Inorganic Chemistry
Article

Inorg. Chem. 2010, 49, 9709–9717 9709
DOI: 10.1021/ic101485a

Low-Coordinate Germylene and Stannylene Heterocycles featuring Sterically Tunable Bis(amido)silyl Ligands

S. M. Ibrahim Al-Rafia, Paul A. Lummis, Michael J. Ferguson, Robert McDonald, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

Received July 24, 2010

A series of monomeric heterocyclic metallylenes [{^{i}Pr$_2$Si(NR)$_2$}M:] (M = Ge and Sn; R = Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$ or SiPh$_3$) have been prepared. Preliminary atom-transfer chemistry involving the new low-valent germylenes with the chalcogen sources Me$_3$NO and S$_8$ yielded the corresponding dimeric oxo- and sulfido complexes (e.g., [{^{i}Pr$_2$Si(NDipp)$_2$}Ge-(μ-E)]$_2$; E = O and S). Structural analyses of the metallylenes and their oxidized products reveal that incorporation of the umbrella-shaped triarylsilyl groups (SiPh$_3$) within the NSiN chelate confers additional steric protection about the group 14 centers relative to a Dipp group. The inclusion of sterically modifiable $-$SiAr$_3$ (Ar = aryl) units as part of a bis(amido) ligand array represents a new approach in this field and holds considerable promise with regard to attaining increasingly higher degrees of steric bulk.

Introduction

The development of sterically encumbered ligands that contain anionic nitrogen donor sites (NR$_2^-$) has played a pivotal role in advancing our overall knowledge of fundamental chemical reactivity throughout the Periodic Table.[1] For example, these studies have led to the discovery of many novel metal-mediated small molecule/bond activation processes which are often elaborated upon later to yield synthetically important catalytic transformations.[2] Moreover amide (or amido) ligand frameworks are prominently featured in the isolation of low-coordinate main group species that exhibit unusual bonding arrangements and reactivity.[3] The widespread success of nitrogen-containing ligands is derived from their ability to act as both σ- and π-donors and their ease of tunability, with the latter property being a direct result of the modular nature of their syntheses; consequently, a significant level of steric and electronic control over chemical reactivity of the ligated element can be achieved.[1−3]

The above-mentioned successes have inspired us to focus research efforts toward the synthesis of new bis(amido) chelates that bear very hindered flanking groups at nitrogen. Specifically, this paper describes the development of the dianionic chelates [NSiN]$^{\mathbf{Dipp}}$ and [NSiN]$^{\mathbf{SiPh3}}$ (Chart 1) and their use to access low-coordinate complexes of Ge(II) and Sn(II). Moreover, illustrative chalcogen atom-transfer chemistry has been explored in order to gauge the relative steric coverage offered by the newly developed NSiN ligands.

Results and Discussion

Ligand Precursor Syntheses. The amine ligand precursors, (RNH)$_2$Si^{i}Pr$_2$ (R = Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$, **1**; R = SiPh$_3$, **2**) were assembled using the general protocol outlined in Scheme 1. Starting from the readily available primary amines, DippNH$_2$ and Ph$_3$Si$-$NH$_2$,[4] the target chelates **1** and **2** were prepared in modest yields via two-step procedures and isolated as colorless moisture-sensitive solids (55 and 67% overall yields for **1** and **2**, respectively).

---

*Corresponding author. E-mail: erivard@ualberta.ca.

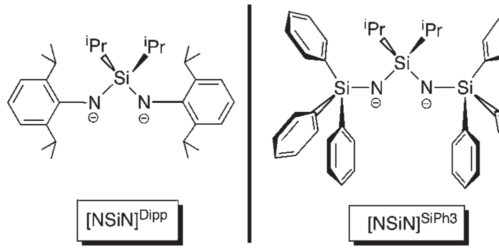
[1] Lappert, M.; Power, P.; Protchenko, A.; Seeber, A. *Metal Amide Chemistry*; John Wiley and Sons Ltd.: West Sussex, UK, 2008.

[2] (a) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (b) Cummins, C. C.; Schaller, C. P.; Van Duyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985. (c) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839. (d) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9. (e) Cummins, C. C. *Chem. Commun.* **1998**, 1777. (f) Macbeth, C. E.; Golombek, A. P.; Young, V. G., Jr.; Yang, C.; Kuzera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, *289*, 938. (g) Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575. (h) Yandulov, D.; Schrock, R. R. *Science* **2003**, *301*, 76. (i) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530. (j) Figueroa, J. S.; Cummins, C. C. *Dalton Trans.* **2006**, 2161. (k) Waterman, R. *Dalton Trans.* **2009**, 18.

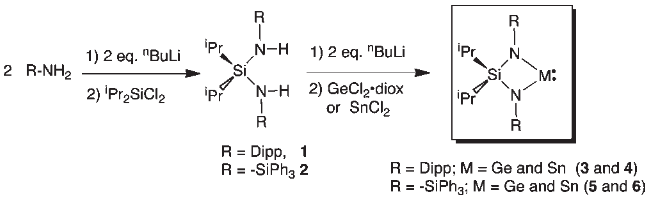
[3] (a) Harris, D. H.; Lappert, M. F. *Chem. Commun.* **1974**, 895. (b) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed.* **1974**, *13*, 134. (c) Veith, M. *Angew. Chem., Int. Ed.* **1975**, *14*, 263. (d) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *Dalton Trans.* **1977**, 2004. (e) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (f) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed.* **1992**, *31*, 1485. (g) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, *68*, 785. (h) Schmidt, E. S.; Jockisch, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1999**, *121*, 9758. (i) Stahl, L. *Coord. Chem. Rev.* **2000**, *210*, 203. (j) Baker, R. J.; Farley, R. D.; Jones, C.; Kloth, M.; Murphy, D. M. *J. Chem. Soc., Dalton Trans.* **2002**, 3844. (k) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113. (l) Wright, R. J.; Brynda, M.; Fettinger, J. C.; Betzer, A. R.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 12498.

[4] Li, Y.; Banerjee, S.; Odom, A. L. *Organometallics* **2005**, *24*, 3272.

Chart 1. Dianionic Bis(amido)silyl Ligands Developed in This Work



Scheme 1. Preparation of the Monomeric Germylenes and Stannylenes, **3**−**6**



The identity of **1** and **2** was established using a combination of NMR and IR spectroscopy, satisfactory elemental analyses (C, H, N), and single-crystal X-ray crystallography (Figure 1). Despite the steric crowding present at the nitrogen centers in both **1** and **2**, all associated metrical parameters, including intrachain Si−N and adjacent Si−C(^{i}Pr) bond distances, were within expected values in accordance with the molecular structures depicted in Scheme 1.

Synthesis of the Monomeric N-heterocyclic Germylenes and Stannylenes, 3−6. In order to verify the ability of our bis(amido)silyl ligands, [NSiN]$^{\mathbf{Dipp}}$ and [NSiN]$^{\mathbf{SiPh3}}$, to stabilize low-coordinate environments, we targeted the preparation of divalent heavy carbene analogues, R_2Ge: and R_2Sn:, termed hereafter as germylenes and stannylenes.[5] Following established procedures,[3d,6,7] the aryl-substituted bis(amine), **1**, was reacted with two equivalents of ^{n}BuLi in Et_2O to generate the dilithiated precursor, [{^{i}Pr$_2$Si(NDipp)$_2$}Li$_2$], Li$_2$[NSiN]$^{\mathbf{Dipp}}$. This reagent could be isolated in pure form as a THF solvate,[8] however, purification was not necessary for our syntheses given that the in situ generated dilithio salt, Li$_2$[NSiN]$^{\mathbf{Dipp}}$, still underwent clean metathesis chemistry with GeCl$_2$·dioxane and SnCl$_2$ to give the target Ge(II) and Sn(II) complexes, [{^{i}Pr$_2$Si(NDipp)$_2$}M:] (M = Ge, **3**; M = Sn, **4**; Scheme 1). High-quality crystals of **3** and **4** were subsequently grown from diethyl ether, and single-crystal X-ray crystallography confirmed the presence of rigorously monomeric heterocycles with dicoordinate Ge(II) and Sn(II) centers. Figure 2 contains the molecular structures of **3** and **4**, while Table 1 lists relevant data associated with structure refinement and solution.

