

## Lewis Base Mediated Autoionization of $\text{GeCl}_2$ and $\text{SnCl}_2$

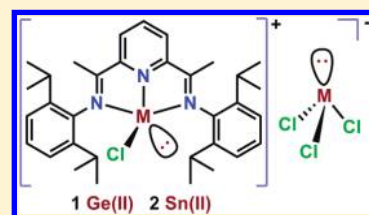
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### Supporting Information

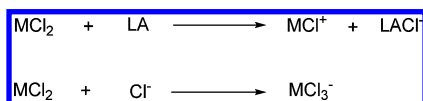
**ABSTRACT:** Cationic and anionic species of heavier low-valent group 14 elements are intriguing targets in main group chemistry due to their synthetic potential and industrial applications. In the present study, we describe the synthesis of cationic ( $\text{MCl}^+$ ) and anionic ( $\text{MCl}_3^-$ ) species of heavier low-valent group 14 elements of germanium(II) and tin(II) by using the substituted Schiff base 2,6-diacetylpyridinebis(2,6-diisopropylanil) as Lewis base (LB). Treatment of LB with 2 equiv of  $\text{GeCl}_2$ :dioxane and  $\text{SnCl}_2$  in toluene gives compounds  $[(\text{LB})\text{Ge}^{\text{II}}\text{Cl}]^+[\text{Ge}^{\text{II}}\text{Cl}_3]^-$  (**1**) and  $[(\text{LB})\text{Sn}^{\text{II}}\text{Cl}]^+[\text{Sn}^{\text{II}}\text{Cl}_3]^-$  (**2**), respectively, which possess each a low-valent cation and an anion. Compounds **1** and **2** are well characterized with various spectroscopic methods and single crystal X-ray structural analysis.



## INTRODUCTION

The chemistry of the heavier group 14 elements has been driven by their industrial applications especially for electronic materials.<sup>1</sup> During the past two decades, chemists have been largely motivated to study the reactivity of compounds with low-valent germanium and tin due to their higher stability when compared with the carbon and silicon analogues.<sup>2,3</sup> Tin dichloride is a very common reducing agent,<sup>4</sup> usually applied for the precipitation of metals such as silver and mercury and for the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . The first step of the autoionization might be the formation of the  $\text{SnCl}_3^-$  anion, which attacks the positively charged metal cation. Already in 1972 G. W. Parshall showed that molten alkyl ammonium salts of  $\text{R}_4\text{N}^+\text{SnCl}_3^-$  could be used for hydrogenation reaction of olefins.<sup>5</sup> Cationic species of low-valent heavier group 14 elements with the composition of  $\text{RM}^+$  (R = halide, organic group) are intriguing to image the reactivity, which combines the ambiphilic nature of a Lewis base and high electrophilicity of a cation.<sup>6</sup> In organic chemistry, carbenes and N-heterocyclic carbenes are well-known.<sup>7</sup> However, to the best of our knowledge, dissociation of a carbene of composition  $\text{R}_2\text{C}$ : to the ionic species  $\text{RC}^+$  and  $\text{R}_3\text{C}^-$  has so far not been observed. These cationic and anionic species of heavier group 14 elements can be prepared by adding a Lewis acid (LA) and a chloride base, respectively, to the neutral  $\text{MCl}_2$  species (Scheme 1).<sup>8</sup>

### Scheme 1. Preparation of Cations and Anions



Moreover, covalently bound substituents on cationic centers of heavier group 14 elements are required to provide steric and electronic stabilization to protect the positively charged species from reactions with solvent and counteranions.<sup>9</sup> It is evident from the pioneering work that the stabilization of  $\text{RGe}^+$  or  $\text{RSn}^+$

cations by cyclopentadienyl-, *N*-isopropyl-2-(isopropylamino)-troponimine-, or cyclophane-group is possible.<sup>10</sup> Notable investigations on four valence electron species  $\text{RM}^+$  with suitable anions have been documented in the literature. Schmidbauer and co-workers<sup>11</sup> isolated an aluminate of a germanium(II) cation. Recently, Baines and colleagues<sup>12</sup> reported the triflate of a germanium(II) cation as byproduct in the synthesis of a cryptand encapsulated germanium dication. Further, Reid and co-workers<sup>13</sup> synthesized and structurally characterized germanium(II) halide complexes with neutral N-donor ligands. Alternatively, an unconventional method for the stabilization of divalent cations of group 14 elements is their coordination to transition metals,<sup>14</sup> which was successfully applied for the synthesis of *trans*- $[(\eta^1\text{-Cp}^*)\text{GeW}(\text{MeCN})\text{-(Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $[\text{L}(\text{OTf})\text{Ge}][\text{W}(\text{CO})_5]$  (L =  $\text{NPhC}(\text{Me})\text{CHC}(\text{Me})\text{NPh}$ ) and  $[(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)\text{SnW}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2][\text{PF}_6]$ ,  $[\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}(\text{H}_2\text{O})\text{-SnW}(\text{CO})_5][\text{CB}_{11}\text{H}_{12}]$ .

