Facile Formation of Rare Terminal Chalcogenido Germanium Complexes with Alkylamidinates as Supporting Ligands

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Received June 16, 1997[⊗]

Abstract: The first characterized amidinate complexes of Ge have been prepared using alkylamidinates as ancillary ligands. Spectroscopic and structural characterization of the two complexes, $(CyNC(Me)NCy)_2Ge^{II}$ (**1**) and $(CyNC(^tBu)NCy)_2Ge^{II}$ (**2**) (Cy = cyclohexyl), revealed that the Ge coordination geometry is distorted tetrahedral in which one of the vertices is occupied by a lone pair of electrons. Both **1** and **2** exhibited one bidentate and one monodentate ("dangling") ligand. Rapid oxidative addition of chalcogen atom sources (styrene sulfide and Se) to these complexes resulted in a series of rare terminal chalcogenido complexes with the formulas $(CyNC(R)-NCy)_2Ge=Ch$ [R = Me, Ch = S (**3**), Se(**4**); R = ^tBu, Ch = S (**5**), Se(**6**)]. The spectroscopic data and X-ray structure of **6** revealed a terminal Ge=Se complex. Mixed amidinato−amido analogues were similarly obtained. For example, $[(CyNC(R)NCy)Ge^{II}[N(SiMe_3)_2]$ (R = Me, ^tBu) react to yield the corresponding terminal chalcogenido complexes. In the case of $[(CyNC(Me)NCy)Ge^{II}[N(SiMe_3)_2]Se$ (**10**), a crystallographic study confirmed the presence of a terminal Ge=Se bond.

Introduction

Recent advances in the preparation of complexes with terminal multiple bonds between the chalcogen elements and Ge or Sn have provided significant results to challenge the idea that such features are unique to the lighter congeners of these elements.[1−7] For example, isolation and structural characterization of species possessing Ge=S, Ge=Se, and Ge=Te moieties have been achieved by virtue of the kinetic stabilization provided by having sterically protecting groups on the Ge center (e.g., $Tbt(CH(SiMe_3)_2)Ge=Te$).[2,8] Additional thermodynamic stability has been applied through the coordination of a base to the group 14 center and was employed to stabilize $[\eta^3-\{(\mu-^tBuN)_2-(SiMeN^tBu)_2\}]GeS$.[3] A series of Sn and Ge terminal chalcogenido complexes were prepared with the versatile supporting ligand octamethyldibenzotetraaza[14]annulene ($Me_8taa^{2−}$).[4] The complexes $[\eta^4-Me_8taa]Ge=E$ (E = S, Se, Te) were all structurally characterized.[4b] The series of compounds bis[(2-pyridyl)-bis(trimethylsilyl)methyl]Ge=E (E = S, Se, Te) has been

reported, and the Se and Te derivatives have been structurally characterized.[5] Bulky alkylamidinate ligands have been demonstrated to provided the supporting environment for a structurally characterized terminal Sn=S complex, $S=Sn(CyNC(^tBu)-NCy)_2$, which is unique in the absence of macrocyclic supporting ligation.[6]

Coincident with our interest in the formation of multiple bonds between the heavy main group elements, we are exploring the effects of ligand geometry on the coordination environments of post transition elements. Part of this systematic study is based on the use of amidinate ligands in the chemistry of group 14 metals. Specifically, we have been exploring the ability of these ligands to stabilize unusual structures and functions in Ge(II/IV) and Sn(II/IV) complexes. Amidinate anions exhibit versatility in binding modes (Chart 1) and, through changes of substituents, should present a flexible system for tuning the effects of changes in steric bulk and electronic properties of the supporting ligand on the product compounds.[9]

Amidinato complexes of tin have been prepared with the metal in both the divalent and tetravalent oxidation states.[6,10−18] However, to our knowledge, there are no structurally characterized germanium analogues. Moreover, these results have been, by and large, limited to use of *N,N'*-bis(trimethylsilyl)benzamidinate-based ligands, $[Me_3SiNC(C_6H_4R)NSiMe_3]$.[10−17] We were interested in the possibility of overcoming this limitation and investigating the effects of changing the various substitu-

