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N−H and N=C Bond Formation via Germanium(III) Diradicaloid Intermediates and C−S Bond Cleavage in Reactions of the Digermyne Ar′GeGeAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$Pr^i{}_2$)$_2$) with Azides

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Reactions of the digermyne Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (**1**) with four different azides R′N_3 (R = Me_3Sn, $^nBu_3Sn$, $PhSCH_2$, or 1-adamantanyl) are described. Treatment of **1** with Me_3SnN_3 or $^nBu_3SnN_3$ afforded the low-valent germanium (II) parent amido derivative, Ar′Ge(μ_2-NH_2)$_2$GeAr′ (**3**) or the high-valent germanium (IV) parent imido derivative, Ar′($^nBu_3Sn$)Ge(μ_2-NH)$_2$Ge(Sn^nBu_3)Ar′ (**4**), respectively. Addition of AdN_3 (Ad =1-admantanyl) yielded a monoimide bridged species Ar′Ge(μ_2-NAd)GeAr′ (**5**). The structure of **5** differs from that of the diradicaloid Ar′Ge(μ_2-$NSiMe_3$)$_2$GeAr′ (**2**), which was previously obtained from the analogous reaction of **1** with Me_3SiN_3. The reaction of **1** with $PhSCH_2N_3$ afforded the germanium ketimide Ar′Ge(SPh)$_2$(N=CH_2) (**6**) containing the imino −N=CH_2 functional group. These reactions demonstrate a remarkable product dependence on the azide substituent. All compounds were spectroscopically and structurally characterized. Both **3** and **4** feature a four-membered Ge_2N_2 core. The structure of **5** is stabilized by CH-π interactions while **6** features a rare example of a π-π interaction between an aromatic ring and a non-aromatic double bond (N=C). The mechanism of formation of **3**−**6** are discussed. It is proposed that **3** and **4** are obtained via diradical imido intermediates followed by H-abstraction from solvents, whereas **6** was formed by the activation of azide group in concert with C−S bond cleavage.

Introduction

Diradicals are thought to play a crucial role in bond breaking and formation processes.[1] Although diradicals are generally highly unstable, the discovery of stable singlet diradicals or diradicaloids based on heavier main group elements has been one of the most interesting recent developments in inorganic main group chemistry.[2−5] Recently we reported the synthesis and characterization of the non-Kekulé singlet diradicaloid, the germanum-centered, imido bridged Ar′Ge(μ_2-$NSiMe_3$)$_2$GeAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$Pr^i{}_2$)$_2$) (**2**), which was obtained from the reaction of digermyne Ar′GeGeAr′ (**1**) with Me_3SiN_3.[4a] We observed that a solution of **2** in several solvents (benzene, toluene, and cyclohexane) gradually faded to pale yellow over time and speculated that hydrogen abstraction from the solvent was the cause. However, we were unable to characterize the product of this reaction adequately. We decided to synthesize a series of imido complexes with different nitrogen substituents related to **2** to throw further light on their reactions with solvents. We also wished to explore the range of imido derivatives of the class Ar′Ge(μ_2-NR′)$_2$GeAr′ to test their

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reactivity with various small molecules. It is noteworthy that, in parallel work, it has been shown that various imido derivatives of transition metals involving Fe(III),[6a] Fe(IV),[6b] and Co(III)[6c] abstract H atoms from reagents or solvents to form iron or cobalt amido complexes. The formation of Ni(II) ketimido complexes via transient Ni(III) imides has also been reported.[7] However, to our knowledge, no similar phenomena have been disclosed for main group 14 imido complexes. In this paper we show that the reactions of Ar′GeGeAr′ with various azides afforded an unexpected variety of products **3**−**6** (Scheme 1), none of which resembles **2**. The common feature of these reactions is the high likelihood of radical involvement.

Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of argon or nitrogen or in a Vacuum Atmospheres HE-43 drybox. Solvents were dried over an alumina column and degassed prior to use. Ar′GeGeAr′[8] and $(C_6H_3\text{-}2,6\text{-}Mes_2)N_3$ (Mes = $C_6H_2\text{-}2,4,6\text{-}Me_3$)[9] were synthesized by literature methods. Me_3SnN_3 (Aldrich, 97%), $^nBu_3SnN_3$ (Aldrich, 98%), $PhSCH_2N_3$ (Aldrich, 95%), and 1-adamantyl azide (AdN_3, Ad = 1-adamantanyl, Aldrich, 97%) were used as received without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument and referenced to known standards. ^2D NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer equipped with a multinuclear probe tuned to ^2D. ^{119}Sn NMR spectra were recorded on a Varian Inova 600 MHz spectrometer (224.2 MHz) and referenced externally to neat $SnMe_4$. The melting points were recorded using a Meltemp apparatus and were not corrected. Infrared data were recorded as Nujol mulls on a Perkin-Elmer PE-1430 instrument.

