Lewis Base Mediated Autoionization of GeCl₂ and SnCl₂

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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 (MCl⁺) and anionic (MCl₃⁻) species of heavier low-valent group 14 elements of germanium(II) and tin(II) by using the substituted Schiff base 2,6-diacyethylpyridinebis(2,6-diisopropyl) as Lewis base (LB). Treatment of LB with 2 equiv of GeCl₂-dioxane and SnCl₂ in toluene gives compounds [(LB)GeCl₂][GeCl₄]⁻ (1) and [(LB)SnCl₂][SnCl₄]⁻ (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.¹ 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.²,³ Tin dichloride is a very common reducing agent,⁴ usually applied for the precipitation of metals such as silver and mercury and for the reduction of Fe³⁺ to Fe²⁺. The first step of the autoionization might be the formation of the SnCl⁻ anion, which attacks the positively charged metal cation. Already in 1972 G. W. Parshall showed that molten alkyl ammonium salts of R₄N⁺SnCl₃⁻ metal cation. Already in 1972 G. W. Parshall showed that molten alkyl ammonium salts of R₄N⁺SnCl₃⁻ could be used for hydrogenation reaction of olefins.⁶ Cationic species of low-valent heavier group 14 elements with the composition of R₂C⁺ (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.⁶ In organic chemistry, carbenes and N-heterocyclic carbenes are well-known.⁷ However, to the best of our knowledge, dissociation of a carbene of composition R₂C⁻ to the ionic species RC⁻ and R₂C⁺ 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 MCl₄ species (Scheme 1).⁸

Moreover, covalently bound substituents on cationic centers of heavier group 14 elements are required to sterically and electronic stabilization to protect the positively charged species from reactions with solvent and counteranions.⁹ It is evident from the pioneering work that the stabilization of RGe⁺ or RSn⁺ cations by cyclopentadienyl-, N-isopropyl-2-(isopropylamino)-troponimine-, or cyclophane-group is possible.¹⁰ Notable investigations on four valence electron species RM⁺ with suitable anions have been documented in the literature. Schmidbaur and co-workers¹¹ isolated an aluminate of a germanium(II) cation. Recently, Baines and colleagues¹² reported the triflate of a germanium(II) cation as byproduct in the synthesis of a cryptand encapsulated germanium dication. Further, Reid and co-workers¹³ 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,¹⁴ which was successfully applied for the synthesis of trans-[η⁷-Cp⁺*GeW(MeCN)₂(Ph₂PCH₂CH₂PPh₂)₂][B(C₆F₅)₄], [L(OTf)Ge][W(CO)₅] (L = NPhC(Me)CHC(Me)NPh) and [(2,6-(Me₂NCH₂)₂C₆H₃)(H₂O)-SnW(P₈PCH₂CH₂PPh₂)][PF₆], [(2,6-(Me₂NCH₂)₂C₆H₃)(H₂O)-SnW(CO)₅][CB₁₁H₁₂], [(LB)GeCl₂][GeCl₄]⁻ (1) and [(LB)SnCl₂][SnCl₄]⁻ (2) have been synthesized by reacting the substituted Schiff base 2,6-diacyethylpyridinebis(2,6-diisopropyl) (LB) with the corresponding metal dichloride. Compounds 1 and 2 have both the cationic [(LB)MCl⁺]⁺ as well as the anionic [MCl₃⁻]⁻ species of their respective low-valent group 14 elements.