As shown above, compounds **3** and **4** adopt similar overall geometries with planar four-membered NSiNM rings (M = Ge and Sn) and trigonal planar coordination involving the chelating nitrogen atoms. The Ge−N and Sn−N bond distances in **3** and **4** were 1.8627(10) and 2.067(2) Å (avg.), respectively, while nearly identical Si−N endocyclic bond lengths were observed in both complexes [1.7471(10) in **3**; 1.745(2) Å avg. in **4**]. Compound **3** represents the first uncomplexed germylene heterocycle featuring an NSiNGe core to be structurally authenticated by crystallography. The analogous Ge(II) heterocycle, [Me$_2$Si(N^{t}Bu)$_2$Ge:] was prepared by Veith as a stable yellow oil, and this species was shown to be monomeric in benzene solvent by cryoscopic measurements.[9,10]

Russell and co-workers recently reported the synthesis of a structurally related tin(II) heterocycle, [{Ph$_2$Si(NDipp)$_2$}Sn:].[7b] As with **4**, a planar NSiNSn unit was present, however the Sn−N bond distances in the diphenylsilane analogue were elongated [2.101(6) and 2.259(5) Å] with respect to those found in **4** [2.067(2) Å (avg.)].[7] Moreover, additional molecular interactions were observed in [{Ph$_2$Si(NDipp)$_2$}Sn:] involving the flanking aryl rings of the Dipp groups and adjacent Sn centers, resulting in the formation of a weakly associated coordination polymer with close intermolecular Sn···η^6 aryl(centroid) contacts of ca. 3.2 Å.[7b] By contrast, compound **4** is rigorously monomeric with no close-range intermolecular interactions observed within 4.0 Å. This difference in solid-state packing is a likely consequence of added intraligand repulsion in **4**. The presence of encumbered ^{i}Pr$_2$Si and Dipp groups within the same heterocycle results in the aryl rings in **4** being pushed even further toward the Sn center, leading to greater steric coverage.[11] This effect is observed both in the solid-state structure of **4**, wherein the Si−N−C(ipso, Dipp) angles are considerably wide [134.98(10) and 137.71(10)°], and via the presence of spectroscopically distinct ^{i}Pr environments within the Dipp ligands (by ^{1}H and ^{13}C{^{1}H} NMR) due to restricted rotation of the Dipp groups. In the less hindered analogue, [{Ph$_2$Si(NDipp)$_2$}Sn:], the exocyclic Si−N−C(ipso, Dipp) angles are reduced to 130.2(2) and 132.7(2)°, while free rotation of the Dipp moieties, and a single ^{i}Pr environment, is observed by NMR spectroscopy at ambient temperature.[7b] The Ge(II) heterocycle **3** possesses a similar overall geometry as its heavier congener **4**, with correspondingly wide Si−N−C(ipso) angles of 139.41(8)° observed.

In order to further expand the potential tunability of our dianionic chelates, we decided to install umbrella-shaped

---

[5] (a) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. (b) Lappert, M. F. *Main Group Metal Chem.* **1994**, *17*, 183. (c) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704. (d) Weidenbruch, M. *J. Organomet. Chem.* **2002**, *646*, 39. (e) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.

[6] (a) Fink, W. *Helv. Chim. Acta* **1964**, *47*, 498. (b) Bush, R. P.; Lloyd, N. C. *J. Chem. Soc. A* **1969**, 257.

[7] (a) Hill, M. S.; Hitchcock, P. B. *Organometallics* **2002**, *21*, 3258. (b) Mansell, S. M.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2008**, *47*, 11367.

[8] Repeating the lithiation of **1** in THF, followed by crystallization of the product from a hexanes/THF mixture, led to the isolation of the dilithiated ligand, Li$_2$[NSiN]$^{\mathbf{Dipp}}$·3THF in quantitative yield. X-ray crystallography showed the structure of this species, prior to desolvation of THF, to be {[NSiN]$^{\mathbf{Dipp}}$Li(THF)$_2$}{Li(THF)$_4$}. See Supporting Information for complete crystallographic details.

[9] (a) Veith, M. *Angew. Chem., Int. Ed.* **1987**, *26*, 1. (b) Veith, M.; Grosser, M. *Z. Naturforsch., B: J. Chem. Sci.* **1982**, *37*, 1375.

[10] For related work on N-heterocyclic germylenes, see (a) Kühl, O.; Lönnecke, P.; Heinicke, J. *Polyhedron* **2001**, *20*, 2215. (b) Tokitoh, N.; Kishikawa, K.; Okazaki, R.; Sasamori, T.; Nakata, N.; Takeda, N. *Polyhedron* **2002**, *21*, 563. (c) Kühl, O. *Coord. Chem. Rev.* **2004**, *248*, 411. (d) Zabula, A. V.; Hahn, F. E.; Pape, T.; Hepp, A. *Organometallics* **2007**, *26*, 1972.

[11] (a) Spencer, D. J. E.; Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108. (b) Stanciu, C.; Richards, A. F.; Fettinger, J. C.; Brynda, M.; Power, P. *J. Organomet. Chem.* **2006**, *691*, 2540. (c) Wolf, R.; Brynda, M.; Ni, C.; Long, G. J.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 6076. (d) Zhu, Z.; Fischer, R. C.; Ellis, B. D.; Rivard, E.; Merrill, W. A.; Olmstead, M. M.; Power, P. P.; Guo, J. D.; Nagase, S.; Pu, L. *Chem.—Eur. J.* **2009**, *15*, 5263.

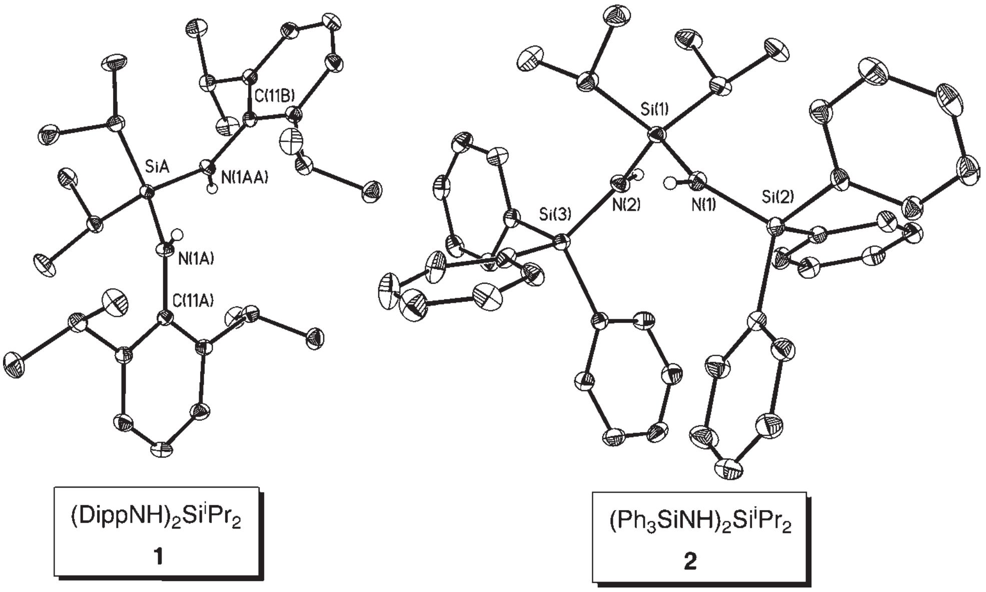


Figure 1. Molecular structures of (DippNH)$_2$Si^{i}Pr$_2$ (**1**) and (Ph$_3$SiNH)$_2$Si^{i}Pr$_2$ (**2**) with thermal ellipsoids presented at the 30% probability level. All carbon-bound hydrogen atoms and solvate molecules have been omitted for clarity. Primed atoms are related to unprimed via a two-fold rotation axis that bisects the N−Si−N angle in **1**. Selected bond lengths (Å) and angles (°) with bracketed values belonging to a second molecule within the asymmetric unit: Compound **1**: Si(1)−N(1) 1.7397(11) [1.7413(11)], Si(1)−C(1) 1.8896(13) [1.8873(13)]; N(1)−Si(1)−N(1)′ 115.04(8) [116.74(8)], C(1)−Si(1)−C(1)′ 116.86(9) [116.82(9)]. Compound **2**: Si(1)−N(1) 1.7391(16), Si(1)−N(2) 1.7402(19), Si(2)−N(1) 1.7228(16), Si(3)−N(2) 1.7182(16), Si(1)−C(1) 1.892(2), Si(1)−C(4) 1.892(2); N(1)−Si(1)−N(2) 114.43(8), Si(1)−N(1)−Si(2) 139.33(10), Si(1)−N(2)−Si(3) 140.09(11), C(1)−Si(1)−C(4) 116.31(9).