$Ar'Ge(\mu_2\text{-}NH_2)_2GeAr'$ (3). To a red solution of 1 (0.201 g, 0.213mmol) in hexane (40 mL) was added dropwise a Me_3SnN_3 (0.137 g, 0.659 mmol) slurry in hexane (20 mL) at 0 °C. The slurry was warmed, and it rapidly gave an orange solution. After further stirring for 1d, unreacted Me_3SnN_3 was recovered by filtration. The filtrate was reduced to dryness, and the yellow powder was redissolved in toluene. Storage of the solution at about −18 °C for one week afforded X-ray-quality crystals of **3**. Yield: 0.097 g, 47%; its melting point, ^1H NMR, and IR spectra are identical to the literature values.[10] mp: 86−88 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.89 (s, 2H, NH_2), 0.97 (d, J_{H-H} = 6.8 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.11 (d, J_{H-H} = 7.2 Hz, 12H, $CH(C\mathit{H}_3)_2$), 2.96 (sept, J_{H-H} = 6.8 Hz, 4H, $C\mathit{H}(CH_3)_2$), 6.95 (d, J_{H-H} = 7.6 Hz, 6H, Ar−H), 7.09−7.13 (m, 12H, Ar−H) ppm. IR (Nujol): ν = 3380 and 3309 cm^{-1} (ν_{NH_2}, weak). A typical NMR experiment involving **1** (0.108 g, 0.114 mmol) and Me_3SnN_3 (0.051 g, 0.245 mmol) was carried out in benzene solvent (50 mL), which, after 1 day, afforded the signals: $^{119}Sn\{^1H\}$ NMR (224 MHz, C_6D_6, 25 °C): δ −33.3 (Me_3SnPh), 125.4 (Me_3SnN_3), 139.4 ($Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$) ppm. A similar NMR experiment was carried out in d_6-benzene. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.00 (m, $CH(C\mathit{H}_3)_2$, $Ar'Ge(\mu_2\text{-}ND_2)_2GeAr'$ and $Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$), 1.31 (m, $CH(C\mathit{H}_3)_2$, $Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$), 2.86 (m, $C\mathit{H}(CH_3)_2$, $Ar'Ge(\mu_2\text{-}ND_2)_2GeAr'$ and $Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$), 6.93−7.30 (m, Ar−H) ppm. ^2D NMR (600 MHz, C_6H_6, 25 °C): δ 0.98 ppm (weak, $Ar'Ge(\mu_2\text{-}ND_2)_2GeAr'$).

$Ar'(^nBu_3Sn)Ge(\mu_2\text{-}NH)_2Ge(Sn^nBu_3)Ar'$ (4). To a red solution of **1** (0.198 g, 0.210mmol) in hexane (50 mL) was added dropwise $^nBu_3SnN_3$ (0.5 mL, 1.8mmol) in hexane (20 mL) at 0 °C with vigorous stirring. The reaction mixture was warmed to room temperature and further stirred for 1d. The resulting yellow solution was concentrated to about 20 mL and stored at about −18 °C for 2 weeks to afford yellow, X-ray-quality crystals of **4**. Yield: 0.065 g, 20%. mp 232 °C (decomp.). NMR: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.87 (t, J_{H-H} = 7.5 Hz, 3H, $CH_2CH_2CH_2C\mathit{H}_3$), 1.03 (t, J_{H-H} = 7.8 Hz, 2H, $C\mathit{H}_2CH_2CH_2CH_3$), 1.27 (sext., J_{H-H} = 7.5 Hz, 2H, $CH_2CH_2C\mathit{H}_2CH_3$), 1.52 (quint, J_{H-H} = 7.2 Hz, 2H, $CH_2C\mathit{H}_2CH_2CH_3$), 2.92 (m, br., $C\mathit{H}Me_2$), 3.08 (sept, $C\mathit{H}Me_2$), 3.57(m, br., $C\mathit{H}Me_2$), 6.94−7.36(m, 9H, Ar−H) (N−*H* resonance not observed). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ 11.37 (^{n}Bu), 15.83 (^{n}Bu), 22.95 ($CH(\mathit{C}H_3)_2$), 25.39 ($CH(\mathit{C}H_3)_2$), 26.18 (^{n}Bu), 26.53 (^{n}Bu), 30.13 ($\mathit{C}H(CH_3)_2$), 123.50 (m-Dipp), 127.54 (*p*-C_6H_3), 128.18 (*m*-C_6H_3) ppm. $^{119}Sn\{^1H\}$ NMR (224 MHz, C_6D_6, 25 °C): δ 99.1 ppm.

$Ar'Ge(\mu_2\text{-}NAd)GeAr'$ (5). To a red solution of **1** (0.298 g, 0.316mmol) in hexane (50 mL) was added dropwise AdN_3 (0.128 g, 0.722 mmol) in hexane (10 mL) at 0 °C. After the reaction mixture had been stirred at room temperature for 1 d, the volume of the solution was reduced to about 10 mL under reduced pressure. Overnight storage of the orange solution at about −18 °C afforded orange X-ray-quality crystals of **5**. Yield: 0.217 g, 63%; mp 254−256 °C. NMR: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.86 (d, J_{H-H} = 6.0 Hz, 24H, $CH(C\mathit{H}_3)_2$), 0.91 (d, J_{H-H} = 6.3 Hz, 24H, $CH(C\mathit{H}_3)_2$), 1.23−1.42 (m), 1.74(m), 3.11 (br) (15H, Ad), 3.57(sept., J_{H-H} = 6.0 Hz, 8H, $C\mathit{H}(CH_3)_2$), 6.92 (d, 6H, Ar−H), 7.09−7.16 (m, 12H, Ar−H) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ 22.89 ($CH(\mathit{C}H_3)_2$), 25.66 ($CH(\mathit{C}H_3)_2$), 30.80 ($\mathit{C}H(CH_3)_2$), 35.79 ($\mathit{C}H(CH_3)_2$), 48.27 (Ad), 63.77 (Ad), 123.66 (m-Dipp), 127.57 (*p*-C_6H_3), 128.21 (*m*-C_6H_3), 130.59 (*p*-$C_6H_3\text{-}2,6\text{-}Pr^i_2$) ppm.

