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FULL PAPER

Oxidative addition to M(II) (M = Ge, Sn) amidinate complexes: routes to group 14 chalcogenolates with hypervalent coordination environments

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Oxidative addition of diphenyl dichalcogenides, PhE–EPh (E = S, Se) to Ge(II) and Sn(II) amidinate complexes is reported. In the case of the bis(alkylamidinato)Ge complexes, Ge(CyNC(R′)NCy) (Cy = cyclohexyl; R′ = Me, ^{t}Bu), six coordinate Ge(IV) compounds were isolated and the structure of $(PhS)_2Ge(CyNC(Me)NCy)$ (**10**) was confirmed by single crystal X-ray diffraction analysis. Mixed amidinato–amido species, $M(CyNC(R')NCy)[N(SiMe_3)_2]$ (M = Ge, Sn; R = Me, ^{t}Bu), react in a similar manner to yield novel bis(phenylchalcogenolate) complexes of Sn and Ge. Spectroscopic features and, in the case of $(PhSe)_2Ge(CyNC(Me)NCy)[N(SiMe_3)_2]$ (**13**), a single crystal structural analysis indicate that this ligand environment appears to favor Ge(IV) complexes with a strong disposition towards a tetrahedral geometry. In these cases, a five coordinate environment for the metal center is avoided by one of the amidinate ligands exhibiting a monodentate coordination mode, which preserves the pseudo-tetrahedral metal coordination geometry. These observations contrast with the Sn(II/IV) analogues which exhibit no such tendency. For example the single crystal structure of $(PhS)_2Sn(CyNC(Me)NCy)[N(SiMe_3)_2]$ (**14**) displays a bidentate ligand and a five coordinate metal coordination geometry. Complex **13** reacts with elemental Se to generate the terminal germanium selenide and regenerate PhSeSePh. Concomitant with this reaction is a rearrangement of the previously monodentate amidinate ligand to a bidentate coordination mode.

Introduction

Amidinate anions, RNC(R′)NR$^-$, have received attention as versatile ancillary ligands for a range of metal complexes. In most cases they appear as bidentate four electron ligands which are either chelating to one metal center or bridging two centers.[1] The steric and, to a lesser extent, the electronic features of these ligands are amenable to manipulation through alterations of the organic substituents. These are among the features that have made amidinates attractive as ligands for main group metal complexes in efforts to design new catalytically active species,[2] molecular precursors to solids[3] and compounds with unusual bonding features and functionalities.[4]

As part of our general investigation of ligand effects on the coordination environments and reactivities of the post-transition elements, we have been interested in employing amidinate ligands in the chemistry of Group 14 metals. Amidinato complexes of tin have been reported with the metal in both the tetravalent and divalent oxidation states.[4a,5] However, the first amidinato complexes of germanium have only recently appeared in the literature.[4,6] Some of these complexes have stimulated theoretical interest.[7] However, very few reactivity studies have appeared for these compounds. While our primary focus has been centered on the ability of these ligands to stabilize rare functionalities and unusual structural features, we have recently observed interesting reactivity for some of these complexes. For example, the M(II) (M = Ge, Sn) species are susceptible to oxidation by elemental chalcogens and many of these complexes are excellent catalysts for the cyclization of aryl isocyanates.[2c,8]

As part of these continuing investigations we now report the oxidative cleavage of the chalcogen–chalcogen bonds of diphenyl dichalcogen compounds (PhE–EPh, E = S, Se) with bis(alkylamidinato)Ge(II) complexes, Ge(CyNC(R′)NCy) (Cy = cyclohexyl; R′ = Me, ^{t}Bu), and mixed amidinato–amido species, $M(CyNC(R')NCy)[N(SiMe_3)_2]$ (M = Ge, Sn; R = Me, ^{t}Bu), to yield novel bis(phenylchalcogenolate) complexes of Sn and Ge. We include some observations on the effects of ligand variation on the structure and reactivity of these species.

Results and discussion

Oxidative addition of diphenyl dichalcogenides to Ge(II) amidinate complexes 1 and 2

Among the M(II) (M = Ge, Sn) species that we have isolated by employing bulky alkylamidinate ligands are those shown in Chart 1. The bis(amidinato)Ge(II) complexes (**1** and **2**) were shown through NMR spectroscopic measurements and by single crystal X-ray diffraction studies to possess one bidentate and one monodentate ("dangling") amidinato ligand and to have geometries based on distorted tetrahedra in which one of the vertices is occupied by a stereochemically active lone pair of electrons.[4b] In contrast, the bis(amidinato)Sn(II) analogues (**3**, and **4**) displayed distorted trigonal bipyramidal geometries with one of the vertices occupied by a lone pair of electrons.[4a] We have attributed these differences to the smaller ionic radius of Ge(II) relative to Sn(II) and to the ability of Sn to more readily accommodate an expanded octet. The observation that one of the amidinate ligands in the Ge(II) complexes was monodentate

