A.; Wang, W. Ge^I-Ge^I coupling reaction induced by a mixture of $CoBr_2$ and a seven-membered N-heterocyclic carbene. *Inorg. Chem.* **2018**, *57*, 2969−2972. (e) Yao, S.; van Wullen, C.; Driess, M. Striking reactivity of ylide-like germylene toward terminal alkynes: [4 + 2] cycloaddition versus C-H bond activation. *Chem. Commun.* **2008**, 5393−5395. (f) Li, Y.; Mondal, K. C.; Stollberg, P.; Zhu, H.; Roesky, H. W.; Stalke, D.; Herbst-Irmer, R.; Fliegl, H. Unusual formation of a N-heterocyclic germylene via homolytic cleavage of a C-C bond. *Chem. Commun.* **2014**, *50*, 3356−3358.

(3) (a) Miller, R. D.; Michl, J. Polysilane high polymers. *Chem. Rev.* **1989**, *89*, 1359−1410. (b) Hayase, S. Polysilanes for semiconductor fabrication. *Prog. Polym. Sci.* **2003**, *28*, 359−381.

(4) (a) Amadoruge, M. L.; Weinert, C. S. Singly bonded catenated germanes: eighty years of progress. *Chem. Rev.* **2008**, *108*, 4253−4294. (b) Wagner, H.; Baumgartner, J.; Müller, T.; Marschner, C. Shuttling germanium atoms into branched polysilanes. *J. Am. Chem. Soc.* **2009**, *131*, 5022−5023. (c) Subashi, E.; Rheingold, A. L.; Weinert, C. S. *Organometallics* **2006**, *25*, 3211−3219. (d) Wang, W.; Inoue, S.; Yao, S.; Driess, M. An unsymmetric substituted digermylene with a Ge(I)−Ge(I) bondand synthesis of a germylene−stannylene with a Ge(I)−Sn(I) bond. *Chem. Commun.* **2009**, 2661−2663.

(5) 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.

(6) Schweizer, J. I.; Scheibel, M. G.; Diefenbach, M.; Neumeyer, F.; Würtele, C.; Kulminskaya, N.; Linser, R.; Auner, N.; Schneider, S.; Holthausen, M. C. A disilene base adduct with a dative Si-Si single bond. *Angew. Chem., Int. Ed.* **2016**, *55*, 1782−1786.

(7) (a) Karsch, H. H.; Deubelly, B.; Riede, J.; Müller, G. $[\{\mu\text{-}[(Me_3Si)C(PMe_2)_2]\}_2Ge_2]_2GeGeCl_2$, a germanediyl-donor germanediyl-acceptor complex containing a mixed-valent Ge_5 Chain. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 674−676. (b) Meyer-Wegner, F.; Nadj, A.; Bolte, M.; Auner, N.; Wagner, M.; Holthausen, M. C.; Lerner, H. W. The perchlorinated silanes Si_2Cl_6 and Si_3Cl_8 as sources of $SiCl_2$. *Chem. - Eur. J.* **2011**, *17*, 4715−4719.

(8) Jutzi, P.; Keitemeyer, S.; Neumann, B.; Stammler, H.-G. Novel heteroleptic germanium(II) compounds from [2,4-Di-tert-butyl-6((dimethylamino)methyl)phenyl]germanium chloride: synthesis, structure, and derivatization. *Organometallics* **1999**, *18*, 4778−4784.

(9) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. Reactivity of pyridyl-1-azaallyl germanium(II) chloride: synthesis of novel lithium germinate $[\{(PhC{\equiv}C)_3Ge\}_3GeLi(Et_2O)_3]$ and Ge(II)-M(I) (M = Cu and Au) adducts. *Organometallics* **2006**, *25*, 2851−2858.

(10) Li, J.; Li, B.; Liu, R.; Jiang, L.; Zhu, H.; Roesky, H. W.; Dutta, S.; Koley, D.; Liu, W.; Ye, Q. A germylene/borane Lewis Pair and the remarkable C = O bond cleavage reaction toward isocyanate and ketone molecules. *Chem. - Eur. J.* **2016**, *22*, 14499−14503.

(11) Setaka, W.; Sakamoto, K.; Kira, M.; Power, P. P. Synthesis and structure of stable tri-*tert*-butylgermyl-substituted stannylene and germylene. *Organometallics* **2001**, *20*, 4460−4462.