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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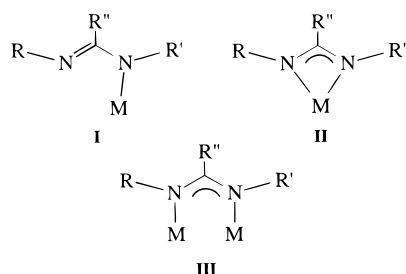
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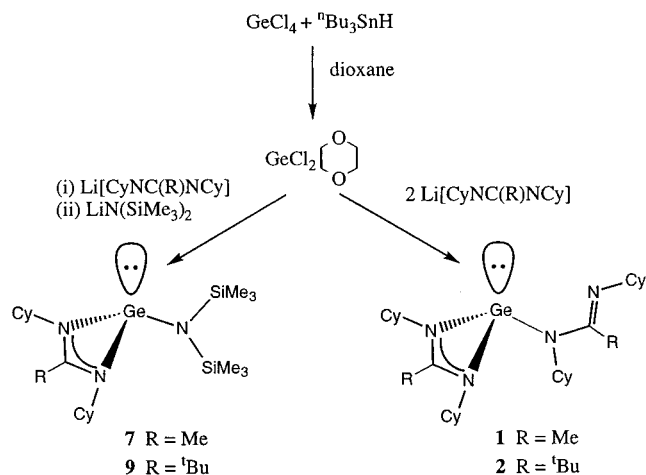(16) Kilimann, U.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1993**, *443*, 35.

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Chart 1

Scheme 1

ents.[6,18] Our investigation of the coordination chemistry of amidinate anions has relied on their generation by the addition of alkyl anion equivalents to carbodiimides.[18,19]

In this report we describe the synthesis of a unique family of bis(amidinato)germanium(II) and mixed (amidinato)(amido)-germanium(II) species. These compounds are easily converted to terminal germanium chalcogenido complexes (Ge=Ch; Ch = S, Se) through oxidation with chalcogen atom sources. These results contribute to the limited number of structurally characterized terminal chalcogenido complexes, and the addition of these new species may help to delineate the features which stabilize and affect the reactivity of such species.

Results and Discussion

Ge(II) Complexes of the (CyNC(R)NCy)⁻ Anions (R = CH₃, CMe₃). The *in situ* preparation of (CyNC(R)NCy)Li (R = Me, ᵗBu; Cy = cyclohexyl) followed by subsequent addition of 0.5 equivalents of GeCl₂(dioxane) generated the Ge(II) complexes **1** and **2** in excellent isolated yields (Scheme 1). Both of these compounds have been characterized by spectroscopic means, microanalysis, subsequent reactivity and single crystal X-ray analysis.

The first indication that these compounds were not isostructural with the previously reported Sn(II) analogues was provided by the room-temperature ¹H NMR spectrum of **2**.[6] Unlike Sn[CyNC(ᵗBu)NCy]₂, which displayed one environment for both the Cy and ᵗBu groups, Ge[CyNC(ᵗBu)NCy]₂ gave two multiplets for the cyclohexyl protons α to nitrogen in a 1:2:1 ratio and two well-separated singlets in a 1:1 ratio for the ᵗBu groups. No coalescence of these signals was observed in the ¹H NMR spectra of **2** up to 375 K.

In contrast, the NMR spectrum for the methyl analogue, Ge[CyNC(Me)NCy]₂, exhibited a single environment for both

the Cy and Me protons. In this case, a variable-temperature ¹H NMR study for **1** over the temperature range 200−300 K showed only a small amount of line broadening which could be attributed to solvent viscosity effects.

Due to these apparently conflicting results, X-ray diffraction studies were undertaken to clarify the geometry of both **1** and **2** (Table 1). Compounds **1** and **2** possess similar geometries which are based on distorted tetrahedra in which one of the vertices is occupied by a stereochemically active lone pair of electrons.[20,21] There were no anomalously short intermolecular contacts. The molecular geometries and atom-numbering schemes are shown in Figures 1 and 2. In contrast to the previously reported Sn[CyNC(ᵗBu)NCy]₂, in which both amidinates were bidentate, **1** and **2** exhibited one bidentate and one monodentate ("dangling") ligand.[6] The free imine nitrogen does not exhibit any obvious interaction with an adjacent metal center.

Taking into account the smaller radius of Ge, the structural features within the bidentate ligand are similar to those of reported Sn(II) and Sn(IV) complexes of related ligands:[6,18] the two nitrogens and bridging carbon atoms for the amidinate ligand lie in a plane which includes the Ge atom with comparable internal angles. The slight differences between the methyl (**1**) and butyl (**2**) analogues (e.g., the angles around N1 and N2) appear to be consistent with the bulk of the group on the methyne carbon.

The Ge−N3 (mondentate ligand) distances are consistently shorter than the Ge−N distances of the bidentate ligand. In addition, the N3 atom is approximately equally disposed with regard to N1 and N2.