$Ar'Ge(SPh)_2(N{=}CH_2)$ (6). To a red solution of **1** (0.176 g, 0.187 mmol) in hexane (40 mL) was added dropwise $PhSCH_2N_3$ (0.5 mL, 3.53 mmol) slurry in hexane (20 mL). After the reaction mixture was stirred at room temperature for 1 d, the yellow solution was concentrated to about 10 mL and stored at −15 °C for 1 week to yield colorless, X-ray-quality crystals of **6**. Yield: 0.02 g, 15%; mp 180−182 °C. NMR: ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.07 (d, J_{H-H} = 6.9 Hz, 12H, $CH(C\mathit{H}_3)_2$), 1.59 (d, J_{H-H} = 6.9 Hz, 12H, $CH(C\mathit{H}_3)_2$), 3.06 (sept, J_{H-H} = 6.9 Hz, 4H, $C\mathit{H}(CH_3)_2$), 4.42 (s, 2H, $NC\mathit{H}_2$), 6.74−6.81 (10H, SPh-*H*), 6.98 (m, 3H, Ar-*H*), 7.16 (m, 6H, Ar-*H*)ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 25 °C): δ 23.16 (CH*Me*2), 26.10 (CH*Me*$_2$), 31.82 (*C*HMe$_2$), 122.65, 123.38, 126.92, 128.63, 129.12, 131.28 (SPh-*C* and Ar-*C*), 136.59 (N*C*H$_2$), 146.15, 147.64 (SPh-*C* and Ar-*C*). IR: 1579 cm^{-1} ($\nu_{N=C}$, weak).

Reaction of 1 with $(C_6H_3\text{-}2,6\text{-}Mes_2)N_3$. To a red solution of **1** (0.183 g, 0.194 mmol) in hexane (40 mL) was added dropwise $(C_6H_3\text{-}2,6\text{-}Mes_2)N_3$ (0.145 g, 0.408mmol) solution in hexane (20 mL). The reaction mixture was stirred at room temperature for 1 d and no color changes were observed. After removal of the solvent under reduced pressure, **1** and $(C_6H_3\text{-}2,6\text{-}Mes_2)N_3$ were recovered on the basis of ^1H NMR spectroscopy.

X-ray Crystallography. Crystals of **3**, **4**, **5**, and **6** were removed from the Schlenk tube under a stream of argon and immediately

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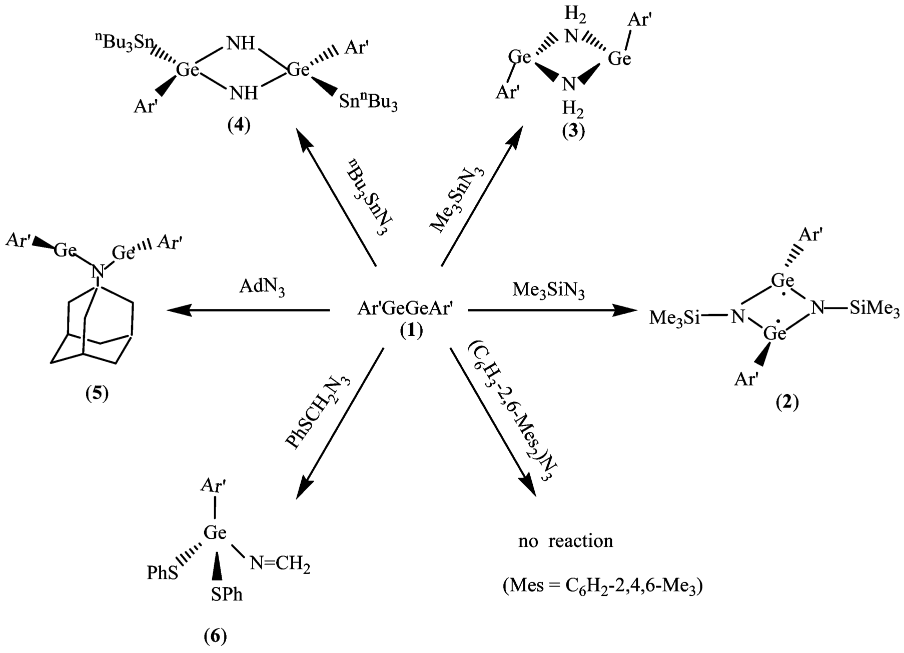
Table 1. Selected X-ray Crystallographic Data for **3**, **4**, **5**, and **6**