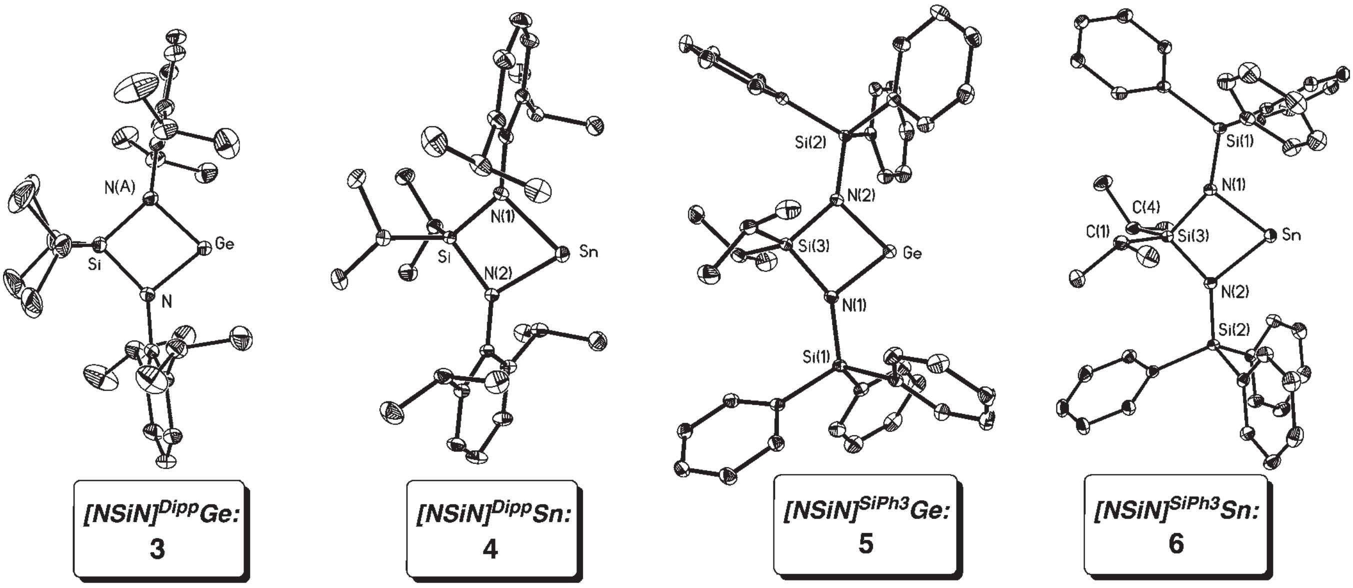


Figure 2. Molecular structures of heterocycles **3**−**6** with thermal ellipsoids at the 30% probability level. Primed atoms for **3** are related to unprimed via a two-fold rotational axis upon which the Ge and Si atoms are located. Selected bond lengths (Å) and angles (°): Compound **3**: Ge(1)−N(1) 1.8627(10), Si(1)−N(1) 1.7471(10); N(1)−Ge(1)−N(1)′ 81.26(6), N(1)−Si(1)−N(1)′ 87.94(7), C(1)−Si(1)−C(1)′ 112.72(12), Si(1)−N(1)−C(11) 139.41(8). Compound **4**: Sn(1)−N(1) 2.0709(12), Sn(1)−N(2) 2.0631(12), Si(1)−N(1) 1.7440(12), Si(1)−N(2) 1.7463(12); N(1)−Sn(1)−N(2) 74.60(5), N(1)−Si(1)−N(2) 91.74(6), C(1)−Si(1)−C(4) 111.87(7), Si(1)−N(1)−C(11) 137.71(10), Si(1)−N(2)−C(31) 134.98(10). Compound **5**: Ge(1)−N(1) 1.8834(14), Ge(1)−N(2) 1.8829(14), Si(1)−N(1) 1.7210(14), Si(2)−N(2) 1.7164(14), Si(3)−N(1) 1.7458(14), Si(3)−N(2) 1.7481(14); N(1)−Ge(1)−N(2) 83.31(6), N(1)−Si(3)−N(2) 91.53(7), C(1)−Si(3)−C(4) 110.52(10), Si(3)−N(1)−Si(1) 146.23(9), Si(3)−N(2)−Si(2) 140.19(9). Compound **6**: Sn(1)−N(1) 2.0888(15), Sn(1)−N(2) 2.0882(15), Si(1)−N(1) 1.7102(16), Si(2)−N(2) 1.7083(16), Si(3)−N(1) 1.7402(16), Si(3)−N(2) 1.7446(16); N(1)−Sn(1)−N(2) 76.28(6), N(1)−Si(3)−N(2) 95.51(8), C(1)−Si(3)−C(4) 109.50(11), Si(3)−N(1)−Si(1) 146.51(10), Si(3)−N(2)−Si(2) 140.14(9).

triarylsilyl groups at the nitrogen-donor sites, [NSiN]^{SiPh3} (Chart 1). The SiAr$_3$ groups (Ar = aryl) not only provide a wide swath of steric bulk that radiates outward from the Si centers, but should allow for further ligand modification via chemical functionalization of the peripheral Ar groups.[12]

The syntheses of the Ge(II) and Sn(II) complexes [{[NSiN]^{SiPh3}}Ge:] (**5**) and [{[NSiN]^{SiPh3}}Sn:] (**6**) proceeded in a similar fashion as for the less hindered Dipp analogues, **3** and **4** (Scheme 1), with the noted exception that the triphenylsilyl-substituted heterocycles exhibited

---

(12) Watkin, J. G.; Click, D. R. Polymerization Catalysts containing Electron Withdrawing Amide Ligands. *WO Patent* 9845039, 1998.

Table 1. Crystallographic Data for Compounds **1**−**5**

	1[b]	**2**[c]	**3**	**4**	**5**
empirical formula	$C_{30}H_{50}N_2Si$	$C_{42}H_{46}N_2Si_3$	$C_{30}H_{48}GeN_2Si$	$C_{30}H_{48}N_2SiSn$	$C_{42}H_{44}GeN_2Si_3$
fw	466.81	663.08	537.38	583.48	733.65
cryst dimens (mm^3)	0.46 × 0.44 × 0.43	0.37 × 0.21 × 0.18	0.40 × 0.37 × 0.36	0.42 × 0.39 × 0.35	0.53 × 0.39 × 0.09
cryst syst	trigonal	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P3_121$	$P2_1$	$C2/c$	$P2_1/c$	$P2_1/n$
unit cell dimensions					
a (Å)	10.2694(3)	10.5347(9)	10.4149(4)	16.6257(7)	8.6077(9)
b (Å)		15.3080(13)	23.1176(8)	11.2475(4)	25.628(3)
c (Å)	46.7860(14)	12.1157(10)	13.4528(5)	17.6079(7)	17.1827(18)
α (°)					
β (°)		111.6950(10)	107.5710(4)	110.7814(4)	91.3020(10)
γ (°)					
V (Å^3)	4273.0(2)	1815.4(3)	3087.9(2)	3078.4(2)	3789.5(7)
Z	6	2	4	4	4
D (g cm^{-3})	1.088	1.213	1.156	1.259	1.286
abs coeff (mm^{-1})	0.102	0.163	1.050	0.888	0.935
T (K)	173(1)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (°)	55.10	52.92	55.00	55.02	55.26
total data	38035	14514	13517	26638	33203
unique data (R_{int})	6589 (0.0201)	7441 (0.0232)	3556 (0.0112)	7080 (0.0116)	8784 (0.0301)
obs data [$I > 2\sigma(I)$]	6421	7063	3371	6777	7290
params	299	425	155	307	433
R_1 [$I > 2\sigma(I)$][a]	0.0331	0.0349	0.0240	0.0208	0.0331
wR_2 [all data][a]	0.0894	0.0940	0.0701	0.0574	0.0983
max/min Δρ (e$^-$ Å^{-3})	0.282/−0.268	0.533/−0.217	0.317/−0.235	0.437/−0.392	0.577/−0.561

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$. [b] Flack parameter = 0.05(8). [c] Flack parameter = 0.17(7).

significantly reduced solubility in organic solvents.[13] As a consequence of the hydrolytically prone Si−N and Ge−N/Sn−N linkages within **5** and **6**, these compounds react readily with trace quantities of moisture to yield $Ph_3Si{-}O{-}SiPh_3$ as a soluble byproduct (identified by X-ray crystallography and ^1H and $^{13}C\{^1H\}$ NMR).[14] However when **5** and **6** are handled under strictly anhydrous conditions, these compounds are quite thermally stable, with no noticeable signs of decomposition in the solid state up to 300 °C (under N_2).

High-quality crystals of **5** and **6** for X-ray diffraction studies were obtained from diethyl ether and their molecular structures are presented as part of Figure 2. These triarylsilyl-capped heterocycles display a higher degree of intramolecular repulsion involving the backbone positioned $^i Pr_2Si$ groups relative to the Dipp analogues, **3** and **4**. These $^i Pr_2Si\cdots SiPh_3$ interactions cause the $-SiPh_3$ moieties to be tilted forward toward the Ge and Sn centers to produce highly distorted Si(endo)−N−Si(exo) angles [Si(3)−N(1)−Si(1,2) angles = 146.23(9) and 140.10(9) for **5**; 146.51(10)° and 140.14(9)° for **6**]. Furthermore, space filling models indicate that the $-SiPh_3$ groups create a much deeper steric pocket about the capping Ge and Sn centers with respect to the coverage offered by the flanking Dipp groups in **3** and **4**, hence the use of triarylsilyl groups as structural motifs is a promising strategy for the stabilization/isolation of low-coordinate environments.

Initial Atom-Transfer Chemistry Involving Germylenes 3 and 5. Divalent germylenes (R_2Ge:) and stannylenes (R_2Sn:) exhibit diverse reaction chemistry due to their dual donor/acceptor nature and proclivity for oxidative bond forming reactions.[5,15] As mentioned earlier, intramolecular steric repulsions within the NSiNM heterocycles **3**−**6** lead to the positioning of the flanking groups at nitrogen (Dipp or $SiPh_3$) in closer proximity to the group 14 center. This effect should be quite useful in uncovering new forms of bonding, whereby kinetic stabilization is required to suppress undesired side-reactions.[16] One such example would be the isolation of heavy analogues of ketones, with the isolation of a stable silicone derivative ($R_2Si{=}O$) being a highly desirable target.[17,18] In order to benchmark the steric coverage offered by our chelates with respect to known ligands, we explored preliminary chalcogen atom-transfer chemistry involving the germylenes **3** and **5** with the goal of isolating hitherto unknown (or rare) examples of Ge=E multiple bonds (E = group 16 element).[5e]

Interaction of the arylamido germylene $[\{[NSiN]^{\mathbf{Dipp}}\}Ge:]$ **3** with the chalcogen sources Me_3NO and S_8 (one atomic equiv) afforded a new Ge product in each case; notably, the products obtained exhibited analogous NMR spectroscopic signatures, suggesting that these products were of similar structure in solution. X-ray

---

[13] For the use of $SiPh_3$ groups in ligands, see:(a) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 6509. (b) Bott, S. G.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1577. (c) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906. (d) Bindl, M.; Stade, R.; Heilmann, E. K.; Picot, A.; Goddard, R.; Fürstner, A. *J. Am. Chem. Soc.* **2009**, *131*, 9468.

