

Synthesis of $M^{II}[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ ($M = Sn, Ge$) from Amidinate Precursors: Active Catalysts for Phenyl Isocyanate Cyclization

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Mixed amidinato amido complexes $[Me_3SiNC(^tBu)NSiMe_3]M[N(SiMe_3)_2]$ ($M = Sn$ **2**, Ge **3**) were prepared by the reaction of $[Me_3SiNC(^tBu)NSiMe_3]Li$ (**1a**) with $SnCl_2$ and $GeCl_2$ (dioxane) in ether. The $N(SiMe_3)_2$ ligand in these compounds is derived from the rearrangement of the $[Me_3SiNC(^tBu)NSiMe_3]^-$ anion with extrusion of tBuCN . The susceptibility of $[Me_3SiNC(^tBu)NSiMe_3]^-$ to rearrangement appears to be dependent on reaction solvent and on the coordinated metal center. Single-crystal X-ray diffraction studies of **2** and **3** are presented. Replacement of Me for tBu in the ligand allowed $[Me_3SiNC(Me)NSiMe_3]_2Sn^{II}$ (**4**) to be isolated, and an X-ray structure of this compound is reported. The isolation of **4** indicates that steric factors also play a role in the stability of $[Me_3SiNC(^tBu)NSiMe_3]^-$. Compounds **2** and **3** are outstanding catalysts for the cyclotrimerization of phenyl isocyanates to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) at room temperature. In contrast, complex **4** catalytically reacts with phenyl isocyanate to produce isocyanate dimer and trimer in a 52:35 ratio.

Introduction

Recent interest in the use of amidinate ligands in the preparation of main group element compounds stems from the recognition that these complexes can exhibit catalytic activity and that these species are useful for fundamental studies of the effects of ligand geometry on the coordination environments of post-transition elements. Amidinates are bidentate, three-atom bridging ligands with the general formula $R'NC(R)NR'^-$. Through modification of the organic substituents on the nitrogen atoms and at the bridge position, rational modifications to the steric and electronic properties of the ligand are possible. This characteristic may be useful in stabilizing desired structural features and generating interesting reactivity characteristics and has resulted in amidinate ligands being employed in the preparation of a variety of main group, transition metal, and f-block element complexes.^{1,2}

Our interest in this area has focused on employing alkyl amidinates in the chemistry of a variety of elements and investigating the effects of variation of R and R' on the features of these products. In general, we have relied on lithium amidinates, which have been prepared by the addition of alkyl anions to the appropriate carbodiimide, as our synthetic access for preparation of these species. For example, bulky trialkyl amidinates provide the environment for the preparation of novel terminal chalcogenido complexes of group 14 metals {e.g., $S=Sn(C_6H_{11}NC(^tBu)NC_6H_{11})_2$, $Se=Ge[C_6H_{11}NC(Me)NC_6H_{11}]-[N(SiMe_3)_2]$ }.^{3,4} In order to further explore the effects of increasing the steric bulk of the amidinate ligand, $[Me_3SiNC(^tBu)NSiMe_3]^-$, prepared by reaction of tBuLi and bis(trimethylsilyl)-carbodiimide, was employed in the synthesis of $[Me_3SiNC(^tBu)NSiMe_3]_2SnCl_2$ ⁵ and $[Me_3SiNC(^tBu)NSiMe_3]_2InCl$.⁶ This

same route was used by Jordan et al. to prepare $[Me_3SiNC(^tBu)NSiMe_3]AlX_2$ ($X = Cl, Me$).⁷ Both the crystallographically determined structural features of the Sn(IV) complex and the diminished reactivity for both the In and Sn complexes in comparison with complexes possessing the less bulky *N,N'*-dicyclohexyl amidinate analogues are consistent with the increased steric demand anticipated for $[Me_3SiNC(^tBu)NSiMe_3]^-$.

The results which we report here began from two points of interest. First, we wished to employ the bulky amidinate $[Me_3SiNC(^tBu)NSiMe_3]^-$ in the preparation of new Sn(II) and Ge(II) complexes. Second, on the basis of our discovery that amidinate complexes of tin(IV) are excellent catalysts for the cyclotrimerization of isocyanates to yield isocyanurates,⁸ we wished to extend our results in this area by applying new amidinate complexes of tin and germanium as catalysts for this reaction. During these attempts we observed some features of the stability of this amidinate ligand and of its lithium salt, $[Me_3SiNC(^tBu)NSiMe_3]Li$, which are pertinent for the utilization of this species. This ligand is susceptible to rearrangement that ultimately yielded, in the case of Sn(II) and Ge(II) metal centers, the mixed amidinato amido complexes $[Me_3SiNC(^tBu)NSiMe_3]M[N(SiMe_3)_2]$ ($M = Sn$ **2**, Ge **3**). Replacement of Me for tBu in the ligand allowed for the isolation of $[Me_3SiNC(Me)NSiMe_3]_2Sn^{II}$ (**4**). These complexes function as effective catalysts for the cyclotrimerization of aryl isocyanates and provide the first report of complexes of Sn(II) and Ge(II/IV) that function in this transformation.

Experimental Section

General Procedure. All reactions were carried out either in a nitrogen-filled drybox or under nitrogen with standard Schlenk-line techniques. Diethyl ether, hexane and THF were distilled under nitrogen from potassium. Deuterated benzene was dried with potassium. MeLi (1.4 M in diethyl ether), tBuLi (1.7 M in hexane), $SnCl_2$ (99.99+%),

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and 1,3-bis(trimethylsilyl)carbodiimide were purchased from Aldrich and used without further purification. $\text{GeCl}_2(\text{dioxane})$ was prepared according to a literature procedure.⁹ NMR spectra were run on a GEMINI 200 MHz spectrometer with deuterated benzene as a solvent and internal standard. Variable temperature NMR spectra were run on a Bruker 500 MHz spectrometer.

