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# Oxidative Addition Versus Substitution Reactions of Group 14 Dialkylamino Metalylenes with Pentafluoropyridine

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Supporting Information

ABSTRACT: Dialkylamino compounds of group 14 elements (Si, Ge, Sn) in the +2 oxidation state supported by benzamidinate ligands were synthesized and treated with pentafluoropyridine. Two different modes of reactivity were observed, depending on the metal atom and the basicity of the substituent at the metal. Pentafluoropyridine undergoes oxidative addition reaction at the Si(II) and Ge(II) atoms whereas at the Sn(II) atom substitution of the NMe<sub>2</sub> group by

the para fluorine of pentafluoropyridine occurs. The C-F bond activation by the lone pair of germanium is the first report of this kind. The Sn(II) fluoride obtained has an elongated Sn-F bond length and can be used as a good fluorinating agent. The compounds were characterized by multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray structural analysis. Single crystal X-ray structural analysis of the tin fluoride shows an asymmetric dimer with weak Sn(II)(F) (F)Sn(II) interactions.

### ■ INTRODUCTION

Heavier carbene analogues of silicon, germanium, and tin are known as silylenes, germylenes, and stannylenes, respectively. Like carbon in carbene, they exhibit the +2 oxidation state. The first stable N-heterocyclic silylene was reported by West et al. in 1994, whereas the first N-heterocyclic germylene was isolated by Veith et al. in 1982.<sup>2</sup> The first monomeric stannylene was synthesized in 1976.<sup>3</sup> Since then a number of room temperature stable silylenes, <sup>4a-g</sup> germylenes, <sup>4h-n</sup> and stannylenes<sup>40,p</sup> were prepared and structurally characterized. Among them the chemistry of functionalized silylenes, germylenes, and stannylenes attracted tremendous attention in the past decade. The advent of these compounds opened an interesting research field of group 14 elements with much attention to compounds containing low valent atoms bearing hydrides, hydroxyl groups, or halides. In 2006, we successfully prepared the first heteroleptic chloro silylene (LSiCl (1), L =  $PhC(NtBu)_2$ ) stabilized by a benzamidinato ligand with tBu substituents on the nitrogen atoms.<sup>5</sup> Later on, we reported the congeners LGeCl (2)<sup>6</sup> and LSnCl (3).<sup>7</sup> These compounds were widely utilized to explore the chemistry of low valent group 14 elements.

In contrast to the ample documentation of chlorides of group 14 elements, reports on fluorides are scarce even if they have found wide application in the laboratory as well as in industry.8 In the literature, the known group 14 fluoro compounds are preferentially in the +4 oxidation state. Only a few examples of organo germanium(II) and tin(II) fluorides are known. 9,10 In contrast to the rich documentation on other silicon halides, the silicon(II) fluorides are scarcely known in literature, because of the lack of convenient synthetic routes and their instability at room temperature. 11 However, very recently we were successful in synthesizing a lead(II) fluoride in the reaction of a  $\beta$ diketiminatolead(II) amine with pentafluoropyridine. 12 In this reaction the NMe2 group at the lead(II) atom was substituted by the para fluorine atom of pentafluoropyridine affording L'PbF (L' =  $HC(CMeNAr)_2$ , Ar =  $2,6-iPr_2C_6H_3$ ). This encouraged us to follow a similar protocol to investigate the general applicability of LE(II)(NR<sub>2</sub>) complexes (L = PhC-(NtBu)2; E = Si, Ge, Sn; R = Me, Pr) to obtain organo Si(II), Ge(II), and Sn(II) fluorides. In addition to this, we are interested to utilize pentafluoropyridine as a fluorinating agent and as an alternative to the widely used trimethyltin fluoride, because the byproduct trimethyltin chloride is highly toxic. For example, studies have proven that trimethyltin chloride could induce hypokalemia in rats which eventually led to their death due to respiratory failure. 13

In a prior publication we reported the preparation of dimethylamino silylene, LSi(NMe<sub>2</sub>) (4), by the reduction of LSiCl<sub>2</sub>(NMe<sub>2</sub>) with potassium.<sup>14</sup> However, to explore the chemistry of dimethylamino silylene in detail, it was essential to develop a more convenient and high yield based protocol. In this regard, very recently we reported the synthesis of various functionalized silylenes (LSiNR<sub>2</sub>) (L = PhC(NtBu)<sub>2</sub>; R = SiMe<sub>3</sub>, Me, iPr, Cy, Ph) by the treatment of LSiCl with the corresponding alkali metal amides. 14b In a similar way, the analogous compounds LGeNiPr<sub>2</sub> (5) and LSnNMe<sub>2</sub> (6) were