Herein, we report the Lewis base mediated autoionization of  $\text{MCl}_2$  to cationic ( $\text{MCl}^+$ ) and anionic ( $\text{MCl}_3^-$ ) species, where M is germanium or tin. Two novel compounds  $[(\text{LB})\text{Ge}^{\text{II}}\text{Cl}]^+[\text{Ge}^{\text{II}}\text{Cl}_3]^-$  (**1**) and  $[(\text{LB})\text{Sn}^{\text{II}}\text{Cl}]^+[\text{Sn}^{\text{II}}\text{Cl}_3]^-$  (**2**) have been synthesized by reacting the substituted Schiff base 2,6-diacetylpyridinebis(2,6-diisopropylanil) (LB) with the corresponding metal dichloride. Compounds **1** and **2** have both the cationic  $[(\text{LB})\text{M}^{\text{II}}\text{Cl}]^+$  as well as the anionic  $[\text{M}^{\text{II}}\text{Cl}_3]^-$  species of their respective low-valent group 14 elements.

## RESULTS AND DISCUSSION

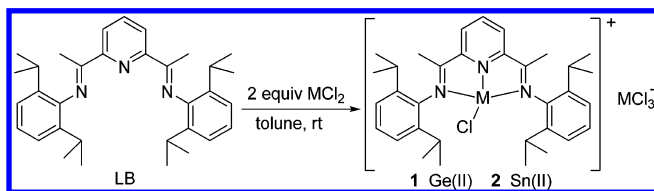
**Synthesis.** The ligand (LB) was treated separately with  $\text{GeCl}_2$ :dioxane and  $\text{SnCl}_2$  in a ratio of 1:2 in toluene at room temperature under a nitrogen atmosphere to afford the compounds

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$[(\text{LB})\text{Ge}^{\text{II}}\text{Cl}]^+[\text{Ge}^{\text{II}}\text{Cl}_3]^-$  (**1**) and  $[(\text{LB})\text{Sn}^{\text{II}}\text{Cl}]^+[\text{Sn}^{\text{II}}\text{Cl}_3]^-$  (**2**), respectively (Scheme 2). Compounds **1** and **2** are highly soluble

**Scheme 2. Synthesis of Compounds 1 and 2**



in polar solvents like tetrahydrofuran (THF) but sparingly soluble in nonpolar solvents indicating the ionic nature of these compounds. Highly saturated solutions of compounds **1** and **2** give crystalline products in an excellent yield (80–85%). Furthermore, they are stable both in solution and in the solid state for a long period of time without any decomposition under an inert gas atmosphere. These compounds have been fully characterized by elemental analysis, solution- as well as solid-state  $^{119}\text{Sn}$  NMR spectroscopy, and single crystal X-ray structural analysis. The  $^1\text{H}$  NMR resonances were assigned by integration and comparison with the signals of the free ligand. In compound **1** especially, aromatic protons resonate downfield ( $\delta$  8.99, 8.88, and 7.15 ppm) in comparison to the free ligand ( $\delta$  8.52, 8.04, and 7.05 ppm), which clearly indicates the coordination of the germanium with the binding sites of the ligand, whereas in compound **2**, the corresponding results have been reciprocated with tin. Another interesting observation in the  $^1\text{H}$  NMR spectrum are the  $\text{CH}_3$  protons of the  $\text{N}=\text{C}-\text{CH}_3$  groups, which exhibit two different resonances (2.64, 2.22 and 2.70, 2.30 ppm for compounds **1** and **2**) in comparison to the free ligand ( $\text{CH}_3$  protons of the  $\text{N}=\text{C}-\text{CH}_3$  groups resonate at 2.31 ppm). We assume that this is probably due to the coordination of the metal ion to the ligand binding sites which result in a different electronic environment for the  $\text{N}=\text{C}-\text{CH}_3$  protons. Accordingly, the  $\text{CH}_3$  carbons of the  $\text{N}=\text{C}-\text{CH}_3$  groups in the  $^{13}\text{C}$  NMR spectrum resonate at two different positions (29.12, 28.16 ppm for **1** and 24.21, 23.21 ppm for **2**), whereas in the free ligand, the resonances are observed at 28.32 ppm. To investigate the electronic environment around the tin centers in compound **2**, the solution- and solid-state  $^{119}\text{Sn}$  NMR spectra were recorded at variable temperatures. The room temperature solution-state  $^{119}\text{Sn}$  NMR spectrum consists of two singlets at  $-60.2$  and  $-435.0$  ppm (Supporting Information Figure S1). These two singlets correspond to two differently coordinated tin(II) atoms present in compound **2**. The available literature data<sup>15</sup> suggest that the broad signal at  $-60.2$  ppm corresponds to the  $\text{SnCl}_3^-$  anion, while the remaining singlet at  $-435.0$  ppm could be assigned to the  $[(\text{LB})\text{SnCl}]^+$  cation. The  $^{119}\text{Sn}$  NMR spectrum of compound **2** at low temperature varying in a range of 298–173 K indicates that the tin center in the  $[(\text{LB})\text{SnCl}]^+$  cation is intact. However, a little broadening observed at 173 K is probably due to inherent freezing properties of the  $\text{THF}-d_8$  solvent which was used for the experiment. In addition, the downfield resonance at  $-60.2$  ppm for the  $\text{SnCl}_3^-$  anion shows a very irregular change in the position at low temperature. This irregular change can be due to coordination of  $\text{THF}-d_8$  solvent molecules to the  $\text{SnCl}_3^-$  anion leading to different geometrical species. To test this hypothesis, solid-state  $^{119}\text{Sn}$  NMR was recorded for compound **2**. The spectra obtained in the range of 282–305 K were virtually unchanged at three different temperatures. The possibility that a rearrangement of the geometry