[Me₃SiNC(^tBu)NSiMe₃]₂Sn[N(SiMe₃)₂] (2). To a solution of bis(trimethylsilyl)carbodiimide (0.300 g, 1.61 mmol) in diethyl ether (30 mL) was added ^tBuLi (0.95 mL, 1.7 M, 1.62 mmol). After 30 min, 0.5 equiv of SnCl₂ (0.153 g, 0.81 mmol) was added. The solution was stirred for 12 h and filtered to remove the white LiCl precipitate. The solvent was removed under vacuum to give a pure off white powder (0.350 g, 83% yield). Mp: 59–60 °C. ¹H NMR (C₆D₆, ppm): 1.04 (s, ^tBu, 9H); 0.44 (s, Si(CH₃)₃, 18H); 0.31 (s, Si(CH₃)₃, 18H). ¹³C NMR (C₆D₆, ppm): 183.9 (s, NC(^tBu)N); 42.7 (s, CCH₃); 29.3 (s, CCH₃); 6.3 (s, Si(CH₃)₃); 3.7 (s, Si(CH₃)₃). Anal. Calcd for C₁₇H₄₅N₃Si₄Sn: C, 39.07; H, 8.68; N 8.04. Found: C, 39.04; H, 8.66; N, 7.80.

[Me₃SiNC(^tBu)NSiMe₃]₂Ge[N(SiMe₃)₂] (3). To a solution of bis(trimethylsilyl)carbodiimide (0.500 g, 2.68 mmol) in diethyl ether (35 mL) was added ^tBuLi (1.58 mL, 1.7 M, 2.69 mmol). After 30 min, 0.5 equiv of GeCl₂(dioxane) (0.311 g, 1.34 mmol) was added. The solution was stirred for 12 h and filtered to remove the white LiCl precipitate. The solvent was removed under vacuum to give a white powder. Crystals were obtained from diethyl ether at –34 °C (0.518 g, 81% yield). ¹H NMR (C₆D₆, ppm, 230 K): 1.01 (s, ^tBu, 9H); 0.36 (s, Si(CH₃)₃, 18H); 0.58 (s, Si(CH₃)₃, 9H); 0.39 (s, Si(CH₃)₃, 9H). ¹³C NMR (C₆D₆, ppm, 230 K): 181.0 (s, NC(^tBu)N); 40.1 (s, CCH₃); 28.9 (s, CCH₃); 2.9 (s, Si(CH₃)₃); 5.8 (s, Si(CH₃)₃); 5.3 (s, Si(CH₃)₃). Anal. Calcd for C₁₇H₄₅N₃Si₄Ge: C, 42.85; H, 9.52; N, 8.82. Found: C, 42.68; H, 9.55; N, 8.86.

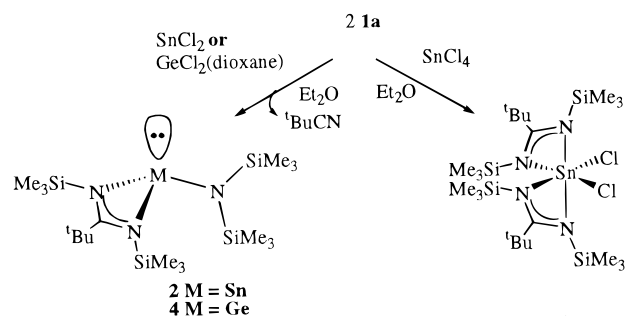
Sn[Me₃SiNC(Me)NSiMe₃]₂ (4). To a solution of bis(trimethylsilyl)carbodiimide (0.500 g, 2.68 mmol) in diethyl ether (35 mL) was added MeLi (1.90 mL, 1.4 M, 2.66 mmol). After 30 min, 0.5 equiv of SnCl₂ (0.254 g, 1.34 mmol) was added. The solution was stirred for 12 h and filtered to remove the white LiCl precipitate. The solvent was removed under vacuum to give a pale yellow powder. Crystals were obtained from diethyl ether at –34 °C (0.370 g, 53% yield). Mp: 90 °C dec. ¹H NMR (C₆D₆, ppm): 1.80 (s, Me, 3H); 0.24 (s, Si(CH₃)₃, 18H). ¹³C NMR (C₆D₆, ppm): 176.0 (s, NC(Me)N); 28.3 (s, Me); 2.5 (s, Si(CH₃)₃). Attempts to obtain satisfactory microanalysis data for this compound have so far been unsuccessful.

Attempted Reaction of Sn[N(SiMe₃)₂] with ^tBuCN. To a solution of 0.160 g (0.36 mmol) of Sn[N(SiMe₃)₂] in 5 mL of ether was added 0.060 g (0.81 mmol) of ^tBuCN. The reaction mixture was stirred for 24 h at room temperature. Removal of solvent under vacuum and isolation of the resultant solid yielded starting material as confirmed by ¹H and ¹³C NMR. A similar reaction with 0.060 g (0.14 mmol) of Sn[N(SiMe₃)₂] and 0.023 g (0.31 mmol) of ^tBuCN in 0.5 mL of C₆D₆ was carried out at 80 °C. No spectral changes were observed over 24 h.

Typical Procedure for the Catalytic Formation of (PhNCO)₃. To complex **3** (0.058 g, 0.122 mmol) was added neat phenyl isocyanate (50 equiv, 0.725 g, 6.09 mmol). A crystalline white solid precipitated out of the yellow solution. After 16 min, the resultant white solid was crushed into a powder and washed with 7 mL of benzene for five repetitions, filtered off, and dried in vacuo to give 0.710 g (98% yield) of (PhNCO)₃. The identity of (PhNCO)₃ was confirmed by comparison of ¹H NMR spectra and melting point with authentic samples.