cmpd	**3**·$4C_7H_8$	**4**	**5**·C_6H_{14}	**6**·$0.5C_6H_{14}$
formula	$C_{88}H_{110}Ge_2N_2$	$C_{84}H_{130}N_2Ge_2Sn_2$	$C_{76}H_{103}NGe_2$	$C_{46}H_{56}NS_2Ge$
formula wt	1341.00	1550.46	1175.82	759.67
color, habit	colorless block	yellow block	orange block	colorless plate
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pbca*	$P2(1)/c$	$C2/c$
a [Å]	12.072(2)	23.066(1)	23.594(1)	42.263(4)
b [Å]	13.241(3)	21.095(1)	12.983(1)	9.943(1)
c [Å]	13.719(3)	32.251(1)	22.881(1)	19.481(1)
α [deg]	109.60(3)			
β [deg]	102.81(3)		112.27(1)	91.44(1)
γ [deg]	103.69(3)			
V [Å^3]	1895.4(10)	15693(1)	6485.9(9)	8183.5(3)
Z	1	8	4	8
$\rho_{calc.}$[g cm^{-3}]	1.175	1.313	1.204	1.233
T [K]	90(2)	90(2)	90(2)	90(2)
μ, mm^{-1}	0.838	1.431	0.969	0.883
no. of reflns	18192	10723	14980	9108
no. of obsd reflns	9096	8162	11937	7834
$R1$, obsd reflns	0.0344	0.0344	0.0378	0.0385
w$R2$, all	0.0964	0.0736	0.1058	0.1113

Scheme 1



covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in a low temperature N_2 stream. The data for **3** and **4** were collected on a Bruker APEX (Mo Kα radiation ($\lambda = 0.71073$ Å) and a CCD area detector), while **5** and **6** were recorded near on a Bruker SMART 1000 (Mo Kα radiation ($\lambda = 0.71073$) and a CCD area detector). For all crystals the SHELX version 6.1 program package was used for the structure solutions and refinements. Absorption corrections were applied using the SADABS program.[11] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-H atoms were refined anisotropically. H atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program.[12] A summary of the data collection parameters for **3**−**6** is provided in Table 1.

Results and Discussion

Reactions. The reactions of **1** with RN_3 (R = $SnMe_3$, Sn^nBu_3, Ad (1-adamantanyl), and $PhSCH_2$) in hexane produced rapid color changes from the intense red color of the precursors to colorless (**3** or **6**), yellow (**4**) or orange (**5**). This is in sharp contrast to the reaction of **1** with Me_3SiN_3 in which a color change from red to deep violet was observed.[4a] The reaction of **1** with terphenyl azide (C_6H_3-2,6-Mes_2)N_3 (Mes = C_6H_2-2,4,6-Me_3), however, produced no color change indicating that no reaction had occurred, which was further confirmed by ^1H NMR spectroscopy.

Treatment of **1** with Me_3SnN_3 afforded a low-valent germanium (II) derivative of the parent amide group $-NH_2$ (**3**), while the reaction with $^nBu_3SnN_3$ afforded a high-valent germanium (IV) derivative of the parent imide group $-NH$ (**4**) (Scheme 2). It can be reasoned that the reactions of **1** with Me_3SnN_3 probably proceeds via the initial formation of a diradicaloid intermediate Ar′Ge(μ_2-$NSnMe_3$)$_2$GeAr′, an

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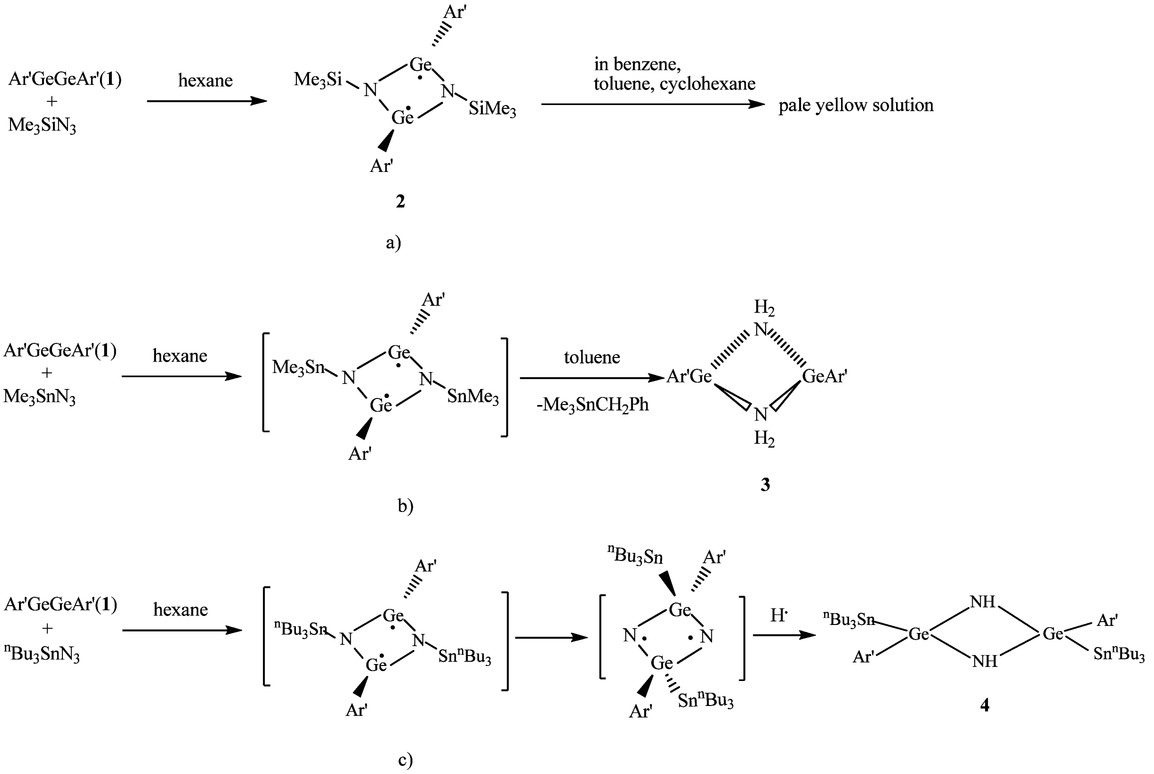
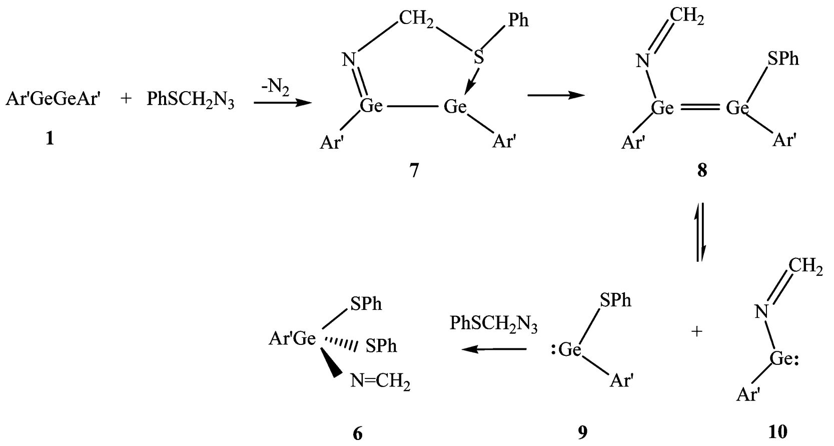
[11] *SADABS, an empirical absorption correction program from the SAINTPlus NT*, version 5.0 package; Bruker AXS: Madison, WI, 1998.