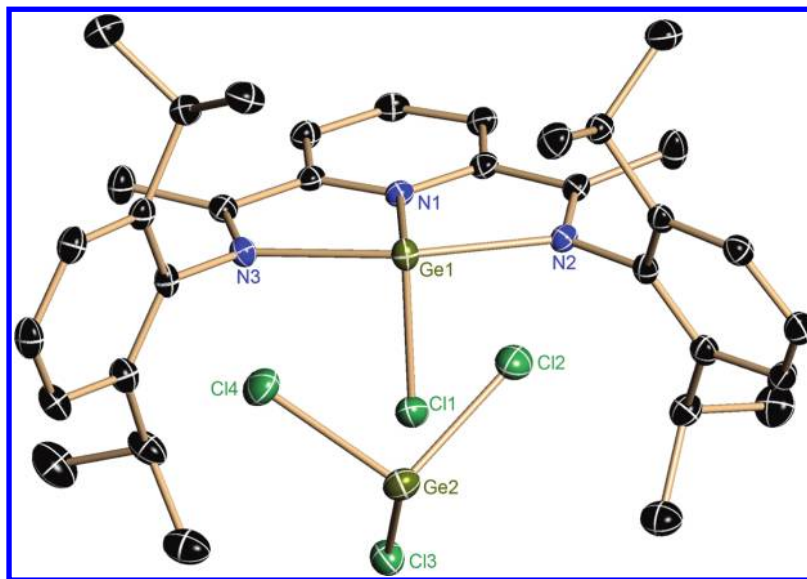
around the tin center of the  $\text{SnCl}_3^-$  anion occurs at low temperature in the absence of a solvent is thus invalidated; the shifts observed in solution-state NMR are rather related to a solvent effect.

**Crystal Structure Analysis.** To establish unambiguously the structural feature of compounds **1** and **2**, single crystal X-ray structural analysis was carried out. Suitable single crystals of **1** and **2** were obtained from saturated toluene solutions at room temperature. Both compounds **1** and **2** are isostructural and crystallize in the triclinic crystal system with space group  $P\bar{1}$  (Table 1). The molecular structures of **1** and **2** reveal that one cation  $[(\text{LB})\text{M}^{\text{II}}\text{Cl}]^+$  and one anion  $[\text{M}^{\text{II}}\text{Cl}_3]^-$  are present in the same crystal lattice where  $\text{M} = \text{Ge}$  for **1** (Figure 1) and  $\text{M} = \text{Sn}$  for **2** (Supporting Information Figure S2). In the cation  $[(\text{LB})\text{M}^{\text{II}}\text{Cl}]^+$ , the metal center is connected to three nitrogen atoms of the ligand (LB) and one chlorine atom. Three nitrogen atoms N1, N2, and N3 of the ligand along with the metal atom M1 form a basal plane. The metal center in the cation  $[(\text{LB})\text{M}^{\text{II}}\text{Cl}]^+$  adopts a distorted square pyramidal geometry if the electron lone pair of M1 is considered at fourth position of the basal plane. The chlorine atom occupies the top of the square pyramid. This arrangement of ligand (LB) gives rise to two five-membered chelating rings. The coordination bond formed by the nitrogen atom N1 and M1 is acting as a bridge between these two rings. In case of compound **1**, the  $\text{Ge}-\text{N}1$ ,  $\text{Ge}-\text{N}2$ , and  $\text{Ge}-\text{N}3$  bond distances are 2.071(2), 2.255(2), and 2.267(2) Å. Other structurally characterized Ge(II) species with N-donor ligands are mostly dicationic, for example,  $[\text{Ge}(\text{Me}_4\text{-cyclam})]^{2+}$  and  $[\text{Ge}(\text{Me}_3\text{-tactn})]^{2+}$  for which the average  $\text{Ge}-\text{N}$  distance is 2.250 and 2.140 Å.<sup>16</sup> However, the  $\text{M}-\text{N}$  bond distances of heavier group 14 elements would be influenced by the metal oxidation state and its coordination number. In compound **2**, the  $\text{Sn}1-\text{N}1$  bond distance (2.286 Å) is significantly shorter than that of  $\text{Sn}1-\text{N}2$  (2.403 Å) and  $\text{Sn}1-\text{N}3$  (2.411 Å). A similar trend is also observed in compound **1**, although the average  $\text{Sn}1-\text{N}$  bond distance (2.366 Å) of **2** is comparatively longer than the average  $\text{Ge}1-\text{N}$  bond length (2.197 Å) of **1**. The angles delaminated at the M1 metal center, within the five-membered chelate rings  $\text{N}1-\text{M}1-\text{N}2$  and  $\text{N}1-\text{M}1-\text{N}3$ , are 73.52(7) and 73.28(7)° for **1**, and 68.71(7) and 68.79(7)° for **2**. In the cation  $[(\text{LB})\text{M}^{\text{II}}\text{Cl}]^+$  of **1** and **2**, the chlorine atom attached to the metal center is oriented nearly perpendicular to the basal plane constituted by the nitrogen atoms N1, N2, and N3 of the ligand with  $\text{M}1-\text{Cl}1$  bond distance of 2.2433(9) and of 2.4359(10) Å, respectively. The average  $\text{N}-\text{M}1-\text{Cl}1$  bond angle is 89.84° and 86.69° for compounds **1** and **2**, respectively. In the anion  $[\text{M}^{\text{II}}\text{Cl}_3]^-$  of **1** and **2**, three chlorine atoms (Cl2, Cl3, and Cl4) are attached to the metal ion M2, resulting in a trigonal pyramidal shape of the anion. The average  $\text{M}2-\text{Cl}$  bond length for **1** and **2** is 2.316 and 2.495 Å, while the average  $\text{Cl}-\text{M}2-\text{Cl}'$  bond angle is 96.37 and 94.32°, respectively. Small differences in the bond lengths and bond angles of **1** and **2** can be explained by the different radii of Sn and Ge. The superposition plot of both the compounds **1** and **2** is depicted in Figure S3. Selected bond distances and bond angles for both compounds are summarized in Table 2.