The results of these analyses clearly explain the ¹H NMR results for **2** and indicate that although **1** exhibits three distinct Cy groups in the solid state, the solution structure is fluxional. Although the mechanism for interconversion of the amidinate groups in complex **1** is not yet clear, it appears that substitution of the methyl group in **1** with a *tert*-butyl group substantially slows this process.[18]

Terminal S and Se Complexes of Ge. Treatment of the two new complexes **1** and **2** with chalcogen sources (e.g., styrene sulfide or Se) followed the redox pathway outlined in Scheme 2. In both cases, the reaction was rapid and complete. Spectroscopic and microanalytical data for both products confirmed the formulas for compounds **3**−**6**. Specifically, the ¹H NMR spectra of [CyNC(Me)NCy]₂GeS (**3**) and [CyNC(Me)-NCy]₂GeSe (**5**) compared favorably to that of the parent **1**. Similarly, the NMR spectra of [CyNC(ᵗBu)NCy]₂GeS (**4**) and [CyNC(ᵗBu)NCy]₂GeSe (**6**) indicated coordinations of the amidinate ligands similar to that observed above for **2**. Furthermore, both COSY and heteroatom (¹³C/¹H) correlation NMR experiments for **4** were consistent with the structure

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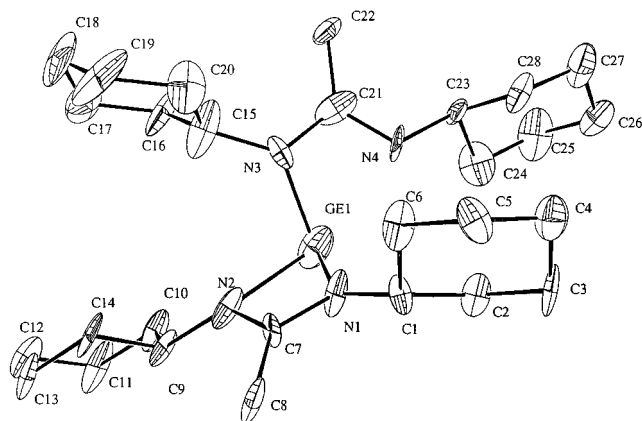
(20) The structure of **1** was refined with observed and unobserved reflections to obtain a better ratio of reflections to parameters (2373/298 = 7.96). Although the crystal quality was not ideal, a higher quality crystal was not available. This analysis established the essential molecular structure which was comparable to that of **2**. Selected bond distances (Å) and bond angles (deg) for **1**: Ge1−N1, 2.037(11); Ge1−N2, 2.158(13); Ge1−N3, 1.935(12); N1−C7, 1.302(19); N2−C7, 1.329(18); N3−C21, 1.364(20); N4−C21, 1.327(18); N1−Ge1−N2, 62.4(4); N1−Ge1−N3, 101.2(5); N2−Ge1−N3, 96.0(4); Ge1−N1−C1, 137.3(10); Ge1−N1−C7, 95.6(9); Ge1−N2−C7, 89.4(9); Ge1−N2−C9, 139.0(9); Ge1−N3−C15, 128.1(10); Ge1−N3−C21, 104.4(9); N1−C7−N2, 111.6(13); N3−C21−N4, 111.4-(12).

(21) Selected bond distances (Å) and bond angles (deg) for **2**: Ge1−N1, 2.040(9); Ge1−N2, 1.993(10); Ge1−N3, 1.903(9); Ge2−N5, 2.043(9); Ge2−N6, 2.090(9); Ge2−N7, 1.898(9); N1−C7, 1.299(15); N2−C7, 1.420(15); N3−C24, 1.419(15); N4−C24, 1.282(16); N1−Ge1−N2, 65.6(4); N1−Ge1−N3, 107.0(4); N2−Ge1−N3, 108.1(4); Ge1−N1−C1, 129.7(7); Ge1−N1−C7, 93.4(7); Ge1−N2−C7, 91.8(7); Ge1−N2−C12, 135.7(7); Ge1−N3−C18, 133.6(7); Ge1−N3−C24, 112.5-(7); N1−C7−N2, 106.8(10); N3−C24−N4, 125.0(11).

Table 1. Crystallographic Data for [CyNC(Me)NCy]$_2$Ge (**1**), [CyNC(^{t}Bu)NCy]$_2$Ge (**2**), [CyNC(^{t}Bu)NCy]$_2$Ge=Se (**6**), and C$_6$H$_{11}$NC(Me)NC$_6$H$_{11}$]Ge[N(SiMe$_3$)$_2$]Se (**10**)

	1	**2**	**6**	**10**
empirical formula	GeN$_4$C$_{28}$H$_{50}$	GeN$_4$C$_{34}$H$_{62}$	SeGeN$_4$C$_{34}$H$_{62}$	GeSeSi$_2$N$_3$C$_{20}$H$_{43}$
fw	515.31	597.46	678.43	533.29
crystal system, space group	monoclinic, $P2_1/c$	monoclinic, Pc	monoclinic, $P2_1/c$	monoclinic, $P2_1/a$
no. of reflns used for unit cell dimens	24	24	24	8192
2θ range (deg)	80−100	40.0−50.0	80−100	3.00−57.0
lattice params				
a (Å)	15.1666(6)	17.2075(21)	17.806(3)	8.8803(1)
b (Å)	11.5652(4)	11.055	9.900(2)	16.5932(2)
c (Å)	16.0374(6)	18.223(3)	20.425(5)	18.2614(3)
β (deg)	99.856(3)	97.029(12)	94.920(16)	97.186(1)
Z value	4	2	4	4
$F(000)$	1110	648	1434	1114
D_{calc}(g·cm^{-3})	1.235	1.157	1.256	1.327
μ (mm^{-1})	1.62	1.37	2.52	2.61
λ (Å)	1.540 56	1.540 56	1.540 56	0.070 93
no. of reflns measd	2509	3690	3740	18456
no. of unique reflns	2373	3690	3588	6781
no. of reflns obsd	1129[20]	3416	1998	5253
no. of atoms	83	202	102	70
no. of variables	298	702	361	417
for significant reflections				
R	0.074	0.057	0.111	0.027
R_w	0.052	0.043	0.087	0.024