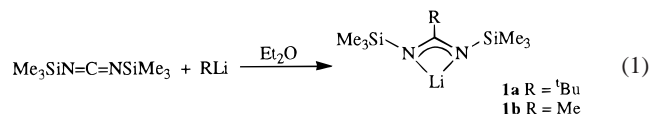
Reaction of 4 with PhNCO To Yield (PhNCO)₃ and (PhNCO)₂. To complex **4** (0.034 g, 0.065 mmol) was added neat phenyl isocyanate (50 equiv, 0.440 g, 3.70 mmol). After 10 min the reaction mixture solidified. The resultant white solid was crushed into a powder and extracted with benzene. The remaining solid (0.154 g, 35% yield) was identified as (PhNCO)₃ by comparison with authentic material. The extracts were combined and dried in vacuo to give 0.228 g (52% yield) of (PhNCO)₂. The identity of (PhNCO)₂ was confirmed by comparison of mp, ¹H NMR spectra,¹⁰ and unit cell parameters with literature values.^{11,12}

Scheme 1



Results and Discussion

The observation that in situ generated [Me₃SiNC(^tBu)NSiMe₃][–]Li (**1a**) was an effective reagent for the introduction of this bulky amidinate into the coordination spheres of Sn,⁵ In,⁶ and Al⁷ along with the fact that the reactivity of Sn(CyNC(R)NCy)₂ (Cy = C₆H₁₁; R = Me, ^tBu) depended on the nature of the R substituent provided the motivating factors that led to our attempt to prepare and investigate the reactivity of the proposed new complex [Me₃SiNC(^tBu)NSiMe₃]₂Sn. All previous syntheses employing **1a** have been performed by first generating this species through the addition of ^tBuLi to Me₃SiN=C=NSiMe₃ in ether (eq 1) followed by metathesis reactions with metal halides. For



example, [Me₃SiNC(^tBu)NSiMe₃]₂SnCl₂ was synthesized in 77% isolated yield following the reaction of **1a** with SnCl₄ (Scheme 1).⁵ Attempting to follow this procedure using a suspension of SnCl₂ in diethyl ether produced a material with a ¹H NMR spectrum inconsistent with the targeted species. The observed spectrum exhibited two signals assigned to trimethylsilyl functions (0.43, 0.30 ppm) and a single resonance for the ^tBu group (1.04 ppm) with integrated ratios indicating four trimethylsilyl groups per *tert*-butyl moiety. On the basis of this data we proposed the connectivity for **2** as indicated in Scheme 1. This was subsequently confirmed by X-ray diffraction, vide infra. On the basis of this formulation the yield of **2** from this reaction procedure is 83%. Interestingly, when this same reaction is performed in the presence of THF the yield of **2** is substantially lower (45% yield).

While the appearance of the amidinato ligand [Me₃SiNC(^tBu)NSiMe₃][–] in **2** is as expected, the bis(trimethylsilyl)amido ligand was not anticipated and likely arises from a rearrangement of the amidinate anion with loss of ^tBuCN. A probable route for this rearrangement is a 1,3 trimethylsilyl shift to form amido and ^tBuCN (Scheme 2). This same transformation was proposed by Jordan et al. when, during their attempts to isolate and structurally characterize **1a**, they obtained the crystal structure of the dimeric species [Li(^tBuCN)⁺[μ-N(SiMe₃)₂][–]]₂ that consisted of N(SiMe₃)₂[–] units bridged by Li cations that were coordinated by ^tBuCN.⁷ All of our attempts to isolate **1a** have so far resulted only in isolation of the identical species as confirmed by comparison of unit cell parameters with those in the literature.⁷ Precedent for 1,3 trimethylsilyl shifts within the

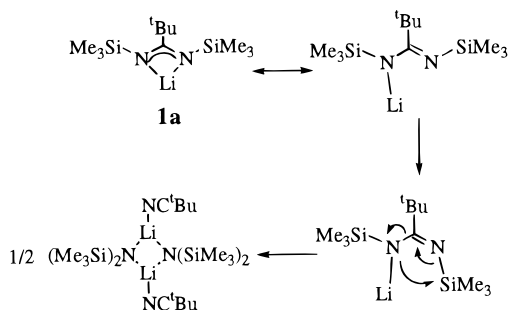
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Scheme 2

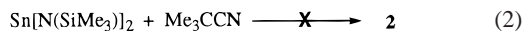


amidinate framework is provided by the common preparative routes to benzamidinate anions $[\text{Me}_3\text{SiNC}(\text{Ar})\text{NSiMe}_3]^-$.² These species are generated by reaction of $\text{LiN}(\text{SiMe}_3)_2$ and ArCN , a synthetic methodology that relies on what is essentially the reverse reaction to that proposed. These rearrangements depend on the presence of trimethylsilyl substituents.

Understanding the conditions that affect the stability of $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]^-$ is a critical factor for the effective use of this ligand. Given the previous isolation of $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]_2\text{SnCl}_2$,⁵ $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]_2\text{InCl}$,⁶ and $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{AlX}_2$ ⁷ ($\text{X} = \text{Cl}, \text{Me}$), steric factors can be ruled out as the sole reason for the observed reorganization.

We have observed that the yield of **2** exhibited a strong solvent dependence with a substantial decrease in yield in the presence of even small amounts of THF. We interpret these results as indicating that **1a** is sensitive to the coordinating ability of the reaction solvent and that in the presence of more strongly coordinated solvents (THF vs diethyl ether) **1a** is less stable. While these observations provide evidence for the solvent-based stability of *N,N'*-bis(trimethylsilyl)amidinates, our previous report of the high-yield syntheses of Sn(IV) and In(III) complexes of $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]^-$ under similar reaction conditions indicates that solvent effects do not offer a complete explanation for the observation that **2** was obtained in an excellent yield as the sole isolated product from the reaction of SnCl_2 and **1a**.