**Solid-State  $^{119}\text{Sn}$  NMR Spectroscopy.** Three tin sites (A, B, and B') are detected in solid-state  $^{119}\text{Sn}$  NMR, in contrast to the two tin resonances detected in solution-state NMR. The isotropic chemical shifts ( $-77.4$  ppm (A),  $-415.4$  ppm (B), and  $-431.5$  ppm (B')) indicated by red arrows in Figure 2, are identified by recording the spectra at two different magic-angle spinning rates (11.0 and 11.8 kHz). The chemical shift

Table 1. Crystal and Structure Refinement Parameters for Compounds 1 and 2

parameters	1·1.5 toluene	2·1.5 toluene
Empirical formula	C <sub>43.50</sub> H <sub>55</sub> Cl <sub>4</sub> N <sub>3</sub> Ge <sub>2</sub>	C <sub>43.50</sub> H <sub>55</sub> Cl <sub>4</sub> N <sub>3</sub> Sn <sub>2</sub>
Formula Weight	906.89	999.09
CCDC no.	862039	862038
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a = 10.330 (3) \text{ \AA}$ $b = 13.013 (3) \text{ \AA}$ $c = 16.873(7) \text{ \AA}$ $\alpha = 93.66 (1)^\circ$ $\beta = 97.33 (1)^\circ$ $\gamma = 103.26 (1)^\circ$	$a = 10.438 (2) \text{ \AA}$ $b = 13.174 (2) \text{ \AA}$ $c = 16.908(4) \text{ \AA}$ $\alpha = 90.68 (1)^\circ$ $\beta = 99.080 (1)^\circ$ $\gamma = 103.21 (1)^\circ$
Volume	2179.4 (12) $\text{\AA}^3$	2226.8 (8) $\text{\AA}^3$
Z	2	2
Density (calcd)	1.382 g/cm <sup>3</sup>	1.490 g/cm <sup>3</sup>
Absorption coefficient	1.658 mm <sup>-1</sup>	0.738 mm <sup>-1</sup>
F (000)	938	1010
Crystal size	0.1 × 0.05 × 0.05 mm	0.1 × 0.05 × 0.05 mm
$\theta$ range for data collection	1.22–26.94°	0.97–20.60°
Limiting indices	$-12 \leq h \leq 13, -14 \leq k \leq 16, -14 \leq l \leq 21$	$-13 \leq h \leq 13, -16 \leq k \leq 16, -21 \leq l \leq 21$
Reflections collected	31860	53144
Independent reflections	64933 ( $R_{\text{int}} = 0.0398$ )	9045 ( $R_{\text{int}} = 0.0628$ )
Completeness to $\theta$	98.2% ( $\theta = 26.83$ )	98.1% ( $\theta = 26.60$ )
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	9181/30/518	9044/96/513
Goodness-of-fit on $F^2$	1.045	1.030
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0253, wR2 = 0.0550$	$R1 = 0.0306, wR2 = 0.0638$
R indices (all data)	$R1 = 0.0332, wR2 = 0.0569$	$R1 = 0.0457, wR2 = 0.0684$
Largest diff. peak and hole	0.387 and $-0.291 \text{ e\AA}^{-3}$	0.939 and $-1.124 \text{ e\AA}^{-3}$