[12] *SHELXTL*, version 5.1; Bruker AXS: Madison, WI, 1998.

Scheme 2



Scheme 3



analogue of the silicon congener **2**. This is followed by Sn−N bond cleavage and loss of the $Me_3Sn\cdot$ radical, whereupon H-atom transfer from the solvent to the nitrogens occurs to afford **3** (Scheme 2b). The tin radical $Me_3Sn\cdot$ is then trapped by H abstraction from benzene or toluene solvent to afford Me_3SnPh or Me_3SnCH_2Ph. This reaction pathway is supported by ^{119}Sn, ^{1}H, and ^{2}D NMR spectroscopy.

The reaction mixture of **1** and Me_3SnN_3 displayed ^{119}Sn NMR signals due to Me_3SnN_3 ($\delta = 125.4$ ppm), $Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$ ($\delta = 139.4$ ppm), and Me_3SnPh ($\delta = -33.3$ ppm) immediately upon mixing the reagents.[13] A signal due to $-NH_2$ ($\delta = 0.89$ ppm) was not observed in the ^{1}H NMR spectrum when the reaction was performed in the deuterated solvent. However, a signal due to $-ND_2$ ($\delta = 0.98$ ppm) was observed in the ^{2}D NMR spectrum. The reaction sequence is also supported by our previous isolation of the silicon analogue (**2**) of $Ar'Ge(\mu_2\text{-}NSnMe_3)_2GeAr'$,[4a] and by work that described the ready formation of metal amido moieties via an H-atom abstraction from solvents by transition metal imido intermediates.[6] In addition, several recent reports have described the H-abstraction by a variety of aminyl radicals.[14] Similarly, a diradicaloid analogue of **2** is formed in the initial step of the reaction of **1** with $^{n}Bu_3SnN_3$.

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[13] Me_3SnPh in CH_2Cl_2: $\delta^{119}Sn = -28.6$ ppm. Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73; Me_3SnN_3 in C_6D_6: $\delta^{119}Sn = 126.0$ ppm (this work).

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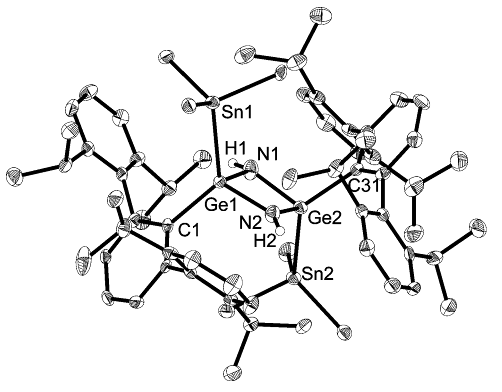

Figure 1. Thermal ellipsoid (50%) drawing of **4**. Hydrogen atoms (except NH) are not shown. Only carbons directly attached to Sn in the Sn^nBu_3 moieties are shown. Selected bond distances (Å) and angles (deg) for **4**: C1−Ge1 2.000(2), Ge1−N2 1.856(2), Ge1−N1 1.841(2), Ge1−Sn1 2.666(1), Ge2−N2 1.856(2), Ge2−N1 1.838(2), Ge2−Sn2 2.636(1), Ge2−C31 1.993(2), C1−Ge1−N1 109.71(1), C1−Ge1−N2 106.50(1), N1−Ge1−N2 83.87(1), Ge1−N1−Ge2 95.34(1), Ge1−N2−Ge2 96.61(1), N1−Ge2−C25 113.16(1), N2−Ge2−C25 109.04(1), Ge1−N1−H2 116.5(1), Ge2−N1−H2 138.8(1), Ge1−N2−H1 132.3(1), Ge2−N2−H1 130.2(1).