RESULTS AND DISCUSSION

Synthesis. The ligand (LB) was treated separately with GeCl₂-dioxane and SnCl₂ in a ratio of 1:2 in toluene at room temperature under a nitrogen atmosphere to afford the compounds...
[(LB)Ge⁴Cl⁺][Ge²Cl₄]⁻ (1) and [(LB)Sn⁴Cl⁺][Sn²Cl₄]⁻ (2), respectively (Scheme 2). Compounds 1 and 2 are highly soluble 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 119Sn NMR spectroscopy, and single crystal X-ray structural analysis. The 1H NMR resonances were assigned by integration and comparison with the signals of the free ligand. In compound 1 especially, aromatic protons resonate downfield (δ 8.99, 8.88, and 7.15 ppm) in comparison to the free ligand (δ 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 1H NMR spectrum are the CH₃ protons of the N=C–CH₃ 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 (CH₃ protons of the N=C–CH₃ 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 N=C–CH₃ protons. Accordingly, the CH₃ carbons of the N=C–CH₃ groups in the 13C 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 119Sn NMR spectra were recorded at variable temperatures. The room temperature solution-state 119Sn 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 data¹⁵ suggest that the broad signal at −60.2 ppm corresponds to the SnCl⁻⁻ anion, while the remaining singlet at −435.0 ppm could be assigned to the [(LB)SnCl⁺]⁺ cation. The ¹¹⁹Sn NMR spectrum of compound 2 at low temperature varying in a range of 298–173 K indicates that the tin center in the [(LB)SnCl⁺]⁺ cation is intact. However, a little broadening observed at 173 K is probably due to inherent freezing properties of the THF-d₈ solvent which was used for the experiment. In addition, the downfield resonance at −60.2 ppm for the SnCl⁻⁻ anion shows a very irregular change in the position at low temperature. This irregular change can be due to coordination of THF-d₈ solvent molecules to the SnCl⁻⁻ anion leading to different geometrical species. To test this hypothesis, solid-state ¹¹⁹Sn 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 SnCl⁻⁻ 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 isorotational and crystallize in the triclinic crystal system with space group P1 (Table 1). The molecular structures of 1 and 2 reveal that one cation [(LB)M⁴Cl⁺]⁺ and one anion [M²Cl₄]⁻ are present in the same crystal lattice where M = Ge for 1 (Figure 1) and M = Sn for 2 (Supporting Information Figure S2). In the cation [(LB)M⁴Cl⁺]⁺, 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 [(LB)M⁴Cl⁺]⁺ 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 Ge–N1, Ge–N2, and Ge–N3 bond distances are 2.071(2), 2.255(2), and 2.267(2) Å. Another structurally characterized Ge(II) species with N-donor ligands are mostly dicationic, for example, [Ge(Me₄-cyclam)]²⁺ and [Ge(Me₃-tacn)]²⁺ for which the average Ge–N distance is 2.250 and 2.140 Å.¹⁶ However, the M–N bond distances of heavier group 14 elements would be influenced by the metal oxidation state and its coordination number. In compound 2, the Sn1–N1 bond distance (2.286 Å) is significantly shorter than that of Sn1–N2 (2.403 Å) and Sn1–N3 (2.411 Å). A similar trend is also observed in compound 1, although the average Sn1–N bond distance (2.366 Å) of 2 is comparatively longer than the average Ge1–N bond length (2.197 Å) of 1. The angles delaminated at the M1 metal center, within the five-membered chelate rings N1–M1–N2 and N1–M1–N3, are 73.52(7) and 73.28(7)° for 1, and 68.71(7) and 68.79(7)° for 2. In the cation [(LB)M⁴Cl⁺]⁺ of 1 and 2, the chloride 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 M1–Cl1 bond distance of 2.4339(9) and of 2.4359(10) Å, respectively. The average N–M1–Cl1 bond angle is 89.84° and 86.69° for compounds 1 and 2, respectively. In the anion [M²Cl₄]⁻ 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 M2–Cl bond length for 1 and 2 is 2.316 and 2.495 Å, while the average Cl1–M2–Cl2 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 ¹¹⁹Sn NMR Spectroscopy. Three tin sites (A, B, and B’) are detected in solid-state ¹¹⁹Sn 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
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. By similarity to the solution-state $^{119}$Sn isotropic chemical shift, site A is assigned to Sn2 in the 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 [(LB)SnCl] cation. The occurrence of two $^{119}$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.
between Sn2 and Sn1 sites which is in agreement with the crystal structure of 2.