**Figure 1.** Molecular structure of  $[(\text{LB})\text{Ge}^{\text{II}}\text{Cl}]^+[\text{Ge}^{\text{II}}\text{Cl}_3]^-$  (1). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

anisotropy  $\delta_{\text{aniso}} = \delta_{zz} - \delta_{\text{iso}}$  is quite large for all three sites ( $-617.5$  ppm (A),  $-750$  ppm (B), and  $-744.7$  ppm (B')) while the asymmetry of the chemical shift anisotropy (CSA) tensor  $\eta_{\text{asym}} = (\delta_{yy} - \delta_{xx})/(\delta_{\text{aniso}})$  is close to 0 for all sites. Values of the asymmetry such as 0.03 for sites A, B', and 0.0 for site B indicate an axially symmetric CSA tensor. The observed large anisotropies are a distinctive feature of tin(II) species.<sup>17</sup> By similarity to the solution-state <sup>119</sup>Sn isotropic chemical shift,

site A is assigned to Sn2 in the  $\text{SnCl}_3^-$  anion (See Supporting information Figure S1). The two latter sites (B and B') share similar values for isotropic and anisotropy chemical shift which can be assigned to Sn1 in the  $[(\text{LB})\text{SnCl}]^+$  cation. The occurrence of two <sup>119</sup>Sn resonances for Sn1 could arise because of polymorphism in the sample, with site B' as a minor component. Indeed, the ratio of summed sideband intensities (A/B/B' 4:3:1) suggests a stoichiometry of 1:1

**Table 2. Selected bond lengths [Å] and angles [°] Parameters for Compounds 1 and 2**

bond lengths and angles	1	2
M(1)–N(1)	2.071(2)	2.286(2)
M(1)–N(2)	2.255(2)	2.403(2)
M(1)–N(3)	2.267(2)	2.411(2)
M(1)–Cl(1)	2.2433(9)	2.4359(10)
M(2)–Cl(2)	2.3100(8)	2.4801(8)
M(2)–Cl(3)	2.3246(9)	2.5190(9)
M(2)–Cl(4)	2.3128(9)	2.4870(8)
N(1)–M(1)–N(2)	73.52(7)	68.71(7)
N(1)–M(1)–N(3)	73.28(7)	68.79(7)
N(2)–M(1)–N(3)	145.99(7)	136.87(7)
N(1)–M(1)–Cl(1)	94.25(6)	88.31(6)
N(2)–M(1)–Cl(1)	87.18(5)	86.18(6)
N(3)–M(1)–Cl(1)	88.09(5)	85.59(6)
Cl(2)–M(2)–Cl(3)	97.18(3)	93.03(3)
Cl(2)–M(2)–Cl(4)	97.17(3)	94.24(3)
Cl(3)–M(2)–Cl(4)	94.75(3)	95.69(3)

between Sn2 and Sn1 sites which is in agreement with the crystal structure of 2.

## CONCLUDING REMARKS

The carbenium ion  $RC_2^+$  and carbanion  $R_3C^-$  analogues of heavier low-valent group 14 elements with the composition of  $RM^+$  and  $R_3M^-$  have potential application in synthesis and industrial processes. In the present study, we have demonstrated a completely new approach to the synthesis of such low-valent cationic and anionic species for heavier group 14 metals by using a Lewis base (LB). Two novel compounds  $[(LB)Ge^IVCl]^+[Ge^{II}Cl_3]^-$  (1) and  $[(LB)Sn^{IV}Cl]^+[Sn^{II}Cl_3]^-$  (2) have been synthesized and well characterized with various spectroscopic techniques and single crystal X-ray structural analysis. Crystal structure analysis reveals that compounds 1 and 2 are isostructural to each other.

## EXPERIMENTAL SECTION

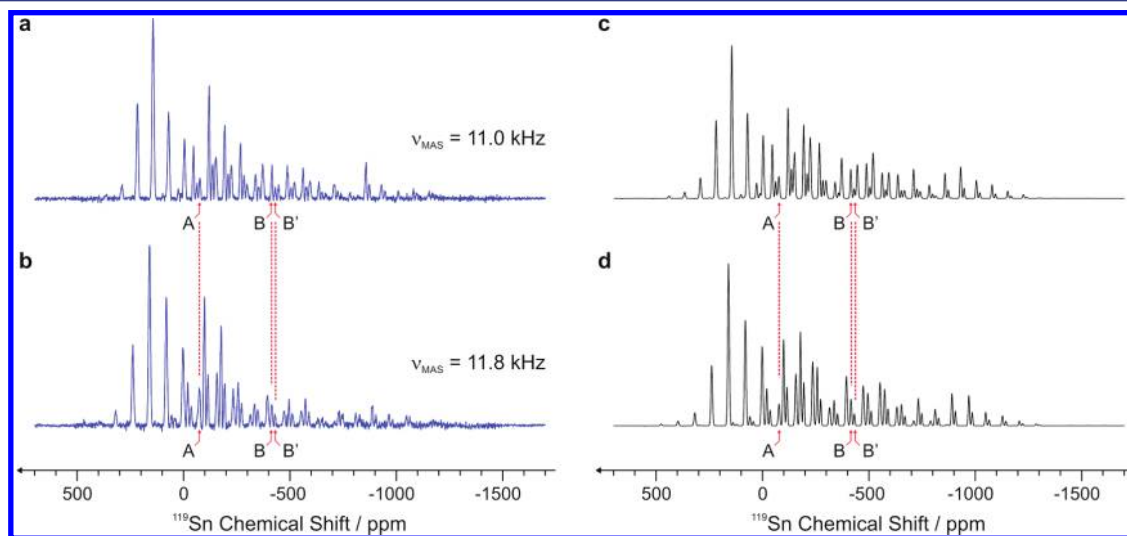
All manipulations were performed in a dry and oxygen free atmosphere ( $N_2$ ) using standard Schlenk-line techniques and inside

a MBraun MB 150-GI glovebox maintained at or below 1 ppm of  $O_2$  and  $H_2O$ . All solvents were dried by a MBraun solvent purifying system prior to use. Substituted Schiff base ligand (LB) was prepared using modified reported procedure. Other chemicals were purchased commercially and used as received. Solution-state  $^1H$ ,  $^{13}C$ , and  $^{119}Sn$  NMR spectra were recorded on a Bruker Avance DRX instrument (300 or 500 MHz). The chemical shifts  $\delta$  are given in ppm with tetramethylsilane ( $^1H$  and  $^{13}C$ ) and  $Me_4Sn$  ( $^{119}Sn$ ) as external standards. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument.

