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Expanding the Steric Coverage Offered by Bis(amidosilyl) Chelates: Isolation of Low-Coordinate *N*-Heterocyclic Germylene Complexes

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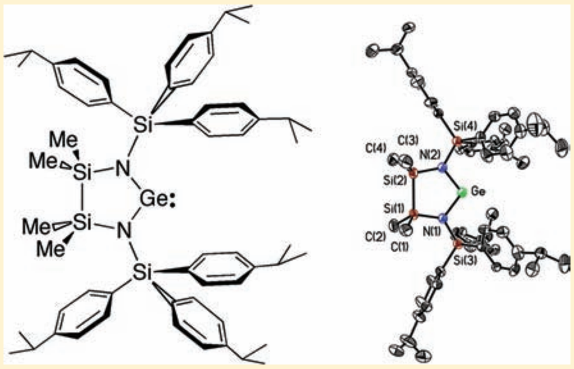
Supporting Information

ABSTRACT: The synthesis and coordination chemistry of a series of dianionic bis(amido)silyl and bis(amido)disilyl, [NSiN] and [NSiSiN], chelates with N-bound aryl or sterically modified triarylsilyl ($SiAr_3$) groups is reported. In order to provide a consistent comparison of the steric coverage afforded by each ligand construct, various two-coordinate *N*-heterocyclic germylene complexes featuring each ligand set were prepared and oxidative S-atom transfer chemistry was explored. In the cases where clean oxidation transpired, sulfido-bridged centrosymmetric germanium(IV) dimers of the general form $[LGe(\mu\text{-}S)]_2$ (L = bis(amidosilyl) ligands) were obtained in lieu of the target monomeric germanethiones with discrete Ge═S double bonds. These results indicate that the reported chelates possess sufficient conformational flexibility to allow for the dimerization of LGe═S units to occur. Notably, the new triarylsilyl groups $(4\text{-}RC_6H_4)_3Si$— (R = ^{t}Bu and ^{i}Pr) still offer considerably expanded degrees of steric coverage relative to the parent congener, —$SiPh_3$, and thus the use of substituted triarylsilyl groups within ligand design strategies should be a generally useful concept in advancing low-coordination main group and transition-metal chemistry.



■ INTRODUCTION

The preparation of complexes that contain ligands with high degrees of steric coverage has had a tremendous influence in expanding the range of chemical transformations that can be mediated by inorganic elements.[1] A parallel strategy that is prominent in synthetic inorganic chemistry is the design of ligand classes with readily modifiable steric and electronic properties, thus enabling key structure−function relationships to be elucidated in a rapid manner. As a consequence, breakthroughs in ligand development can translate into the discovery of novel bond activation processes[2] and often provides access to new bonding environments throughout the Periodic Table.[3]

With the above-mentioned concepts in mind, there has been considerable focus on exploring the synthesis and coordination chemistry of complexes supported by silylamido chelates. Silylamido ligands each contain Si−N linkages as part of their chelate backbones, and hallmarks of these ligands include their ease of synthesis and the ability to alter the ligand donor properties by changing the substituent bound at either the intraligand silicon or nitrogen centers.[1e,4,5]

Motivated by our prior work involving formally dianionic bis(amido)silyl [NSiN] ligands,[6] we now introduce a series of [NSiSiN] chelates bearing elongated tetramethyldisilyl, $-SiMe_2-SiMe_2-$, backbones in conjunction with new sterically expanded triarylsilyl, $(4\text{-}RC_6H_4)_3Si-$, umbrella-shaped moieties (R = ^{t}Bu and ^{i}Pr).[7] By combining the greater radial bulk offered by the new triarylsilyl side groups with the tighter steric pocket inherent to an [NSiSiN] chelate, we hope to prepare low-coordinate complexes with concomitantly unique forms of chemical bonding and/or reactivity. Specifically, this paper describes the preparation of reactive two-coordinate germylene complexes supported by new bulky silylamido ligands and subsequent atom transfer chemistry involving these low valent Ge(II) complexes and elemental sulfur.[8] A further rationale for exploring the coordination chemistry of Ge(II) is that germanium can be regarded as a steric atomic model for first row transition metals, thus the chemistry in this paper should serve as a guide for the future use of our sterically hindered silylamido ligands in the realm of d-block chemistry.

■ 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[9] manufactured by Innovative Technology, Inc., and degassed (freeze−pump−thaw method) and stored under an atmosphere of nitrogen prior to use. *n*-Butyl lithium (1.6 M solution in hexanes), $GeCl_2\cdot$dioxane, $SnCl_2$, $Li[NH_2]$, magnesium, iodine, and elemental sulfur were purchased from Aldrich and used as received. Dichloroditolylsilane and dichlorotetramethyldisilane were obtained from Gelest, degassed (freeze−pump−thaw), and

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Table 1. Crystallographic Data for Compounds 2−5

	2	3	4·tol·THF	5
empirical formula	$C_{28}H_{46}GeN_2Si_2$	$C_{28}H_{46}N_2Si_2Sn$	$C_{67}H_{108}Ge_2N_4SiOS_2Si_4$	$C_{27}H_{33}ClSi$
fw	539.44	585.54	1307.2	421.07
cryst dimens (mm^3)	0.61 × 0.29 × 0.18	0.64 × 0.53 × 0.22	0.32 × 0.10 × 0.07	0.48 × 0.40 × 0.37
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimensions				
a (Å)	13.5706(4)	9.1347(5)	9.960(2)	10.1381(3)
b (Å)	15.5783(5)	10.0168(5)	14.101(3)	11.5933(4)
c (Å)	14.5196(4)	19.1344(10)	15.228(3)	11.6907(4)
α (deg)	90	76.6557(5)	102.871(3)	83.9233(3)
β (deg)	97.2967(3)	86.6259(5)	93.857(3)	65.1785(3)
γ (deg)	90	66.6516(5)	107.097(2)	89.4459(3)
V (Å^3)	3044.69(13)	1562.99(14)	1972.6(8)	1239.19(7)
Z	4	2	1	2
ρ (g cm^{-3})	1.177	1.244	1.100	1.128
abs coeff (mm^{-1})	1.102	0.911	0.913	0.213
T (K)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	55.18	55.10	50.50	55.26
total data	26915	14072	14188	11052
unique data (R_{int})	7038 (0.0159)	7151 (0.0072)	7124 (0.0641)	5692 (0.0095)
obs data [$I > 2\sigma(I)$]	6181	6802	5240	5111
params	298	302	363	262
R_1 [$I > 2\sigma(I)$]^a	0.0250	0.0186	0.0870	0.0497
wR_2 [all data]^a	0.0763	0.0586	0.2703	0.1428
max/min $\Delta\rho$ (e$^-$ Å^{-3})	0.467/−0.309	0.531/−0.332	1.865/−1.461	0.963/−0.491

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

stored under an N_2 atmosphere prior to use. Anhydrous Me_3NO (Aldrich) was recrystallized from a dry and degassed DMF/hexanes mixture (−35 °C). 4-^{i}PrC_6H_4Br, 4-^{t}BuC_6H_4Br, Li[NHDipp] (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$), and MesCNO (Mes = 2,4,6-Me$_3$C$_6$H$_2$) were prepared according to literature procedures.[10−13] ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded with either Varian iNova-400 or iNova-500 spectrometers and referenced externally to SiMe$_4$ (^{1}H, ^{13}C{^{1}H}, and ^{29}Si). Elemental analyses and mass spectrometry were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded with a 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 from either a Schlenk tube under a stream of nitrogen, or from 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.[14] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo or Cu Kα radiation, with the crystal cooled to −100 °C. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXS-97[15] (compounds **2**, **4**, **5**, **7**, **12**, and **13**) and SIR97[16] (compound **3**), or using the Patterson search/structure expansion facilities within the DIRDIF-2008[17] and SHELXD[18] program suites (compound **2**). Refinements were completed using the program SHELXL-97.[15] 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 4:* The following distance restraints were applied to the solvent tetrahydrofuran molecules: O—C, 1.43(1); C—C, 1.53(1) Å. The solvent toluene molecule phenyl ring was constrained to be an idealized hexagon with C—C distances of 1.39 Å, and C22S—C27S and C26S—C27S distances restrained to be 2.51(2) Å.

Compound 7: The Si−C31A and Si−C31B distances (involving disordered positions for the ipso carbon of one of the 4-isopropylphenyl groups) were constrained to be equal (within 0.02 Å) during the refinement.

Compound 12: The geometries of the isopropyl groups defined by atoms C27B to C29B and C47B to C49B (the minor orientations) were restrained to be the same as that of C37 to C39. Additionally, the phenyl rings defined by atoms C21A to C26A, C21B to C26B, C31B to C36B, C41A to C46A, and C41B to C46B were constrained to be idealized hexagons with C−C distances of 1.39 Å.

Compound 13: Attempts to refine peaks of residual electron density as disordered or partial-occupancy hexane solvent molecules were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure as incorporated in *PLATON*.[19] A total solvent accessible void volume of 591 Å^3 with a total electron count of 89 (consistent with two molecules of solvent hexane or one molecule per asymmetric unit) was found in the unit cell. The C44B−C47B, C47B−C48B, and C47B−C49B distances were restrained to be 1.51(1) Å. The C17−C18A, C17−C19A, C17−C18B, and C17−C19B distances were restrained to be the same by the *SHELX* **SAME** instruction. Additionally, the phenyl ring defined by carbon atoms C41B to C46B was constrained to be an idealized hexagon with C−C distances of 1.39 Å.