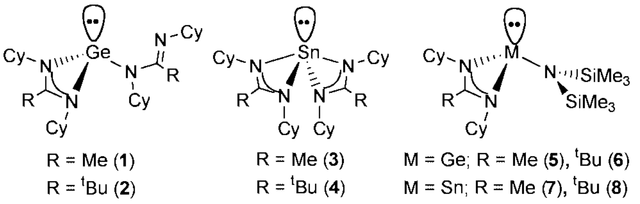

Chart 1

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provided some motivation to prepare mixed ligand species (**5**–**8**).[2c,4b,8]

Some general trends in reactivity of **1**–**8** have been noted. In particular, these compounds are susceptible to oxidation by chalcogen atom sources (*e.g.* elemental S and Se and episulfides) to yield interesting terminal chalcogenides and polychalcogenido species such as those shown in Chart 2.[2c,4] It is noteworthy that all of these complexes continue to display the structural preferences described above. The Ge(IV) species favor pseudo-tetrahedral based geometries even in the presence of a pendant base from the "dangling" amidinate nitrogen and in spite of the increased oxidation state and associated Lewis acidity of the Ge center. Similarly, the geometry of the Sn(II) complexes is maintained upon oxidation to Sn(IV). We have never observed the monodentate amidinate ligand for Sn.

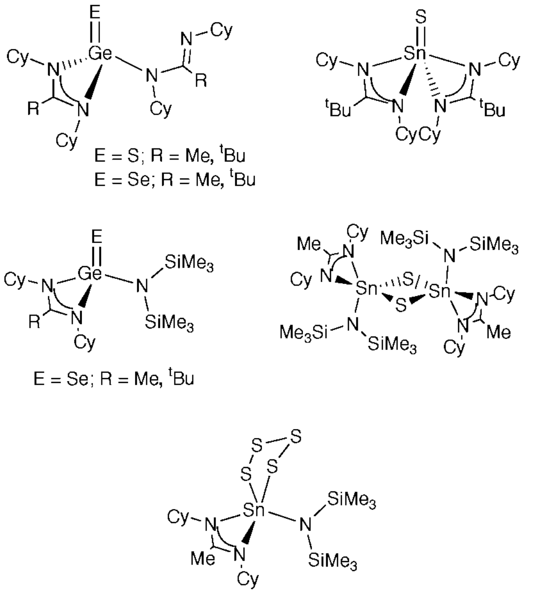
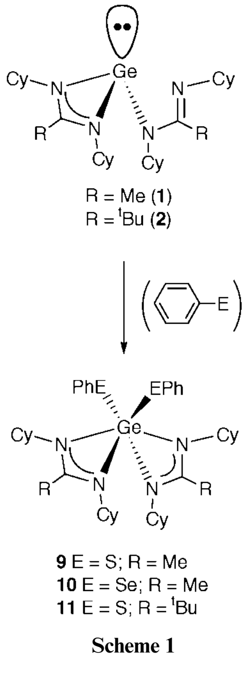


Chart 2

Oxidative addition of diphenyl disulfide and diphenyl diselenide occurs rapidly to complexes **1** and **2**. The products of these reactions are the result of cleavage of the chalcogen–chalcogen bond and formation of the corresponding bis(phenylchalcogenolate)M(IV) complexes **9**–**11** in high yields (Scheme 1). The most obvious change in the NMR spectra for the products of these reactions is the appearance of aromatic signals with integrated intensities consistent with the formulation of the products. Diphenyl ditelluride does not react with **1** or **2**, even at elevated temperatures, a feature that is likely due to the weaker oxidizing power of this reagent.



Scheme 1

Table 1 Selected bond lengths [Å] and angles [°] for $[C_6H_{11}NC(Me)NC_6H_{11}]_2Ge[SeC_6H_5]_2$ (**10**)

Se(1)–Ge	2.4698(14)	N(1)–C(13)	1.322(12)
Se(2)–Ge	2.4790(17)	N(1)–C(6)	1.466(12)
Se(1)–C(34)	1.926(5)	N(2)–C(13)	1.313(12)
Se(2)–C(40)	1.940(5)	N(2)–C(12)	1.465(12)
Ge–N(1)	1.955(7)	N(3)–C(27)	1.313(14)
Ge–N(4)	1.978(8)	N(3)–C(20)	1.468(14)
Ge–N(3)	2.062(9)	N(4)–C(27)	1.310(14)
Ge–N(2)	2.105(7)	N(4)–C(26)	1.472(14)
Ge–C(27)	2.467(10)	C(13)–C(14)	1.515(14)
Ge–C(13)	2.468(9)	C(27)–C(28)	1.520(15)
C(34)–Se(1)–Ge	105.7(2)	C(13)–N(1)–Ge	95.8(6)
C(40)–Se(2)–Ge	106.3(2)	C(6)–N(1)–Ge	130.0(6)
N(1)–Ge–N(4)	154.9(4)	C(13)–N(2)–C(12)	124.1(8)
N(1)–Ge–(3)	96.5(3)	C(13)–N(2)–Ge	89.3(6)
N(4)–Ge–(3)	64.1(4)	C(12)–N(2)–Ge	146.6(6)
N(1)–Ge–N(2)	64.4(3)	C(27)–N(3)–C(20)	121.6(10)
N(4)–Ge–N(2)	98.2(3)	C(27)–N(3)–Ge	91.2(7)
N(3)–Ge–N(2)	89.9(3)	C(20)–N(3)–Ge	145.5(8)
N(1)–Ge–Se(1)	99.8(2)	C(27)–N(4)–C(26)	131.0(10)
N(4)–Ge–Se(1)	98.5(2)	C(27)–N(4)–Ge	95.0(7)
N(3)–Ge–Se(1)	97.5(2)	C(26)–N(4)–Ge	131.0(8)
N(2)–Ge–Se(1)	163.3(2)	N(2)–C(13)–N(1)	110.5(8)
N(1)–Ge–Se(2)	96.6(2)	N(2)–C(13)–C(14)	124.0(9)
N(4)–Ge–Se(2)	99.2(3)	N(1)–C(13)–C(14)	125.4(9)
N(3)–Ge–Se(2)	161.0(2)	N(4)–C(27)–N(3)	109.6(9)
N(2)–Ge–Se(2)	83.5(2)	N(4)–C(27)–C(28)	125.7(12)
Se(1)–Ge–Se(2)	93.71(6)	N(3)–C(27)–C(28)	124.6(12)
C(13)–N(1)–C(6)	127.8(8)		