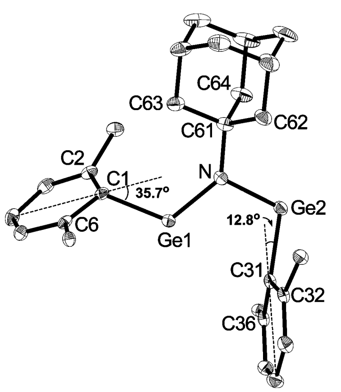

Figure 2. Thermal ellipsoid (50%) drawing of **5**. Hydrogen atoms and C_6H_3-2,6-Pr^i_2 (except ipso carbon atoms) are not shown. Selected bond distances (Å) and angles (deg): C1−C2 1.426(3), C1−C6 1.424(3), Ge1−C1 2.049(2), Ge1−N 1.849(1), Ge2−N 1.891(2), N−C61 1.502(3), C31−C32 1.411(3), C31−C36 1.418(3), C61−C62 1.540(3), C61−C63 1.532(3), N−C61 1.502(3), C6−C1−C2 116.38(9), Ge1−C1−C2 128.00(6), Ge1−C1−C6 107.55(4), C1−Ge1−N 118.82(8), Ge1−N−C61 134.09(4), Ge2−N−C61 114.15(3), Ge1−N−Ge2 111.38(9), N−Ge2−C31 104.99(8), Ge2−C31−C32 112.04(5), Ge2−C31−C36 127.73(6), C36−C31−C32 118.02(9).

This is also followed by N−Sn bond cleavage and the formation of a new aminyl diradical[14,15] $\{^nBu_3Sn(Ar)'Ge(\mu\text{-}N\bullet)\}_2$, which forms **4** via H-atom abstraction (Scheme 2c). The reasons why these reactions produce **3** and **4** from the addition of the Me_3SnN_3 and $^nBu_3SnN_3$ to **1** are unclear at present.

Reaction of **1** with excess AdN_3 yielded a novel monoimido bridged species **5** (Scheme 1). It seems that steric crowding prevents the isolation of a cyclic Ge_2N_2 diradicaloid species analogous to **2**. It is noteworthy that **1** displays no reaction with the even bulkier terphenyl azide (C_6H_3-2, 6-Mes_2)N_3. The structure of **5** resembles that of Ar′Sn(μ_2-$NSiMe_3$)SnAr′, which was obtained by the reaction of Me_3SiN_3 with Ar′SnSnAr′.[16]

Reaction of **1** with excess $PhSCH_2N_3$ afforded a germanium (IV) ketimide **6** featuring the imino $-N{=}CH_2$ group. It is proposed (without mechanistic evidence) that this reaction proceeds via the sequence given in Scheme 3, during which the cleavage of C−S bond occurs in the conversion of **7** to **8** followed by dissociation of **8** to afford **9** and **10**. The C−S bond is readily cleaved by numerous transition metal complexes,[17] but a similar reaction for multiple bonded compounds of main group elements is unknown.[18] This reaction has provided a new route to a metal ketimide ($MN{=}CR_2$) (M = metal). **6** is the first example of a main-group metal ketimide featuring the parent $-N{=}CH_2$ group.[19]

Structures. The molecular structure of **3** is essentially identical to that previously reported. However, in the earlier report **3** was obtained by a straightforward route involving treatment of Ar′GeCl with liquid NH_3.[10] For the current structure, the compound crystallized in a different space group with a different number of toluene solvate molecules (4 vs 1.5). Otherwise there are no significant differences (see Supporting Information for more details). The structure of **4**, $Ar'^nBu_3SnGe(\mu_2\text{-}NH)_2GeSn^nBu_3Ar'$(Figure 1), is dimeric with a Ge_2N_2 core that has an almost planar arrangement with a rhombohedral shape and with an acute angle near 84° at the germaniums and a wider angle near 97° at the nitrogens. The germanium centers have tetrahedral coordination geometries, and the terphenyl groups are arranged in a trans fashion across the ring. The nitrogen centers have trigonal planar coordination in the case of N1 and a somewhat pyramidalized coordination in the case of N2 as shown by the sum of the angles at N1 of 359° and at N2 of 349°. The Ge−N1 bond lengths (1.841 (2), 1.838 (2) Å) are slightly shorter than Ge−N2 bond lengths (1.856 (2), 1.856 (2) Å) consistent with the different nitrogen coordination geometries. The Ge−N distances are slightly longer than the reported range 1.801−1.829 Å in several Ge(IV)−NH imido species, for example, the Ge−N(H) bond lengths of 1.811−1.818 Å in $[iPrC_6H_3NSiMe_3Ge(NH_2)_2]_2NH$[20] or 1.807−1.828 Å in $[iPrC_6H_3NSiMe_3Ge(NH_2)_2NH]_3$,[21] in