Synthetic Procedures. *Preparation of (DippNH)$_2$Si$_2$Me$_4$ (1).*[20] To a solution of Li[NHDipp] (1.043 g, 5.69 mmol) in 10 mL of cold (−35 °C) Et$_2$O was added dropwise a cold (−35 °C) solution of ClSiMe$_2$SiMe$_2$Cl (0.532 g, 2.84 mmol) in 5 mL of Et$_2$O. The resulting mixture was slowly warmed to room temperature and stirred for 12 h to give a yellow solution over a white precipitate. The reaction mixture was then filtered through Celite and the volatiles were removed to yield **1** as a light yellow oil (1.300 g, 98%). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.25 (s, 12H, SiCH_3), 1.21 (d, 24H, $^3J_{HH}$ = 7.2 Hz, CH(CH_3)$_2$), 2.28 (s, 2H, NH), 3.47 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), and 7.07−7.18 (m, 6H, ArH). ^{13}C{^{1}H} NMR (100 MHz,

Table 2. Crystallographic Data for Compounds 7, 12, and 13

	7	12	13
empirical formula	$C_{27}H_{35}NSi$	$C_{55}H_{78}GeN_2Si_4$	$C_{148}H_{188}Ge_2N_4S_2Si_6$
fw	401.65	988.17	2400.86
cryst dimens (mm^3)	0.61 × 0.21 × 0.16	0.39 × 0.31 × 0.22	0.22 × 0.12 × 0.09
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
unit cell dimensions			
a (Å)	15.0786(16)	18.6549(5)	15.3279(11)
b (Å)	6.8829(7)	16.2623(4)	16.5942(12)
c (Å)	23.297(3)	21.0055(5)	16.8715(13)
α (deg)	90	90	62.851(3)
β (deg)	93.6135(14)	116.4250(10)	66.564(4)
γ (deg)	90	90	83.170(4)
V (Å^3)	2413.0(4)	5706.7(2)	3493.2(4)
Z	4	4	1
ρ (g cm^{-3})	1.106	1.150	1.141
abs coeff (mm^{-1})	0.110	1.800	1.668
T (K)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	52.80	138.88	140.40
total data	18635	28066	23551
unique data (R_{int})	4941 (0.0351)	10446 (0.0317)	12426 (0.0423)
obs data [$I > 2\sigma(I)$]	3734	8581	8900
params	352	694	696
R_1 [$I > 2\sigma(I)$]^a	0.0371	0.0675	0.0722
wR_2 [all data]^a	0.1018	0.1928	0.2328
max/min $\Delta\rho$ (e$^-$ Å^{-3})	0.238/−0.233	0.846/−1.623	1.279/−0.829

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

C_6D_6): δ = 1.1 ($SiCH_3$), 26.4 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 124.0 (ArC), 124.8 (ArC), 140.6 (ArC), and 144.7 (ArC). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = −7.9. IR (FT-IR microscope, cm^{-1}): 3384 [m, ν(N−H)]. Anal. calcd. for $C_{29}H_{51}N_2Si_2$: C, 71.98; H, 10.62; N, 5.79. Found: C, 71.04; H, 10.30; N, 5.76.

*Preparation of [($Me_2SiNDipp)_2Ge$:] **(2)**.* A solution of ^{n}BuLi (3.5 mL, 1.6 M solution in hexanes, 5.6 mmol) was slowly added to a solution of **1** (1.30 g, 2.80 mmol) in 6 mL of Et_2O at −35 °C. The resulting mixture was warmed to room temperature and stirred for 2 h, recooled to −35 °C, and then slowly added to a slurry of $GeCl_2$·dioxane (0.648 g, 2.80 mmol) in 7 mL of Et_2O. The reaction mixture was then warmed to room temperature and allowed to stir for 15 h to give an orange solution over a white precipitate (LiCl). Filtration of the mixture through Celite gave an amber solution, which afforded **2** as pale orange waxy solid upon removal of the volatiles (1.314 g, 88%). Recrystallization of **2** from hexanes/Et_2O at −35 °C resulted in the formation of large plate-shaped orange crystals of suitable quality for X-ray crystallography. ^1H NMR (400 MHz, C_6D_6): δ = 0.22 (s, 12H, $SiCH_3$), 1.17 (d, 12H, $^3J_{HH}$ = 7.2 Hz, $CH(CH_3)_2$), 1.29 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.55 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), and 7.08−7.18 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 0.8 ($SiCH_3$), 23.0 ($CH(CH_3)_2$), 27.5 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 123.9 (ArC), 125.5 (ArC), 139.6 (ArC), and 146.4 (ArC). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = −2.5. HR-MS, EI (m/z): calcd. for [M^+]: 540.24115. Found: 540.24176 (Δppm =1.1). Mp (°C) = ca. 80 (turns red), 126−132 (melts). Anal. calcd. for $C_{28}H_{46}GeN_2Si_2$: C, 62.34; H, 8.59; N, 5.19. Found: C, 62.02; H, 8.83; N, 4.86.

*Preparation of [($Me_2SiNDipp)_2Sn$:] **(3)**.* A solution of ^{n}BuLi (0.623 mL, 1.6 M solution in hexanes, 1.00 mmol) was slowly added to a solution of **1** (0.231 g, 0.50 mmol) in 5 mL of Et_2O at −35 °C. The resulting mixture was warmed to room temperature and stirred for 2 h, then recooled to −35 °C, and slowly added to a slurry of $SnCl_2$ (0.105 g, 0.55 mmol) in 5 mL of Et_2O. Afterward, the reaction mixture was warmed to room temperature and stirred for 15 h to give a deep yellow solution over a white precipitate (LiCl). Filtration of the mixture through Celite yielded a pale yellow solution, which afforded a pale yellow solid once the solvent was removed (0.266 g, 91%). This product was recrystallized from cold (−35 °C) Et_2O to give **3** as yellow rhomboid-shaped crystals. ^1H NMR (400 MHz, C_6D_6): δ = 0.27 (s, 12H, $SiCH_3$), 1.15 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.32 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.68 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 7.07−7.10 (m, 2H, ArH), and 7.19 (d, 4H, $^3J_{HH}$ = 8.0 Hz, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 2.2 ($SiCH_3$), 23.2 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 123.8 (ArC), 124.5 (ArC), 141.5 (ArC), and 145.4 (ArC). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = −2.2. HR-MS, EI (m/z): calcd. for [M^+]: 586.22217. Found: 586.22284 (Δppm =1.1). Mp (°C): 169−171. Anal. calcd for $C_{28}H_{46}N_2Si_2Sn$: C, 57.43; H, 7.92; N, 4.78. Found: C, 57.56; H, 8.06; N, 4.86.

*Preparation of [($Me_2SiNDipp)_2Ge(\mu$-S)]$_2$ **(4)**.* Elemental sulfur (8.3 mg, 0.26 mmol) and **2** (0.149 g, 0.261 mmol) were combined in 5 mL of Et_2O and the resulting reaction mixture was then stirred for 24 h. Removal of the volatiles yielded a white microcrystalline powder from which X-ray quality crystals of **4** (needles) were subsequently grown from a solution of toluene and THF at −35 °C (34 mg, 22%). ^1H NMR (400 MHz, C_6D_6): δ = 0.06 (s, 12H, $SiCH_3$), 1.04 (br, 12H, $CH(CH_3)_2$), 1.23 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 3.46 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), and 7.02−7.08 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ = 1.2 (br, $SiCH_3$), 26.3 ($CH(CH_3)_2$), 27.1 ($CH(CH_3)_2$), 28.2 ($CH(CH_3)_2$), 125.0 (ArC), 126.1 (ArC), 140.0 (ArC), and 148.3 (ArC). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = −2.5. Mp (°C): 215 (dec.). Anal. calcd. for $C_{56}H_{92}Ge_2N_4S_2Si_4$: C, 58.84; H, 8.11; N, 4.90; S: 5.61. Found: C, 58.84; H, 8.08; N, 4.82; S, 5.71.

*Synthesis of (4-^{i}Pr$C_6H_4)_3$SiCl **(5)**.* The Grignard reagent, (4-^{i}PrC_6H_4)MgBr was first prepared by slowly adding 4-^{i}PrC_6H_4Br (29.38 g, 0.148 mol) in 75 mL of THF (75 mL) to dried magnesium metal (4.20 g, 0.170 mol) in 75 mL of THF, followed by heating of the solvent to reflux overnight. The resulting brown solution of (4-^{i}PrC_6H_4)MgBr was then filtered into a separate flask and, then, slowly added via cannula to a solution of $SiCl_4$ (5.65 mL, 0.049 mol) in 50 mL of THF at −78 °C. A yellow-green solution was obtained which was then warmed to room temperature and heated to reflux for 2 days to yield a pale yellow solution. A 15 mL portion of 1,4-dioxane was then added to precipitate the MgX_2 byproduct (in the form of MgX_2·dioxane; X = Cl and/or Br), and the resulting heterogeneous mixture was filtered. Removal of the volatiles from the filtrate afforded a colorless solid that was recrystallized from hexanes (ca. 75 mL; −35 °C) to give **5** as colorless X-ray quality crystals (7.635 g, 36%). ^1H NMR (500 MHz, C_6D_6): δ = 1.07 (d, 18H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 2.63 (septet, 3H, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 7.07 (d, 6H, $^3J_{HH}$ = 8.0 Hz, ArH), and 7.77 (d, 6H, $^3J_{HH}$ = 8.0 Hz, ArH). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 23.8 ($CH(CH_3)_2$), 34.4 ($CH(CH_3)_2$), 126.6 (ArC), 131.0 (ArC), 136.0 (ArC), and 151.6 (ArC). $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6): δ = 1.9. HR-MS, EI (m/z): calcd. for [M]$^+$: 422.20105. Found: 422.20269 (Δppm = 0.3). Mp (°C): 156−168. Anal. calcd. for $C_{27}H_{33}ClSi$: C, 77.01; H, 7.90. Found: C, 76.79; H, 7.50.