Figure 1. Molecular structure and atom-numbering scheme for [CyNC(Me)NCy]$_2$Ge (**1**) (Cy = cyclohexyl).[20] Hydrogen atoms have been omitted for clarity.

Figure 2. Molecular structure and atom-numbering scheme for one of the two molecules in the asymmetric unit for the structure of [CyNC(^{t}Bu)NCy]$_2$Ge (**2**) (Cy = cyclohexyl).[21] Hydrogen atoms have been omitted for clarity.

proposed in Scheme 2. Finally, the ^{77}Se NMR spectrum (δ = 1023.8 vs Me$_2$Se) of **6** is comparable to that of a structurally characterized germaselenone which appeared at δ = 940.6.[2b]

In order to validate the terminal Ge=Ch bond in these materials, we undertook an investigation of the structure of **6** by single-crystal X-ray diffraction (Table 1). These structural results demonstrate the salient bonding features shown in Figure 3.[22] From Figure 3 it is clear that the most outstanding structural feature in this molecule is the terminal Ge=Se bond. The Ge−Se bond length of 2.196 Å correlates favorably with the comparable reports in the literature of (cf. 2.247 and 2.180 Å).[2b,4b]

The distorted tetrahedral Ge coordination geometry in this complex is similar to that of the Ge(II) starting material (**2**) with the Ge−Se vector residing in the site previously occupied by the lone electron pair. The coordination sphere of Ge is completed by the nitrogen atoms of one bidentate (N3, N4) and one monodentate amidinate (N1). The gross features (e.g., internal angles of the Ge−N3−C24−N4 cycle) of both amidi-

nate ligands and their relative disposition are very similar to those of **2**. Not surprisingly, the three Ge(IV)−N bonds for **6** are shorter than those of the Ge(II) starting material. The Se−Ge−N angles range from 120.0(5) to 122.3(4)°.

Ge(II) Complexes with Mixed-Ligand Systems. The observation that one of the amidinate ligands in both the Ge(II) complexes and the terminal Ge^{IV}=Ch complexes is monodentate prompted us to consider substitution of this ligand with a simple amido ligand. Complexes **1**−**6** appear to be essentially equal to mixed amidinato−amido species. On the basis of accessibility and the previous synthesis of Ge^{II}[N(SiMe$_3$)$_2$]$_2$, we chose to investigate the substitution of the dangling amidinate with the N(SiMe$_3$)$_2$ moiety. It should be noted that reaction of Ge^{II}[N(SiMe$_3$)$_2$]$_2$ with a chalcogen is rapid and yields the expected bridging system (μ-Ch)$_2${Ge[N(SiMe$_3$)$_2$]$_2$}$_2$.[23]

The mixed-ligand species **7** and **9** were obtained by the stepwise reaction of GeCl$_2$(dioxane) with 1 equiv of lithium

(22) Selected bond distances (Å) and bond angles (deg) for **6**: Ge−Se, 2.196(4); Ge−N1, 1.86(1); Ge−N3, 2.01(1); Ge1−N4, 1.99(1); N1−C7, 1.42(2); N2−C7, 1.27(2); N3−C24, 1.29(2); N4−C24, 1.35(2); N1−Ge−N3, 106.4(6); N1−Ge−N4, 108.9(6); N3−Ge−N4, 65.6(6); Ge−N1−C7, 119.8(11); C1−N1−C7, 123.9(13); Ge−N3−C24, 92.4(11); Ge−N4−C24, 91.7(11); N3−C24−N4, 109.9(16); Se1−Ge1−N1, 120.0(5); Se1−Ge1−N3, 122.3(4); Se1−Ge1−N4, 121.4(4).