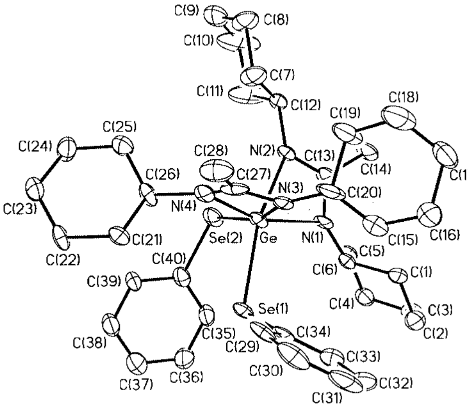


Fig. 1 Molecular structure of $[C_6H_{11}NC(Me)NC_6H_{11}]_2Ge[SeC_6H_5]_2$ (**10**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Observation of single Me groups and a single type of Cy group in the ^1H and ^{13}C NMR spectra of **9** and **10** is consistent with our previously reported findings and indicative of fluxional species.[4b] However, similar observations with the ᵗBu analogue, **11**, were at odds with our prior observations that Ge complexes of this ligand exhibit hindered internal motion and reduced fluxionality compared with their Me analogues.

In order to clarify the geometry of these complexes, a crystallographic study was performed on **10** (Fig. 1). This analysis revealed a monomeric Ge(IV) species in a distorted octahedral coordination sphere that included the four nitrogen atoms of the two chelating amidinate anions and was completed by two *cis*-phenylselenolate ligands. Table 1 presents a summary of selected bond distances and angles for **10**. The unusual six coordinate geometry exhibited by the Ge center in this complex contrasts with our previous observations for bis(amidinate) germanium complexes shown in Charts 1 and 2.

The two amidinate ligands in 10 are only very slightly different and in both cases the two nitrogen atoms and the bridging carbon atoms of the ligands lie in a plane which includes the Ge atom (Σ internal angles = 360°). Ligand bite angles of 64.1(4)° and 64.4(3)° are similar to the corresponding angles in previously reported complexes.[4b,6] The equivalence of the C–N bond lengths within N–C–N frameworks of the amidinates as well as their magnitudes (range from 1.322(12) to 1.310(14) Å) indicate that the π electrons within the ligands are delocalized.

The termini of the amidinate ligand can be divided into two types, the *cis*-NCy groups (N(2), N(3)) and *trans*-NCy groups (N(1), N(4)). The *cis*-GeN bond lengths (Ge–N(3) 2.062(9), Ge–N(2) 2.105(7) Å) are slightly longer than the *trans*-GeN distances (Ge–N(1) 1.955(7), Ge–N(4) 1.978(8) Å). This feature is likely due to a combination of the relative steric congestion experienced by the two groups and the effect of the *trans* oriented SePh groups.

The few reported Ge^{IV} complexes with phenylselenolate ligands all exhibit four coordinate geometries.[9] In **10,** the nearly equal Ge–Se bond lengths of 2.4698(14) and 2.4790(17) Å are longer than in the reported complexes (range 2.34–2.39 Å)[9] and the angles around the two Se centers (C(34)–Se(1)–Ge 105.7(2), C(40)–Se(2)–Ge 106.3(2)°) are larger than in these compounds. Both of these observations are consistent with the sterically crowded six coordinate Ge center that was observed for **10**.

We found the appearance of a six coordinate Ge center in **10** all the more surprising given the increased steric congestion of this geometry compared to that of **1** and to other reported complexes of these ligands. In contrast to the solid state structural observation of distinct Cy groups, the Cy moieties appear to be equivalent in the room temperature ^{1}H and ^{13}C NMR spectra thus indicating that complex **10** has a fluxional solution structure. Similar observations have been noted for six coordinate Sn(IV) complexes of these ligands.[5a]

While diphenyl disulfide and diphenyl diselenide react readily with complex **1** to form **9** and **10** and the corresponding Ge(IV) bis(phenylthiolato) complex **11** can be prepared by reaction of **2** with diphenyl disulfide, the reaction of **2** with diphenyldiselenide follows a different course. This reaction generates a mixture of products from which we have only been able to isolate $(CyNC(^tBu)NCy)Ge(SePh)_3$.[10] This result, while still under investigation, seems to indicate that the increase in steric bulk provided by the substitution of Me for ^{t}Bu in the amidinate ligand can have substantial effects on the reactivity and stability of complexes of this anion.