*Synthesis of (4-^{t}Bu$C_6H_4)_3$SiCl **(6)**.* A 500 mL three-necked round-bottom flask equipped with a magnetic stirring bar and a condenser was flushed with nitrogen and then charged with dried magnesium turnings (1.1 g, 0.046 mol), 10 mL of THF, and a small crystal of iodine. The mixture was stirred at room temperature until the color of the iodine faded away and a solution of 1-bromo-4-tert-butylbenzene (6.0 g, 0.028 mol) in 20 mL of THF was then added dropwise. The resulting brown solution was refluxed overnight, cooled to room temperature, and then filtered to remove unreacted magnesium. This solution of aryl magnesium bromide was then added dropwise to a cold (−78 °C) solution of $SiCl_4$ (1.07 mL, 9.35 mmol) in 20 mL of THF. The reaction mixture was allowed to warm to room temperature and then refluxed overnight to yield a pale green solution. Removal of the volatiles from the solution afforded a white powder that was redissolved in 15 mL of THF, and then, 6 mL of 1,4-dioxane was added. The resulting slurry was stirred for 2 h, and the precipitates were allowed to settle; then, the mother liquor was filtered through Celite to yield a colorless filtrate. Removal of the volatiles from the filtrate gave **6** as a white powder that was then recrystallized from THF (5 mL) to yield spectroscopically pure **6** as colorless crystals (1.87 g, 43%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.34$ (s, 27H, $C(CH_3)_3$), 7.43 (d, 6H, $^3J_{HH} = 8.4$ Hz, Ar*H*), and 7.60 (d, 6H, $^3J_{HH} = 8.4$ Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 31.4$ ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 125.2 (Ar*C*), 130.0 (Ar*C*), 135.3 (Ar*C*), and 153.8 (Ar*C*). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): $\delta = 1.9$. Mp (°C): 233−235. HR-MS, EI (*m/z*): calcd. for $[M]^+$: 462.25086. Found: 462.25095 (Δppm = 0.2).

*Synthesis of (4-^{i}PrC$_6$H$_4$)$_3$SiNH$_2$ (**7**).* (4-^{i}PrC$_6$H$_4$)$_3$SiCl (6.435 g, 0.0152 mol) and $LiNH_2$ (0.456 g, 0.0199 mol) were combined in 25 mL of THF and the resulting white slurry was stirred overnight. A slightly turbid reaction mixture was obtained, and the volatiles were removed under vacuum. The product was extracted with 50 mL of hexanes, and the LiCl salt was removed by filtration. The resulting filtrate was cooled to −35 °C to give a crop of colorless crystals, while further concentration and cooling of the mother liquor yielded additional pure **7** as a white solid (combined yield of both crops = 4.896 g, 80%). ^1H NMR (500 MHz, C_6D_6): $\delta = 0.83$ (br. s, 2H, NH_2), 1.13 (d, 18H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 2.70 (septet, 3H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 7.14 (d, 6H, $^3J_{HH} = 8.0$ Hz, Ar*H*), and 7.72 (d, 6H, $^3J_{HH} = 8.0$ Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 24.1$ ($CH(CH_3)_2$), 34.5 ($CH(CH_3)_2$), 126.3 (Ar*C*), 134.9 (Ar*C*), 136.0 (Ar*C*), and 150.3 (Ar*C*). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): $\delta = -16.8$. HR-MS, EI (*m/z*): calcd. for $[M]^+$: 401.25388. Found: 401.25374 (Δppm = 3.9). Mp (°C): 65−70. Anal. calcd. for $C_{27}H_{35}NSi$: C, 80.74; H, 8.78; N, 3.49. Found: C, 80.42; H, 8.66; N, 3.48.

*Synthesis of (4-^{t}BuC$_6$H$_4$)$_3$SiNH$_2$ (**8**).* Compound **6** (1.50 g, 3.2 mmol) and $LiNH_2$ (0.10 g, 4.4 mmol) were combined in 12 mL of THF and the reagent mixture was stirred for 2 days at room temperature to give a colorless solution. The solvent was then removed *in vacuo* to yield a white powder. The product was then extracted with 20 mL of Et_2O, and the resulting slurry was filtered through Celite to give a colorless solution. Removal of the volatiles from the filtrate afforded spectroscopically pure **8** as a white powder (0.41 g, 28%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.32$ (s, 27H, $C(CH_3)_3$), 7.38 (d, 6H, $^3J_{HH} = 8.1$ Hz, Ar*H*), and 7.57 (d, 6H, $^3J_{HH} = 8.1$ Hz, Ar*H*); the N−*H* resonance could not be located. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 31.4$ ($C(CH_3)_3$), 34.9 ($C(CH_3)_3$), 124.9 (Ar*C*), 133.6 (Ar*C*), 135.2 (Ar*C*), and 152.5 (Ar*C*). HR-MS, EI (*m/z*): calcd. for $[M]^+$: 443.30036. Found: 443.30084 (Δppm = 1.1). IR (FT-IR microscope, cm^{-1}): 3390 [br, ν(N−H)]. Mp (°C): 167−169. Anal. calcd. for $C_{30}H_{41}NSi$: C, 81.20; H, 9.31; N, 3.16. Found: C, 81.03; H, 9.07; N, 3.08.

*Preparation of [(4-^{i}PrC$_6$H$_4$)$_3$SiNH]$_2$Si(tolyl)$_2$ (**9**).* (4-^{i}PrC$_6$H$_4$)$_3$SiNH$_2$ (0.774 g, 1.92 mmol) was dissolved in 8 mL of Et_2O and cooled to −35 °C. A solution of ^{n}BuLi (1.20 mL, 1.6 M solution in hexanes, 1.92 mmol) was then added dropwise, followed by stirring for 3 h. The resulting slurry was then cooled to −35 °C, and neat di-*p*-tolyldichlorosilane (0.259 mL, 1.01 mmol) was then added followed by stirring at room temperature overnight. The reaction mixture was then filtered to yield a colorless filtrate, and the volatiles were then removed from the filtrate under vacuum. The crude product was then recrystallized from hexanes (−35 °C) to yield **9** as a white microcrystalline solid (0.568 g, 58%). ^1H NMR (400 MHz, C_6D_6): $\delta =$ 1.14 (d, 36H, $^3J_{HH} = 6.8$ Hz, $CH(CH_3)_2$), 1.78 (br. s, 2H, N*H*), 2.08 (s, 6H, tolyl-CH_3), 2.71 (septet, 6H, $^3J_{HH} = 6.8$ Hz, $CH(CH_3)_2$), 6.87 (d, 4H, $J = 8.0$ Hz, tolyl-Ar*H*), 7.05 (d, 12H, $J = 8.0$ Hz, Ar*H*), 7.55 (d, 4H, $^3J_{HH} = 8.0$ Hz, tolyl-Ar*H*), and 7.67 (d, 12H, $^3J_{HH} = 8.0$ Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 21.5$ (tolyl-CH_3), 24.0 ($CH(CH_3)_2$), 34.4 ($CH(CH_3)_2$), 126.1 (Ar*C*), 128.4 (Ar*C*), 134.7 (Ar*C*), 135.6 (Ar*C*), 135.9 (Ar*C*), 136.4 (Ar*C*), 138.7 (Ar*C*), and 149.8 (Ar*C*). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): $\delta = -17.1$ (−*Si*Ar$_3$) and −20.4 (−*Si*(tolyl)$_2$−). IR (FT-IR microscope, cm^{-1}): 3330 [br, ν(N−H)]. Mp (°C): 178−181. Anal. calcd. for $C_{68}H_{82}N_2Si_3$: C, 80.73; H, 8.17; N, 2.77. Found: C, 80.95; H, 8.06; N, 2.77.

*Synthesis of [(4-^{i}PrC$_6$H$_4$)$_3$SiNHSiMe$_2$]$_2$ (**10**).* (4-^{i}PrC$_6$H$_4$)$_3$SiNH$_2$ (1.04 g, 2.60 mmol) was dissolved in 20 mL of Et_2O and cooled to −35 °C, and a solution of ^{n}BuLi (1.62 mL, 1.6 M solution in hexanes, 2.60 mmol) was added dropwise. The reaction mixture was then stirred for 3 h, cooled to −35 °C, and dichlorotetramethyldisilane (0.245 mL, 1.32 mmol) was then added. The resulting cloudy white suspension was then warmed to room temperature, stirred for 16 h, and filtered through Celite. Removal of the volatiles from the filtrate (in vacuo) afforded a viscous yellow oil that was freed from residual LiCl (as evidenced by a flame test) by redissolving the crude material in 10 mL of hexanes, followed by filtration through Celite. Removal of the solvent from the filtrate gave **10** as a spectroscopically pure pale yellow oil (0.92 g, 77%). ^1H NMR (300 MHz, C_6D_6): $\delta = 0.18$ (s, 12H, $Si(CH_3)_2$), 1.02 (br, 2H, N*H*), 1.14 (d, 36H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 2.71 (septet, 6H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 7.14 (d, 12H, $^3J_{HH} = 8.0$ Hz, Ar*H*), and 7.83 (d, 12H, $^3J_{HH} = 8.0$ Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 2.0$ ($Si(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 34.5 ($CH(CH_3)_2$), 126.5 (Ar*C*), 135.2 (Ar*C*), 136.3 (Ar*C*), and 150.3 (Ar*C*). $^{29}Si\{^1H\}$ NMR (79.5 MHz, C_6D_6): $\delta = -7.2$ (s) and −16.6 (s). IR (FT-IR microscope, cm^{-1}): 3349 [m, ν(N−H)]. EI-MS (*m/z*): 459 {[(4-^{i}PrC$_6$H$_4$)$_3$SiNHSiMe$_2$]$^+$, 6%}, 401 {[(4-^{i}PrC$_6$H$_4$)$_3$SiNH$_2$]$^+$, 38%}, {[(4-^{i}PrC$_6$H$_4$)$_3$Si]$^+$, 22%}. Anal. calcd. for $C_{58}H_{50}N_2Si_4$: C, 75.92; H, 8.79; N, 3.05. Found: C, 74.29; H, 8.84; N, 2.81; despite repeated attempts the analyses were consistently low in C (ca. 2%).