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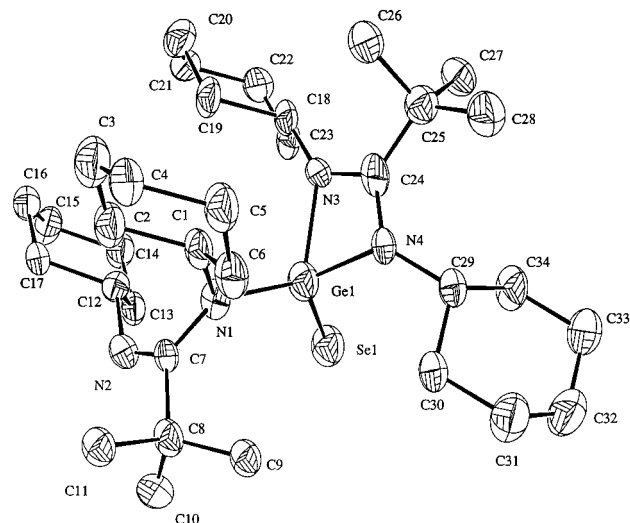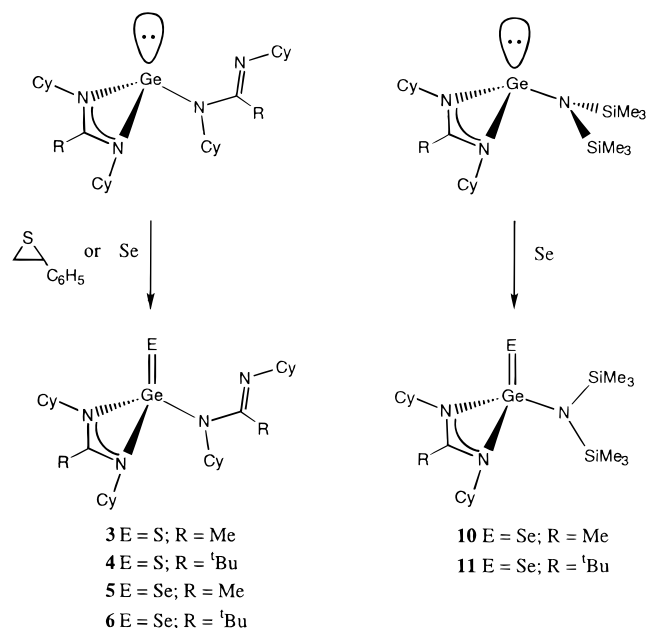
Figure 3. Molecular structure and atom-numbering scheme for [CyNC-('Bu)NCy]₂Ge=Se (**6**) (Cy = cyclohexyl).[22] Hydrogen atoms have been omitted for clarity.

Scheme 2

3 E = S; R = Me
4 E = S; R = 'Bu
5 E = Se; R = Me
6 E = Se; R = 'Bu

10 E = Se; R = Me
11 E = Se; R = 'Bu

amidinate followed by addition of 1 equiv of lithium amide (Scheme 1). Only in the case of CyNC('Bu)NCy]₂GeCl (**8**) was the intermediate species isolated and characterized. The ¹H NMR spectrum of CyNC('Bu)NCy]₂GeN(SiMe₃)₂ (**9**) displays a broadened singlet for the trimethylsilyl groups relative to that of CyNC(Me)NCy]₂GeN(SiMe₃)₂ (**7**), indicative of hindered rotation of the amido ligand.

These Ge(II) species also readily react with elemental selenium to yield the chalcogenido complexes [CyNC(Me)NCy]₂Ge-[N(SiMe₃)₂]Se (**10**) [CyNC('Bu)NCy]₂Ge[N(SiMe₃)₂]Se (**11**). Both COSY and heteroatom (¹³C/¹H) correlation NMR experiments for **11** were consistent with the connectivity shown in Scheme 2. As in the case of **9**, the NMR spectrum of **11** indicates that there is hindered rotation around Ge−N(SiMe₃)₂ bond. The appearance of a ⁷⁷Se NMR resonance at δ = 1115.6 vs Me₂Se for **10** is similar to the case of **6** and appropriate for a terminal function.[2b]

A single-crystal X-ray diffraction analysis provided the detailed connectivity of **10** (Table 1). From Figure 4 it is clear that **10**, like **6**, is a terminal Ge chalcogenido species.[24] Again, the Ge coordination geometry in this complex is that of a
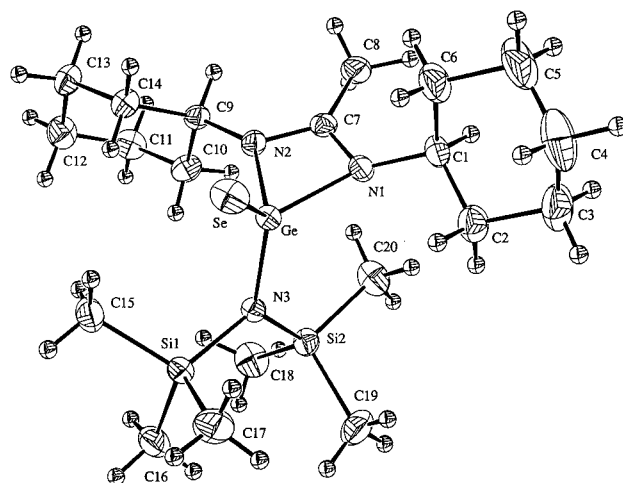