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synthesized from **2** and **3**, respectively. Herein we report the synthesis of benzamidinato dialkylamino germylene and stannylene [LENR<sub>2</sub>, L = PhC(NtBu)<sub>2</sub>; E = Ge, R = iPr (**5**); and E = Sn, R = Me (**6**)] and the different modes of reactivity of **4**–**6** with pentafluoropyridine. In contrast to the behavior of LSiNMe<sub>2</sub> and LGeNiPr<sub>2</sub> toward pentafluoropyridine, where oxidative addition of one C–F bond occurs at the Si(II) and Ge(II) atoms, the NMe<sub>2</sub> group in LSnNMe<sub>2</sub> undergoes substitution by the para fluorine atom of pentafluoropyridine. Also we show by some preliminary results that the new Sn(II)F compound might function as an effective and soluble fluorinating agent in organometallic chemistry.

#### ■ RESULTS AND DISCUSSION

The reaction of LGeCl (2) with LiNiPr<sub>2</sub> at room temperature afforded LGeNiPr<sub>2</sub> (5) in good yield. Similarly, the reaction of LSnCl with LiNMe<sub>2</sub> yielded LSnNMe<sub>2</sub> (6) (Scheme 1).

Scheme 1. Preparation of 4, 5, and 6

$$Ph \xrightarrow{\text{fBu}} Ph \xrightarrow{\text{liNR}_2} Ph \xrightarrow{\text{liNR}_2}$$

Compounds 5 and 6 were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The  $^1H$  NMR spectrum of 5 shows a singlet ( $\delta$  1.13 ppm) corresponding to the tBu group and two other singlets ( $\delta$  1.31 and 1.61 ppm) originating from the methyl protons of the NiPr $_2$  group. The CH protons of the iPr groups resonate at 3.53 and 3.80 ppm indicating the difference in chemical environment for each of the iPr groups due to the presence of a lone pair of electrons at the germanium atom in different proximity. The tBu groups in 6 resonate at  $\delta$  0.97 ppm and the NMe $_2$  resonance appears at 3.32 ppm. The  $^{119}$ Sn NMR spectrum of 6 exhibits a singlet ( $\delta$  16.57 ppm).

After the successful preparation of the dialkyl amino functionalized silylene, germylene, and stannylene stabilized by the benzamidinato ligand, we treated them with pentafluoropyridine to obtain the corresponding fluorides LE(II)F (E = Si, Ge, and Sn), inspired by our recent success in obtaining L'PbF from L'PbNMe $_2$  and pentafluoropyridine.

But the reaction of LSiNMe<sub>2</sub> (4) with pentafluoropyridine followed a different route, leading to the formation of  $LSiF(NMe_2)(C_5F_4N)$  (7) (Scheme 2). The reaction proceeds through the oxidative addition of one of the C-F bonds of  $C_sF_sN$  to the silicon(II) atom. Moreover, the reaction resembles our previous report in which the para fluorine atom of the pentafluoropyridine is activated by silylenes. 15 The <sup>1</sup>H NMR spectrum of compound 7 shows two singlets ( $\delta$  0.70, 1.08 ppm) for the *t*Bu protons and one singlet ( $\delta$  2.87 ppm) corresponding to the NMe<sub>2</sub> group. The <sup>29</sup>Si NMR spectrum exhibits a doublet ( $\delta$  –100.25 ppm) with a coupling constant of  $J(^{29}\text{Si}-^{19}\text{F}) = 310.99 \text{ Hz. The }^{19}\text{F NMR spectrum of compound}$ 7 shows two doublets ( $\delta$  –133.29, –93.75 ppm) corresponding to the fluorine atoms in the  $C_5F_4N$  moiety and a singlet ( $\delta$ -84.68 ppm) originating from the fluorine atom bound to the silicon atom. Compound 7 crystallizes in the space group  $P\overline{1}$ with one molecule in the asymmetric unit. (Figure 1) The