[14] For spectroscopic data, see: (a) Blankenship, C.; Cremer, S. E. *J. Organomet. Chem.* **1989**, *371*, 19. Crystals of non-solvated $Ph_3SiOSiPh_3$ and those containing toluene solvate were isolated in separate reactions, and identified by comparison of their unit cell parameters with those found in the literature: (b) Glidwell, C.; Liles, D. C. *Acta Crystallogr.* **1978**, *B34*, 124. (c) Honle, W.; Manriquez, V.; von Schnering, H. G. *Acta Crystallogr.* **1990**, *C46*, 1982.

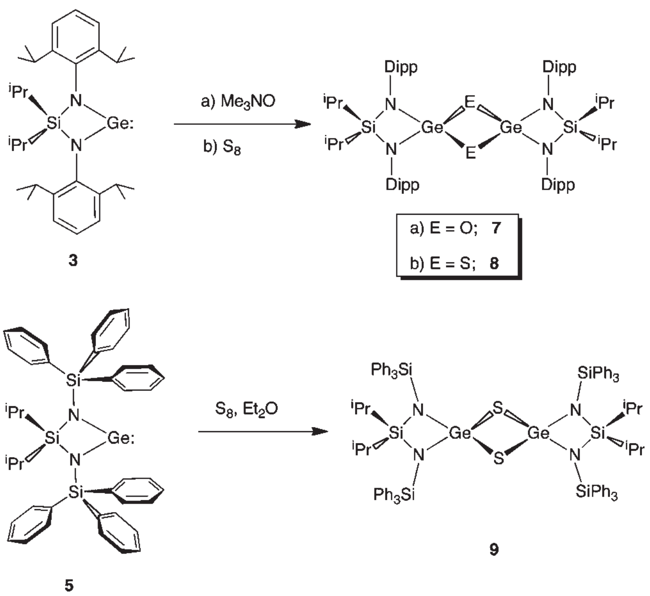
[15] (a) Veith, M.; Nötzel, M.; Huch, V. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1264. (b) Klein, B.; Neumann, W. P. *J. Organomet. Chem.* **1994**, *465*, 119. (c) Rakebrandt, H. −J.; Klingebiel, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1264.

[16] Power, P. P. *Chem. Rev.* **1999**, *99*, 3463.

[17] (a) Robison, R.; Kipping, F. S. *J. Chem. Soc. Trans.* **1908**, *24*, 25. (b) Tokitoh, N.; Okazki, R. *Coord. Chem. Rev.* **2000**, *210*, 251. (c) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625.

[18] (a) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268. (b) Yao, S.; Brym, M.; van Wüllen, C.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4159. (c) Yao, S.; Xiong, Y.; Driess, M. *Chem. Commun.* **2009**, 6466. (d) Yao, S.; Xiong, Y.; Driess, M. *Chem.—Eur. J.* **2010**, *16*, 1281.

Scheme 2. Chalcogen Transfer Chemistry Used to Generate the Oxo- and Sulfido-Bridged Germane Dimers (**7**−**9**)



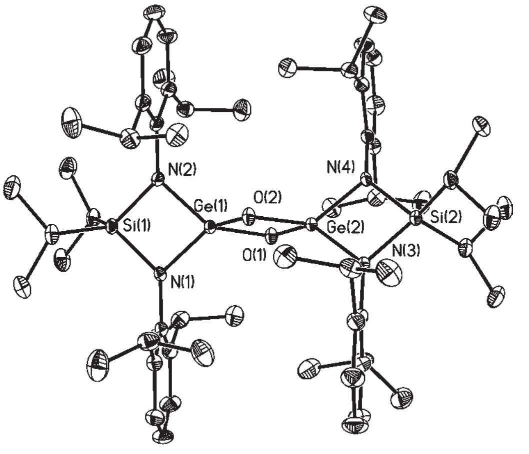


Figure 3. Molecular structure of **7** [{[NSiN]^{Dipp}}Ge(μ-O)]$_2$ with thermal ellipsoids presented at the 30% probability level. All hydrogen atoms and ether solvate molecules omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)−O(1) 1.8045(18), Ge(1)−O(2) 1.8063(19), Ge(2)−O(1) 1.8044(19), Ge(2)−O(2) 1.8032(18), Ge(1)−N(1) 1.828(2), Ge(1)−N(2) 1.833(2), Ge(2)−N(3) 1.830(2), Ge(2)−N(4) 1.828(2), Si(1)−N(1) 1.768(2), Si(1)−N(2) 1.763(2), Si(1)−C(1) 1.879(3), Si(1)−C(4) 1.877(3), Si(2)−N(3) 1.761(2), Si(2)−N(4) 1.762(2), Si(2)−C(7) 1.878(30, Si(2)−C(10) 1.878(3); O(1)−Ge(1)−O(2) 86.43(8), N(1)−Ge(1)−N(2) 84.10(10), O(1)−Ge(2)−O(2) 86.51(8), N(1)−Si(1)−N(2) 87.95(11), C(1)−Si(1)−C(4) 112.08(14), Si(1)−N(1)−C(21) 134.65(19), Si(1)−N(2)−C(41) 135.79(19), Ge(1)−N(1)−C(21) 131.27(19), Ge(1)−N(2)−C(41) 129.17(19), N(3)−Si(2)−N(4) 87.78(11), C(7)−Si(2)−C(10) 111.86(14), Si(2)−N(3)−C(61) 135.34(19), Si(2)−N(4)−C(81) 134.57(19), Ge(2)−N(3)−C(61) 130.43(18), Ge(2)−N(4)−C(81) 130.12(18).

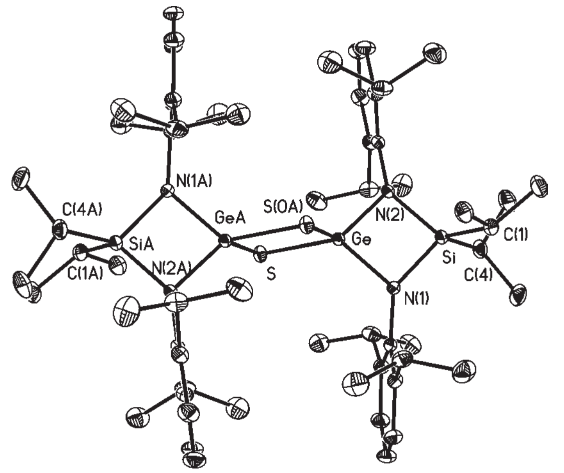


Figure 4. Molecular structure of **8** [{[NSiN]^{Dipp}}Ge(μ-S)]$_2$ with thermal ellipsoids presented at the 30% probability level. All hydrogen atoms and ether solvate molecules omitted for clarity. Primed atoms related to unprimed by an inversion center. Selected bond lengths (Å) and angles (°): Ge(1)−S(1) 2.1992(3), Ge(1)−S(1)′ 2.2577(3), Ge(1)−N(1) 1.8344(9), Ge(1)−N(2) 1.8471(9), Si(1)−N(1) 1.7606(9), Si(1)−N(2) 1.7675(10), Si(1)−C(1) 1.8925(13), Si(1)−C(4) 1.8755(13); S(1)−Ge(1)−S(1)′ 95.956(10), Ge(1)−S(1)−Ge(1)′ 84.043(10), N(1)−Ge(1)−N(2) 83.65(4), N(1)−Si(1)−N(2) 88.19(4), C(1)−Si(1)−C(4) 109.35(6), Si(1)−N(1)−C(11) 137.62(9), Si(1)−N(2)−C(31) 138.00(8), Ge(1)−N(1)−C(11) 128.19(7), Ge(1)−N(2)−C(31) 128.18(7).

crystallography substantiated the successful transfer of chalcogen atoms to germanium in both instances and revealed the formation of the corresponding oxo- and sulfido-bridged dimers, [{^{i}Pr$_2$Si(NDipp)$_2$}Ge(μ-E)]$_2$ (E = O and S, **7** and **8**, Scheme 2, Figures 3 and 4).

The oxo-bridged dimer [{[NSiN]^{Dipp}}Ge(μ-O)]$_2$ **7** contains planar NSiNGe and Ge$_2$O$_2$ arrays that are mutually rotated by 73.0 and 71.6°, with average endocyclic Ge−O and Ge−N bond lengths of 1.805(4) and 1.830(5) Å. A related amide-substituted 1,3-cyclodigermoxane, [Ge{N(SiMe$_3$)$_2$}$_2$(μ-O)]$_2$, was synthesized by Lappert and co-workers through the direct reaction of the germanium(II) bisamide, Ge{N(SiMe$_3$)$_2$}$_2$ with molecular oxygen.[19] Dimeric [Ge{N(SiMe$_3$)$_2$}$_2$(μ-O)]$_2$ features a similar planar Ge$_2$O$_2$ core, as in **7** with Ge−O distances ranging from 1.804(11) to 1.836(10) Å and accompanying Ge−N distances that vary from 1.8317(10) to 1.830(10) Å.[19] For further comparison, the centrosymmetric diarylgermone dimer, [(2,6-Et$_2$C$_6$H$_3$)$_2$Ge(μ-O)]$_2$, exhibited an average Ge−O bond length of 1.817(3) Å and an endocyclic O−Ge−O angle of 87.6(1)°;[20] this O−Ge−O bond angle compares well with those found in **7** [86.43(8) and 86.51(8)°]. Notably, the Ge−N distances in **7** are ca. 0.03 Å shorter than in **3**, while the intraring N−Ge−N angles are slightly wider in **7** [84.10(6) and 83.79(10)°] relative to the corresponding angle of 81.26(6)° in the Ge(II) precursor **3**. The decrease in the observed Ge−N bond lengths upon oxidation of **3** with Me$_3$NO is likely due to a reduction in the covalent radii on going from a formal Ge(II) site in **3** to a Ge(IV) center in **7**.[21]

The formation of a dimeric arrangement in **7** underscores the difficulty associated with isolating a monomeric germanone (R$_2$Ge=O) under ambient conditions; a major factor for the lack of success thus far lies in the highly polar nature of the Ge−O π-bond, which makes this unit prone to dimerization/oligomerization to yield thermodynamically more stable σ-linkages (and the formation of extended Ge−O rings and/or chains).[22−24]

---

(19) Ellis, D.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1992**, 3397.