Figure 4. Molecular structure and atom-numbering scheme for [C₆H₁₁-NC(Me)NC₆H₁₁]Ge[N(SiMe₃)₂]Se (**10**) (Cy = cyclohexyl).[24]

distorted tetrahedron with the Ge−Se vector residing on one of the vertices at a slightly longer distance (2.2212(3) Å) than in **6** but comparable to those of literature species.[2b,4b] The coordination sphere of Ge is completed by the nitrogen atoms of one bidentate (N1, N2) amidinate and the bis(trimethylsilyl)amido nitrogen (N3). The internal angles of the planar Ge−N1−C7−N2 cycle are reminiscent of those in the bidentate ligands in **1**, **2**, and **6**. The amido nitrogen (N3) is planar with the plane of this ligand rotated out of the plane of the amidinate ligand (torsional angles: N1−Ge−N3−Si1 = 165.2°, N1−Ge−N3−Si2 = −9.04°, Se−Ge−N3−Si1 = 21.72°). The three Ge(IV)−N bonds are very similar to those of **6**, and the Se−Ge−N angles are slightly smaller and range from 115.18(5) to 121.03(5)°.

Conclusion

Terminal chalcogenido germanium complexes have been prepared from a unique family of bis(amidinato)germanium-(II) and mixed (amidinato)(amido)germanium(II) compounds. These results add significantly to the limited number of structurally characterized terminal chalcogenido complexes. These new species will help to delineate the steric and electronic features which stabilize and influence the reactivity of such species.

The structural studies presented above show that Ge(II) and Ge(IV) complexes with these ligand environments have a strong disposition toward a tetrahedral coordination geometry. This tendency led to the systematic observation of dangling ligands in the bis(amidinate) systems. This contrasts with reported Sn(II/IV) analogues. In addition, amidinate anions have been shown to be excellent ancillary ligands for Ge complexes with fairly well-defined structural features.

Preparation of these relatively stable Ge=Ch species is allowing a thorough study of their reactivity. Our preliminary efforts in this regard (i.e., investigation of 2+2 cycloadditions and atom transfer reactions) are promising and will be the subject of future reports.

Experimental Section

General Considerations. All manipulations were carried out in a Vacuum Atmospheres drybox or on a vacuum line using standard

(24) Selected bond distances (Å) and bond angles (deg) for **10**: Ge−Se, 2.2212(3); Ge−N1, 1.9946(15); Ge−N2, 1.9572(15); Ge−N3, 1.8410(15); N1−C7, 1.3367(24); N2−C7, 1.3209(24); N3−Si1, 1.7723(15); N3−Si2, 1.7542(15); ; Se−Ge−N1, 115.18(5); Se−Ge−N2, 121.03(5); Se−Ge−N3, 120.52(5); N1−Ge−N2, 67.14(6); N1−Ge−N3, 114.05(6); N2−Ge−N3, 107.42(6); Ge−N1−C7, 92.12(11); Ge−N2−C7, 92.06(11); N1−C7−N2, 108.54(16).

Schlenk techniques. Solvents were distilled under nitrogen from Na/K alloy. $GeCl_2(dioxane)^{25}$ was prepared by literature procedures. ^{t}BuLi, MeLi, $LiN(SiMe_3)_2$, and dicyclohexylcarbodiimide were used as received from Aldrich.

NMR spectra were run on a Gemini 200 MHz or Bruker 500MHz spectrometer with deuterated benzene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system. Satisfactory CHN microanalysis was obtained for all products.

$Ge[C_6H_{11}NC(Me)NC_6H_{11}]_2$ (1). To a solution of dicyclohexylcarbodiimide (0.889 g, 4.32 mmol) in diethyl ether (40 mL) was added MeLi (3.08 mL, 1.4 M, 4.32 mmol). After 30 min, $GeCl_2$(diox) (0.50 g, 2.16 mmol) was added. The solution was stirred for 12 h, filtered to remove the white LiCl precipitate, and evaporated to dryness. Colorless crystals were obtained from hexanes at -34 °C (1.73 g, 78% yield). ^{1}H NMR (C_6D_6, ppm): 3.29 (br, C_6H_{11}, 4H); 2.02$-$1.16 (m, C_6H_{11}, 40H); 1.64 (s, Me, 6H). ^{13}C NMR (C_6D_6, ppm): 163.0 (s, NCN); 56.3, 35.8, 26.5, 26.3 (4s, C_6H_{11}); 12.6 (s, Me).