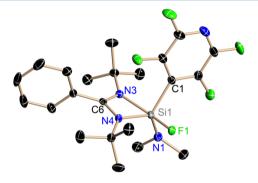


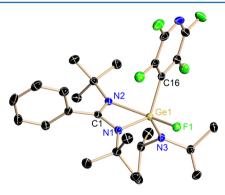
Figure 1. Molecular structure of 7. The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths  $[\mathring{A}]$  and angles  $[\deg]$ : Si1–F1 1.6563(8), Si1–C1 1.9343(13), Si1–N1 1.7035(12), Si1–N3 1.9652(11), Si1–N4 1.8115(11); N3–Si1–N4 69.04(5), N1–Si1–F1 96.80(5), C1–Si1–F1 88.58(5).

coordination polyhedron around the silicon atom features a distorted trigonal bipyramidal geometry. The Si-F and Si-C bond lengths are 1.6563(8) Å and 1.9343(13) Å, respectively.

The reaction of LGeNiPr<sub>2</sub> (5) with pentafluoropyridine  $(C_5F_5N)$  in toluene in a 1:1 molar ratio at room temperature (Scheme 2) leads to the formation of the LGeF(NiPr<sub>2</sub>)- $(C_5F_4N)$  (8) through an oxidative addition pathway in contrast to our expectation of a metathesis reaction. Such a reaction at the amino substituted Ge(II) atom is surprising, and this is the

Scheme 2. Preparation of 7, 8, and 9

first report of a C-F bond activation by a germylene lone pair. It should be noted that the activity of the lone pair is highly influenced by the functionalities attached to the germanium atom. For instance, there is no reaction between LGeCl (2) and C<sub>5</sub>F<sub>5</sub>N. Among the amino functionalized germylenes, LGeN-(SiMe<sub>3</sub>)<sub>2</sub> (see Supporting Information for preparation) does not react with C<sub>5</sub>F<sub>5</sub>N, even at an elevated temperature of 60 °C, but LGeNMe, (see Supporting Information for preparation) reacts very slowly at room temperature. The reaction of LGeNMe<sub>2</sub> with C<sub>5</sub>F<sub>5</sub>N proceeds in an uncontrolled protocol, and we were not able to isolate a clean product. However, <sup>1</sup>H and <sup>19</sup>F NMR spectra clearly indicate the formation of 4dimethylaminotetrafluoropyridine (4-NMe<sub>2</sub>C<sub>5</sub>F<sub>4</sub>N), the byproduct of a metathesis reaction. We assume that both metathesis and oxidative addition occur in parallel in the case of LGeNMe<sub>2</sub>. The reaction of 2 with C<sub>5</sub>F<sub>5</sub>N is comparatively faster, and it is unidirectional. From these observations it can be concluded that the reactivity of the lone pair is tuned by the basicity of the functional group attached to the germanium atom. Obviously an increased basic nature results in the higher activity of the lone pair. The <sup>1</sup>H NMR spectrum of 8 shows two singlets ( $\delta$  0.56 and 1.12 ppm) corresponding to the two tBu groups. The methyl protons of the iPr groups appear as two close doublets ( $\delta$  1.38 and 1.41 ppm) and the CH protons resonate ( $\delta$  3.92 ppm) as a septet. The <sup>19</sup>F NMR spectrum shows two broad signals ( $\delta$  -130.54 and -92.37 ppm) originating from the fluorine atoms of the C<sub>5</sub>F<sub>4</sub>N unit and a sharp resonance ( $\delta$  –91.34 ppm) corresponding to the fluorine atom bonded to the germanium atom. Compound 8 crystallizes in the monoclinic space group  $P2_1/n$  and the coordination environment around the germanium is distorted trigonal bipyramidal similar to that of compound 7. (Figure 2) The Ge-F bond length is 1.8009(8) Å, and the Ge-C bond length shows 1.9944(14) Å.

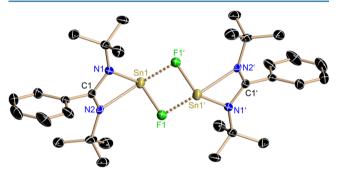


**Figure 2.** Molecular structure of **8**. The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths  $[\mathring{A}]$  and angles  $[\deg]$ : Ge1-F1 1.8009(8), Ge1-N3 = 1.8024(11), Ge1-C16 1.9944(14), Ge1-N1 1.9054(12), Ge1-N2 2.1623(12); N1-Ge1-N2 64.47(5), C16-Ge1-F1 87.74(5), N3-Ge1-F1 98.56(5).