(20) Masamune, S.; Batcheller, S. A.; Park, J.; Davis, W. M.; Yamashita, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1888.

(21) Bokii, N. G.; Yu, T.; Struchkov, T.; Kolesnikov, S. P.; Rogozhin, I. S.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim* **1975**, *4*, 812.

(22) (a) Trinquier, G.; Barthelat, J. C.; Satge, J. *J. Am. Chem. Soc.* **1982**, *104*, 5931. (b) Kapp, J.; Remko, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 5745.

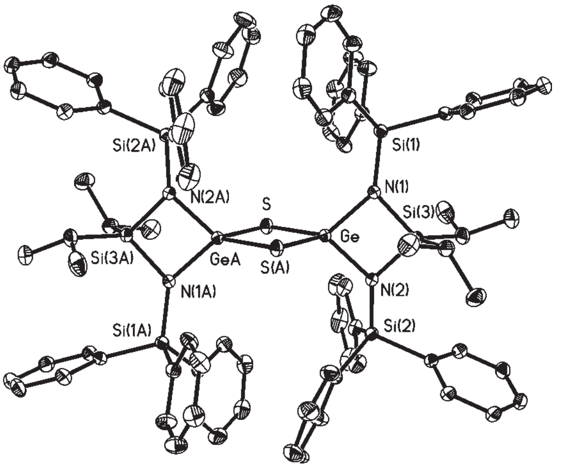


Figure 5. Molecular structure of [{[NSiN]$^{\mathrm{SiPh_3}}$}Ge(μ-S)]$_2$ **9** with thermal ellipsoids presented at the 30% probability level with primed atoms related to nonprimed by an inversion center. All hydrogen atoms and ether solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)−S(1) 2.2197(5), Ge(1)−S(1)′ 2.2484(5), Ge(1)−N(1) 1.8534(13), Ge(1)−N(2) 1.8519(13), Si(1)−N(1) 1.7337(14), Si(2)−N(2) 1.7326(14), Si(3)−N(1) 1.7704(14), Si(3)−N(2) 1.7675(14); S(1)−Ge(1)−S(1)′ 94.28(2), N(1)−Ge(1)−N(2) 85.38(6), N(1)−Si(3)−N(2) 90.49(6), C(1)−Si(3)−C(4) 110.96(9), Si(3)−N(1)−Si(1) 131.13(8), Si(3)−N(2)−Si(2) 134.47(8), Ge(1)−N(1)−Si(1) 136.91(8), Ge(1)−N(2)−Si(2) 133.22(8).

Notably, Veith's heterocyclic germylene, [$\mathrm{Me_2Si(N^tBu)_2}$-Ge:], also participates in smooth oxo-transfer chemistry with $\mathrm{Me_3NO}$, however due to the reduced steric bulk in this system relative to **3**, a trimeric product [{$\mathrm{Me_2Si(N^tBu)_2}$}-Ge(μ-O)]$_3$ containing a $\mathrm{Ge_3O_3}$ core was obtained.[15a]

The sulfido dimer [{[NSiN]$^{\mathrm{Dipp}}$}Ge(μ-S)]$_2$ (**8**) (Figure 4) has an overall structure that mirrors the oxo-bridge dimer **7** with the primary difference being the presence of an expanded $\mathrm{Ge_2S_2}$ core [Ge−S = 2.1992(3) and 2.2577(3) Å] due to the larger covalent radius of S relative to O.[25] It is salient to mention that an example of a stable monomeric germanethione has been isolated at ambient temperature, [Tbt(Tip)Ge═S] (Tbt = 2,4,6-{$\mathrm{(Me_3Si)_2CH}$}-$\mathrm{C_6H_2}$; Tip = 2,4,6-$\mathrm{^iPr_3C_6H_2}$),[26,27] and that this species contains a significantly short Ge−S distance [2.049(3) Å] that is consistent with a Ge═S double bond. Inspection of the structures of **7** and **8** reveals that the flanking Dipp groups can readily twist away from the germanium-chalcogen rings, thus providing a pathway for the dimerization of any putative Ge═O and Ge═S double bonds initially formed. In addition, the relative positions between the Dipp groups in **7** and **8** and the Ge centers in these dimers are similar to that found in the precursor **3** as evidenced by only minor deviations in the Si−N−C(ipso, Dipp) angles in all three complexes. This suggests that the degree of repulsion between the cofacial Dipp groups in the dimers **7** and **8** was minimal. In order to more thoroughly compare the steric effects created by the Dipp and $\mathrm{SiPh_3}$ groups within our chelates, we explored analogous chalcogen-transfer chemistry with the triarylsilyl-substituted germylene, **5**.

Interaction of the $\mathrm{Ph_3Si}$-flanked germylene [{[NSiN]$^{\mathrm{SiPh_3}}$}-Ge:] (**5**) with $\mathrm{Me_3NO}$ did not yield any products that could be isolated in pure form. However treatment of **5** with elemental sulfur yielded a clean product that was marginally soluble in diethyl ether. Single-crystal X-ray crystallography (Figure 5), later identified the compound as the sterically congested germanethione dimer [{[NSiN]$^{\mathrm{SiPh_3}}$}Ge(μ-S)]$_2$ (**9**). As with the less hindered derivative [{[NSiN]$^{\mathrm{Dipp}}$}Ge(μ-S)]$_2$ (**8**), the $\mathrm{Ge_2S_2}$ core in **9** was found to be planar with similar Ge−S distances of 2.2197(5) and 2.2484(5) Å and with slightly narrower intraring S−Ge−S angles of 94.28(2)°; the Ge−S bond lengths in **9** are in the range expected for single bonds (2.17−2.25 Å).[26b] Particularly noteworthy is the significant degree of intramolecular repulsion in **9** involving proximal $\mathrm{SiPh_3}$ groups that are mutually located on the same side of the plane created by the central $\mathrm{Ge_2S_2}$ core. These $-\mathrm{SiPh_3}\cdots\mathrm{Ph_3Si}-$ interactions lead to very large molecular distortions, as revealed by a widening of the *Ge-N-Si*Ph$_3$ angles [*Ge-N-Si*Ph$_3$ angles = 133.22(8) and 136.91(8)°] relative to in the less-hindered precursor **5** [121.13(8) and 127.42(8)°]. This effect is in stark contrast to the sulfido-dimer **8** where little perturbation of the Dipp groups is observed relative to the free germylene **3**. It is tempting to postulate that the addition of bulk to the aryl groups in **9** would result in further repulsion between the $\mathrm{SiAr_3}$ units and a steric preference for monomeric species with discrete Ge═O and Ge═S double bonds. Fortunately the synthesis of related ligands featuring substituted $\mathrm{SiAr_3}$ groups should be feasible,[28] thus enabling us to directly test our hypothesis in the near future.

Conclusions

A series of low-coordinate group 14 complexes featuring sterically encumbered bis(amido)silyl ligands has been reported. The ligand systems employed are hindered enough to facilitate the isolation of rigorously monomeric, two-coordinate germylenes and stannylenes, and preliminary work indicates that these species undergo clean chalcogen-transfer chemistry with $\mathrm{Me_3NO}$ and $\mathrm{S_8}$ to give centrosymmetric dimers with $\mathrm{Ge_2E_2}$ cores (E = O and S). The structural data in this paper suggests that [NSiN]$^{\mathrm{SiPh_3}}$ and related ligands featuring modified triarylsilyl groups would be useful for supporting low-coordination environments involving transition-metal elements.[29] Consequently, we are currently exploring this avenue of study in our laboratory.

---

(23) Khabashesku, V. N.; Boganov, S. E.; Kudin, K. N.; Margrave, J. L.; Nefedov, O. M. *Organometallics* **1998**, *17*, 5041.

(24) (a) Barrau, J.; Rima, G.; Lavayssière, H.; Dousse, G.; Satgé, J. *J. Organomet. Chem.* **1983**, *246*, 227. (b) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 1087. (c) Weidenbruch, M.; Sturmann, M.; Kilian, H.; Pohl, S.; Saak, W. *Chem. Ber.* **1997**, *130*, 735. (d) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *J. Organomet. Chem.* **2001**, *636*, 130. (e) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Organomet. Chem.* **2004**, *689*, 1337.

(25) Cordero, B.; Gómez, V.; Platero-Plats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(26) (a) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811.

(27) For reports concerning base-stabilized germanethiones, see: (a) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed.* **1989**, *28*, 1237. (b) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457.

(28) (a) Steele, A. R.; Kipping, F. S. *J. Chem. Soc.* **1929**, 357. (b) Maruoka, K.; Ito, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975. (c) Osakada, K.; Koizumi, T.; Sarai, S.; Yamamoto, T. *Organometallics* **1998**, *17*, 1868. (d) Lambert, J. B.; Lin, L. *J. Org. Chem.* **2001**, *66*, 8537.