$Ge[C_6H_{11}NC(CMe_3)NC_6H_{11}]_2$ (2). To a solution of dicyclohexylcarbodiimide (1.24 g, 6.00 mmol) in diethyl ether (50 mL) was added ^{t}BuLi (3.55 mL, 1.7 M, 6.00 mmol). After 30 min, $GeCl_2$(diox) (0.700 g, 3.00 mmol) was added. The solution was stirred for 12 h, filtered to remove the white LiCl precipitate, and evaporated to dryness. Pale yellow crystals were obtained from a 50:50 mixture of hexamethyldisiloxane/hexanes at -34 °C (3.05 g, 85% yield). ^{1}H NMR (C_6D_6, ppm): 4.10 (br, C_6H_{11}, 1H); 3.77 (br, C_6H_{11}, 2H); 3.50 (br, C_6H_{11}, 1H); 2.35$-$1.17 (m, C_6H_{11}, 40H); 1.61 (s, CMe_3, 9H); 1.17 (s, CMe_3, 9H).

$[C_6H_{11}NC(Me)NC_6H_{11}]_2GeS$ (3). To a solution of **1** (0.152 g, 0.30 mmol) in hexanes (5 mL) was added styrene sulfide (0.061 g, 0.45 mmol). Product slowly precipitated out of solution. The solution was stirred for 12 h and filtered, and the product was crystallized from ether at -34 °C (0.12 g, 75% yield of colorless crystals of **3**). ^{1}H NMR (C_6D_6, ppm): 3.27 (br, C_6H_{11}, 4H); 2.12$-$1.04 (m, C_6H_{11}, 40H); 1.49 (s, Me, 6H).

$[C_6H_{11}NC(CMe_3)NC_6H_{11}]_2GeS$ (4). To a solution of **2** (0.110 g, 0.184 mmol) in hexanes (5 mL) was added styrene sulfide (0.037 g, 0.28 mmol). Product slowly precipitated out of solution. The solution was stirred for 12 h, filtered, and crystallized from ether at -34 °C (0.087 g, 75% yield of colorless crystals of **4**). ^{1}H NMR (C_6D_6, ppm): 4.07 (br, C_6H_{11}, 1H); 3.71 (br, C_6H_{11}, 2H); 3.22 (br, C_6H_{11}, 1H); 2.67$-$0.90 (m, C_6H_{11}, 40H); 1.70 (s, CMe_3, 9H); 1.07 (s, CMe_3, 9H).

$[C_6H_{11}NC(Me)NC_6H_{11}]_2GeSe$ (5). To a solution of **1** (1.00 g, 1.94 mmol) in ether (15 mL) was added 1 equiv of selenium (0.154 g, 1.94 mmol). The solution was stirred for 12 h and evaporated to dryness. Colorless crystals were obtained from ether at -34 °C (1.02 g, 89% yield). ^{1}H NMR (C_6D_6, ppm): 3.30 (br, C_6H_{11}, 4H); 2.15$-$0.85 (m, C_6H_{11}, 40H); 1.50 (s, Me, 6H).

$[C_6H_{11}NC(CMe_3)NC_6H_{11}]_2GeSe$ (6). To a solution of **2** (0.300 g, 0.500 mmol) in ether (10 mL) was added 1 equiv of selenium (0.040 g, 0.500 mmol). The solution was stirred for 12 h and evaporated to dryness. Crystals were obtained from ether at -34 °C (0.25 g, 85% yield of colorless crystals of **6**). ^{1}H NMR (C_6D_6, ppm): 4.03 (br, C_6H_{11}, 1H); 3.75 (br, C_6H_{11}, 2H); 3.23 (br, C_6H_{11}, 1H); 2.70$-$0.90 (m, C_6H_{11}, 40H); 1.71 (s, CMe_3, 9H); 1.07 (s, CMe_3, 9H). ^{13}C NMR (C_6D_6, ppm): 178.7 (s, NCN); 162.5 (s, NCN); 32.2 (s, Me); 28.6 (s, Me). ^{77}Se NMR (C_6D_6, ppm vs Me_2Se): 1023.8 (s, GeSe).

$[C_6H_{11}NC(Me)NC_6H_{11}]GeN(SiMe_3)_2$ (7). To a solution of dicyclohexylcarbodiimide (0.445 g, 2.16 mmol) in diethyl ether (25 mL) was added MeLi (1.54 mL, 1.4 M, 2.16 mmol). After 30 min, the solution was added to 1 equiv of $GeCl_2$(diox) (0.500 g, 2.16 mmol) in diethyl ether (25 mL). The solution was stirred for 6 h, and 1 equiv of lithium bis(trimethylsilylamide) (0.361 g) was then added. The solution was stirred for another 12 h and filtered to remove the white LiCl precipitate. The solvent was removed under vacuum, at which point an intractable yellow oil was observed as the sole product (0.90 g, 92% yield). ^{1}H NMR (C_6D_6, ppm): 3.05 (br, C_6H_{11}, 2H); 2.00$-$1.02 (m, C_6H_{11}, 20H); 1.29 (s, Me, 3H); 0.46 (s, $SiMe_3$, 18H).