*Preparation of [{tolyl$_2$Si[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (**11**).* Compound **9** (0.259 g, 0.256 mmol) was dissolved in 7 mL of Et_2O and cooled to −35 °C, and ^{n}BuLi (320 μL, 1.6 M solution in hexanes, 0.512 mmol) was added dropwise; the reaction mixture was then allowed to warm to room temperature and stirred for 3 h. This solution was then added dropwise to $GeCl_2$·dioxane (59 mg, 0.26 mmol) in 4 mL of Et_2O and stirred overnight to yield a cloudy white mixture. The resulting LiCl precipitate was separated by filtration, and the volatiles were removed from the yellow filtrate to give a white solid that was recrystallized from Et_2O at −35 °C to give an analytically pure sample of **11** as a colorless microcrystalline solid (95 mg, 34%). ^1H NMR (500 MHz, C_6D_6): $\delta = 1.08$ (d, 36H, $^3J_{HH} = 6.5$ Hz, $CH(CH_3)_2$), 2.08 (s, 6H, tolyl-CH_3), 2.63 (septet, 6H, $^3J_{HH} = 6.5$ Hz, Ar$CH(CH_3)_2$), 6.86 (d, 4H, $^3J_{HH} = 7.5$ Hz, tolyl-ArH), 7.00 (d, 12H, $^3J_{HH} = 8.0$ Hz, ArH), 7.47 (d, 4H, $^3J_{HH} = 7.5$ Hz, tolyl-ArH), and 7.65 (d, 12H, $^3J_{HH} = 8.0$ Hz, ArH). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 21.5$ (tolyl−CH_3), 23.9 ($CH(CH_3)_2$), 34.3 ($CH(CH_3)_2$), 126.1 (Ar*C*), 128.7 (Ar*C*), 133.8 (Ar*C*), 134.7 (Ar*C*), 135.6 (Ar*C*), 136.5 (Ar*C*), 139.1 (Ar*C*), and 149.9 (Ar*C*). $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): $\delta = -3.1$ (−*Si*(tolyl)$_2$−) and −18.9 (−*Si*Ar$_3$). Mp (°C): 245−248. Anal. calcd. for $C_{68}H_{80}GeN_2Si_3$: C, 75.46; H, 7.45; N, 2.59. Found: C, 75.23; H, 7.46; N, 2.56.

*Synthesis of [{Me$_4$Si$_2$[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (**12**).* Silylamine **10** (0.377 g, 0.410 mmol) was dissolved in 14 mL of Et_2O and cooled to −35 °C, and ^{n}BuLi (0.513 mL, 1.6 M solution in hexanes, 0.82 mmol) was added; the reaction mixture was then allowed to warm to room temperature and stirred for 3 h. This resulting solution was then added dropwise to $GeCl_2$·dioxane (95 mg, 0.41 mmol) in 3 mL of Et_2O and stirred overnight to yield a cloudy yellow mixture. The precipitate was separated by filtration, and the volatiles were removed form the filtrate to give a tacky yellow solid. This product was recrystallized from 5 mL of a 5:1 hexanes/hexamethyldisiloxane mixture at −35 °C to yield pale yellow crystals of **12** of suitable quality for single-crystal X-ray crystallography (154 mg, 38%). ^1H NMR (500 MHz, C_6D_6) $\delta = 0.21$ (s, 12H, $Si(CH_3)_2$), 1.12 (d, 36H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 2.67 (septet, 6H, $^3J_{HH} = 7.0$ Hz, $CH(CH_3)_2$), 7.13 (d, 12H, $^3J_{HH} = 8.0$ Hz, Ar*H*), and 7.87 (d, 12H, $^3J_{HH} = 8.0$ Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 2.8$ ($Si(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 34.4 ($CH(CH_3)_2$), 126.2 (Ar*C*), 135.4 (Ar*C*), 137.0 (Ar*C*), and 150.3 (Ar*C*).

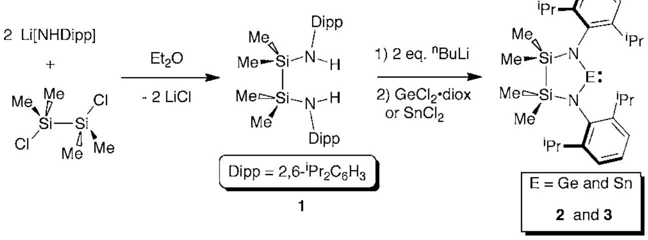
^{29}Si{^{1}H} NMR (80 MHz, C_6D_6): δ = −7.2 (−*Si*Me$_2$*Si*Me$_2$−) and −16.6 (−*Si*Ar$_3$). Mp (°C): 80−83 (dec.). Anal. calcd. for $C_{58}H_{78}GeN_2Si_4$: C, 70.49; H, 7.96; N, 2.83. Found: C, 70.83; H, 7.96; N, 2.79.

*Preparation of [{[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$Si(tolyl)$_2$}Ge(μ-S)]$_2$ (**13**).* To a mixture of **11** (81 mg, 0.075 mmol) and elemental sulfur (2.4 mg, 0.075 mmol) was added 10 mL of Et_2O. The reaction mixture was stirred overnight at room temperature to give a white suspension that was then filtered through Celite to obtain a pale yellow solution. Removal of volatiles from the filtrate afforded **13** as a white powder (73 mg, 87% yield). X-ray quality crystals were obtained by cooling a solution of **13** in 2:1 hexanes/hexamethyldisiloxane mixture (6 mL) at −35 °C for 3 days. ^{1}H NMR (500 MHz, C_6D_6) δ = 1.14 (d, 36H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 2.03 (s, 6H, tolyl-C*H*$_3$) 2.67 (septet, 6H, $^3J_{HH}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 6.71 (d, 4H, $^3J_{HH}$ = 7.5 Hz, Ar*H*), 6.83 (br. d, 12H, $^3J_{HH}$ = 6.5 Hz, Ar*H*), 7.20 (d, 4H, $^3J_{HH}$ = 7.5 Hz, Ar*H*), and 7.41 (br. d, 12H, $^3J_{HH}$ = 6.5 Hz, Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 21.6 (tolyl-CH$_3$), 24.1 (CH(CH$_3$)$_2$), 34.4 (CH(CH$_3$)$_2$), 125.7 (Ar*C*), 132.4 (Ar*C*), 134.2 (Ar*C*), 136.5 (Ar*C*), 137.3 (Ar*C*), 139.1 (Ar*C*), and 149.1 (Ar*C*); one Ar*C* resonance could not be located. Mp (°C): >260. Anal. calcd. for $C_{136}H_{160}Ge_2N_4S_2Si_6$: C, 73.29; H, 7.24; N, 2.51. Found: C, 73.45; H, 7.20; N, 2.60.

■ RESULTS AND DISCUSSION

Bis(amidosilyl) [NSiSiN] Chelates and Associated Low-Coordinate Group 14 Element Chemistry. As mentioned in the Introduction, we have been exploring ligand design strategies as a means to access low-coordinate main group complexes with novel reactivity. An area that would benefit from such ligand advances would be the synthesis of a silicon analogue of a ketone, termed a silanone, LSi═O (L = bidentate ligand) or R_2Si═O. This molecular class has been the target of scientific investigation for over 100 years but has thwarted isolation in the condensed phase, as the Si═O double bonds in these targets are anticipated to be highly reactive due to their polarized nature. The isolation of a silanone will therefore require sufficient steric shielding from the proximal ligands in order to suppress the thermodynamically favored formation of oligomers.[21] Although Tamao and co-workers have very recently reported the elegant synthesis of a monomeric germanone R_2Ge═O,[22] these species and their heavier chalcogen derivatives (e.g., R_2Ge═S) are still quite rare.[8] Drawing inspiration from *N*-heterocyclic carbene chemistry[23] and keeping the above-mentioned synthetic targets in mind, we decided to prepare low-coordinate, *N*-heterocyclic Group 14 complexes featuring 5-membered rings (Scheme 1). It was reasoned that the expanded chelate ring size relative to our previously reported 4-membered heterocycles, such as Ge-[NSiN]^{Dipp} ([NSiN]^{Dipp} = [^{i}Pr$_2$Si(NDipp)$_2$]),[6a] would place the flanking aryl (Dipp) groups in closer proximity to the Group 14 (tetrel) element, thus leading to a more sterically crowded coordination environment.