**Solid-State NMR.** Compound 2 was loaded under an inert atmosphere into a 4.0 mm MAS rotor. All spectra were recorded on a wide-bore 9.4 T instrument (400 MHz,  $^1H$  Larmor frequency) at magic-angle spinning rates of 11 or 11.8 kHz.  $^{119}Sn$  chemical shifts are given in reference to  $Me_4Sn$ , using the sharp resonance of tetracyclohexyltin as external calibration. A cross-polarization contact time of 3.5 ms was employed, with an effective acquisition time of 4 ms and a recycling delay of 1 s. The full sideband pattern was acquired by the variable offset cumulative spectrum technique,<sup>18</sup> recording 9 subspectra spanning each a 75.2 kHz spectral window, and each time moving the  $^{119}Sn$  rf carrier frequency by 37.6 kHz. The number of scans ranges from 50176 to 71680 per subspectrum, for a total measurement time ranging from 5 to 8 days per spectrum. The temperature was calibrated externally using the  $^1H$  chemical shift of nickelocene.<sup>19</sup>

**Synthesis of 2,6-Diacetylpyridinebis(2,6-diisopropylanil) (LB).** The ligand (LB) was synthesized by a modified reported procedure.<sup>20</sup> The 2,6-diisopropylaniline (7.34 mL, 38.61 mmol) was added to the absolute ethanol (50 mL) solution of 2,6-diacetylpyridine (3.00 g, 18.38 mmol). After the addition of a few drops of glacial acetic acid, the solution was refluxed for 6 h. Volatiles were removed under reduced pressure to afford a yellow colored solid product. The product was crystallized from ethanol at low temperature which gives a white colored crystalline compound (yield 7.34 g, 83%).  $^1H$  NMR (500 MHz,  $THF-d_8$ , TMS, 25 °C):  $\delta$  8.52 (d, 2H, Py- $H_m$ ), 8.04 (t, 1H, Py- $H_p$ ), 7.05 (m, 6H, Ar- $H$ ), 2.83 (sept, 4H, Ar- $CH(CH_3)_2$ ), 2.31 (s, 6H,  $N=CCH_3$ ), 1.18 (m, 24 H,  $CHCH_3$ ) ppm.  $^{13}C$  NMR (500 MHz,  $THF-d_8$ , TMS, 25 °C):  $\delta$  167.04 (N=C), 155.25 (Py- $C_o$ ), 146.25 (Ar- $C_{ip}$ ), 135.69 (Ar- $C_o$ ), 123.75 (Ar- $C_p$ ), 123.02 (Py- $C_p$ ), 122.57 (Py- $C_m$ ), 122.30 (Ar- $C_m$ ), 28.32 (N=C- $CH_3$ ), 23.21 ( $CH(CH_3)_2$ ), 17.15 ( $CH(CH_3)_2$ ) ppm.

**Synthesis of  $[(LB)GeCl]^+[GeCl_3]^-$  (1).** The solution of ligand LB (500 mg, 1.03 mmol) in toluene (50 mL) was added to solid  $GeCl_2$ -dioxane (480 mg, 2.07 mmol) at room temperature (25 °C).



**Figure 2.** Solid-state  $^{119}Sn$  NMR cross-polarization spectra of compound 2 at 11.0 kHz (a and c) and 11.8 kHz (b and d). Experimental (a and b) and simulated (c and d) spectra, as obtained from the fitting of spinning sideband intensities.



The reaction mixture was stirred for 12 h at this temperature. Then, all volatiles were removed under vacuum. The residue was washed with *n*-hexane (50 mL) to afford a red colored solid. The crude compound was again dissolved in a minimum amount of toluene and filtered through the pad of Celite in a medium porosity frit. The filtrate was stored 3 days at room temperature to give a red crystalline compound suitable for single crystal analysis (yield 654 mg, 82%). Elemental analysis (%) calcd for  $C_{47}H_{51}Cl_4N_3Ge_2$  (953.08): C, 59.23; H, 6.24; N, 4.41. Found: C, 59.76; H, 6.34; N, 4.89.  $^1H$  NMR (500 MHz, THF- $d_8$ , TMS, 25 °C):  $\delta$  8.99 (t, 1H, Py- $H_p$ ), 8.88 (d, 2H, Py- $H_m$ ), 7.15 (m, 6H, Ar- $H$ ), 2.83 (sept, 4H, CH(CH $_3$ ) $_2$ ), 2.64 (s, 3H, N=C-CH $_3$ ), 2.22 (s, 3H, N=C-CH $_3$ ), 1.15 (m, 24H, CH(CH $_3$ ) $_2$ ) ppm.  $^{13}C$  NMR (500 MHz, THF- $d_8$ , TMS, 25 °C):  $\delta$  150.14 (N=C), 139.25 (Py- $C_o$ ), 138.21 (Ar- $C_p$ ), 137.23 (Ar- $C_o$ ), 134.55 (Ar- $C_p$ ), 127.02 (Py- $C_p$ ), 124.57 (Py- $C_m$ ), 123.30 (Ar- $C_m$ ), 29.12 (N=C-CH $_3$ ), 28.16 (N=C-CH $_3$ '), 25.29 (CH(CH $_3$ ) $_2$ ), 24.31 (CH'(CH $_3$ ) $_2$ ), 19.35 (CHCH $_3$ ), 18.65 (CHCH $_3$ ') ppm. EI-MS:  $m/z$  (%) 590 (100) [(LB)GeCl] $^+$ , 178 (100) [GeCl $_3$ ] $^+$ .