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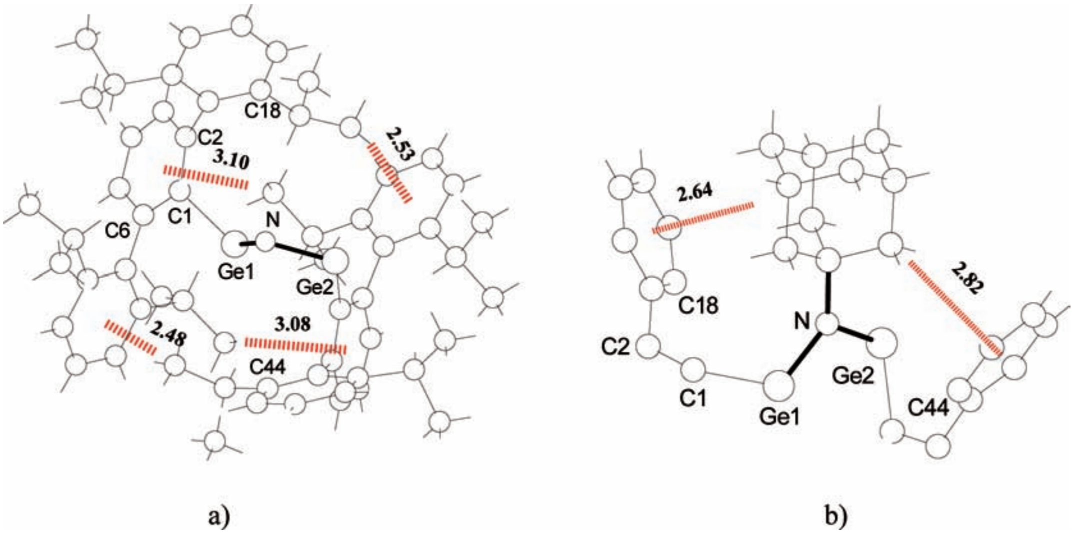

a) b)

Figure 3. Intramolecular CH-π interactions in **5** between (a) two Ar′ ligands (2.48−3.10 Å); (b) Ar′ and the adamantanyl ligand (2.64−2.82 Å).

which the nitrogens bridge two germaniums, and have planar coordination geometry.

The structure of **5** is illustrated in Figure 2. It can be seen that an adamantanyl imido unit bridges two Ar′Ge moieties. The two Ge−N lengths (Ge1−N 1.849(1), Ge2−N 1.891(2) Å) are slightly different but similar to those in **4** and are consistent with single bonding. The Ge1···Ge2 separation (3.089(1) Å) is much longer than a normal Ge−Ge single bond (average 2.44 Å).[22] The coordination geometry at the nitrogen atom is planar (sum of interligand angles = 359.6°). The Ge1−N−C61 (134.09°) and Ge2−N−C61 (114.15°) angles are dissimilar, and the shorter Ge1−N bond is associated with the wider Ge1−N−C61 angle. Significantly, deformations of the trigonal planar geometries at the ipso C1 and C31 atoms are also observed. The C1−Ge1 bond subtends an angle of about 35.7° with respect to the averaged plane of the C1 aryl ring. The corresponding Ge2−C31 deviation is about 12.8°. As a result, the corresponding phenyl ring geometries are distorted with some C−C bond lengthening. The C1−C2 (1.426 (3) Å) and C1−C6 (1.424 (3) Å) bond lengths are marginally longer than those of C31−C32 (1.411 (3) Å) and C31−C36 (1.418 (3) Å), consistent with the higher degree of distortion (35.7° vs 12.8°). The preference of the singly bridged imido structure and the distortion of the geometry at the ipso C atoms are likely a result of crowding as is evident from the intramolecular interactions involving CH(CH_3 or CH_2)-π electron interactions in the range 2.48−3.10 Å between terphenyl and adamantanyl substitutents as shown in Figure 3. The existence of CH-π interactions in a range of molecules is well-known and could be a controlling influence in the observed structural conformations.[23]

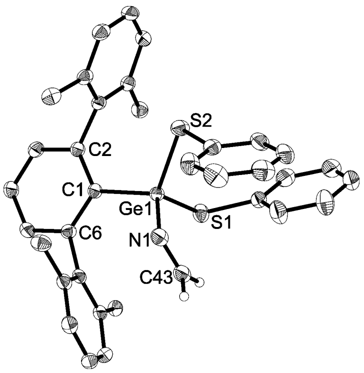

Figure 4. Thermal ellipsoid (50%) drawing of **6**. Hydrogen atoms (except $N{=}CH_2$ hydrogen atoms) and C_6H_3-2,6-Pr^i_2 (except ipso carbon atoms) are not shown. Selected bond distances (Å) and angles (deg) for **6**: C1−C2 1.407(2), C1−C6 1.412(3), C1−Ge1 1.970(2), Ge1−N1 1.862(2), N1−C43 1.258(3), Ge1−S1 2.253(6), Ge1−S2 2.223(6), C2−C1−C6 119.16(6), C2−C1−Ge1 121.05(3), C6−C1−Ge1 119.66(3), C1−Ge1−N1 111.52(7), Ge1−N1−C43 120.28(6), N1−Ge1−S1 112.70(6), N1−Ge1−S2 105.44(6), S1−Ge1−S2 111.43(2).