Unlike 4 and 5 the reaction of LSnNMe<sub>2</sub> (6) with pentafluoropyridine affords the anticipated LSnF (9) in a metathesis reaction (Scheme 2) together with the formation of 4-dimethylaminotetrafluoropyridine (4-NMe<sub>2</sub>C<sub>5</sub>F<sub>4</sub>N). The reaction achieved full conversion within 10 min. The  $^1$ H NMR spectrum of the crude reaction mixture indicates the complete disappearance of the resonance for NMe<sub>2</sub> ( $\delta$  3.31 ppm) of 6, and the formation of a new resonance ( $\delta$  2.54 ppm) for 4-

dimethylaminotetrafluoropyridine. This reaction is comparable with the synthesis of 4-dimethylaminotetrafluoropyridine from dimethyl amine or trimethylsilyl-dimethylamine (Me<sub>3</sub>SiNMe<sub>2</sub>) and C<sub>5</sub>F<sub>5</sub>N. <sup>16a,b</sup> The energy required for the cleavage of the C-F bond is compensated by the formation of the C-N bond. In addition, the different modes of reactivity shown by Ge(II) and Sn(II) with pentafluoropyridine are comparable to the oxidative addition versus arene elimination reaction of Ar<sub>2</sub>Ge(II) and  $Ar_2Sn(II)$  [Ar =  $C_6H_3$ -2,6- $(C_6H_3$ -2,6-iPr<sub>2</sub>)<sub>2</sub>] with ammonia and hydrogen as reported by Power et al. <sup>16c</sup> The tBu resonance in the <sup>1</sup>H NMR spectrum of compound 9 appears at 1.09 ppm and the <sup>19</sup>F NMR spectrum shows the resonance at  $\delta$  –98.06 ppm. The <sup>119</sup>Sn NMR spectrum exhibits an upfield resonance  $(\delta -210.92 \text{ ppm})$  when compared with that of the starting material ( $\delta$  16.57 ppm). However, the Sn-F coupling was not observed in the spectra. The 119Sn NMR spectrum of 9 at a reduced temperature of -60 °C in toluene-d<sub>8</sub> showed a broad resonance at  $\delta$  –283.93 ppm.

Storing a saturated solution of 9 in toluene at -4 °C in a freezer afforded single crystals suitable for X-ray diffraction investigation. 9 crystallizes in the space group  $P2_1/c$ , and it exists as a dimer in which two molecules are connected by weak intermolecular Sn···F bonds (Figure 3). However, Lappert et al.



**Figure 3.** Molecular structure of **9.** The anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Sn1-F1 2.0796(11), Sn1-F1′ 2.338, Sn1-N1 2.1980(14), Sn1-N2 2.254(9); N1-Sn1-N2 59.83(17), N1-Sn1-F1 97.18(5), N2-Sn1-F1 86.24(15).

reported a compound with  $Sn(\mu-F)_2Sn$  structure where all four Sn-F bonds are equal each with a bond distance of 2.156 Å. 10a In compound 9 the Sn-F bond lengths are 2.0796(11) and 2.338 Å respectively showing the weak association of the two molecules. This represents the first example where such an arrangement of Sn(II)(F) (F)Sn(II) was observed for a Sn(II)-Fcompound. Each Sn atom adopts a distorted square pyramidal geometry with the lone pair of electrons in the axial position. The base of the square pyramid is constituted by two nitrogen atoms from the amidinate ligand, and the two fluorine atoms of the Sn-F and Sn···F bonds. The dimeric arrangement of 9 in solution was confirmed by osmometric molecular mass determination in toluene. From these observations, it should be noted that the absence of clear splitting of the 119Sn resonance may be due to the presence of two chemically nonequivalent fluorine atoms with respect to the Sn atom. The Sn-F bond length of 2.0796(11) Å in 9 is of special interest when compared with those of the monomeric organotin fluorides containing Sn(IV) atoms. For example, the Sn-F bond lengths in  $Me_2[(PhMe_2Si)_3C]SnF,^{17}$   $Ph_2[(TMS)_3C]-SnF,^{17}$  and  $Mes_3SnF^{18}$  are 1.965, 1.965, and 1.961 Å,