(29) (a) Tsai, Y.-C.; Lin, Y.-M.; Yu, J.-S. K.; Hwang, J.-K. *J. Am. Chem. Soc.* **2006**, *128*, 13980. (b) Tsai, Y.-C.; Lu, Y.-M.; Lin, Y.-M.; Hwang, J.-K.; Yu, J.-S. *Chem. Commun.* **2007**, 4125.

Table 2. Crystallographic Data for Compounds **6**−**9**

	6	**7**	**8**	**9**
empirical formula	$C_{42}H_{44}N_2Si_3Sn$	$C_{68}H_{116}Ge_2N_4O_4Si_2$	$C_{64}H_{106}Ge_2N_4OS_2Si_2$	$C_{92}H_{108}Ge_2N_4O_2S_2Si_6$
fw	779.75	1255.01	1213.01	1679.66
cryst dimens (mm^3)	0.46 × 0.24 × 0.08	0.49 × 0.45 × 0.12	0.49 × 0.45 × 0.12	0.52 × 0.45 × 0.40
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	P-1	$P2_1/n$	P-1
unit cell dimensions				
a (Å)	8.6497(7)	12.8221(6)	14.0842(6)	11.766(2)
b (Å)	25.761(2)	15.7103(7)	14.8807(7)	13.955(3)
c (Å)	17.1292(13)	19.1054(9)	16.6170(8)	15.759(3)
α (°)		82.9780(10)		65.862(2)
β (°)	91.3450(10)	78.9340(10)	105.8690(10)	72.296(2)
γ (°)		79.303(10)		71.013(2)
V (Å^3)	3815.8(5)	3696.4(3)	3349.9(3)	2188.5(7)
Z	4	4	2	1
D (g cm^{-3})	1.357	1.128	1.203	1.274
abs coeff (mm^{-1})	0.796	0.890	1.036	0.866
T (K)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (°)	55.06	50.50	55.10	55.30
total data	33 162	16 911	29 458	19 736
unique data (R_{int})	8760 (0.0228)	16 911 (0.0323)	7700 (0.0156)	10 089 (0.0096)
observed data [$I > 2\sigma(I)$]	7616	13 235	7028	9505
params	433	696	375	530
R_1 [$I > 2\sigma(I)$]^a	0.0284	0.0411	0.0211	0.0313
wR_2 [all data]^a	0.0787	0.1229	0.0582	0.0903
difference map $\Delta\rho$ (e$^-$ Å^{-3})	0.559/−0.695	1.164/−0.584	0.444/−0.197	0.995/−0.330

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Experimental Section

General. All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[30] manufactured by Innovative Technology, Inc., degassed (freeze−pump−thaw method), and stored under an atmosphere of nitrogen prior to use. Triphenylchlorosilane, *n*-butyl lithium (2.5 M solution in hexanes), $GeCl_2 \cdot$dioxane, $SnCl_2$, elemental sulfur, 2,6-diisopropylaniline, and lithium amide were purchased from Aldrich and used as received. Dichlorodiisopropylsilane was obtained from Gelest, degassed (freeze−pump−thaw), and stored over molecular sieves under an N_2 atmosphere prior to use. Anhydrous trimethylamine *N*-oxide was recrystallized from dry and degassed DMF (−30 °C). LiNHDipp (Dipp = 2,6-$^i Pr_2C_6H_3$) was prepared according to a literature procedure.[31] ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra were recorded on Varian Inova-400 spectrometer and referenced externally to $SiMe_4$ (^{1}H, ^{13}C{^{1}H}, and ^{29}Si) and $SnMe_4$ (^{119}Sn). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded using Nic-Plan FTIR microscope. Melting points were obtained in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray Crystallography. Crystals of appropriate quality for X-ray diffraction studies were removed either from a Schlenk tube under a stream of nitrogen or a vial (glovebox) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen.[32] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα radiation, with the crystal cooled to −100 °C. The data were corrected for absorption[33] through use of a multiscan model (SADABS[34] [**2**, **5**, **6**] or TWINABS[35] [**7**]) or through Gaussian integration from indexing of the crystal faces (**1**, Li_2[NSiN]^{Dipp}, **3**, **4**, **8**, **9**). Structures were solved using the direct methods programs SHELXS-97[36] (**1**, Li_2[NSiN]^{Dipp}, **2**, **7**, **9**) and SIR97[37] (**5**, **6**, **8**) or the Patterson search/structure expansion facilities within the DIRDIF-2008[38] program system (**3**, **4**). Refinements were completed using the program SHELXL-97.[31] Hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon or nitrogen atoms and were given thermal parameters 20% greater than those of their parent atoms. See Tables 1 and 2 for a listing of crystallographic data.

Special Refinement Conditions. Compound **7**: The crystal used for data collection exhibited nonmerohedral twinning. Both components were indexed with the program CELL_NOW.[39] The second twin component can be related to the first component by a 180° rotation about the [1 0 0] axis in reciprocal space and the [1 −0.135 −0.144] axis in real space. Integration intensities for the reflections from the two components were written into a SHELXL-97 HKLF 5 reflection file with the data integration program SAINT (version 7.68 A)[40] using all reflection data (exactly and partially overlapped and nonoverlapped). The following restraints were applied to the disordered solvent Et_2O molecules: O−C, 1.43(1); C−C, 1.53(1); C···C, 2.34(2); and O···C, 2.42(2) Å.

Compound **9**: The following restraints were applied to the disordered solvent Et_2O molecules: O−C, 1.430(4); C−C, 1.530(4); C···C, 2.340(8); and O···C, 2.420(8) Å.

---

(30) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(31) Patton, J. T.; Feng, S. C.; Abboud, K. A. *Organometallics* **2001**, *20*, 3399.

(32) Hope, H. *Prog. Inorg. Chem.* **1995**, *43*, 1.

(33) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(34) Sheldrick, G. M. *SADABS*, version 2008/1; Universität Göttingen: Göttingen, Germany, 2008.

(35) Sheldrick, G. M. *TWINABS*, version 2008/2; Universität Göttingen: Göttingen, Germany, 2008.

(36) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(37) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(38) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. *DIRDIF-2008*; Crystallography Laboratory, Radboud University: Nijmegen, The Netherlands, 2008.

(39) Sheldrick, G. M. *CELL_NOW*, version 2008/2; Universität Göttingen: Göttingen, Germany, 2008.

(40) Sheldrick, G. M. *SAINT*, version 7.68A; Bruker AXS Inc.: Madison, WI, 2008.

Synthetic Procedures. Preparation of Ph_3Si-NH_2. [4] Thirty mL of THF was added to a precooled mixture of Ph_3SiCl (6.02 g, 20.4 mmol) and $LiNH_2$ (0.519 g, 22.4 mmol) at −78 °C. The reaction mixture was then warmed to room temperature and stirred overnight to eventually yield a pale-pink solution. The solvent was then removed under vacuum to give an off-white oil. Addition of 50 mL dry diethyl ether to the oil resulted in the precipitation of a white solid (presumably LiCl), and the mixture was filtered using a filter-tipped cannula. The solvent was then removed from the colorless filtrate to give a white solid that was recrystallized from hexane (ca. −30 °C) to give pure $Ph_3Si{-}NH_2$ as a colorless solid (4.5 g, 80% yield). ^1H NMR (C_6D_6): δ 0.75 (br, 2H, $-NH_2$), 7.16−7.19 (m, 9H, Ar*H*), and 7.62−7.64 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 128.1 (ArC), 129.8 (ArC), 135.6 (ArC), and 137.3 (ArC). NMR spectroscopic data were also obtained in $CDCl_3$ and matched those reported previously.[4]

Preparation of $(DippNH)_2Si^iPr_2$ (1). To a white slurry of LiNHDipp (1.67 g, 9.1 mmol) in 35 mL of Et_2O at −78 °C was added dropwise $^iPr_2SiCl_2$ (0.85 mL, 4.7 mmol). The reaction mixture was subsequently warmed to room temperature and stirred for 6 h. The resulting white slurry was filtered with a filter-tipped cannula to give a clear colorless solution. Concentration of the filtrate to ca. 20 mL followed by cooling to ca. −30 °C produced large colorless blocks of **1** after 2 days (1.16 g, 55%); these crystals were of suitable quality for X-ray crystallography. ^1H NMR (C_6D_6): δ 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$, $-Si^iPr_2-$), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 24H, $CH(CH_3)_2$, Dipp), 1.23 (septet, $^3J_{HH}$ = 6.6 Hz, 2H, $CH(CH_3)_2$, $-Si^iPr_2-$), 2.93 (s, 2H, N*H*), 3.67 (septet, $^3J_{HH}$ = 6.6 Hz, 4H, $CH(CH_3)_2$, Dipp), and 7.06−7.14 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.3 ($CH(CH_3)_2$, $-Si^iPr_2-$), 18.5 ($CH(CH_3)_2$, $-Si^iPr_2-$), 24.0 ($CH(CH_3)_2$, Dipp), 28.6 ($CH(CH_3)_2$, Dipp), 123.7 (ArC), 124.0 (ArC), 140.1 (ArC), and 143.6 (ArC). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −11.8. Mp (°C): 104−106. IR (FT-IR microscope): 3394 cm^{-1} (m, ν(N−H)). Anal. calcd for $C_{30}H_{50}N_2Si$: C, 77.19; H, 10.80; N, 6.00. Found: C, 77.17; H, 10.98; N, 6.05.