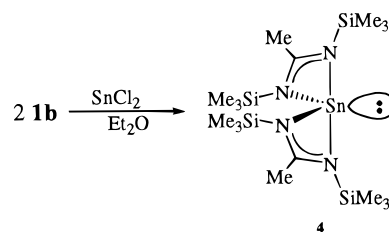
Our results appear to indicate that the stability of the amidinate anion in **1a** is affected by interaction with the Sn(II) metal center. The possibility that complex **2** in fact arises from an insertion reaction of tBuCN into the Sn–N bond of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ coupled with a 1,3 trimethylsilyl shift can be excluded on the basis of our observation that these two species do not produce **2** under the reaction conditions reported above (eq 2). This observation further suggests that the in situ



generation of **1a** by the reaction of tBuLi and $\text{Me}_3\text{SiNCNSiMe}_3$ does indeed proceed according to eq 1. Interestingly, we have also observed that **2** does not undergo further rearrangement/elimination to give tBuCN and $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ even under forcing conditions (100 °C) or variation of the solvent.

We attempted to explore the effect of the Lewis acidity of the coordinated metal center on the stability of $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]^-$ through the synthesis of Ge(II) analogues of this amidinate. Replacing SnCl_2 in the reaction with **1a** by GeCl_2 (dioxane) provides a means of increasing the Lewis acidity of the metal center. Thus, reaction of an ether solution of **1a** and a suspension of GeCl_2 (dioxane) in ether in a 2:1 ratio followed the pathway outlined in Scheme 1. Spectroscopic characterization of the product of this reaction, **3**, clearly indicated it to be the analogue of **2**. The smaller Ge(II) center causes the steric

Scheme 3



demands of the ligands to be more pronounced in the case of **3**, which is reflected in the broadening of the ^1H and ^{13}C NMR resonances attributed to the $\text{N}(\text{SiMe}_3)_2$ moiety. This hindered fluxionality enables the two trimethylsilyl groups to be distinguished at 230 K. Definitive confirmation of the structure of this complex was provided by single-crystal X-ray analysis of **3**.

The less sterically demanding species $[\text{Me}_3\text{SiNC}(\text{Me})\text{NSiMe}_3]^- \text{Li}^+$ (**1b**) is easily synthesized by the reaction of MeLi and $\text{Me}_3\text{SiNCNSiMe}_3$ in ether (eq 1) and provides a means of exploring the role of sterics in the stability of **1a** and in the synthesis of **2** and **3**. We employed the methyl analogue **1b** in a reaction with SnCl_2 as represented in Scheme 3. In this case, the ^1H and ^{13}C NMR spectra of the product **4** indicated no rearrangement of the amidinate and that we had isolated the bis(amidinate) complex. X-ray structural analysis of **4** confirmed these observations. The isolation of **4** suggests that $[\text{Me}_3\text{SiNC}(\text{Me})\text{NSiMe}_3]^-$ is less susceptible to the 1,3 trimethylsilyl shift observed for the tBu -substituted species. In addition, the effective use of this species provides further evidence that the ether solutions of **1a** and **1b** do, in fact, contain the amidinate species. Interestingly, complex **4** appears to be stable to the rearrangement that was observed for the generation of **2** even when heated to greater than 70 °C.

These results offer corroborating evidence that the coordinated metal center (Sn(II) or Ge(II)) plays a role in the stability of these bulky amidinate ligands. Furthermore, the sterics of the substituents on the methyne carbon do play a role in the stability of bis(trimethylsilyl) amidinate ligands.

Structural Studies of $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{M}[\text{N}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Sn } \mathbf{2}, \text{Ge } \mathbf{3}$). Single-crystal X-ray analyses of complexes **2** and **3** confirmed the proposed connectivities and gave the structural parameters of the amidinates employed in this study. A summary of the data collections is provided in Table 1.

Figures 1 and 2 provide the molecular geometries and atom-numbering schemes for **2** and **3**, respectively, and show that the two complexes adopt similar coordination geometries. Furthermore, the metal centers in these mixed-ligand species are similar to recently reported analogues $[(\text{CyNC}(\text{R})\text{NCy})\text{Sn}[\text{N}(\text{SiMe}_3)_2]]$ ($\text{R} = \text{Me}, \text{tBu}$)⁸ and $[(\text{CyNC}(\text{R})\text{NCy})\text{Ge}[\text{N}(\text{SiMe}_3)_2]]$ ($\text{R} = \text{Me}, \text{tBu}$)⁴ which reside in distorted tetrahedral environments with one vertex occupied by a stereochemically active lone pair of electrons. The result is an overall pyramidal ligand array around the M(II) centers which consists of one bidentate amidinate and the bis(trimethylsilyl)amido nitrogen center. The coordination environments of the Sn(II) centers in these species also exhibit some structural similarities to recently reported triamidostannates^{13–15} and to $[\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}\{\eta^2\text{-(NtBu)S}\}]^-$.¹⁶