Table 1. Crystal and Structure Refinement Parameters for Compounds 7, 8, and (9),

parameters	7	8	(9) <sub>2</sub>
CCDC No.	899944	899945	899946
empirical formula	$C_{22}H_{29}F_5N_4Si$	$C_{26}H_{37}F_5GeN_4$	$C_{30}H_{46}F_2N_4Sn_2$
formula weight	472.58	573.18	738.09
crystal system	triclinic	monoclinic	monoclinic
space group	$P\overline{1}$	$P2_1/n$	$P2_1/c$
unit cell dimensions	a = 9.2560(10)  Å	a = 15.1223(8)  Å	a = 10.149(3)  Å
	b = 10.2020(10)  Å	b = 19.2483(10)  Å	b = 9.614(2)  Å
	c = 13.9106(10)  Å	c = 19.8868(10)  Å	c = 16.921(2)  Å
	$\alpha = 93.480(10)^{\circ}$	$\beta = 112.045(2)^{\circ}$	$\beta = 99.62(2)^{\circ}$
	$\beta = 92.283(10)^{\circ}$		
	$\gamma = 115.677(10)^{\circ}$		
volume, Z	1178.48(19) Å <sup>3</sup> , 2	5365.4(5) Å <sup>3</sup> , 8	1627.8(6) Å <sup>3</sup> , 2
density (calcd)	$1.332 \text{ Mg/m}^3$	$1.419 \text{ Mg/m}^3$	$1.506 \text{ Mg/m}^3$
absorption coefficient	0.156 mm <sup>-1</sup>	1.198 mm <sup>-1</sup>	1.570 mm <sup>-1</sup>
F (000)	496	2384	744
crystal size/mm	$0.1 \times 0.1 \times 0.08$	$0.15 \times 0.1 \times 0.05$	$0.325 \times 0.290 \times 0.277$
$\theta$ range for data collection	1.471 to 27.894°.	1.458 to 27.523°.	2.035 to 26.788°
limiting indices	$-12 \le h \le 12$	$-19 \le h \le 19$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-25 \le k \le 23$	$-12 \le k \le 12$
	$-18 \le l \le 18$	$-25 \le l \le 25$	$-21 \le l \le 21$
reflections collected	31603	98347	40528
independent reflections	$5626 (R_{\text{int}} = 0.0332)$	12312 ( $R_{\text{int}} = 0.0364$ )	$3475 (R_{\rm int} = 0.0284)$
completeness to $\theta$	99.9% ( $\theta = 25.242^{\circ}$ )	$100.0\% \ (\theta = 25.242^{\circ})$	$100.0\% \ (\theta = 25.242^{\circ})$
refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
data/restraints/parameters	5626/0/297	12312/0/669	3475/107/209
goodness-of-fit on $F^2$	1.008	1.033	1.087
final R indices $[I > 2\sigma(I)]$	R1 = 0.0358, wR2 = 0.0872	R1 = 0.0247, wR2 = 0.0576	R1 = 0.0180, wR2 = 0.0409
R indices (all data)	R1 = 0.0433, wR2 = 0.0909	R1 = 0.0299, wR2 = 0.0593	R1 = 0.0205, wR2 = 0.0422
largest diff. peak and hole	$0.332 \text{ and } -0.269 \text{ e } \text{Å}^{-3}$	$0.375 \text{ and } -0.273 \text{ e } \text{Å}^{-3}$	$0.511 \text{ and } -0.392 \text{ e Å}^{-3}$

respectively. The extended Sn-F bond length of 9 is an interesting feature which is due to the larger ionic radius of Sn(II) compared to that of Sn(IV). This increases the reactivity in the case of Sn(II) fluorides when compared with those of Sn(IV) fluorides. Interestingly, the Sn-F bond length in 9 is still larger than that in L'SnF (1.988 Å) [L' = HC(CMeNAr)<sub>3</sub>, still larger than that in L'SnF (1.988 Å) Ar =  $2,6-iPr_2C_6H_3$ ] which we reported previously. Subsequently compound 9 is presumed to have a large synthetic utility as an effective fluorinating agent that does not cause hazardous byproducts like Me<sub>3</sub>SnCl. To investigate the fluorinating ability of 9 we treated this compound with organic and inorganic substrates. The preliminary results from our laboratory show the clean conversion of Me<sub>3</sub>SiCl, PhCOCl, and CH(SiMe<sub>3</sub>)<sub>2</sub>PCl<sub>2</sub> to Me<sub>3</sub>SiF, PhCOF, and CH(SiMe<sub>3</sub>)<sub>2</sub>PF<sub>2</sub> respectively, and the formations of products were confirmed from the corresponding resonances in the <sup>19</sup>F NMR spectra. Note that the conversion of CH(Me<sub>3</sub>Si)<sub>2</sub>PCl<sub>2</sub> to CH(Me<sub>3</sub>Si)<sub>2</sub>)-PF<sub>2</sub> was completed in a few minutes at room temperature in the presence of 2 equiv of 9 whereas the same conversion using Me<sub>3</sub>SnF will take more than 6 h toward completeness at an elevated temperature of 60 °C.