Oxidative addition of diphenyl dichalcogenides to Ge(II) and Sn(II) amidinate complexes 5 and 7

Diphenyl disulfide and diphenyl diselenide also add rapidly to the mixed ligand complexes **5** and **7** according to Scheme 2. Again the products of these reactions complexes **12**–**15** are M(IV) species with two phenylchalcogenolate ligands derived from the cleavage of the chalcogen–chalcogen bonds. Compounds **12**–**15** display very similar NMR spectral data with the key features being the appearance of equivalent phenyl groups and with the amidinate providing a single set of resonances for the Cy groups. While these observations suggest similar structures for **12**–**15**, the fluxionality that has been observed for similar complexes prompted us to investigate the solid state structures of **13** and **14** by single crystal X-ray crystallography.

Complex **13** crystallized with two independent molecules in the asymmetric unit, each of which displayed similar bonding parameters. Consistent with our proposals, the structural analysis of **13** (Fig. 2) revealed it to be a monomeric species which, in contrast to **10**, displayed the characteristic "dangling" amidinate ligand. Coordination of the amidinate ligand in a monodentate fashion preserves a metal coordination environment based on a pseudo-tetrahedral geometry rather than achieving the five coordinate environment possible *via* bidentate coordination. The coordination sphere of Ge is completed by a bis(trimethylsilyl)amido group and two phenylselenolate moieties. The observed pseudo-tetrahedral Ge coordination geometry (average interligand angle of 109.4°) is consistent with our previous observations for Ge complexes of alkylamidinates.[4b] A summary of bond distances and angles for **13** is provided in Table 2.

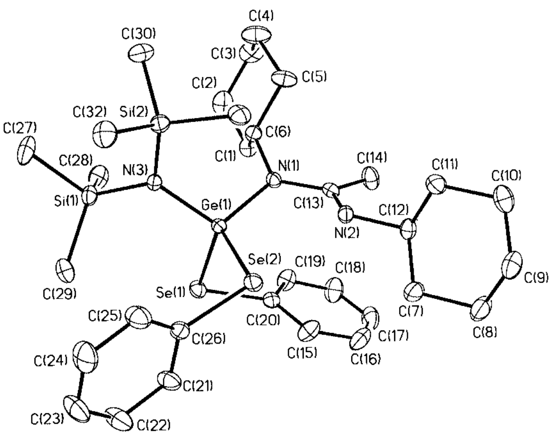
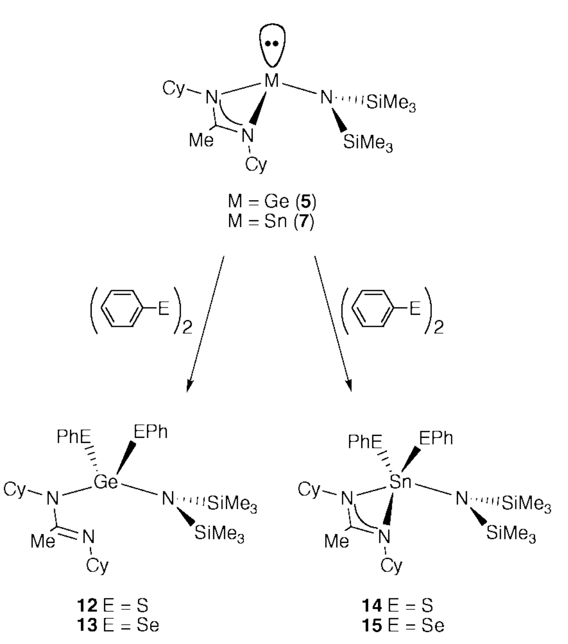


Fig. 2 Molecular structure for one of the independent molecules of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SeC_6H_5]_2$ (**13**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.



Scheme 2

The Ge–N bond lengths are similar for both the amido and monodentate amidinato ligands. Furthermore, the pertinent nitrogen centers (N(1), N(3)) are planar (sum to 360°). Consistent with the localized valence structure for **13** presented in Scheme 2, the bond lengths (N(2)–C(13), 1.272(3) Å) and one defining angle (C(13)–N(2)–C(12), 121.5(3)°) for the uncoordinated nitrogen atom support the imine formulation for this center. The phenylselenolate ligands exhibit bonding parameters that are similar to the few reported Ge complexes possessing these ligands with an average Ge–Se distance of 2.373 Å and an average Ge–Se–Ph angle of 97.98°.[9]

Complex **14** also crystallized with two independent molecules in the asymmetric unit and with no significant differences in