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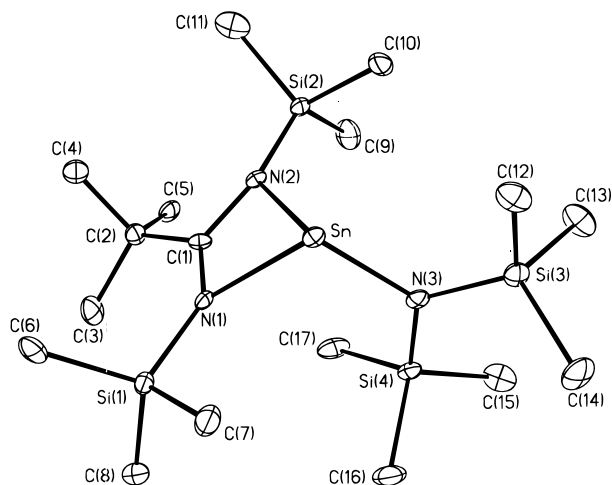
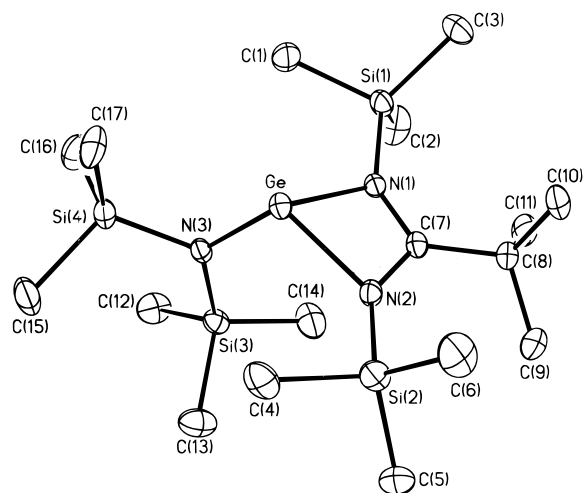
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Table 1. Crystal Data for Compounds $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{Sn}[\text{N}(\text{SiMe}_3)_2]$ (**2**), $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{Ge}[\text{N}(\text{SiMe}_3)_2]$ (**3**), and $\text{Sn}[\text{Me}_3\text{SiNC}(\text{Me})\text{NSiMe}_3]_2$ (**4**)^a

empirical formula	$\text{C}_{17}\text{H}_{45}\text{N}_3\text{Si}_4\text{Sn}$ (2)	$\text{C}_{17}\text{H}_{45}\text{N}_3\text{Si}_4\text{Ge}$ (3)	$\text{C}_{16}\text{H}_{42}\text{N}_4\text{Si}_4\text{Sn}$ (4)
fw	522.59	476.51	521.59
temp (K)	113(1)	203(2)	203(2)
λ (Å)	0.71073	0.71073	0.71073
space group	$P2_1/c$	$P2_1/n$	$Pbcn$
unit cell dimens (Å, deg)	$a = 15.071(1)$ $b = 10.712(1)$ $c = 18.290(1)$ $\beta = 112.12(1)$	$a = 14.791(1)$ $b = 10.176(1)$ $c = 19.542(2)$ $\beta = 111.806(1)$	$a = 10.998(1)$ $b = 12.1543$ $c = 20.084(2)$
vol (Å ³)	2735.4(8)	2730.9(4)	2684.6(4)
Z	4	4	4
density (Mg/m ³) (calcd)	1.269	1.159	1.290
abs coeff (mm ⁻¹)	1.12	1.304	1.138
R (F _o)	0.042	0.0442	0.0362
R _w (F _o ²)	0.060	0.0886	0.0975

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$

**Figure 1.** Molecular structure and atom numbering scheme for $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{Sn}[\text{N}(\text{SiMe}_3)_2]$ (**2**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.**Figure 2.** Molecular structure and atom numbering scheme for $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{Ge}[\text{N}(\text{SiMe}_3)_2]$ (**3**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Complexes **2** and **3** both exhibit two M–N(amidinate) bond distances (Tables 2 and 3) which are only slightly different. As expected, the average M–N(amidinate) distance is shorter for the Ge complex (**3**) with the corresponding distances in **2** (2.229–(4) Å) being slightly longer than in $[(\text{CyNC}(\text{tBu})\text{NCy})\text{Sn}[\text{N}(\text{SiMe}_3)_2]]$ (2.204(4) Å), which is indicative of increased bulk for the amidinate ligand in **2**. The amido nitrogen atoms in both

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Me}_3\text{SiNC}(\text{tBu})\text{NSiMe}_3]\text{Sn}[\text{N}(\text{SiMe}_3)_2]$ (**2**)

Distances			
Sn–N(1)	2.236(4)	Si(2)–C(11)	1.855(7)
Sn–N(2)	2.221(4)	Si(2)–C(9)	1.861(7)
Sn–N(3)	2.121(5)	Si(2)–C(10)	1.858(7)
Si(1)–N(1)	1.748(5)	Si(4)–N(3)	1.739(5)
Si(1)–C(8)	1.850(7)	Si(4)–C(17)	1.864(7)
Si(1)–C(6)	1.862(7)	Si(4)–C(15)	1.868(7)
Si(1)–C(7)	1.878(6)	Si(4)–C(16)	1.858(7)
Si(3)–N(3)	1.726(5)	N(1)–C(1)	1.331(7)
Si(3)–C(13)	1.878(7)	N(2)–C(1)	1.355(7)
Si(3)–C(12)	1.861(7)	C(1)–C(2)	1.523(8)
Si(3)–C(14)	1.860(7)	C(2)–C(5)	1.520(9)
Si(2)–N(2)	1.730(5)	C(2)–C(4)	1.532(8)
		C(2)–C(3)	1.534(8)