### CONCLUSION

Dialkylamino functionalized group 14 metalylenes LSiNMe<sub>2</sub> (4), LGeNiPr<sub>2</sub> (5), and LSnNMe<sub>2</sub> (6) were synthesized, and the reaction of these compounds with pentafluoropyridine was probed. C–F bond activation of pentafluoropyridine occurred at the Si(II) and the Ge(II) atoms of 4 and 5 followed by the oxidative addition to yield LSiF(NMe<sub>2</sub>)( $C_5F_4N$ ) (7) and LGeF(NiPr<sub>2</sub>)( $C_5F_4N$ ) (8). The formation of 8 is the first

example of the C-F bond activation at a Ge(II) atom. Unlike 4 and 5, compound 6 undergoes the expected metathesis reaction with pentafluoropyridine affording LSnF (9) with an elongated Sn-F bond. Preliminary experiments show that compound 9 is a promising mild fluorinating agent. Application of 9 for synthesizing organometallic fluoride compounds are under progress in our laboratory, and such results will be reported in due course.

## **■ EXPERIMENTAL SECTION**

Syntheses were carried out under an inert gas atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques. Other manipulations were accomplished in a dinitrogen filled glovebox. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. Compounds 1,  $^{\rm Sb}$  2,  $^6$  3,  $^7$  and 4  $^{\rm 14b}$  were prepared as reported in the literature.  $^{\rm 1}$ H,  $^{\rm 13}$ C, and  $^{\rm 29}$ Si NMR spectra were recorded with a Bruker Avance DPX 200 or a Bruker Avance DRX 300 spectrometer, using  $\rm C_6D_6$  as solvent. Chemical shifts  $\delta$  are given relative to SiMe<sub>4</sub>. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were carried out in the Analytischen Labor der Anorganischen Chemie der Universität Göttingen. Molecular mass determination was performed with a KNAUER vapor pressure osmometer.

**Synthesis of 5.** Toluene (50 mL) was added to a Schlenk flask (100 mL) containing **2** (2 g, 5.88 mmol) and LiN*i*Pr<sub>2</sub> (0.62 g, 5.88 mmol). The reaction mixture was stirred at room temperature for 6 h. The solution was filtered, and the solvent was reduced in vacuo to about 10 mL and stored at -32 °C in a freezer for two days to obtain **5** as a white crystalline product. (1.92 g, 81%). Elemental analysis (%) calcd for C<sub>21</sub>H<sub>37</sub>GeN<sub>3</sub> (405.22): C, 62.40; H, 9.23; N, 10.40; Found: C, 62.74; H, 9.10; N, 10.89. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.13

(s, 18 H,  $C(CH_3)_3$ ), 1.31 (s, 6 H,  $CH(CH_3)_2$ ), 1.61 (s, 6H,  $CH(CH_3)_2$ ), 3.53 (br, 1H,  $CH(CH_3)_2$ ), 3.80 (br, 1H,  $CH(CH_3)_2$ ), 6.95–7.22 (m, 5H, Ph) ppm. EI-MS: m/z 405 [M $^+$ ].

**Synthesis of 6.** To a Schlenk flask (100 mL) containing 3 (2 g, 5.19 mmol) and LiNMe<sub>2</sub> (0.26 g, 5.19 mmol) was added toluene (50 mL) at -60 °C. The reaction mixture was allowed to warm to room temperature and stirring was continued for 6 h. The solution was filtered, and concentrated in vacuo to about 10 mL and stored at -32 °C in a freezer for two days to obtain 6 as a white crystalline product. (1.53 g, 75%). Elemental analysis (%) calcd for  $C_{17}H_{29}N_3Sn$  (395.14): C, 51.80; H, 7.42; N, 10.66; Found: C, 52.05; H, 7.26; N, 10.78. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 25 °C):  $\delta$  0.98 (s, 18 H,  $C(CH_3)_3$ ), 3.32 (s, 6 H,  $C(CH_3)_2$ ), 6.96–7.10 (m, 5H, Ph) ppm. <sup>119</sup>Sn NMR (111 MHz,  $C_6D_6$ ):  $\delta$  16.57 ppm. EI-MS: m/z 395 [M<sup>+</sup>].