Synthesis of $(Ph_3SiNH)_2Si^iPr_2$ (2). To a solution of Ph_3SiNH_2 (2.53 g, 9.14 mmol) in 30 mL dry diethyl ether was added dropwise one equiv of ^{n}BuLi (3.66 mL, 9.15 mmol, 2.5 M solution in hexanes) at 0 °C. The reaction mixture was then warmed at room temperature and stirred for 3 h. The resulting white slurry was cooled at −78 °C, then 0.82 mL of $Cl_2Si^iPr_2$ (0.5 equiv., 4.57 mmol) was added dropwise. After which the reaction was warmed to room temperature and stirred overnight. The resulting mixture was filtered through Celite to give pale-orange colored solution, and subsequent removal of volatiles afforded an orange-colored oil that was recrystallized from diethyl ether (−35 °C) to give colorless crystals of **2** after 3 days (2.05 g, 67%). ^1H NMR (C_6D_6): δ 0.69 (septet, $^3J_{HH}$ = 7.6 Hz, 2H, $CH(CH_3)_2$, $-Si^iPr_2-$), 0.95 (d, $^3J_{HH}$ = 7.6 Hz, 12H, $CH(CH_3)_2$, $-Si^iPr_2-$), 1.06 (br, 2H, N*H*), 7.13−7.18 (m, 18H, Ar*H*), and 7.71−7.74 (m, 12H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.4 ($CH(CH_3)_2$, $-Si^iPr_2-$), 18.5 ($CH(CH_3)_2$, $-Si^iPr_2-$), 128.1 (Ar*C*), 129.9 (Ar*C*), 136.1 (Ar*C*), and 137.3 (Ar*C*). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): −18.2 (s, $-SiPh_3$), 1.2 (s, $-Si^iPr_2-$). Mp (°C): 121−123. IR (FT-IR microscope): 3334 cm^{-1} (m, ν(N−H)). Anal. calcd for $C_{42}H_{46}N_2Si_3$: C, 76.08; H, 6.99; N, 4.22. Found: C, 75.82; H, 6.82; N, 4.22.

Preparation of $[^iPr_2Si(NDipp)_2]Li_2\cdot 3THF$, $\{Li_2[NSiN]^{Dipp}\cdot 3THF\}$. Compound **1** (0.163 g, 0.35 mmol) was dissolved in 5 mL of hexanes, and this solution was cooled to −35 °C. To this solution was added ^{n}BuLi (2.5 M solution in hexanes, 280 μL, 0.70 mmol), and stirring of the reaction mixture for 30 min resulted in the formation of a white slurry. THF (1 mL) was then added, followed by stirring for 30 min to yield a pale-yellow, clear solution. The volume of the solution was then concentrated to ca. 2 mL, and subsequent cooling to −35 °C resulted in the formation of clear crystals of suitable quality for X-ray analysis. This analysis revealed the presence of the mixed dilithio adduct, $[\{^iPr_2Si(NDipp)_2\}Li(THF)_2][Li(THF)_4]$. These crystals rapidly released THF upon exposure to vacuum to yield a pure material containing three equivalents of THF per $[NSiN]^{Dipp}$ ligand. Yield of $\{Li_2[NSiN]^{Dipp}\cdot 3THF\}$ = 0.238 g (0.34 mol, 98%). ^1H NMR (C_6D_6): δ 1.18 (m, 12H, THF), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 24H, $CH(CH_3)_2$, Dipp), 1.36 (d, $^3J_{HH}$ = 7.2 Hz, 12H, $CH(CH_3)_2$, $-Si^iPr_2-$), 1.56 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, $CH(CH_3)_2$, $-Si^iPr_2-$), 3.24 (m, 12H, THF), 4.04 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$, Dipp), 6.90 (t, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), and 7.24 (d, $^3J_{HH}$ = 7.5 Hz, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.9 ($CH(CH_3)_2$, $-Si^iPr_2-$), 21.9 ($CH(CH_3)_2$, $-Si^iPr_2-$), 25.1 ($CH(CH_3)_2$, Dipp), 25.5 (β-C (THF)), 27.4 ($CH(CH_3)_2$, Dipp), 68.1 (α-C (THF)), 115.1 (Ar*C*), 123.3 (Ar*C*), 141.7 (Ar*C*), and 157.1 (Ar*C*). Mp (°C) 132−134. Anal. calcd for $\{Li_2[NSiN]^{Dipp}\cdot 3THF\}$ $C_{42}H_{72}O_3N_2Li_2Si$: C, 72.58; H, 10.44; N, 4.03. Found: C, 72.54; H, 10.41; N, 4.03.

Preparation of $[\{^iPr_2Si(NDipp)_2\}Ge:]$, $[NSiN]^{Dipp}Ge$ (3). To a solution of **1** (0.233 g, 0.50 mmol) in 6 mL of Et_2O was added dropwise two equiv of ^{n}BuLi (2.5 M solution in hexanes, 0.40 mL, 1.00 mmol) at −35 °C. The reaction mixture was warmed to room temperature and stirred for 1.5 h to give a pale-yellow solution. This solution was then added dropwise to a cold (−35 °C) slurry of $GeCl_2\cdot$dioxane (0.115 g, 0.50 mmol) in 5 mL of Et_2O. Upon the addition of the lithiated ligand, a purple color was generated which dissipated rapidly upon stirring. After the addition was complete, an orange solution was seen over a white precipitate. The reaction was then warmed to ambient temperature and stirred overnight. Filtration of the resulting mixture yielded an orange filtrate from which **3** was isolated as a tan-colored solid upon removal of the volatiles (0.251 g, 94%). X-ray quality crystals of **3** (colorless plates) were subsequently obtained by slowly cooling a solution of **3** in Et_2O to −35 °C (2 days). ^1H NMR (C_6D_6): δ 1.02 (d, $^3J_{HH}$ = 7.2 Hz, 12H, $CH(CH_3)_2$, Dipp), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 24H, $CH(CH_3)_2$, Dipp, and $^iPr_2Si$, coincident; confirmed by an $^1H-^{13}C$ HMQC correlation experiment), 1.71 (septet, $^3J_{HH}$ = 6.8 Hz, 2H, $CH(CH_3)_2$, $-Si^iPr_2-$), 3.80 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$, Dipp), 7.10 (m, 2H, Ar*H*), and 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.2 ($CH(CH_3)_2$, Dipp), 23.5 ($CH(CH_3)_2$, Dipp), 24.2 ($CH(CH_3)_2$, $-Si^iPr_2-$), 28.5 ($CH(CH_3)_2$, $-Si^iPr_2-$), 123.5 (ArC), 124.4 (ArC), 142.6 (ArC), and 144.1 (ArC). Mp (°C): 171−173. Anal. calcd for $C_{30}H_{48}GeN_2Si$: C, 67.05; H, 9.00; N, 5.21. Found: C, 66.84; H, 9.29; N, 5.09.

Preparation of $[\{^iPr_2Si(NDipp)_2\}Sn:]$, $[NSiN]^{Dipp}Sn$ (4). To a solution of **1** (0.270 g, 0.58 mmol) in 6 mL of Et_2O was added dropwise a solution of ^{n}BuLi (2.5 M solution in hexanes, 0.463 mL, 1.16 mmol). The resulting colorless solution was then stirred for 1.5 h and added dropwise to a cold (−35 °C) slurry of $SnCl_2$ (0.128 g, 0.68 mmol) in 4 mL of Et_2O. After the addition was complete (time of addition = 15 min.), a red-brown solution was observed over unreacted $SnCl_2$. The reaction mixture was then warmed to ambient temperature and stirred for 2 days. The resulting orange slurry was filtered through Celite, and the volatiles were removed from the orange filtrate collected to give a yellow solid (0.336 g, quantitative yield). Crystals of suitable for X-ray crystallography were subsequently grown by cooling a saturated solution of **4** in Et_2O to −35 °C to afford yellow rods. ^1H NMR (C_6D_6): δ 1.04 (d, $^3J_{HH}$ = 7.6 Hz, 12H, $CH(CH_3)_2$, Dipp), 1.28 (br, 24H, $CH(CH_3)_2$, Dipp and $^iPr_2Si$, coincident; confirmed by an $^1H-^{13}C$ HMQC correlation experiment), 1.57 (septet, $^3J_{HH}$ = 7.6 Hz, 2H, $CH(CH_3)_2$, $-Si^iPr_2-$), 3.90 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, $CH(CH_3)_2$, Dipp), 7.02 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), and 7.20 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.4 ($CH(CH_3)_2$, Dipp), 23.3 ($CH(CH_3)_2$, Dipp), 24.1 ($CH(CH_3)_2$, $-Si^iPr_2-$), 28.0 ($CH(CH_3)_2$, $-Si^iPr_2-$), 123.2 (ArC), 123.4 (ArC), 143.6 (ArC), and 144.8 (ArC). $^{119}Sn\{^1H\}$ NMR (C_6D_6): δ 536. Mp (°C): 129−131. Anal. calcd for $C_{30}H_{48}N_2SiSn$: C, 61.75; H, 8.29; N, 4.80. Found: C, 60.22; H, 8.65; N, 4.41.