Angles			
N(1)–Sn–N(2)	60.6(2)	N(3)–Si(4)–C(16)	110.9(3)
N(1)–Sn–N(3)	103.9(2)	C(17)–Si(4)–C(15)	104.6(3)
N(2)–Sn–N(3)	99.0(2)	C(17)–Si(4)–C(16)	107.6(3)
N(1)–Si(1)–C(8)	114.6(3)	C(15)–Si(4)–C(16)	106.4(3)
N(1)–Si(1)–C(6)	113.6(3)	C(1)–N(1)–Si(1)	142.8(4)
N(1)–Si(1)–C(7)	104.5(3)	C(1)–N(1)–Sn	92.6(3)
C(8)–Si(1)–C(6)	110.6(3)	Si(1)–N(1)–Sn	121.5(2)
C(8)–Si(1)–C(7)	107.2(3)	C(1)–N(2)–Si(2)	144.8(4)
C(6)–Si(1)–C(7)	105.5(3)	C(1)–N(2)–Sn	92.6(3)
N(3)–Si(3)–C(13)	111.8(3)	Si(2)–N(2)–Sn	122.3(2)
N(3)–Si(3)–C(12)	112.5(3)	Si(3)–N(3)–Si(4)	120.1(3)
N(3)–Si(3)–C(14)	112.2(3)	Si(3)–N(3)–Sn	113.5(2)
C(13)–Si(3)–C(12)	105.7(3)	Si(4)–N(3)–Sn	126.1(2)
C(13)–Si(3)–C(14)	108.8(3)	N(1)–C(1)–N(2)	113.6(5)
C(12)–Si(3)–C(14)	105.4(3)	N(1)–C(1)–C(2)	125.1(5)
N(2)–Si(2)–C(11)	116.1(3)	N(2)–C(1)–C(2)	121.3(5)
N(2)–Si(2)–C(9)	113.2(3)	C(1)–C(2)–C(5)	111.0(5)
N(2)–Si(2)–C(10)	104.4(3)	C(1)–C(2)–C(4)	108.0(5)
C(11)–Si(2)–C(9)	110.4(3)	C(1)–C(2)–C(3)	111.8(5)
C(11)–Si(2)–C(10)	105.8(3)	C(5)–C(2)–C(4)	110.1(5)
C(9)–Si(2)–C(10)	105.8(3)	C(5)–C(2)–C(3)	107.1(5)
N(3)–Si(4)–C(17)	114.1(3)	C(4)–C(2)–C(3)	108.8(5)
N(3)–Si(4)–C(15)	112.7(3)		

compounds have planar geometries with metal–N_{amido} distances of 2.121(5) Å for **2** and 1.9101(19) Å in **3** which are comparable when adjusted for the relative covalent radii of Ge and Sn.¹⁷

The two N atoms and central C of the amidinate frameworks are in distorted trigonal planar environments resulting in planar amidinate ligands in both **2** and **3**. The corresponding C–N bond lengths (average for both compounds 1.34(1) Å) are consistent with delocalization of the π bond in the N–C–N unit of the ligand.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Me₃SiNC(^tBu)NSiMe₃]₂Ge[N(SiMe₃)₂]₂ (**3**)

Distances			
Ge–N(3)	1.9101(19)	Si(3)–C(14)	1.857(3)
Ge–N(1)	2.037(2)	Si(3)–C(13)	1.870(3)
Ge–N(2)	2.042(2)	Si(3)–C(12)	1.868(3)
Ge–C(7)	2.445(2)	Si(4)–N(3)	1.740(2)
Si(1)–N(1)	1.745(2)	Si(4)–C(17)	1.871(3)
Si(1)–C(1)	1.853(3)	Si(4)–C(16)	1.870(3)
Si(1)–C(2)	1.864(3)	Si(4)–C(15)	1.874(3)
Si(1)–C(3)	1.866(3)	N(1)–C(7)	1.334(3)
Si(2)–N(2)	1.749(2)	N(2)–C(7)	1.338(3)
Si(2)–C(4)	1.858(3)	C(7)–C(8)	1.533(3)
Si(2)–C(6)	1.858(3)	C(8)–C(9)	1.532(4)
Si(2)–C(5)	1.867(3)	C(8)–C(11)	1.537(4)
Si(3)–N(3)	1.743(2)	C(8)–C(10)	1.540(4)
Angles			
N(3)–Ge–N(1)	104.84(8)	C(17)–Si(4)–C(16)	105.86(16)
N(3)–Ge–N(2)	104.96(8)	N(3)–Si(4)–C(15)	112.03(13)
N(1)–Ge–N(2)	65.65(8)	C(17)–Si(4)–C(15)	105.94(16)
N(3)–Ge–C(7)	112.61(8)	C(16)–Si(4)–C(15)	107.80(16)
N(1)–Ge–C(7)	33.08(8)	C(7)–N(1)–Si(1)	144.41(18)
N(2)–Ge–C(7)	33.19(8)	C(7)–N(1)–Ge	90.49(15)
N(1)–Si(1)–C(1)	104.13(12)	Si(1)–N(1)–Ge	122.50(11)
N(1)–Si(1)–C(2)	114.02(14)	C(7)–N(2)–Si(2)	143.17(18)
C(1)–Si(1)–C(2)	106.96(16)	C(7)–N(2)–Ge	90.18(15)
N(1)–Si(1)–C(3)	114.24(14)	Si(2)–N(2)–Ge	121.29(11)
C(1)–Si(1)–C(3)	107.89(15)	Si(4)–N(3)–Si(3)	120.07(11)
C(2)–Si(1)–C(3)	109.06(17)	Si(4)–N(3)–Ge	112.46(10)
N(2)–Si(2)–C(4)	104.81(12)	Si(3)–N(3)–Ge	127.24(11)
N(2)–Si(2)–C(6)	112.61(13)	N(1)–C(7)–N(2)	111.6(2)
C(4)–Si(2)–C(6)	107.25(15)	N(1)–C(7)–C(8)	123.8(2)
N(2)–Si(2)–C(5)	114.30(13)	N(2)–C(7)–C(8)	124.4(2)
C(4)–Si(2)–C(5)	107.82(14)	N(1)–C(7)–Ge	56.43(12)
C(6)–Si(2)–C(5)	109.60(16)	N(2)–C(7)–Ge	56.64(12)
N(3)–Si(3)–C(14)	114.35(12)	C(8)–C(7)–Ge	166.10(17)
N(3)–Si(3)–C(13)	111.97(13)	C(9)–C(8)–C(7)	111.9(2)
C(14)–Si(3)–C(13)	107.00(17)	C(9)–C(8)–C(7)	107.5(2)
N(3)–Si(3)–C(12)	111.89(13)	C(7)–C(8)–C(11)	110.4(2)
C(14)–Si(3)–C(12)	104.57(16)	C(9)–C(8)–C(10)	109.5(2)
C(13)–Si(3)–C(12)	106.47(15)	C(7)–C(8)–C(10)	107.9(2)
N(3)–Si(4)–C(17)	111.94(12)	C(11)–C(8)–C(10)	109.6(2)
N(3)–Si(4)–C(16)	112.81(13)		

Replacing the organic substituents of the amidinate with bulkier groups leads to increased steric crowding around the metal center. A comparison of the angles around the amidinate N atoms of **2** and [(CyNC(^tBu)NCy)Sn[N(SiMe₃)₂]]⁸ supports this idea by exhibiting the effects anticipated for the relative interactions of Cy and bulkier SiMe₃ substituents with the central ^tBu groups (Chart 1). These steric effects are even more pronounced in the case of **3** and help to justify the spectroscopic features noted above.