**Synthesis of 8.** To a toluene solution (30 mL) of **5** (1 g, 2.46 mmol) in a Schlenk flask (100 mL) pentafluoropyridine (0.43 g, 2.59 mmol) dissolved in toluene (10 mL) was added slowly at room temperature and stirred for 4 h. The solution was concentrated to dryness, the solid residue was redissolved in toluene (20 mL), and stored at -4 °C in a freezer for a day to obtain single crystals of **8**. (1.04 g, 74%). Elemental analysis (%) calcd for C<sub>26</sub>H<sub>37</sub>F<sub>5</sub>GeN<sub>4</sub> (574.22): C, 54.48; H, 6.51; N, 9.77; Found: C, 55.06; H, 6.23; N, 9.89. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.56 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.12 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.37 (d, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.85–3.98 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.74–7.04 (m, 5H, Ph) ppm. <sup>19</sup>F NMR (188.29 MHz, C<sub>6</sub>D<sub>6</sub>): δ –91.34 (s, 1F, Ge-F), –92.37 (br, 2F, o-F), –130.54 (br, 2F, m-F) ppm.

**Synthesis of 9.** Pentafluoropyridine (0.45 g, 2.66 mmol) dissolved in toluene (10 mL) was added slowly to a toluene solution (30 mL) of 6 (1 g, 2.53 mmol) in a Schlenk flask (100 mL) at room temperature and stirred for 30 min. The solution was concentrated to dryness, the white residue was dissolved in toluene (15 mL), and stored at  $-4\,^{\circ}\mathrm{C}$  for two days to obtain single crystals of 9. (0.76 g, 81%). Elemental analysis (%) calcd for  $\mathrm{C_{15}H_{23}FN_2Sn}$  (370.09): C, 48.82; H, 6.28; N, 7.59; Found: C, 48.71; H, 6.10; N, 7.34. <sup>1</sup>H NMR (300 MHz,  $\mathrm{C_6D_6}$ ) 5 °C): δ 1.09 (s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>), 6.94–6.97 (m, 5H, Ph) ppm. <sup>19</sup>F NMR (188.29 MHz,  $\mathrm{C_6D_6}$ ): δ -98.06 ppm. <sup>119</sup>Sn NMR (111 MHz,  $\mathrm{C_6D_6}$ ): δ -210.92 ppm. EI-MS: m/z 351 [M<sup>+</sup>-F].

Crystal Structure Determination. Single crystals were selected from a Schlenk flask under an argon atmosphere and covered with perfluorated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow supplied by the X-TEMP2 device. 19 An appropriate crystal was selected using a polarizing microscope, fixed on the tip of a MiTeGen MicroMount, transferred to a goniometer head, and shock cooled by the crystal cooling device. The data for 7, 8, and 9 were collected from these shock-cooled crystals at 100(2) K. 19 The data for 7 and 9 were collected on an Incoatec Mo microfocus source<sup>20</sup> equipped with Helios mirror optics and an APEX II detector at a D8 goniometer. The data for 8 was measured on a Bruker TXS Mo rotating anode with Helios mirror optics and an APEX II detector at a D8 goniometer. Important data are summarized in Table 1. Both diffractometers used Mo  $K_{\alpha}$  radiation,  $\lambda = 71.073$  pm. The data for all structures were integrated with SAINT, 21 and an empirical absorption correction (SADABS)<sup>22</sup> was applied. The structures were solved by direct methods (SHELXS-97)<sup>23a</sup> and refined by full-matrix leastsquares methods against  $F^2$  (SHELXL-97) $^{23\mathrm{b,c}}$  within the SHELXLE GUI. GUI.  $^{23\mathrm{d}}$  All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their  $U_{\mathrm{iso}}$  values constrained to equal 1.5 times the  $U_{\mathrm{eq}}$  of their pivot atoms for terminal sp $^3$  carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length and angle restraints and anisotropic displacement parameter restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table 1.

#### ASSOCIATED CONTENT

### **S** Supporting Information

Preparation of LGeNMe<sub>2</sub> and LGeN(SiMe<sub>3</sub>)<sub>2</sub> and CIF files for compounds 7–9. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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