Table 2 Selected bond lengths [Å] and angles [°] for one of the independent molecules of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2]$-$[SeC_6H_5]_2$ (**13**)

Ge(1)–N(3)	1.840(2)	N(1)–C(13)	1.395(4)
Ge(1)–N(1)	1.859(2)	N(1)–C(6)	1.489(3)
Ge(1)–Se(2)	2.3522(5)	N(2)–C(13)	1.272(3)
Ge(1)–Se(1)	2.4009(5)	N(2)–C(12)	1.467(4)
Se(1)–C(20)	1.925(3)	C(13)–C(14)	1.514(4)
Se(2)–C(26)	1.934(3)		
N(3)–Ge(1)–N(1)	108.87(11)	C(13)–N(2)–C(12)	121.5(3)
N(3)–Ge(1)–Se(2)	111.98(7)	Si(1)–N(3)–Si(2)	120.99(14)
N(1)–Ge(1)–Se(2)	113.81(7)	Si(1)–N(3)–Ge(1)	121.12(14)
N(3)–Ge(1)–Se(1)	110.26(7)	Si(2)–N(3)–Ge(1)	117.88(13)
N(1)–Ge(1)–Se(1)	104.13(8)	N(2)–C(13)–N(1)	117.3(3)
Se(2)–Ge(1)–Se(1)	107.484(17)	N(2)–C(13)–C(14)	124.2(3)
C(20)–Se(1)–Ge(1)	96.23(9)	N(1)–C(13)–C(14)	118.4(3)
C(26)–Se(2)–Ge(1)	99.67(9)	C(45)–N(5)–C(44)	121.3(3)
C(13)–N(1)–C(6)	123.8(2)	Si(4)–N(6)–Si(3)	120.84(14)
C(13)–N(1)–Ge(1)	118.45(18)	Si(4)–N(6)–Ge(2)	121.65(13)
C(6)–N(1)–Ge(1)	117.60(19)		

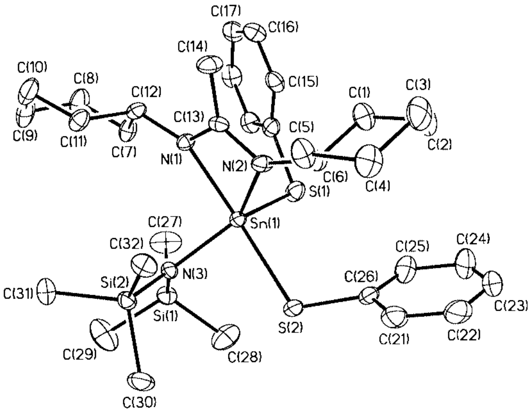


Fig. 3 Molecular structure for one of the independent molecules of $[C_6H_{11}NC(Me)CN_6H_{11}]Sn[N(SiMe_3)_2][SC_6H_5]_2$ (**14**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

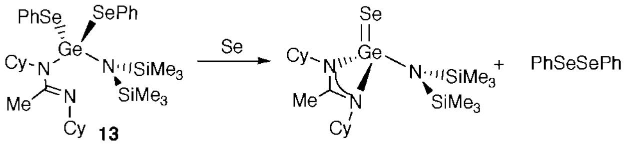
metrical parameters between the two species (Fig. 3). While the Sn coordination sphere in **14** is comprised of a similar ligand set as **13**, **14** exhibited a bidentate amidinate ligand rather than the monodentate coordination observed in **13**. The result is a distorted trigonal bipyramidal environment for the Sn(IV) center in **14**.

A selection of bond distances and angles for **14** are provided in Table 3. Examination of this data confirms that the amidinate ligands bind asymmetrically to the Sn(IV) centers and suggest an assignment of N(1) as pseudo-axial and N(2) as pseudo-equatorial. The relative Sn–N bond distances (*i.e.* axial greater than equatorial) are consistent with this formulation. Based on this arrangement the other pseudo-axial group is a phenylthiolato ligand (S(2)). The equatorial plane is then defined by the amido nitrogen, one amidinate nitrogen and the second phenylthiolato ligand. The angles within this plane are irregular but sum to 358° in the case of Sn(1) and 356° for Sn(2). The expected bond length difference between the pseudo-axial and pseudo-equatorial groups is reflected in the two Sn–S distances of each molecule. The Sn–S distances correlate favorably with the few comparable structural reports of bis(phenylthiolato) with five coordinate geometries.[11]

The amidinate ligands form planar metallocycles with the Sn centers (Σ internal angles = 360°). As anticipated for the bidentate coordination mode, the alkyl amidinate ligands exhibit a delocalized π bond over the N–C–N backbone as reflected in the C–N bond lengths ranging from 1.303(4) to 1.336(4) Å.