Structural Study of [Me₃SiNC(Me)NSiMe₃]₂Sn (4**).** In order to confirm the structural features of **4** and to provide metrical details for the new amidinate in this complex, a single-crystal X-ray study of this complex was performed. Complex **4** (Figure 3, Table 4) possesses two bidentate amidinate ligands and has a molecular geometry derived from a distorted trigonal bipyramid in which one of the pseudoequatorial sites is occupied by a lone pair of electrons. The electron pair lies on a molecular C₂ axis making N(2)/N(2A) the pseudoaxial positions with N(1)/N(1A) the pseudoequatorial ligands. Planarity of the amidinate rings is confirmed by the fact that the sum of the internal angles of the MNCN cycle is 360°. The axial Sn–N(2) bond lengths are slightly longer (2.397(2) Å) than the Sn–N(1) equatorial bond lengths (2.224(2) Å), a feature which is similar to the previously reported cyclohexyl analogues.³

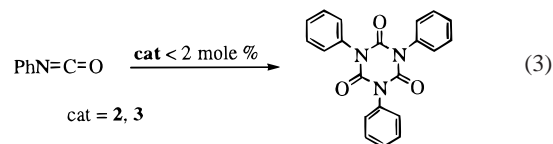
A comparison of the angles around the amidinate N atoms of **4** with those of **2**, **3**, and [(CyNC(^tBu)NCy)Sn[N(SiMe₃)₂]]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Sn[Me₃SiNC(Me)NSiMe₃]₂ (**4**)

Distances			
Sn–N(1A)	2.224(2)	Si(1)–C(2)	1.870(3)
Sn–N(1)	2.224(2)	Si(2)–N(2)	1.734(2)
Sn–N(2A)	2.397(2)	Si(2)–C(4)	1.858(3)
Sn–N(2)	2.397(2)	Si(2)–C(5)	1.866(4)
Si(1)–N(1)	1.740(2)	Si(2)–C(6)	1.868(4)
Si(1)–C(1)	1.856(3)	N(1)–C(7)	1.345(4)
Si(1)–C(3)	1.866(3)	N(2)–C(7)	1.317(4)
		C(7)–C(8)	1.508(4)
Angles			
N(1A)–Sn–N(1)	95.36(12)	C(4)–Si(2)–C(5)	108.68(17)
N(1A)–Sn–N(2A)	158.63(8)	N(2)–Si(2)–C(6)	111.89(15)
N(1)–Sn–N(2A)	99.15(8)	C(4)–Si(2)–C(6)	108.71(18)
N(1A)–Sn–N(2)	99.15(8)	C(5)–Si(2)–C(6)	108.18(18)
N(1)–Sn–N(2)	58.63(8)	C(7)–N(1)–Si(1)	126.93(19)
N(2A)–Sn–N(2)	148.84(11)	C(7)–N(1)–Sn	95.26(17)
N(1)–Si(1)–C(1)	107.91(13)	Si(1)–N(1)–Sn	137.80(13)
N(1)–Si(1)–C(3)	110.23(15)	C(7)–N(2)–Si(2)	130.5(2)
C(1)–Si(1)–C(3)	108.58(18)	C(7)–N(2)–Sn	88.38(17)
N(1)–Si(1)–C(2)	113.11(15)	Si(2)–N(2)–Sn	135.83(13)
C(1)–Si(1)–C(2)	107.61(18)	N(2)–C(7)–N(1)	116.8(2)
C(3)–Si(1)–C(2)	109.26(18)	N(2)–C(7)–C(8)	122.2(3)
N(2)–Si(2)–C(4)	105.93(14)	N(1)–C(7)–C(8)	120.9(3)
N(2)–Si(2)–C(5)	113.32(15)		

is provided in Chart 1. These data clearly indicate the decreased steric demands of [Me₃SiNC(Me)NSiMe₃][–] relative to the ^tBu analogue and place this species as even more svelte than (CyNC(^tBu)NCy)[–].

Catalytic Reactions of Phenyl Isocyanate with Complexes 2–4. We have observed that amidinate complexes of Sn(IV) are outstanding catalysts for the cyclotrimerization of aryl isocyanates to yield triaryl isocyanurates (eq 3).⁸ In an effort to



elucidate the generality of this observation and the features which dictate the activity and selectivity in this reaction, we have now extended the complexes employed in this reaction to include **2–4**. To our knowledge this is the first application of Sn(II) species or Ge(II/IV) in this reaction.