Scheme 1. Synthesis of the Bis(amido)disilyl Germylene and Stannylene Heterocycles [(Me$_2$SiNDipp)$_2$E:] (E = Ge and Sn; 2 and 3)



Starting from the known bis(amine) **1**,[20] we were able to prepare the monomeric germylene and stannylene complexes, [(Me$_2$SiNDipp)$_2$E:] (E = Ge and Sn; **2** and **3**) in high yields of 88 and 91%, respectively. The germanium heterocycle **2** was obtained as an orange solid of modest stability in the solid state (decomposition noted at 80 °C under N_2), while its tin congener was isolated as a thermally stable yellow solid (Mp = 169−171 °C). As shown in Figure 1, compounds **2** and **3** adopt monomeric structures in the solid state with the peripheral, nitrogen-bound Dipp groups oriented orthogonal to the ENSiSiN ring planes (E = Ge and Sn). In each heterocycle, slight canting of the SiMe$_2$ groups relative to one another was observed with N−Si−Si−N intraring torsion angles of 11.58(6)° and 22.17(6)° for **2** and **3**, respectively. As expected, the Dipp substituents were also bent considerably forward toward the Ge and Sn centers, as evidenced by the narrow C(ipso, Dipp)−N−E angles of 113.99(12)° *avg.* and 117.12(13)° *avg.* for compounds **2** and **3**. For comparison, the Dipp groups within the four-membered [NSiNE] chelates [{^{i}Pr$_2$Si(NDipp)$_2$}E:] (E = Ge and Sn) were also orthogonal to the inorganic ring planes, but were positioned further away from the Group 14 centers as indicated by significantly wider C(ipso, Dipp)−N−E angles of 124.96(8)° (E = Ge) and 126.30(13)° *avg.* (E = Sn).[6a] The backbone Si−Si distances in heterocycles **2** [2.3339(5) Å] and **3** [2.3269(5) Å] were nearly identical within experimental error and are in the range expected for Si−Si single bonds.[24]

Compound **2** represents the first heterocyclic, two-coordinate, germylene that contains a disilane unit as part of the ring skeleton.[25] Notably, structurally related Sn(II) disilylamino complexes, [(Me$_2$SiNR)$_2$Sn]$_{1\text{ or }2}$ (R = alkyl groups) were prepared by the group of Wrackmeyer.[26] When bulky side groups were appended to nitrogen (e.g., R = ^{t}Bu), monomeric stannylenes were observed in solution; however upon decreasing the steric bulk of the substituent at nitrogen, dimerization via intermolecular Sn···N interactions transpired and in some instances, monomer−dimer equilibria were identified using variable-temperature ^{1}H and ^{119}Sn NMR studies.[26] While our hindered stannylene **3** is stable indefinitely at room temperature and in the presence of light, the less-sterically protected Sn complexes of Wrackmeyer slowly decompose in solution when exposed to ambient light; this process generally leads to ligand redistribution to give the homoleptic complexes [(Me$_2$SiNR)$_2$]$_2$Sn.[26]

The high degrees of thermal stability, coupled with the monomeric nature of the germylene and stannylene complexes **2** and **3**, suggest that the consitituent [NSiSiN]^{Dipp} chelates are promising ligands for the stabilization of other reactive inorganic bonding environments.[27] As a starting point, we explored chalcogen atom transfer chemistry between the two-coordinate germylene [(Me$_2$SiNDipp)$_2$Ge:] **2** and elemental sulfur in order to potentially access a rare example of a stable species featuring an unsupported Ge═S double bond.[8a] Treatment of **2** with an atomic equivalent of sulfur resulted in the gradual bleaching of the initially orange colored solution and the eventual recovery of a white microcrystalline solid. X-ray crystallographic analysis later revealed the successful installation of a sulfur atom at Ge; however in place of isolating the desired monomeric germanethione, a dimeric complex [(Me$_2$SiNDipp)$_2$Ge(μ-S)]$_2$ (**4**) was obtained (eq 1; Figure 1).

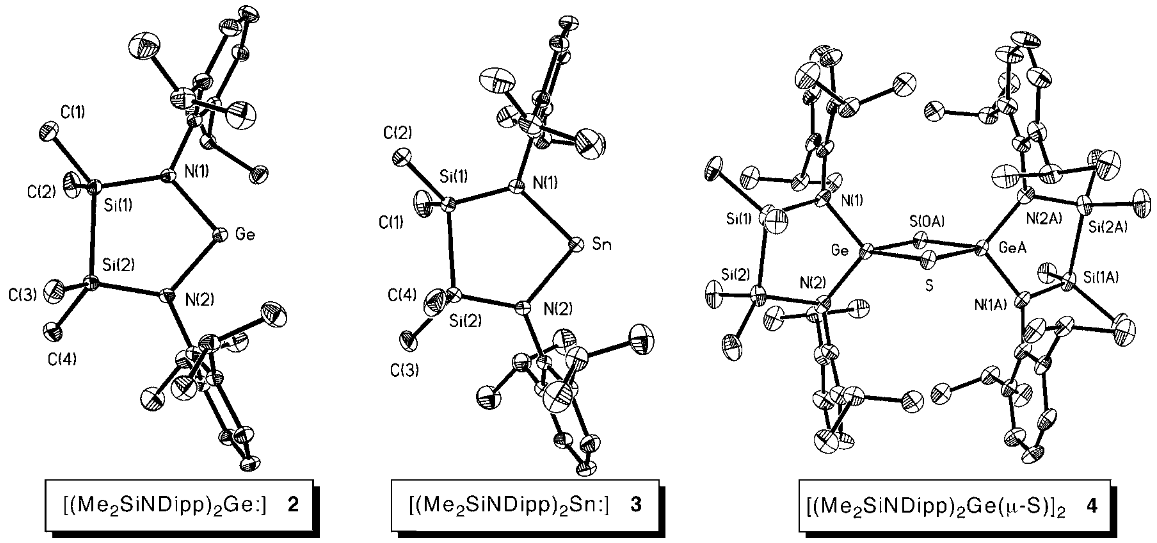
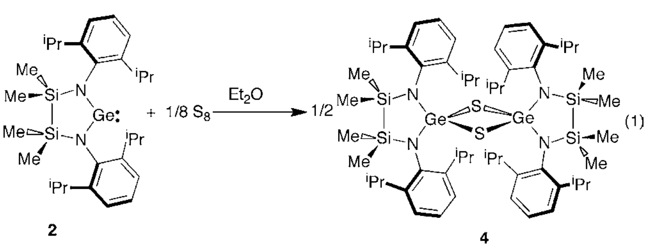


Figure 1. Molecular structures of [(Me$_2$SiNDipp)$_2$}E:] (E = Ge and Sn; **2** and **3**) and [(Me$_2$SiNDipp)$_2$Ge(μ-S)]$_2$ (**4**) with thermal ellipsoids presented at the 30% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Compound **2**: Ge−N(1) 1.8615(10), Ge−N(2) 1.8623(10), N(1)−Si(1) 1.7535(11), N(2)−Si(2) 1.7560(11), Si(1)−Si(2) 2.3339(5); N(1)−Ge-N(2) 98.75(5), Si(1)−N(1)−Ge 122.49(6), Si(2)−N(2)−Ge 121.70(6), Si(1)−N(1)−C(11) 123.50(8), C(11)−N(1)−Ge 113.93(8), Si(2)−N(2)−C(31) 124.26(8), C(31)−N(2)−Ge 114.05(8), N(1)−Si(1)−Si(2) 97.41(4), N(2)−Si(1)−Si(2) 98.00(4). Compound **3**: Sn−N(1) 2.0597(11), Sn−N(2) 2.0646(11), N(1)−Si(1) 1.7477(11), N(2)−Si(2) 1.7533(12), Si(1)−Si(2) 2.3269(5); N(1)−Sn-N(2) 93.35(4), Si(1)−N(1)−Sn 121.05(6), Si(2)−N(2)−Sn 120.45(6), Si(1)−N(1)−C(11) 122.10(9), C(11)−N(1)−Sn 116.79(8), Si(2)−N(2)−C(31) 121.93(9), C(31)−N(2)−Sn 117.44(8), N(1)−Si(1)−Si(2) 99.47(4), N(2)−Si(1)−Si(2) 100.24(4). Compound **4**: Ge−S 2.2763(17), Ge−S′ 2.2245(17), Ge−N(1) 1.853(5), Ge−N(2) 1.840(6), N(1)−Si(1) 1.765(6), N(2)−Si(2) 1.792(6), Si(1)−Si(2) 2.303(3); S−Ge−S(A) 93.39(6), Ge−S−Ge 86.61(6), N(1)−Ge-N(2) 101.7(2), Ge−N(1)-C(11) 127.3(4), Ge−N(2)−C(31) 130.2(4), N(1)−Si(1)−Si(2) 96.9(2), N(2)−Si(1)−Si(2) 98.2(2).