Table 3 Selected bond lengths [Å] and angles [°] for one of the independent molecules of $[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2]$-$[SC_6H_5]_2$ (**14**)

Sn(1)–N(3)	2.070(2)	S(2)–C(26)	1.777(4)
Sn(1)–N(2)	2.140(3)	N(1)–C(13)	1.303(4)
Sn(1)–N(1)	2.213(2)	N(1)–C(12)	1.463(4)
Sn(1)–S(1)	2.4158(10)	N(2)–C(13)	1.336(4)
Sn(1)–S(2)	2.4854(10)	N(2)–C(6)	1.468(4)
S(1)–C(20)	1.781(4)	C(13)–C(14)	1.516(4)
N(3)–Sn(1)–N(2)	135.18(11)	C(13)–N(1)–C(12)	124.8(3)
N(3)–Sn(1)–N(1)	95.56(10)	C(13)–N(1)–Sn(1)	93.1(2)
N(2)–Sn(1)–N(1)	60.05(10)	C(12)–N(1)–Sn(1)	142.1(2)
N(3)–Sn(1)–S(1)	116.44(8)	C(13)–N(2)–C(6)	130.0(3)
N(2)–Sn(1)–S(1)	106.28(8)	C(13)–N(2)–Sn(1)	95.4(2)
N(1)–Sn(1)–S(1)	104.03(8)	C(6)–N(2)–Sn(1)	133.8(2)
N(3)–Sn(1)–S(2)	88.81(8)	Si(2)–N(3)–Si(1)	121.65(15)
N(2)–Sn(1)–S(2)	98.23(8)	Si(2)–N(3)–Sn(1)	116.18(15)
N(1)–Sn(1)–S(2)	152.35(8)	Si(1)–N(3)–Sn(1)	119.88(14)
S(1)–Sn(1)–S(2)	98.29(3)	N(1)–C(13)–N(2)	111.3(3)
N(6)–Sn(2)–N(5)	140.30(10)	N(1)–C(13)–C(14)	124.3(3)
C(20)–S(1)–Sn(1)	105.61(11)	N(2)–C(13)–C(14)	124.3(3)
C(26)–S(2)–Sn(1)	114.00(13)		



Scheme 3

Exchange reactions of bis(phenylchalcogenolato)Ge(IV) complexes

The mixed ligand bis(phenylselenolato)Ge(IV) complex **13** exhibits ligand exchange reactivity as shown in Scheme 3. Complex **13** reacts cleanly with elemental selenium to form the corresponding terminal selenide, with elimination of diphenyl diselenide. This reaction provides a qualitative measure of the relative stabilities of the terminal selenido species *versus* the bis(diphenylselenido) complex. Concomitant with this reaction is a rearrangement of the amidinate ligand around the Ge(IV) center. The previously monodentate amidinate ligand now becomes bidentate and the pseudo-tetrahedral geometry of the Ge center remains intact.

The corresponding bis(phenylthiolato) complex **12** $(CyNC(Me)NCy)_2Ge(SPh)_2$ however, does not react with elemental Se or styrene sulfide at room temperature. The relative oxidizing power and Ge–E bond strength of Se *versus* S may rationalize the lack of reactivity with Se but the fact that styrene sulfide did not react with **12** is still under investigation.

Conclusions

A series of bis(phenylchalcogenolate) complexes of Ge and Sn have been prepared through the oxidative addition of diphenyl disulfide and diphenyl diselenide to a family of bis(amidinato)Ge(II) and mixed amidinato–amido-Ge(II) and -Sn(II) complexes. Structural studies confirm the geometric features of these species and indicate that this ligand environment appears to favor Ge(IV) complexes with a strong disposition towards either a tetrahedral or an octahedral geometry. In all observed cases a five coordinate environment is avoided by one of the amidinate ligands exhibiting a monodentate coordination mode thus preserving a pseudo-tetrahedral metal coordination geometry. This contrasts with the Sn(II/IV) analogues which exhibit no such tendency.

Experimental

General procedure

All manipulations were carried out in either a Vacuum

Table 4 Crystal data for compounds $[C_6H_{11}NC(Me)NC_6H_{11}]_2Ge[SeC_6H_5]_2$ (**10**), $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SeC_6H_5]_2$ (**13**), and $[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2][SC_6H_5]_2$ (**14**)

Empirical formula	$C_{40}H_{60}GeN_4Se$ (**10**)	$C_{32}H_{53}GeN_3Se_2Si_2$ (**13**)	$C_{32}H_{53}N_3S_2Si_2Sn$ (**14**)
Formula weight	827.43	766.46	718.76
T/K	163(2)	203(2)	203(2)
λ/Å	0.71073	0.71073	0.71073
Crystal symmetry	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	10.953(2)	10.828(1)	13.234(2)
b/Å	19.181(4)	25.140(3)	15.834(2)
c/Å	18.909(4)	26.674(3)	19.023(2)
α/°			88.728(2)
β/°	94.72(3)	98.304(2)	80.465(2)
γ/°			67.232(2)
V/Å^3	3959(1)	7185(1)	3621.0(7)
Z	4	8	4
D_c/Mg m^{-3}	1.388	1.417	1.318
μ/mm^{-1}	2.645	2.971	0.912
R (F_o)	0.0708	0.0366	0.0393
R_w (F_o^2)	0.1931	0.0610	0.0791

Atmospheres drybox or under nitrogen using standard Schlenk-line techniques. Diethyl ether and hexane were purified using a system developed by Anhydrous Engineering. Deuterated benzene was distilled under nitrogen from Na/K alloy. Diphenyl disulfide, diphenyl diselenide, diphenyl ditelluride, and elemental selenium were purchased from Aldrich and used without further purification. Complexes **1**, **2**, **5**, and **7** were prepared by literature procedures.[4,8] NMR spectra were run on a GEMINI 200 MHz 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.