(12) The molar ratio of 3:4 referred to stoichiometric synthesis of compound **1**.

(13) Li, Y.; Mondal, K. C.; Lübben, J.; Zhu, H.; Dittrich, B.; Purushothaman, I.; Parameswaran, P.; Roesky, H. W. A functionalized Ge_3-compound with a dual character of the central germanium atom. *Chem. Commun.* **2014**, *50*, 2986−2989.

(14) (a) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. Trigermaallene and 1,3-digermasilaallene. *Organometallics* **2005**, *24*, 197−199. (b) Mondal, T.; Dutta, S.; De, S.; Thirumalai, D.; Koley, D. Donor stabilized diatomic gr.14 E_2 (E = C-Pb) molecule D-E_2-D (D= NHC, *a*NHC, ^{N}NHC, NHSi, NHGe, cAAC, cAASi, cAAGe): a theoretical insight. *J. Phys. Chem. A* **2019**, *123*, 565−581.

(15) For a similar 1,2-group shift, see: (a) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. Isomeric forms of divalent heavier group 14 element hydrides: characterization of Ar'(H)GeGe(H)Ar' and $Ar'(H)_2GeGeAr'{\cdot}PMe_3$ (Ar' = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-$Pr^i{}_2$). *J. Am. Chem. Soc.* **2003**, *125*, 3204−3205. (b) Phillips, A. D.; Hino, S.; Power, P. P. A reversible valence equilibrium in a heavier main group compound. *J. Am. Chem. Soc.* **2003**, *125*, 7520−7521.

(16) See Supporting Information for the experimental and computational details.

(17) Blomberg, M. R. A.; Siegbahn, P. E. M.; Svensson, M. Mechanisms for the reactions between methane and the neutral transition metal atoms from yttrium to palladium. *J. Am. Chem. Soc.* **1992**, *114*, 6095−6102.

(18) Dauber, P.; Hagler, A. T. Crystal packing, hydrogen bonding, and the effect of crystal forces on molecular conformation. *Acc. Chem. Res.* **1980**, *13*, 105−112.

(19) The formation of **4** can also be considered a formal nitrene insertion into a Ge−Ge bond. See reference: Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. Reactions of the heavier group 14 element alkyne analogues Ar'EEAr' (Ar' = C_6H_3-2,6(C_6H_3-2,6-Pr^i2)2; E = Ge, Sn) with unsaturated molecules: probing the character of the EE multiple bonds. *J. Am. Chem. Soc.* **2005**, *127*, 17530−17541.

(20) (a) Barrau, J.; Rima, G. Stable germanium analogs of carbenes, imines, ketones, thiones, selones and tellones. *Coord. Chem. Rev.* **1998**, *178−180*, 593−622. (b) Böserle, J.; Zhigulin, G.; Ketkov, S.; Jambor, R.; Ružička, A.; Dostál, L. Diverse reactivity of a boraguanidinato germylene toward organic pseudohalides. *Dalton Trans.* **2018**, *47*, 14880−14883. (c) Klein, B.; Neumann, W. P. Chemie der schweren carben-analogen R_2M (M = Si, Ge, Sn) XIX*. Reaktionen von stabilem diaminogermylen und -stannylen Me_2Si-$(^tBuN)_2M$ (M = Ge, Sn) mit organischen aziden. *J. Organomet. Chem.* **1994**, *465*, 119−126.

(21) Hintermann, L. Experiment syntheses of N-heterocyclic carbine precursor imidazolium salts IPrHCl, IMesHCl and IXyHCl. *Beilstein J. Org. Chem.* **2007**, *3*, 22.

(22) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. N-Heterocyclic carbene stabilized digermanium(0). *Angew. Chem., Int. Ed.* **2009**, *48*, 9701−9704.

(23) One typical procedure to prepare LLi is as follows: at room temperature, *n*BuLi (37.8 mL, 2.5 M solution in *n*-heptane, 94.5 mmol) was slowly added to a solution of LH (8.84 g, 90 mmol) in *n*-hexane (100 mL) to afford a white suspension. After being stirred for 3 h, the suspension was filtered, and the insoluble stuff was then washed by *n*-hexane (2 × 10 mL) and dried under a vacuum to obtain pure LLi as a white powder (8.16 g, 87%).