(25) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

$[C_6H_{11}NC(CMe_3)NC_6H_{11}]GeCl$ (8). To a solution of dicyclohexylcarbodiimide (0.267 g, 1.30 mmol) in diethyl ether (20 mL) was added ^{t}BuLi (0.76 mL, 1.7M, 1.30 mmol). After 30 min, 1 equiv of $GeCl_2$-(diox) (0.300 g, 1.30 mmol) was added. The solution was stirred for 12 h, filtered to remove the white LiCl precipitate, and evaporated to dryness to give a white solid. ^{1}H NMR (C_6D_6, ppm): 3.62 (br, C_6H_{11}, 2H); 2.12$-$0.90 (m, C_6H_{11}, 20H); 1.20 (s, CMe_3, 9H).

$[C_6H_{11}NC(CMe_3)NC_6H_{11}]GeN(SiMe_3)_2$ (9). To a solution of **8** (0.130 g, 0.350 mmol) in ether (10 mL) was added 1 equiv of lithium bis(trimethylsilylamide) (0.217 g, 0.350 mmol). The solution was stirred for 12 h, filtered, and evaporated to dryness. White crystals were obtained from ether at room temperature (0.13 g, 77% yield). ^{1}H NMR (C_6D_6, ppm): 3.72 (br, C_6H_{11}, 2H); 2.20$-$0.95 (m, C_6H_{11}, 20H); 1.11 (s, CMe_3, 9H); 0.50 (br s, $SiMe_3$, 18H).

$[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2]Se$ (10). To a solution of **7** (0.98 g, 2.15 mmol) in diethyl ether (30 mL) was added 1 equiv of selenium (0.17 g, 2.15 mmol). The solution was stirred for 24 h and evaporated to dryness, leaving behind a yellow powder. Clear, colorless crystals were obtained from 75:25 diethyl ether/hexanes at -34 °C (0.85 g, 74% yield). ^{1}H NMR (C_6D_6, ppm): 2.98 (br, C_6H_{11}, 2H); 2.10$-$0.85 (m, C_6H_{11}, 20H); 1.16 (s, Me, 3H); 0.53 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6, ppm): 170.0 (s, NCN); 55.3, 35.1, 33.6, 25.4 (4s, C_6H_{11}); 11.8 (s, Me); 6.1 (s, $SiMe_3$). ^{77}Se NMR (C_6D_6, ppm vs Me_2Se): 1115.6 (s, GeSe).

$[C_6H_{11}NC(CMe_3)NC_6H_{11}]Ge[N(SiMe_3)_2]Se$ (11). To a solution of **9** (0.050 g, 0.101 mmol) in C_6D_6 (0.5 mL) was added 1 equiv of selenium (0.008 g, 0.101 mmol). ^{1}H NMR (C_6D_6, ppm): 3.67 (br, C_6H_{11}, 2H); 2.75$-$0.90 (m, C_6H_{11}, 20H); 1.11 (s, CMe_3, 9H); 0.84 (b, $SiMe_3$, 9H); 0.33 (b, $SiMe_3$, 9H). ^{13}C NMR (C_6D_6, ppm): 175.7 (s, NCN); 57.7, 37.1, 34.3, 25.9, 25.4 (5s, C_6H_{11}); 38.1 (s, CMe_3); 28.0 (s, Me); 7.0, 5.8 (br s, $SiMe_3$).

X-ray Crystallography. For compounds **1**, **2**, and **6** a summary of the data collection is provided in Table 1. Intensity data were collected on a Rigaku diffractometer at -153 °C using the $\theta-2\theta$ scan technique for crystals mounted on glass fibers. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of a favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma(I)$]. Anomalous dispersion effects were included in the F_c values. All calculations were performed using the NRCVAX package. Full details of the data collection and refinement and final atomic coordinates are reported in the Supporting Information.

For compound **7**, a summary of the data collection is provided in Table 1. Intensity data were collected on a Siemens SMART CCD diffractometer at -153 °C using the ω (0.3° scans) scan technique for crystals mounted on glass fibers. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of a favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma(I)$]. Anomalous dispersion effects were included in the F_c values. All calculations were performed using the NRCVAX package. Full details of the data collection and refinement and final atomic coordinates are reported in the Supporting Information.

Supporting Information Available: COSY and HETCOR spectra for compounds **4** and **11**, listings providing crystallographic data and details of the structural solutions, tables of atomic positions, thermal parameters, and bond distances and angles, and ORTEP drawings and unit cell diagrams for compounds **1**, **2**, **6**, and **10** (60 pages). See any current masthead page for ordering and Internet access instructions.