Syntheses

$[C_6H_{11}NC(Me)NC_6H_{11}]_2Ge[SC_6H_5]_2$ (9). To a solution of **1** (0.300 g, 0.583 mmol) in diethyl ether (25 ml) was added 1 equiv of diphenyl disulfide (0.127 g). The solution was allowed to react for 12 h and evaporated to dryness. White crystals were obtained from hexane at −34 °C (0.33 g, 78% yield). ^{1}H NMR (C_6D_6): δ 7.72, (m, C_6H_5, 4H); 7.08 (m, C_6H_5, 6H); 3.39 (br, C_6H_{11}, 4H); 2.16–0.89 (m, C_6H_{11}, 40H); 1.57 (s, Me, 6H). ^{13}C NMR (C_6D_6): δ 161.6 (s, N*C*MeN); 136.8, 136.2, 129.2, 125.5 (4s, C_6H_5); 56.0, 34.1, 26.9, 25.5 (4s, C_6H_{11}); 13.0 (s, C*C*H_3). Calc. for $C_{40}H_{60}N_4GeS_2$: C, 65.49; H, 8.24; N, 7.64. Found: C, 65.87; H, 8.54; N, 7.06%.

$[C_6H_{11}NC(Me)NC_6H_{11}]_2Ge[SeC_6H_5]_2$ (10). To a solution of **1** (0.187 g, 0.363 mmol) in diethyl ether (20 ml) was added 1 equiv of diphenyl diselenide (0.113 g). The solution was allowed to react for 12 h and evaporated to dryness. Yellow crystals were obtained from diethyl ether at −34 °C (0.27 g, 90% yield). ^{1}H NMR (C_6D_6): δ 7.89, (m, C_6H_5, 4H); 7.04 (m, C_6H_5, 6H); 3.42 (br, C_6H_{11}, 4H); 2.05–0.95 (m, C_6H_{11}, 40H); 1.59 (s, Me, 6H). ^{13}C NMR (C_6D_6): δ 162.4 (s, N*C*MeN); 138.5, 135.0, 127.9, 126.4 (4s, C_6H_5); 56.1, 34.5, 27.2, 26.6 (4s, C_6H_{11}); 13.5 (s, C*C*H_3). Calc. for $C_{40}H_{60}N_4GeSe_2$: C, 58.06; H, 7.31; N, 6.77. Found: C, 57.72; H, 7.75; N, 6.67%.

$[C_6H_{11}NC(^tBu)NC_6H_{11}]_2Ge[SC_6H_5]_2$ (11). To a solution of **2** (0.098 g, 0.164 mmol) in hexane (4 ml) was added 1 equiv of diphenyl disulfide (0.036 g). The solution was allowed to react for 1 h and evaporated to dryness. White crystals were obtained from hexane at −34 °C (0.12 g, 91% yield). ^{1}H NMR (C_6D_6): δ 7.95, (m, C_6H_5, 4H); 7.05 (m, C_6H_5, 6H); 3.98 (br, C_6H_{11}, 4H); 2.25–0.98 (m, C_6H_{11}, 40H); 1.32 (s, ^{t}Bu, 18H). ^{13}C NMR (C_6D_6): δ 168.0 (s, N*C(*CH_3)N); 135.8, 129.3, 128.1, 125.6 (4s, C_6H_5); 58.3, 34.0, 26.8, 26.0 (4s, C_6H_{11}); 30.7 (s, C(*C*H_3)$_3$); 15.8 (s, *C(*CH_3)$_3$). Calc. for $C_{46}H_{72}N_4GeS_2$: C, 67.56; H, 8.87; N, 6.85. Found: C, 67.70; H, 8.90; N, 6.629%.

$[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SC_6H_5]_2$ (12). To a solution of **5** (0.126 g, 0.277 mmol) in hexane (5 ml) was added 1 equiv of diphenyl disulfide (0.061 g). The solution was allowed to react for 2.5 h and evaporated to dryness. White crystals were obtained from hexane at −34 °C (0.14 g, 72% yield). ^{1}H NMR (C_6D_6): δ 7.78 (m, C_6H_5, 4H); 7.02 (m, C_6H_5, 6H); 3.35 (br, C_6H_{11}, 2H); 1.92–0.81 (m, C_6H_{11}, 20H); 1.71 (s, Me, 3H); 0.38 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6): δ 158.5 (s, N*C*MeN); 136.1, 135.9, 134.0, 127.5 (4s, C_6H_5); 57.6, 34.4, 26.6, 26.3 (4s, C_6H_{11}); 16.6 (s, C*C*H_3); 6.2 (s, $SiMe_3$). Calc. for $C_{32}H_{53}N_3Si_2GeS_2$: C, 57.14; H, 7.94; N, 6.25. Found: C, 57.14; H, 7.83; N, 6.27%.