Triaryl isocyanurates are known to enhance the stability of polyurethane networks and coating materials with respect to thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.^{10,18–28} A variety of isocyanate trimerization catalysts has been described with a majority of

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Chart 1

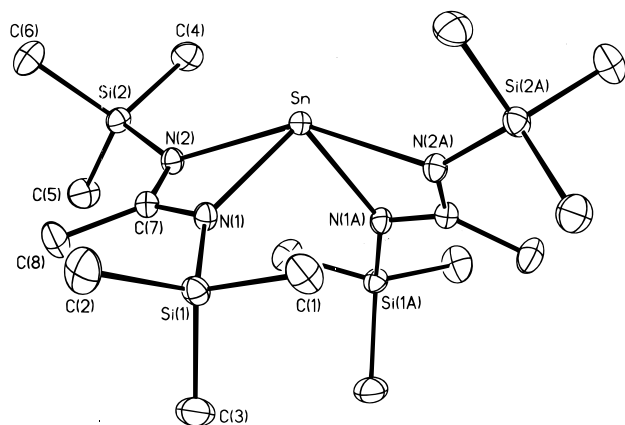
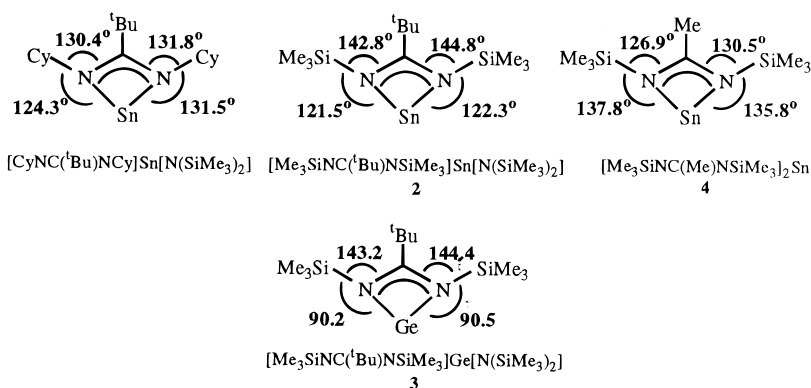


Figure 3. Molecular structure and atom-numbering scheme for Sn- $[Me_3SiNC(Me)NSiMe_3]_2$ (4). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Table 5. Data for the Cyclotrimerization of Phenyl Isocyanate to Yield Triphenyl Isocyanurates^a

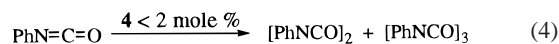
catalyst	time (min)	isolated yield of trimer (%)
$[Me_3SiNC(tBu)NSiMe_3]Sn[N(SiMe_3)_2]$ (2)	210	94
$[Me_3SiNC(tBu)NSiMe_3]Ge[N(SiMe_3)_2]$ (3)	16	98
$Sn[Me_3SiNC(Me)NSiMe_3]_2$ (4)	10	35 (52% dimer)
$[CyNC(Me)NCy]Sn[N(SiMe_3)_2]S_4^b$	12	95
$P(MeNCH_2CH_2)_3N^c$	2	94
CsF^d	20	80.2
Net_3	20	0
$AcOK$	20	0

^a All reactions carried out in neat phenyl isocyanate at room temperature. ^b Data from ref 8. ^c Data from ref 18. ^d Data from ref 21.

the conventional catalysts being anions or neutral Lewis bases.^{10,18–25} Some metal-based catalysts have been described and a Lewis acid pathway could be envisioned for these systems.^{26–28} Conventional catalysts for isocyanurate formation suffer from low activity necessitating severe conditions, poor selectivity resulting in byproducts, and difficulty in separating the catalysts from the product.

The catalytic activity of species 2–4 along with data for some representative reported catalysts is summarized in Table 5. From these data it is clear that the new complexes which we report exhibit catalytic activity that is superior or comparable to known catalysts. For example, in the presence of 50 equiv of isocyanate (2 mol % catalyst), complex 3 generates a 98% isolated yield of pure triphenyl isocyanurate within 16 min at room temperature. These results place this complex as one of the most active and selective species reported to catalyze eq 3.

A comparison of our reported Sn(IV) catalyst, $[CyNC(Me)NCy]Sn[N(SiMe_3)_2]S_4$,⁸ and the Sn(II) complexes 2 and 4 is instructive. While these species exhibited selectivity comparable to that of the Sn(IV) compound, they have substantially slower reaction rates. Similarly, 2 is also much less active than the analogous Ge(II) species 3. These two observations suggest that the Lewis acidity of the metal center plays a role in the activity of these complexes. The metal coordination environment also appears to be a factor in the selectivity of isocyanurate formation. Our results indicate that the complexes 2 and 3 exhibit a high degree of selectivity in generating only isocyanurate (95–98% yield). In contrast, the bis(amidinate) complex 4, while quite active in reaction with phenyl isocyanate, displayed a selectivity for the formation of phenyl isocyanate dimer (eq 4) with an approximate 2:3 ratio of trimer:dimer formation.



Catalysts 2–4 can be recycled without apparent loss of activity. When active catalyst systems were probed by ¹H NMR, nothing but the starting complex was observed, no byproducts were evident, and no degradation of the starting material was noticed.

Conclusions

The bulky amidinate $[Me_3SiNC(tBu)NSiMe_3]^-$ has been used in the preparation of novel mixed-ligand Sn(II) and Ge(II) species. A rearrangement of this ligand via trimethylsilyl migration and nitrile elimination generates a bis(trimethylsilyl)-amido ligand and provides ultimate products with the formulas $[Me_3SiNC(tBu)NSiMe_3]M[NSiMe_3]$. The propensity for this rearrangement is dependent on reaction solvent and on the coordinated metal center. Furthermore, the isolation of $[Me_3SiNC(Me)NSiMe_3]_2Sn$ (4) indicates that steric factors also play a role in the stability of $[Me_3SiNC(tBu)NSiMe_3]^-$. The reported complexes exhibit catalytic activity toward the cyclotrimerization and cyclodimerization of isocyanates and represent unique catalysts for these transformations. These results add to our mechanistic of this transformation and provide some evidence for a Lewis acid pathway and for the role of Sn coordination environment in dimer/trimer selectivity.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Crystal data, positional and thermal parameters, and selected interatomic distances and angles for complex 2. CIF files for the structural determinations of complexes 3 and 4. These materials are available free of charge via the Internet at <http://pubs.acs.org>.