**Synthesis of [(LB)SnCl] $^+$ [SnCl $_3$ ] $^-$  (2).** Compound 2 was synthesized by a similar procedure as compound 1 using SnCl $_2$  (394 mg, 2.07 mmol) instead of GeCl $_2$ ·dioxane. A saturated toluene solution of compound 2 gives yellow colored crystals suitable for structural analysis (yield 759 mg, 85%). Elemental analysis (%) calcd for  $C_{47}H_{51}Cl_4N_3Sn_2$  (1045.22): C, 54.01; H, 5.69; N, 4.02. Found: C, 54.56; H, 5.34; N, 4.39.  $^1H$  NMR (500 MHz, THF- $d_8$ , 25 °C, TMS):  $\delta$  9.01 (t, 1H, Py- $H_p$ ), 8.89 (d, 2H, Py- $H_m$ ), 7.17 (m, 6H, Ar- $H$ ), 3.05 (sept, 4H, CH(CH $_3$ ) $_2$ ), 2.70 (s, 3H, N=C-CH $_3$ ), 2.30 (s, 3H, N=C-CH $_3$ '), 1.16 (m, 24H, CH(CH $_3$ ) $_2$ ) ppm.  $^{13}C$  NMR (500 MHz, THF- $d_8$ , TMS, 25 °C):  $\delta$  147.04 (N=C), 138.25 (Py- $C_o$ ), 136.25 (Ar- $C_p$ ), 135.69 (Ar- $C_o$ ), 133.75 (Ar- $C_p$ ), 125.02 (Py- $C_p$ ), 122.57 (Py- $C_m$ ), 122.30 (Ar- $C_m$ ), 28.32 (N=C-CH $_3$ ), 27.36 (N=C-CH $_3$ '), 24.21 (CH(CH $_3$ ) $_2$ ), 23.21 (CH'(CH $_3$ ) $_2$ ), 18.15 (CHCH $_3$ ), 17.35 (CHCH $_3$ ') ppm.  $^{119}Sn$  NMR (500 MHz, THF- $d_8$ , Me $_4$ Sn, 25 °C):  $\delta$  -60.27 and -435.07 ppm. EI-MS:  $m/z$  (%) 636 (100) [(LB)SnCl] $^+$ , 224 (100) [SnCl $_3$ ] $^+$ .

**Crystal Structure Determination.** Suitable single crystals for X-ray structural analysis of compounds 1 and 2 were mounted at low temperature under nitrogen atmosphere by applying the X-TEMP-2 device.<sup>21</sup> The diffraction data for compound 1 were collected at 100 K on Bruker TXS-Mo rotating anode with Helios mirror optics and an APEX II detector with D8 goniometer. Data for 2 were collected at 100 K on SMART APEX Quazar with INCOATEC Ag microsource with mirror optics ( $\lambda = 0.56086$  Å). The data were integrated with SAINT<sup>22</sup> and an empirical absorption correction with TWINABS<sup>23</sup> for 1 and SADABS<sup>24</sup> for 2 was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on  $F^2$  (SHELXL v 0.477).<sup>25</sup> 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  $U_{iso}$  values constrained to 1.5  $U_{eq}$  of their pivot atoms for terminal sp $^3$  carbon atoms and 1.2 times for all other carbon atoms (Table 1).

## ASSOCIATED CONTENT

### Supporting Information

CIF files for 1 and 2, solution-state  $^{119}Sn$  NMR, and molecular structure of 2. 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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## REFERENCES