$[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SeC_6H_5]_2$ (13). To a solution of **5** (0.400 g, 0.881 mmol) in hexane (10 ml) was added 1 equiv of diphenyl diselenide (0.275 g). The solution was allowed to react for 4 h and evaporated to dryness. White crystals were obtained from hexane at −34 °C (0.60 g, 84% yield). ^{1}H NMR (C_6D_6): δ 7.90 (m, C_6H_5, 4H); 7.05 (m, C_6H_5, 6H); 3.40 (br, C_6H_{11}, 2H); 1.97–0.82 (m, C_6H_{11}, 20H); 1.66 (s, Me, 3H); 0.38 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6): δ 159.1 (s, N*C*MeN); 136.9, 130.7, 128.8, 127.6 (4s, C_6H_5); 57.2, 34.6, 26.7, 26.2 (4s, C_6H_{11}); 16.2 (s, C*C*H_3); 6.3 (s, $SiMe_3$). Calc. for $C_{32}H_{53}N_3Si_2GeSe_2$: C, 50.14; H, 6.92; N, 5.48. Found: C, 50.57; H, 7.07; N, 5.36%.

$[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2][SC_6H_5]_2$ (14). To a solution of **7** (0.225 g, 0.450 mmol) in hexane (6 ml) was added 1 equiv of diphenyl disulfide (0.098 g). The solution was allowed to react for 12 h and evaporated to dryness. White crystals were obtained from hexane at −34 °C (0.24 g, 74% yield). ^{1}H NMR (C_6D_6): δ 7.76, (m, C_6H_5, 4H); 6.98 (m, C_6H_5, 6H); 3.01 (br, C_6H_{11}, 2H); 1.72–0.98 (m, C_6H_{11}, 20H); 1.28 (s, Me, 3H); 0.46 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6): δ 165.8 (s, N*C*MeN); 136.0, 135.7, 128.5, 126.6 (4s, C_6H_5); 56.2, 34.4, 25.7, 13.4 (4s, C_6H_{11}); 26.3 (s, C*C*H_3); 6.0 (s, $SiMe_3$). Calc. for $C_{32}H_{53}N_3Si_2SnS_2$: C, 53.47; H, 7.43; N, 5.85. Found: C, 53.64; H, 7.45; N, 5.78%.

$[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2][SeC_6H_5]_2$ (15). To a solution of **7** (0.200 g, 0.400 mmol) in hexane (6 ml) was added 1 equiv of diphenyl diselenide (0.125 g). The solution was allowed to react for 12 h and evaporated to dryness. Yellow crystals were obtained from hexane at −34 °C (0.27 g, 82% yield). ^{1}H NMR (C_6D_6): δ 7.78, (m, C_6H_5, 4H); 6.95 (m, C_6H_5, 6H); 3.01 (br, C_6H_{11}, 2H); 1.75–0.97 (m, C_6H_{11}, 20H); 1.30 (s, Me, 3H); 0.48 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6): δ 166.0 (s, N*C*MeN); 137.9, 130.4, 129.1, 128.9 (4s, C_6H_5); 56.4, 34.9, 26.3, 14.1 (4s, C_6H_{11}); 26.8 (s, C*C*H_3); 6.6 (s, $SiMe_3$). Calc. for

$C_{32}H_{53}N_3Si_2SnSe_2$: C, 47.30; H, 6.57; N, 5.17. Found: C, 47.42; H, 6.64; N, 5.10%.

$[C_6H_{11}NC(Me)NC_6H_{11}][N(SiMe_3)_2]Ge{=}Se$ from $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SeC_6H_5]_2$. To a solution of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SeC_6H_5]_2$ (0.055 g, 0.072 mmol) in 0.5 ml C_6D_6 was added elemental selenium (11 mg, 0.14 mmol). The reaction was complete after 2 h at 60 °C. Identity of the product was confirmed by comparison of NMR spectra of authentic samples of $[C_6H_{11}NC(Me)NC_6H_{11}][N(SiMe_3)_2]Ge{=}Se$ and $(C_6H_5Se)_2$. No other species were observed.

Reactions

Of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SC_6H_5]_2$ with Se. To a solution of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SC_6H_5]_2$ (0.055 g, 0.082 mmol) in 0.5 ml C_6D_6 was added elemental selenium (26 mg, 0.33 mmol). The sample was heated at 60 °C for 12 h and monitored by ^1H NMR. No change in the starting material was observed.

Of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SC_6H_5]_2$ with styrene sulfide. To a solution of $[C_6H_{11}NC(Me)NC_6H_{11}]Ge[N(SiMe_3)_2][SC_6H_5]_2$ (0.040 g, 0.059 mmol) in 0.5 ml C_6D_6 was added styrene sulfide (32 mg, 0.24 mmol). The sample was heated at 60 °C for 2 days and monitored by ^1H NMR. No change in the starting material was observed.

Crystallography

Crystallographic data for compounds **10**, **13** and **14** are presented in Table 4.

CCDC reference number 186/1908.

See http://www.rsc.org/suppdata/dt/a9/a909228e/ for crystallographic files in .cif format.

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