2

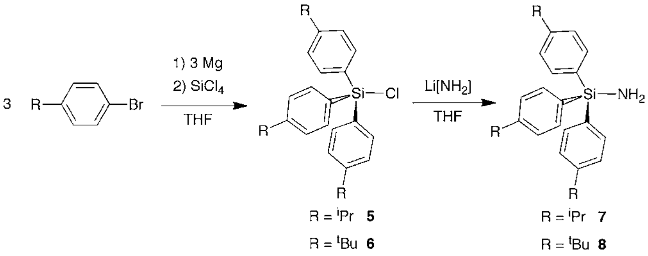
4

As shown in Figure 1, compound **4** adopts a centrosymmetric structure comprised of two GeNSiSiN heterocycles joined by a central Ge$_2$S$_2$ array. The overall geometry of this germanium sulfide complex is reminiscent of that observed within the previously reported dimers, [{^{i}Pr$_2$Si(NDipp)$_2$}Ge(μ-S)]$_2$ and [{^{i}Pr$_2$Si(NSiPh$_3$)$_2$}Ge(μ-S)]$_2$.[6a] For example, the Ge−S distances in **4** were 2.2245(17) and 2.2763(17) Å, while in the above-mentioned dimers featuring [NSiN] chelates, distances in the range of 2.1992(3)−2.2577(3) Å were observed.[6a] The Ge−S distances in **4** are consistent with the presence of Ge−S single bonds,[8b] and these bond lengths are expectedly lengthened in comparison to the Ge=S double bond distance of 2.049(3) Å found in [Tbt(Trip)Ge=S] (Tbt = 2,4,6-{(Me$_3$Si)$_2$CH}$_3$C$_6$H$_2$; Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).[8a,b] The backbone-positioned SiMe$_2$ groups in **4** are mutually twisted in comparison to the nearly eclipsed Me$_2$Si-SiMe$_2$ arrangement found in the Ge(II) precursor **2**, as evidenced by widened N−Si−Si−N torsion angles of 23.6(3)° in **4** versus 11.58(6)° in **2**; this effect is likely due to an increase in intraligand Dipp···SiMe$_2$ repulsion in the oxidized dimer [(Me$_2$SiNDipp)$_2$Ge(μ-S)]$_2$ (**4**). Another potential indicator of intraligand repulsion would be the presence of substantial widening of the Ge−N−C(ipso, Dipp) angles as the cofacial Dipp groups in **4** are pushed away from each other (and away from the Ge centers). In compound **4**, the average Ge−N−C(ipso, Dipp) angles were 128.8(5)° and indicate that the Dipp groups in this complex subtend at an angle that is only ca. 3° wider than in the precursor **2**. This data suggests that, despite some increase in intraligand repulsion involving the Dipp groups in **4**, the overall level of intraligand strain in this dimer is still relatively low, thus the dimerization of putative [(Me$_2$SiNDipp)$_2$}Ge=S] units can still proceed to form **4**.

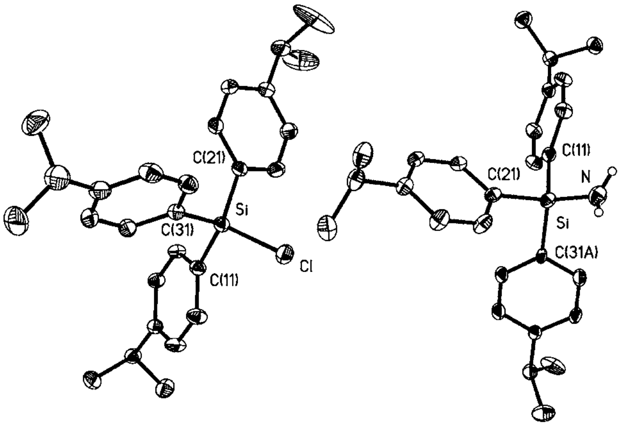
Synthesis of Ligand Frameworks Bearing Sterically Expanded Triarylsilyl Groups, (4-RC$_6$H$_4$)$_3$Si− (R = ^{i}Pr and ^{t}Bu). We have demonstrated in earlier work that replacement of Dipp groups by "umbrella-shaped" triphenylsilyl, −SiPh$_3$, moieties within [NSiN] chelates leads to an increase in the overall steric bulk of the resulting ligand.[6a] Building upon this concept, we targeted the synthesis of sterically expanded analogues in which the flanking triarylsilyl groups contained pendant ^{t}Bu and ^{i}Pr groups at the para-positions of the aryl rings, (4-RC$_6$H$_4$)$_3$Si− (R = ^{i}Pr and ^{t}Bu).

Somewhat to our surprise, examples of species with the desired triarylsilyl motifs (4-RC$_6$H$_4$)$_3$Si− (R = ^{i}Pr and ^{t}Bu) were unknown in the literature prior to our investigations. Consequently, new synthetic routes to the requisite nucleophilic silylamine ligand precursors (4-RC$_6$H$_4$)$_3$SiNH$_2$ (R = ^{i}Pr and ^{t}Bu) had to be developed. The first step in the general procedure outlined in Scheme 2 involved the preparation of the hindered triarylsilylchlorides, (4-RC$_6$H$_4$)$_3$SiCl (R = ^{i}Pr and ^{t}Bu; **5** and **6**), via the condensation of in situ generated aryl Grignard reagents 4-RC$_6$H$_4$MgBr with SiCl$_4$. Fortunately the selective installation of three aryl groups at silicon was possible in a high yield, and conversion of the chlorosilanes **5** and **6** into the target silylamines (4-RC$_6$H$_4$)$_3$SiNH$_2$ (R = ^{i}Pr and ^{t}Bu; **7** and **8**) was readily accomplished by treating the chlorosilanes with a slight excess of Li[NH$_2$] in THF. The hindered silane reagents **5**−**8** were each obtained as lipophilic, moisture-

Scheme 2. Synthesis of the Hindered Triarylchlorosilane and Triarylsilylamine Precursors 5−8



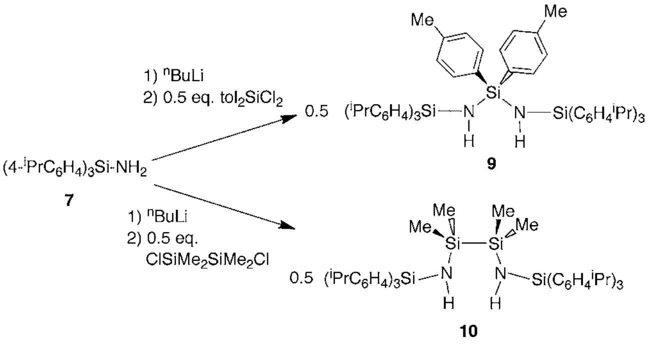
sensitive colorless solids, while the ^{i}Pr-substituted (cumyl) derivatives **5** and **7** were characterized further by single-crystal X-ray crystallography (Figure 2); the metrical parameters for both **5** and **7** were within expected values and thus no further discussion is required.



$(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiCl}$ **5** $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}_2$ **7**

Figure 2. Molecular structures of $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiCl}$ (**5**) and $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}_2$ (**7**) with thermal ellipsoids at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity; values due to a disordered 4-^{i}PrC$_6$H$_4$ group in **7** are listed in brackets. Selected bond lengths [Å] and angles [deg]. **5**: Si−Cl 2.0841(6), Si−C(11) 1.8573(17), Si−C(21) 1.8605(18), Si−C(31) 1.8569(18); Cl−Si−C angles: 107.41(6) to 111.64(8), C−Si−C angles: 110.44(8) to 111.64(8). **7**: Si−N 1.7144(16), Si−C(11) 1.8679(15), Si−C(21) 1.8721(15), Si−C(31) 1.881(4) [1.884(5)]; N−Si−C angles: 105.3(6) to 113.6(4); C−Si−C angles: 103.4(3) to 109.8(5).

Scheme 3. Synthesis of the Silyl and Disilyl Bis(Amine) Ligand Precursors $[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}]_2\text{Si(tolyl)}_2$ (9) and $[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNHSiMe}_2]_2$ (10)



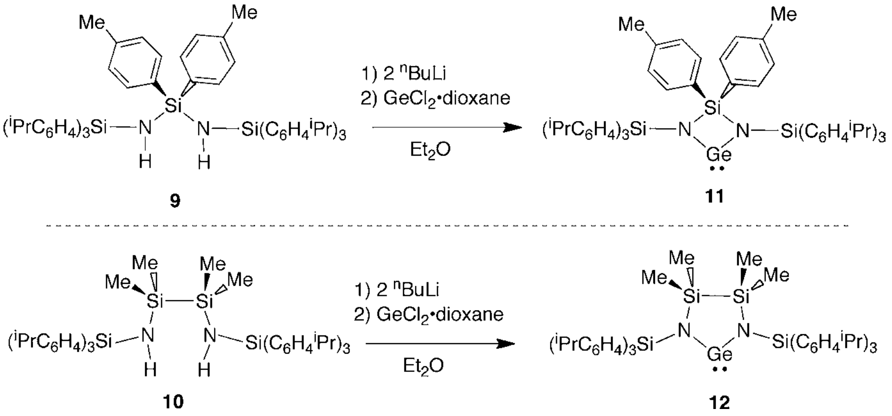
With the silylamine $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}_2$ (**7**) in hand, both the monosilyl $[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}]_2\text{Si(tolyl)}_2$ **9** and disilyl-bridged $[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNHSiMe}_2]_2$ **10** ligand precursors were then prepared using the straightforward one-pot procedures outlined in Scheme 3. In the case $[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiNH}]_2\text{Si(tolyl)}_2$ **9**, the presence of the backbone-positioned tolyl groups were used to add structural rigidity to the ligand framework and to serve as spectroscopic handles. Both bis(amine) precursor **9** and **10** were obtained as analytically pure, moisture-sensitive materials in 58 and 77% yields, respectively, and exhibited NMR and IR spectral data consistent with the assigned structures. We encountered considerable difficulties when we attempted to construct the ligand analogues to **9** and **10** with para-^{t}Bu substituents in place of ^{i}Pr. For example, when $^i\text{Pr}_2\text{SiCl}_2$ was reacted with in situ generated $[(4\text{-}{}^t\text{BuC}_6\text{H}_4)_3\text{SiNH}]\text{Li}$, complex product mixtures were obtained from which the desired *tert*-butylated silylbis(amine) ligand precursors could not be isolated in pure form. One contributing reason for the lack of success lies in the extreme solubility of these *tert*-butylated derivatives that precluded further purification of the impure products by fractional crystallization; moreover, attempts to triturate the oily products with $\text{Me}_3\text{SiOSiMe}_3$ or lyophilization with benzene also failed to yield tractable products. Motivated by the successful use of ^{i}Pr-bound aryl groups within ligand designs to aid in crystallization/purification,[28] we focused our remaining synthetic efforts on [NSiN] and [NSiSiN] chelates bearing $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{Si}$− substituents at the ligating nitrogen atoms.