Synthesis of [{^{i}Pr$_2$Si(NSiPh$_3$)$_2$}Ge:], [NSiN]^{SiPh3}Ge (5). To a solution of **2** (95 mg, 0.14 mmol) in 10 mL of Et_2O was added dropwise two equiv of ^{n}BuLi (2.5 M solution in hexanes, 0.120 mL, 0.30 mmol) at −35 °C. The reaction was warmed to room temperature and stirred overnight to give a yellow solution. The solution was then added dropwise to a cold (−35 °C) slurry of $GeCl_2 \cdot$dioxane (0.035 g, 0.15 mmol) in 5 mL of Et_2O. The solution turned red-yellow immediately, and the formation of a white precipitate was observed. The reaction was then warmed to ambient temperature and stirred overnight. Filtration of the resulting mixture yielded a clear yellow filtrate from which **5** was isolated as a yellow-colored solid upon removal of the volatiles (88 mg, 84%). X-ray quality crystals (colorless) of **5** were subsequently obtained by slowly cooling a solution in Et_2O (−35 °C, 5 days). ^{1}H NMR (C_6D_6): δ 0.81 (septet, $^3J_{HH}$ = 6.4 Hz, 2H, C*H*(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 0.87 (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH(C*H*$_3$)$_2$, −Si^{i}Pr$_2$−), 7.15−7.17 (m, 18H, Ar*H*), and 7.78−7.80 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 15.0 (*C*H(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 17.0 (CH(*C*H$_3$)$_2$, −Si^{i}Pr$_2$−), 128.2 (Ar*C*), 129.9 (Ar*C*), 136.4 (Ar*C*), and 137.3 (Ar*C*). Mp (°C): 196−198. Anal. calcd for $C_{42}H_{44}GeN_2Si_3$: C, 68.75; H, 6.04; N, 3.82. Found: C, 68.76; H, 5.61; N, 3.79.

Synthesis of [{^{i}Pr$_2$Si(NSiPh$_3$)$_2$}Sn:], [NSiN]^{SiPh3}Sn (6). To a solution of **2** (0.100 g, 0.15 mmol) in 10 mL of Et_2O was added dropwise two equiv of ^{n}BuLi (2.5 M solution in hexanes, 0.120 mL, 0.30 mmol) at −35 °C. The reaction was warmed to room temperature and stirred overnight to give a yellow solution. The solution was then added dropwise to a cold (−35 °C) slurry of $SnCl_2$ (0.029 g, 0.15 mmol) in 5 mL of Et_2O. The reaction was then warmed to ambient temperature and stirred overnight to give a bright-yellow solution over white precipitate. Filtration of the resulting mixture yielded a bright-yellow filtrate from which **6** was isolated as a yellow-colored solid upon removal of the volatiles (93 mg, 79%). Crystals of **6** (yellow blocks) were grown by cooling a saturated ether solution to −35 °C for 5 days. ^{1}H NMR (C_6D_6): δ 0.80 (septet, $^3J_{HH}$ = 7.2 Hz, 2H, C*H*(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 0.94 (d, $^3J_{HH}$ = 7.2 Hz, 12H, CH(C*H*$_3$)$_2$, -Si^{i}Pr$_2$-), 7.16−7.19 (m, 18H, Ar*H*), and 7.77−7.79 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 15.8 (*C*H(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 17.5 (CH(*C*H$_3$)$_2$, −Si^{i}Pr$_2$−), 128.1 (Ar*C*), 129.7 (Ar*C*), 136.3 (Ar*C*), and 138.9 (Ar*C*). ^{119}Sn{^{1}H} NMR (C_6D_6): δ 527. Mp (°C): 113−115. Anal. calcd for $C_{42}H_{44}N_2Si_3Sn$: C, 64.69; H, 5.69; N, 3.59. Found: C, 65.02; H 5.81; N 3.57.

Preparation of [{^{i}Pr$_2$Si(NDipp)$_2$}Ge(μ-O)]$_2$, {[NSiN]^{Dipp}-Ge(μ-O)}$_2$ (7). Toluene (10 mL) was added to a mixture of **3** (60 mg, 0.11 mmol) and trimethylamine *N*-oxide (8.3 mg, 0.12 mmol) in a 20 mL scintillation vial in a glovebox. The reaction mixture was stirred overnight at ambient temperature and resulted in the formation of a clear pale-yellow solution. The solution was filtered through Celite, and volatiles were removed in vacuo to obtain **7** (colorless solid), which was recrystallized from hexanes (−35 °C, 7 days). Yield: 48 mg (78%). ^{1}H NMR (C_6D_6): δ 0.94 (d, $^3J_{HH}$ = 7.5 Hz, 24H, CH(C*H*$_3$)$_2$, −Si^{i}Pr$_2$−), 1.04 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$, Dipp), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$), Dipp), 1.58 (septet, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 3.77 (septet, $^3J_{HH}$ = 6.9 Hz, 8H, C*H*(CH$_3$)$_2$, Dipp), and 6.99−7.10 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 19.3 (*C*H(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 19.0 (CH(*C*H$_3$)$_2$, −Si^{i}Pr$_2$−), 26.2 (*C*H(CH$_3$)$_2$, Dipp), 28.4 (CH(*C*H$_3$)$_2$, Dipp), 123.9 (Ar*C*), 125.7 (Ar*C*), 138.2 (Ar*C*), and 146.9 (Ar*C*). Mp (°C): > 300. Anal. calcd. for $C_{60}H_{96}Ge_2N_4O_2Si_2$ C, 65.11; H 8.74; N, 5.06. Found: C, 64.02; H, 8.68; N, 5.03.

Preparation of [{^{i}Pr$_2$Si(NDipp)$_2$}Ge(μ-S)]$_2$, {[NSiN]^{Dipp}-Ge(μ-S)}$_2$ (8). Ten mL of dry ether was added to a mixture of **4** (60 mg, 0.11 mmol) and one equiv of sulfur (3.7 mg, 0.12 mmol) in a 20 mL scintillation vial in a glovebox. The reaction mixture was stirred overnight at ambient temperature, which resulted in the formation of a clear yellow solution. The solution was filtered through Celite, and volatiles were removed in vacuo to give white solid, which was recrystallized from a toluene/hexanes mixture (5:1 ratio, −35 °C, 10 days). Yield of **8**: 58 mg (91%). ^{1}H NMR (C_6D_6): δ 0.91 (d, $^3J_{HH}$ = 7.5 Hz, 24H, C*H*(C*H*$_3$)$_2$, −Si^{i}Pr$_2$−), 1.20 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(C*H*$_3$)$_2$, Dipp), 1.29 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(C*H*$_3$), Dipp), 1.44 (septet, $^3J_{HH}$ = 7.5 Hz, 4H, C*H*-(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 3.96 (septet, $^3J_{HH}$ = 7.0 Hz, 8H, C*H*(CH$_3$)$_2$, Dipp), and 6.99−7.17 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 15.6 (*C*H(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 18.7 (CH(*C*H$_3$)$_2$, −Si^{i}Pr$_2$−), 27.6 (*C*H(CH$_3$)$_2$, Dipp), 28.2 (CH(*C*H$_3$)$_2$, Dipp), 124.2 (Ar*C*), 125.6 (Ar*C*), 138.3 (Ar*C*), and 147.6 (Ar*C*). Mp (°C): > 300. Anal. calcd for $C_{60}H_{96}Ge_2N_4S_2Si_2$: C, 63.27; H, 8.50; N, 4.92. Found: C, 63.55; H, 8.80; N, 4.59.

Synthesis of [{^{i}Pr$_2$Si(NSiPh$_3$)$_2$}Ge(μ-S)]$_2$, {[NSiN]^{SiPh3}-Ge(μ-S)}$_2$ (9). Diethyl ether (10 mL) was added to a mixture of **5** (51 mg, 0.070 mmol) and sulfur (2.2 mg, 0.069 mmol) in a 20 mL scintillation vial in a glovebox. The reaction mixture was stirred for 24 h and resulted in the formation of white slurry. The reaction was filtered, and the volatiles were removed from the filtrate in vacuo to give a white solid. X-ray quality crystals of **9** were obtained by redissolving the product in Et_2O (8 mL), followed by layering with hexanes (−35 °C, 9 days). Yield: 18 mg (35%). ^{1}H NMR (C_6D_6): δ −0.02 (septet, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 0.51 (d, $^3J_{HH}$ = 7.5 Hz, 12H, CH(C*H*$_3$)$_2$, −Si^{i}Pr$_2$−), 1.15 (septet, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*(CH$_3$)$_2$, −Si^{i}Pr$_2$−), 1.28 (d, $^3J_{HH}$ = 7.5 Hz, 12H, CH(C*H*$_3$)$_2$, −Si^{i}Pr$_2$−), 6.97 (t, $^3J_{HH}$ = 7.5 Hz, 24H, Ar*H*), 7.12 (t, $^3J_{HH}$ = 7.5 Hz, 12H, Ar*H*), and 7.65 (d, $^3J_{HH}$ = 7.5 Hz, 24H, Ar*H*). The ^{13}C{^{1}H} NMR spectrum was uninformative due to the low solubility of the product. Mp (°C): > 300. Anal. calcd for $C_{92}H_{108}Ge_2N_4O_2S_2Si_6$ (**9**$\cdot$2 Et_2O): C, 65.80; H 6.49; N, 3.34. Found: C, 65.35; H, 6.53; N, 3.23.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council (NSERC-Discovery Grant) and the Canada Foundation for Innovation (CFI-LOF Grant). In addition the authors would like to thank the University of Alberta for start-up funding and Alberta Innovates for an Alberta Ingenuity New Faculty Award (E.R.) and a Ph.D. fellowship (S.M.I.A). We also thank Mr. Mark Miskolzie for assistance with acquiring ^{119}Sn{^{1}H} NMR data.

Supporting Information Available: X-ray crystallographic data in CIF format and the molecular structure of Li$_2$-[NSiN]$^{Dipp}\cdot$6THF along with selected bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.