- (1) (a) Marygarian, A. M. *Photodetectors and Fiber Optics*; Academic Press: San Diego, CA, 2001; pp 369–458. (b) Shemkunas, M. P.; Petuskey, W. T.; Chizmeshya, A. V. G.; Leinenweber, K.; Wolf, G. H. *J. Mater. Res.* **2004**, *19*, 1392–1399. (c) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372. (d) Power, P. P. *Appl. Organometal. Chem.* **2005**, *19*, 488–493. (e) Spike, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85–87. (f) Richards, A. F.; Brynda, M.; Olmstead, M. M.; Power, P. P. *Organometallics* **2004**, *23*, 2841–2844. (g) Richards, A. F.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4071–4074. (h) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67–86. (i) Braunschweig, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1156–1158. (j) Saur, I.; Garcia Alonso, S.; Barrau, J. *Appl. Organometal. Chem.* **2005**, *19*, 414–428. (k) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511.
- (2) (a) Mandal, S. K.; Roesky, H. W. *Chem. Commun.* **2010**, *46*, 6016–6041. (b) Nava, M.; Reed, C. A. *Organometallics* **2011**, *30*, 4798–4800. (c) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155–215. (d) West, R.; Moser, D. F.; Guzei, I. A.; Lee, G.-H.; Naka, A.; Li, W.; Zabala, A.; Bukalov, S.; Leites, L. *Organometallics* **2006**, *25*, 2709–2711. (e) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969–990. (f) Krummenacher, I.; Oschwald, C.; Rügger, H.; Breher, F. Z. *Anorg. Allg. Chem.* **2007**, *633*, 2354–2361.
- (3) (a) Willey, G. R.; Somasundaram, U.; Aris, D. R.; Errington, W. *Inorg. Chim. Acta* **2001**, *315*, 191–195. (b) Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszczuk, M. *Inorg. Chem.* **1972**, *11*, 1402–1409. (c) Ejfler, J.; Szafert, S.; Jiao, H.; Sobota, P. *New J. Chem.* **2002**, *26*, 803–805. (d) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Eur. J. Inorg. Chem.* **2007**, 2488–2495. (e) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Eur. J. Inorg. Chem.* **2007**, 4897–4905.
- (4) (a) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839–842. (b) Zheng, L.; Wang, B.; Chi, Y.; Song, S.; Fan, C.; Chen, G. *Dalton Trans.* **2012**, *41*, 1630–1634.
- (5) Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 8716–8719.
- (6) (a) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Chem.—Eur. J.* **2009**, *15*, 3945–3950. (b) Gaspar, P. P. In *Organosilicon Chemistry VI*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 2005; Vol. 2, p 10.
- (7) (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92. (c) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304–5313.
- (8) (a) Lee, V. Y.; Sekiguchi, A. *Acc. Chem. Res.* **2007**, *40*, 410–419. (b) Stender, M.; Phillips, A. D.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 5314–5315. (c) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655. (d) Steiner, A.; Stalke, D. *Inorg. Chem.* **1995**, *34*, 4846–4853. (e) Rugar, P. A.; Staroverov, V. N.; Ragonna, P. J.; Baines, K. M. *J. Am. Chem. Soc.* **2007**, *129*, 15138–15139. (f) Apostolico, L.; Mahon, M. F.; Molloy, K. C.; Binions, R.; Blackman, C. S.; Carmalt, C. J.; Parkin, I. P. *Dalton Trans.* **2004**, 470–470.
- (9) Rugar, P. A.; Bandyopadhyay, R.; Cooper, B. F. T.; Stinchcombe, M. R.; Ragonna, P. J.; Macdonald, C. L. B.; Baines, K. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5155–5158.

(10) (a) Jutzi, P.; Kohl, F.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 59–60. (b) Hani, R.; Geanangel, R. A. *J. Organomet. Chem.* **1985**, *293*, 197–205. (c) Jutzi, P.; Kohl, F.; Krüger, C.; Wolmershäuser, G.; Hofmann, P.; Stauffert, P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 70. (d) Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564–1575. (e) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123–9126. (f) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650–4655.

(11) (a) Probst, T.; Steigelmann, O.; Riede, J.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1397–1398. (b) Schmidbaur, H.; Schier, A. *Organometallics* **2008**, *27*, 2361–2395.

(12) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Science* **2008**, *322*, 1360–1363.

(13) Cheng, F.; Dyke, J. M.; Ferrante, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Dalton Trans.* **2010**, *39*, 847–856.

(14) (a) Filippou, A. C.; Philippopoulos, A. L.; Schnakenburg, G. *Organometallics* **2004**, *23*, 4503–4512. (b) Saur, I.; Alonso, S. G.; Gornitzka, H.; Lemierre, V.; Chrostowska, A.; Barrau, J. *Organometallics* **2005**, *24*, 2988–2996. (c) Filippou, A. C.; Philippopoulos, A. L.; Schnakenburg, G. *Organometallics* **2003**, *22*, 3339–3341. (d) Jambor, R.; Kasna, B.; Koller, S. G.; Strohmam, C.; Schurmann, M.; Jurkschat, K. *Eur. J. Inorg. Chem.* **2010**, 902–908.

(15) Coddington, J. M.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2223–2227.

(16) Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5152–5154.

(17) Eichler, B. E.; Phillips, B. L.; Power, P. P.; Augustine, M. P. *Inorg. Chem.* **2000**, *39*, 5450–5453.

(18) Massiot, D.; Farnan, I.; Gautier, N.; Trumeau, D.; Trokiner, A.; Coutures, J. P. *Solid State Nucl. Magn. Reson.* **1995**, *4*, 241–248.

(19) Heise, H.; Köhler, F. H.; Xie, X. *J. Magn. Reson.* **2001**, *150*, 198–206.

(20) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728–8740.

(21) (a) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178. (b) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619.

(22) SAINT V7.46/V7.66; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2008.

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

(24) Sheldrick, G. M. *SADABS 2008/2*; Universität Göttingen: Göttingen, Germany, 2008.

(25) Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.