The structure of **6** (Figure 4) shows that the coordination geometry at germanium is tetrahedral with a terminal $-N{=}CH_2$ group bound to Ge. The Ge−N (1.862 (2) Å) is close to that found in Ar′Ge−N(Ph)CC(Ph)N-GeAr′ and Ar′Ge{(TCNE)}$_3${(GeAr′)}$_3$ (Ge−N 1.801 (4)−1.859 (4)),[16] which contain $-N{=}CRR'$ (R, R′ = organic) groups. The N−C bond length (1.258 (3) Å) is consistent with an N=C double bond.[24] The Ge1−N1−C43 bond angle (120.28(6)°) is quite different from the Mo−N−C angles, for example, 163.20(1)° in $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_3(\mu_1\text{-}NCH_2)$ $(\mu_2\text{-}NCH_2)$ and 177.99(2)° in $H_2CNMo(N[^tBu]Ar)_3$ (Ar = 3,5-$(CH_3)_2C_6H_3$),[19a] consistent with the presence of a stereochemically active lone pair at N (1). This is consistent with a shorter N−C bond length (1.258(3) Å) in **6**, which may be comparable to those in the linear Mo=N=C units (N−C 1.275(1) Å in $(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_3(\mu_1\text{-}NCH_2)$ $(\mu_2\text{-}NCH_2)$ and 1.299(7) Å in $Mo(N[^tBu]Ar)_3(\mu_1\text{-}NCH_2)$ (Ar = 3,5-$(CH_3)_2C_6H_3$)).[19b]

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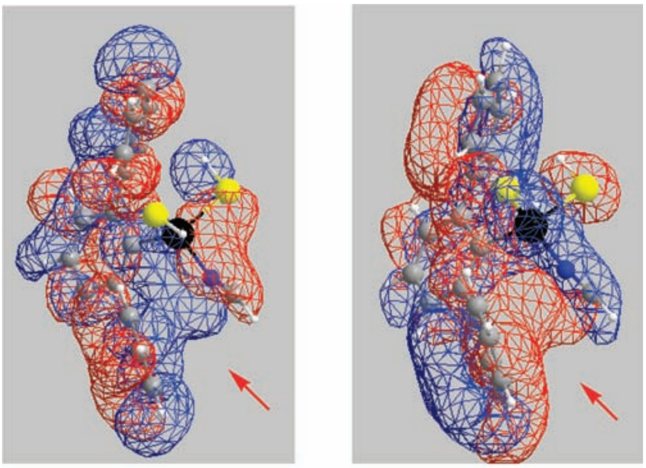

(a) HOMO-17 (b) HOMO-18

Figure 5. Two molecular orbitals of $\mathrm{Ar^{\#}Ge(SH)_2NCH_2}$ (HF/3-21G)[28] showing π(N=C)-π(arene) interactions. The red and blue colors represent two different phases and the blue (a) and red (b) colored regions indicated by the arrows represent the interaction overlaps. Color code for atoms: gray (C), blue (N), white (H), yellow (S), and black (Ge).

The plane of the $-\mathrm{N{=}CH_2}$ moiety is approximately parallel to that of one phenyl (the angle between planes is ca. 10.7°), and the distance between the N atom and phenyl ring is about 3.2 Å, suggesting a π-π interaction between the N=C unit and the phenyl ring.[25] Attractive interactions between π-systems have been recognized for over 20 years as important factors in the structure of biological systems, crystal packing, and molecular recognition.[26] To date, most experimental and theoretical attention has been focused on aromatic pairs as model systems for π-π interactions. However, studies of non-aromatic species have largely been limited to systems with interactions to tetracyanoethene (TCNE).[25] Compound **6** is a rare example that contains an interaction between an aromatic ring and a non-aromatic π bond.[27] Figure 5 shows two molecular orbitals exhibiting π(N=C)-π(arene) interaction in a similar but simpler molecule $\mathrm{Ar^{\#}Ge(SH)_2NCH_2}$ ($\mathrm{Ar^{\#}} = (\mathrm{C_6H_3\text{-}2,\,6\text{-}Mes_2})$).

Conclusion

This work has demonstrated that a diversity of germanium−nitrogen compounds, a germanium amide, two imido derivatives, or a ketimide, can be synthesized by the treatment of the multiple bonded digermyne Ar′GeGeAr′ (**1**) with a variety of azides. The results indicate that several different processes involving unusual intermediates, for example, a Ge(III) imido diradicaloid, Ge(IV) aminyl radical, C−S bond cleavage, N−H and N=C bond formation, and intra CH-π(arene) and π(N=C)-π(arene) interactions probably occur. It also suggests that a wider range of Ge−N compounds could be made by the treatment of digermynes with other azides. The isolation of a large range of other heavier main group element or even transition metal element amido or imido by reactions of the recently synthesized species REER (E =Si,[29] Sn,[29] Pb,[29] Cr,[30] Fe,[31] Co,[31] Zn,[32] Cd,[32] Hg,[32] R = alkyl, aryl, and silyl groups) with a variety of azides $\mathrm{R'N_3}$ (e.g., R′ = $\mathrm{Me_3Si}$, $\mathrm{Me_3Sn}$, $\mathrm{{}^{n}Bu_3Sn}$, $\mathrm{PhSCH_2}$, 1-adamantyl, $\mathrm{C_6H_5}$, $\mathrm{C_6H_3\text{-}2,6\text{-}Pr^{i}{}_2}$) is probable.

Acknowledgment. We are grateful to the National Science Foundation (CHE-0641020) for financial support.

Supporting Information Available: X-ray data (CIFs) for **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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