In order to access low-valent germylene complexes, we followed the established procedure[6a] outlined in Scheme 4. The required dilithio-amide precursors, $\{\text{tolyl}_2\text{Si}[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiN}]_2\}\text{Li}_2$ and $\{[\text{Me}_2\text{Si}(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiN}]_2\}\text{Li}_2$, were each generated in situ via the reaction of the bis(amines) **9** and **10** with 2 equiv of ^{n}BuLi in diethyl ether, and then reacted with $\text{GeCl}_2\cdot\text{dioxane}$ to afford the air- and moisture-sensitive germylenes $[\{\text{tolyl}_2\text{Si}[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiN}]_2\}\text{Ge:}]$ (**11**) and $[\{\text{Me}_4\text{Si}_2[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiN}]_2\}\text{Ge:}]$ (**12**) in moderate yields. Compounds **11** and **12** were obtained as colorless and pale yellow air- and moisture-sensitive solids, respectively, with the germylene **11** decomposing at 245 °C under a nitrogen atmosphere, while the disilylamido germylene heterocycle **12** exhibited a much lower decomposition temperature of 80 °C. We were unable to verify the solid state structure of the **11** by X-ray crystallography; however, crystals of **12** of suitable quality for single-crystal X-ray crystallography were obtained from a cold (−35 °C) hexanes/$\text{Me}_3\text{SiOSiMe}_3$ solution (Figure 3).

The five-membered germylene heterocycle $[\{\text{Me}_4\text{Si}_2[(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{SiN}]_2\}\text{Ge:}]$ (**12**) is monomeric in the solid state (Figure 3) with a planar GeNSiSiN ring and mutually eclipsed backbone SiMe$_2$ groups [N(1)−Si(1)−Si(2)−N(2) torsion angle = 1.74(6)°]. What is evident upon inspection of the structure of **12** is that the flanking nitrogen-bound $(4\text{-}{}^i\text{PrC}_6\text{H}_4)_3\text{Si}$ groups serve to create a much tighter steric pocket about the Ge center when compared to the Dipp analogue $[(\text{Me}_2\text{SiNDipp})_2\text{Ge:}]$ (**2**). The backbone Si−Si bond length in **12** [2.3400(15) Å] is the same within experimental error as the related linkage in **2**, while the Ge−N bond lengths in **12** [1.875(3) and 1.886(3) Å] are typical for single bonding interactions and suggest a lack of appreciable Ge−N π-bonding within the heterocycle.

The Ge(II) centers within the monomeric germylenes **11** and **12** were expected to undergo facile oxidation chemistry to yield stable products with germanium centers in the +4 oxidation state. As anticipated, the bis(amido)germylene **11**

Scheme 4. Synthesis of the Germylene Complexes [{tolyl$_2$Si[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (11) and [{Me$_4$Si$_2$[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (12)



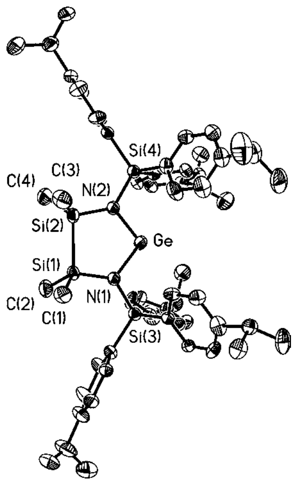


Figure 3. Molecular structure of [{Me$_4$Si$_2$[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (**12**) with thermal ellipsoids at a 30% probability level. All hydrogen atoms and disordered 4-^{i}PrC$_6$H$_4$ groups have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge−N(1) 1.875(3), Ge−N(2) 1.886(3), Si(1)−Si(2) 2.3400(15), Si(1)−N(1) 1.744(3), Si(2)−N(2) 1.745(3), N(1)−Si(3) 1.732(3), N(2)−Si(4) 1.737(3); N(1)−Ge-N(2) 101.46(13), N(1)−Si(1)−Si(2) 99.30(11), N(2)−Si(2)−Si(1) 99.53(11), Ge−N(1)-Si(1) 119.99(17), Ge−N(1)-Si(3) 110.55(15), Ge−N(2)-Si(2) 119.56(17), Ge−N(2)-Si(4) 110.07(15).

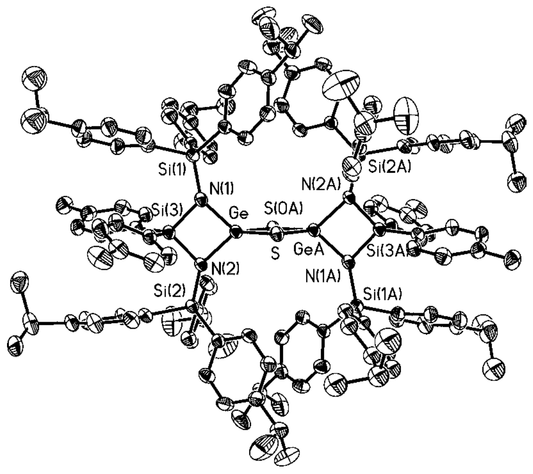


Figure 4. Molecular structure of [{[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$Si(tolyl)$_2$}Ge-(μ-S)]$_2$ (**13**) with hydrogen atoms and solvate molecules omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge−S 2.2253(10), Ge−S′ 2.2392(9), Ge−N(1) 1.837(3), Ge−N(2) 1.850(3), N(1)−Si(1) 1.738(3), N(1)−Si(3) 1.764(3), N(2)−Si(2) 1.741(3), N(2)−Si(3) 1.762(3); S−Ge−S′ 95.14(3), Ge−S−Ge′ 84.86(3), N(1)−Ge−N(2) 85.68(12), Ge−N(1)−Si(1) 142.01(18), Ge−N(2)−Si(2) 141.76(17), Ge−N(1)−Si(3) 91.85(14), Ge−N(2)−Si(3) 91.43(12), N(1)−Si(3)−N(2) 85.68(12).

reacted rapidly with elemental sulfur; however as with **2**, the product obtained was a sulfido-linked dimer, [{(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$Si(tolyl)$_2$}Ge(μ-S)]$_2$ (**13**). Due to the high lipophilicity of **13**, the use of hexamethyldisiloxane as a cosolvent of crystallization was required to obtain crystals of suitable quality for X-ray crystallography. The refined structure of **13** is presented in Figure 4 and reveals the formation of a dimeric germanethione containing a similar Ge$_2$S$_2$ diamond core arrangement as in **2** and **4**; however in **13**, the Ge$_2$S$_2$ unit is much more sterically shielded as a result of interdigitating cumyl groups (4-^{i}PrC$_6$H$_4$) that are positioned on each side of the Ge$_2$S$_2$ core. Furthermore, the close intraligand interactions between the cumyl side groups results in significant intraligand repulsion which is manifested in the form of wide *Ge−N−Si*Ar$_3$ angles of 141.76(17) and 142.01(18)°. For comparison, the related angles in [^{i}Pr$_2$Si(NSiPh$_3$)$_2$Ge(μ-S)]$_2$ were, on average, considerably narrower [135.07(11)°].[6a] Despite the substantial buckling of the (4-^{i}PrC$_6$H$_4$)$_3$Si− groups in **13**, the Ge−S bond lengths [2.2253(10) and 2.2392(9) Å] were similar to the Ge−S bond lengths noted within related sulfido-bridged Ge(IV) complexes featuring silylamido chelates [2.1992(3) to 2.2577(3)].[6a]

Unfortunately our attempts to react the sterically shielded germylene [{Me$_4$Si$_2$[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}Ge:] (**12**) with elemental sulfur failed to yield clean products that could be structurally authenticated. When the reaction of **12** with one atom equiv of sulfur was conducted, significant amounts (ca. 20−30%) of unreacted **12** were noted along with another major product (ca. 50% spectroscopic yield). Increasing the amount of sulfur in the reaction to 2 equiv improved the spectroscopic yield of the major species to ca. 60%; however our efforts to separate this product from the remaining byproducts (at least four by ^{1}H NMR) via fractional crystallization were unsuccessful. At this stage we are unsure if monomeric germanium polysulfides, such as {Me$_4$Si$_2$[(4-^{i}PrC$_6$H$_4$)$_3$SiN]$_2$}-Ge(S)$_x$ (x = 2, 3, ...), are formed as in the case of the reaction of Tbt(Trip)Ge: with S$_8$,[8] or if bridging sulfido Ge−S$_x$−Ge interactions are present. Moreover attempts to selectively oxidize **12** with Me_3NO or $MesCNO$[13] to give the germanium(IV) oxo complex $\{Me_4Si_2[(4\text{-}^iPrC_6H_4)_3SiN]_2\}Ge(O)$ gave multiple products as evidenced by NMR spectroscopy. Interestingly, a number of downfield positioned $SiMe_2$ resonances (relative to in **12**) were observed and suggested that oxidation of the backbone Si−Si linkages in **12** to give siloxane moieties, $-SiMe_2OSiMe_2-$, transpired. Support for this mode of reactivity exists in the literature wherein the oxidation of Si−Si linkages by Me_3NO has been reported by various groups.[29]

