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Note

Synthesis and characterization of β-diketiminate germanium(II) and tin(II) bromides

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ABSTRACT

The equimolar reaction of a β-diketiminate lithium salt LLi(OEt$_2$) [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] with either GeBr$_2$ or SnBr$_2$ in diethyl ether affords the synthetically useful monomeric β-diketiminate-element halides LGeBr (**1**) and LSnBr (**2**), respectively. Both are soluble in hydrocarbon solvents, stable in inert atmosphere, and have been characterized by elemental analysis, NMR spectroscopy, and single-crystal X-ray diffraction analysis.

1. Introduction

Halides of group 14 elements are important precursors for a variety of new reactions. Dihalogermylenes, GeX$_2$ (X = F, Cl, Br, I), were the first known divalent species that had been studied and reviewed as starting materials and intermediates in organogermanium chemistry in 1973 [1]. Cp*GeCl was the first example of a monohalide with the general composition RMX (M = Ge, Sn; R = organic group; X = halide) prepared in 1987 [2], followed by the tin analogue RSnCl (R = C(SiMe$_3$)$_2$C$_5$H$_4$N-2) in 1988 [3]. After 10 years Filippou et al. were successful in preparing a germanium bromide dimer, [Cp*GeBr]$_2$ [4]. In 2006 our group reported the synthesis and structure of the first monomeric chloro silylene [{PhC(N*t*Bu)$_2$}SiCl] [5]. More recently we described the synthesis of a Lewis base (NHC) stabilised dichloro silylene [6], which has the potential for further reactions and may have the same impact like GeCl$_2$·dioxane. Filippou et al. published the *N*-heterocyclic carbene adduct of dibromosilylene [7]. In the literature there are numerous reports known on the synthesis of fluoro, chloro, and iodo derivatives of compounds with low valent group 14 elements. This is in contrast to the corresponding bromo derivatives [8]. Independently, Lappert et al. and we reported on the β-diketiminate of lead(II) bromo derivative [9,10], and very recently So et al. described the synthesis of monomeric bromo silylene [{PhC(N*t*Bu)$_2$}SiBr] [11], by the reaction of the silicon(I) compound [{PhC(N*t*Bu)$_2$}Si]$_2$ [12] with elemental bromine. Herein we outline the preparation and characterization of the monomeric LGeBr (**1**) and LSnBr (**2**) [L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] compounds.

2. Result and discussion

The reaction of the β-diketiminato lithium salt LLi(OEt$_2$) with GeBr$_2$ and SnBr$_2$ in diethyl ether gave the monomeric compounds LMBr (M = Ge (**1**); M = Sn (**2**)) with three-coordinate metal atoms (Scheme 1).

Compounds **1** and **2** are well soluble in common organic solvents, including benzene, THF, *n*-hexane, and *n*-pentane. Compounds **1** and **2** are characterized by NMR spectroscopy, EI-mass spectrometry, and elemental analysis. The ^{119}Sn NMR spectrum of **2** exhibits a singlet at δ −180.47 ppm. In Table 1 we summarise the ^{119}Sn NMR data of all four halogen derivatives of tin(II) compounds with the same β-diketiminate ligand. These data are in the expected range for the high field fluorine compound and low field iodine derivative.

The molecular structures of **1** and **2** are shown in Figs. 1 and 2. The X-ray single-crystal structures of **1** and **2** show that they are monomeric and isostructural. The metal atoms adopt three-coordinate sites, and reside in a distorted-tetrahedral environment with one vertex occupied by a lone pair of electrons. The structural feature of **1** and **2** is similar to the corresponding chloro derivative [13]. In compounds **1** and **2** the backbone of the chelating ligand is essentially planar and the metal atom is slightly shifted from the best C$_3$N$_2$-plane (23.5° in **1** and 23.7° in **2**). However, the bond angle of N(1)–Ge(1)–N(2) (90.80(6)°) in **1** is larger than the corresponding angle in **2** (N(1)–Sn(1)–N(2) 85.33(5)°), indicating the even lower tendency of tin to hybridize [14]. The bond length of N–Ge (1.9824(14) and 1.9934(14) Å) in **1** is slightly shorter than the corresponding N–Sn bond length in **2** (2.1758(13) and 2.1883(13) Å), as expected. This indicates that the ionic interactions of the central metal atom with the ligand decrease from Ge to Sn due to the difference of the atomic radii (Ge(II) 0.93 Å, Sn(II) 1.12 Å).

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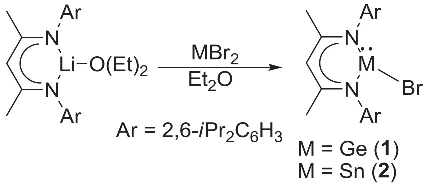

Scheme 1. Preparation of compounds **1** and **2**.

Table 1
^{119}Sn NMR data of Sn(II) compounds.