### CONCLUDING REMARKS

The carbenium ion RC:+ and carbanion R3C− analogues of heavier low-valent group 14 elements with the composition of RM:+ and R3M− 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)GeCl]+[GeCl3])− and ([(LB)SnCl]+[SnCl3])− 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 isomorphous to each other.

### EXPERIMENTAL SECTION

All manipulations were performed in a dry and oxygen free atmosphere (N2) using standard Schlenk-line techniques and inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of O2 and H2O. 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, 13C, and 119Sn NMR spectra were recorded on a Bruker Avance DRX instrument (300 or 500 MHz). The chemical shifts δ are given in ppm with tetramethylsilane (δH and δ13C) and Me4Sn (δ119Sn) as external standards. Elemental analyses were performed by the Analytisches Labor des Institutes für Anorganische Chemie der Universität Göttingen. El-MS were measured on a Finnigan Mat 8230 or a Varian MAT CHS 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. 119Sn chemical shifts are given in reference to Me4Sn, 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, recording 9 subspectra spanning each a 75.2 kHz spectral window, and each time moving the 119Sn rf carrier frequency by 37.6 kHz. The number of scans ranges from 50 176 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.15

#### Synthesis of 2,6-Diacetylpyridinebis(2,6-disopropylbischloro) GeCl (LB)

The ligand (LB) was synthesized by a modified reported procedure. The 2,6-diisopropylaniline (7.34 mL, 38.61 mmol) was crystallized from ethanol at low temperature which gives a white crystalline compound (yield 7.34 g, 83%).1HN M R (500 MHz, THF-d8, 25 °C): δ 8.82 (d, 2H, Py−Hδ), 8.04 (t, 1H, Py−Hδ), 7.05 (m, 6H, Ar−H), 2.83 (sept, 4H, Ar−CH(CH3)2), 1.18 (m, 24 H, CH(CH3)2).13CN M R (300 or 500 MHz, THF-d8, 25 °C): δ 167.04 (N=C=), 155.25 (Py=C), 146.25 (Ar−Cip), 135.69 (Ar−Cip), 123.75 (Ar−Cip), 123.02 (Py−C), 122.57 (Py−C), 122.30 (Ar−Cip), 28.32 (N=C−CH3), 23.21 (CH(CH3)2), 17.15 (CH(CH3)2) ppm.13CN M R (300 or 500 MHz, THF-d8, 25 °C): δ 167.04 (N=C=), 155.25 (Py=C), 146.25 (Ar−Cip), 135.69 (Ar−Cip), 123.75 (Ar−Cip), 123.02 (Py−C), 122.57 (Py−C), 122.30 (Ar−Cip), 28.32 (N=C−CH3), 23.21 (CH(CH3)2), 17.15 (CH(CH3)2) ppm.13CN M R (300 or 500 MHz, THF-d8, 25 °C): δ 167.04 (N=C=), 155.25 (Py=C), 146.25 (Ar−Cip), 135.69 (Ar−Cip), 123.75 (Ar−Cip), 123.02 (Py−C), 122.57 (Py−C), 122.30 (Ar−Cip), 28.32 (N=C−CH3), 23.21 (CH(CH3)2), 17.15 (CH(CH3)2) ppm.13CN M R (300 or 500 MHz, THF-d8, 25 °C): δ 167.04 (N=C=), 155.25 (Py=C), 146.25 (Ar−Cip), 135.69 (Ar−Cip), 123.75 (Ar−Cip), 123.02 (Py−C), 122.57 (Py−C), 122.30 (Ar−Cip), 28.32 (N=C−CH3), 23.21 (CH(CH3)2), 17.15 (CH(CH3)2) ppm.
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 (%) calc for C_{47}H_{51}Cl_{4}N_{3}Sn_{2} (1045.22): C, 54.01; H, 5.69; N, 4.02. Found: C, 59.76; H, 6.34; N, 4.89. 

**REFERENCES**


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**ASSOCIATED CONTENT**

Supporting Information

CIF files for 1 and 2, solution-state \textsuperscript{119}Sn NMR, and molecular structure of 2. This material is available for free 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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