■ CONCLUSION

In this work, we report new silylamido chelates featuring elongated Si−Si bonds within a [NSiSiN] ligand backbone and introduce the sterically expanded triarylsilyl group, $-Si(C_6H_4{}^iPr)_3$, as a structural motif in ligand design. Although these chelates provided increased steric coverage relative to pre-existing silylamido bidentate ligands, our initial attempts to isolate rare examples of three-coordinate germanium compounds with terminal Ge═S double bonds led to the formation of dimeric germanes with exclusively σ-bonded Ge_2S_2 arrays. These results suggest that a high degree of structural flexibility is present within the newly developed amidosilyl ligands, thus allowing higher than expected coordination numbers to be attained. Despite such challenges, the ease of synthesis and high level of substituent control, make the general silylamino ligand class introduced in this paper of widespread interest to those seeking to access new inorganic element bonding modes and reactivity profiles via ligand design.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. (b) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. (c) Eaborn, C. *J. Organomet. Chem.* **1982**, *239*, 93. (d) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (e) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9. (f) Cummins, C. C. *Chem. Commun.* **1998**, 1777. (g) Power, P. P. *J. Organomet. Chem.* **2004**, *689*, 3904. (h) MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530. (i) Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905. (j) Wolczanski, P. T. *Chem. Commun.* **2009**, 740.

(2) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8732. (b) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861. (c) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (d) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527. (e) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6252. (f) Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790. (g) Ni, C.; Ellis, B. D.; Long, G. J.; Power, P. P. *Chem. Commun.* **2009**, 2332. (h) Takaoka, A.; Mankad, N. P.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 8440. (i) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. *Science* **2011**, *334*, 780.

(3) (a) Okazaki, R.; Tokitoh, N. *Acc. Chem. Res.* **2000**, *33*, 625. (b) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136. (c) Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310*, 844. (d) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Science* **2008**, *322*, 1360. (e) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201. (f) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877. (g) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (h) Li, J.; Schenk, C.; Goedecke, C.; Frenking, G.; Jones, C. *J. Am. Chem. Soc.* **2011**, *133*, 18622.

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

(5) (a) Bradley, D. C.; Hursthouse, M. B.; Rodesiler, P. F. *J. Chem. Soc., Chem. Commun.* **1969**, 14. (b) Fisher, K. J.; Bradley, D. C. *J. Am. Chem. Soc.* **1971**, *93*, 2058. (c) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *Dalton Trans.* **1976**, 2268. (d) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *Dalton Trans.* **1976**, 2275. (e) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Orgamometallics* **1982**, *1*, 918. (f) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445. (g) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 756. (h) Brynda, M.; Herber, R.; Hitchcock, P. B.; Lappert, M. F.; Nowik, I.; Power, P. P.; Protchenko, A.; Ruzicka, A.; Steiner, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4333. (i) Wright, R. J.; Brynda, M.; Fettinger, J. C.; Betzer, A. R.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 12498.

(6) (a) Al-Rafia, S. M. I.; Lummis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Inorg. Chem.* **2010**, *49*, 9709 and references therein. For recent reports involving related chelates, see. (b) Yang, D.; Guo, J.; Wu, H.; Ding, Y.; Zheng, W. *Dalton. Trans.* **2012**, 2187. (c) West, J. K.; Stahl, L. *Organometallics* **2012**, *31*, 2042.

(7) For the effective use of $SiAr_3$ groups (Ar = Ph or tolyl) in ligand design, see: (a) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1987**, *109*, 6509. (b) Danopoulos, A. A.; Redshaw, C.; Vaniche, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 1061. (c) Bindl, M.; Stade, R.; Heilman, E. K.; Picot, A.; Goddard, R.; Fürstner, A. *J. Am. Chem. Soc.* **2009**, *131*, 9468. (d) Suzuki, E.; Komuro, T.; Kanno, Y.; Okazaki, M.; Tobita, H. *Organometallics* **2010**, *29*, 1839. (e) Malassa, A.; Herzer, N.; Görls, H.; Westerhausen, M. *Dalton Trans.* **2010**, 5356. (f) Li, J.; Stasch, A.; Schenk, C.; Jones, C. *Dalton Trans.* **2011**, 10448.

(8) For related studies involving chalcogen atom transfer to germylenes, see: (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. (c) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (d) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457. (e) Yao, S.; Xiong, Y.; Driess, M. *Chem.—Eur. J.* **2010**, 1281.

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

(10) Marvel, C. S.; Johnston, H. W.; Meier, J. W.; Mastin, T. W.; Whitson, J.; Himel, C. M. *J. Am. Chem. Soc.* **1944**, *66*, 914.

(11) Hall, M. A.; Xi, J.; Lor, C.; Dai, S.; Pearce, R.; Dailey, W. P.; Eckenhoff, R. G. *J. Med. Chem.* **2010**, *53*, 5667.

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

(13) (a) Bode, J. W.; Hachisu, Y.; Matsuura, T.; Suzuki, K. *Tetrahedron Lett.* **2003**, *44*, 3555. (b) Barybin, M. V.; Diaconescu, P. L.; Cummins, C. C. *Inorg. Chem.* **2001**, *40*, 2892.

(14) Hope, H. *Prog. Inorg. Chem.* **1993**, *41*, 1.

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

(16) 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.

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

(18) Schneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772.

(19) (a) Sluis, P. v.; der; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194. (b) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34. (c) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7. (d) *PLATON−a multipurpose crystallographic tool*. Utrecht University, Utrecht, The Netherlands.

(20) Jäger, F.; Roesky, H. W.; Dorn, H.; Shah, S.; Noltemeyer, M.; Schmidt, H.-G. *Chem. Ber./Receuil* **1997**, *130*, 399.

(21) (a) Steele, A. R.; Kipping, F. S.; Dickinson, R.; Chapman, A. C. *J. Chem. Soc.* **1929**, 357. (b) Maruoka, K.; Ito, T.; Araki, T.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975. (c) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (d) Tokitoh, N.; Kishikawa, K.; Okazaki, R.; Sasamori, T.; Nakata, N.; Takeda, N. *Polyhedron* **2002**, *21*, 563. (e) Witnall, R.; Andrews, L. *J. Phys. Chem.* **1985**, *89*, 3261. (f) Khabashesku, V. N.; Boganov, S. E.; Kudin, K. N.; Margrave, J. L.; Nefedov, O. M. *Organometallics* **1998**, *17*, 5041. (g) Xiong, Y.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7562. (h) Muraoka, T.; Abe, K.; Haga, Y.; Nakamura, T.; Ueno, K. *J. Am. Chem. Soc.* **2011**, *133*, 15365.

(22) Li, L.; Fukawa, T.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *Nature Chem.* DOI: 10.1038/NCHEM.1305.

(23) (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J. *Acc. Chem. Res.* **1999**, *32*, 913. For examples of analogous heavy Group 14 element systems, see (c) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714. (d) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F. -R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485. (e) Mansell, S. M.; Herber, R.; Nowik, I.; Ross, D. H.; Russell, C. A.; Wass, D. F. *Inorg. Chem.* **2011**, *50*, 2252 and references therein.

(24) Choi, N.; Asano, K.; Ando, W. *Organometallics* **1995**, *14*, 3146.

(25) For examples of four-coordinate Ge(IV) complexes with NSiSiN chelates, see: Wannagat, v. U.; Seifert, R.; Schlingmann, M. *Z. Anorg. Allg. Chem.* **1978**, *439*, 83.

(26) (a) Horschler, K.; Stader, C.; Wrackmeyer, B. *Inorg. Chim. Acta* **1986**, *117*, L39. (b) Stader, C.; Wrackmeyer, B.; Schlosser, D. *Z. Naturforsch. B* **1988**, *43*, 288. (c) Wrackmeyer, B.; Stader, C.; Horchler, K.; Zhou, H.; Schlosser, D. *Inorg. Chim. Acta* **1990**, *176*, 205.

(27) (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (b) West, R. *Polyhedron* **2002**, *21*, 467. (c) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. (d) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273. (e) Wang, Y.; Robinson, G. H. *Dalton Trans.* **2012**, 337. (f) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. *Chem. Sci* **2012**, *3*, 659.

(28) (a) Stanciu, C.; Richards, A. F.; Fettinger, J. C.; Brynda, M.; Power, P. P. *J. Organomet. Chem.* **2006**, *691*, 2540. (b) Rivard, E.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 10047 and references therein.

(29) (a) Sakurai, H.; Hirama, K.; Nakadaira, Y.; Kabuto, C. *J. Am. Chem. Soc.* **1987**, *109*, 6880. (b) Kwak, Y. −W.; Lee, I. −S.; Baek, M. −K.; Lee, U.; Choi, H. −J.; Ishikawa, M.; Naka, A.; Ohshita, J.; Lee, K. −H.; Kunai, A. *Organometallics* **2006**, *25*, 48. (c) Kai, H.; Ohshita, J.; Ohara, S.; Nakayama, N.; Kunai, A.; Lee, I. −S.; Kwak, Y. −W. *J. Organomet. Chem.* **2008**, *693*, 3490.