Compound[a]	^{119}Sn NMR (δ, ppm)
LSnF [15]	−371.52
LSnCl [13]	−224
LSnBr [this work]	−180.47
LSnI [15]	−107.33

[a] L = HC(CMeNAr)$_2$; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

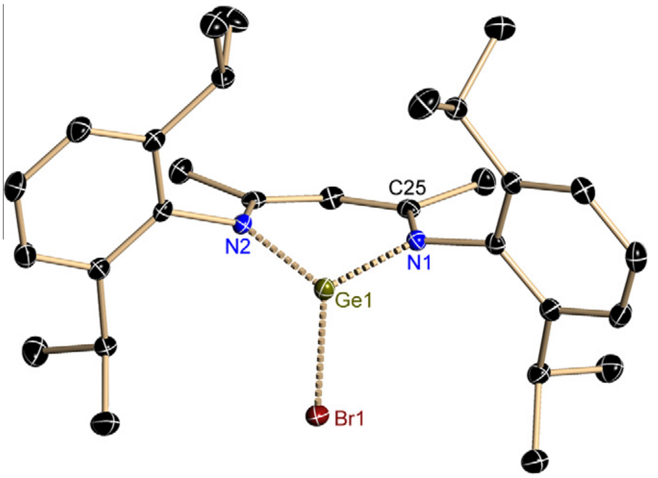

Fig. 1. Molecular structure of **1**. Anisotropic displacement parameters are depicted at the 50% probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1–Br1 2.5064(3), Ge1–N1 1.9934(14), N1–C25 1.326(2); N1–Ge1–N2 90.80(6), N1–Ge1–Br1 92.58(4), and Ge1–N1–C25 124.91(11).

3. Conclusion

In summary we have prepared the β-diketiminate germanium(II) and tin(II) bromides. These two compounds are prone to be the potential precursors for the preparation of compounds with low valent germanium and tin atoms.

4. Experimental

All manipulations were performed in a dry and oxygen-free atmosphere (N$_2$ or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system. Compound LLi·OEt$_2$ was prepared by literature procedure [13]. Other chemicals were purchased and used as received. ^{1}H, ^{19}F, and ^{119}Sn NMR spectra were recorded on a Bruker instrument and referenced to the deuterated solvent in the case of ^{1}H NMR spectra. ^{19}F and ^{119}Sn NMR spectra were referenced to CFCl$_3$ and SnMe$_4$. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Mass spectra were obtained on a Finnigan Mat 8230 instrument. Melting points were measured in a sealed glass tube and are not corrected.

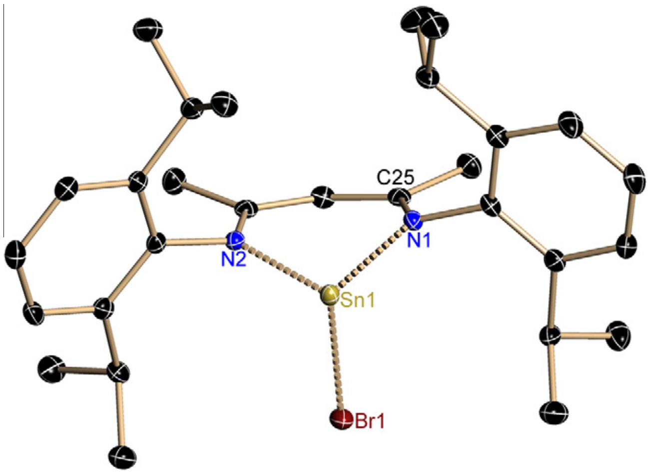

Fig. 2. Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1–Br1 2.6373(2), Sn1–N1 2.1758(13), N1–C25 1.337(2); N1–Sn1–N2 85.33(5), N1–Sn1–Br1 93.35(3), and Sn1–N1–C25 123.82(10).

4.1. LGeBr (**1**)

A solution of LLi(OEt$_2$) (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of GeBr$_2$ (0.230 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered off, and the solvent was partially reduced (ca. 15 mL). Storing the solution in a freezer at −32 °C overnight afforded colorless crystals of **1**, which are suitable for X-ray diffraction analysis. Yield: 0.480 g (85%). M.p. 214 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.03–7.18 (m, 6H, Ar-*H*), 5.22 (s, 1H, γ-C*H*), 4.01 (sept, 2H, C*H*(CH$_3$)$_2$), 3.13 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.48 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (q, 12H, CH(C*H*$_3$)$_2$), 1.00 (d, 6H, CH(C*H*$_3$)$_2$) ppm. EI-MS (70 eV): *m/z* (%): 570 (100) [M]$^+$. *Anal.* Calc. for C$_{29}$H$_{41}$BrGeN$_2$(570.17): C, 61.09; H, 7.25; N, 4.91. Found: C, 60.46; H, 7.10; N, 4.87%.

4.2. LSnBr (**2**)

A solution of LLi(OEt$_2$) (0.498 g, 1.0 mmol) in diethyl ether (20 mL) was added drop by drop to a stirred suspension of SnBr$_2$ (0.280 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for another 12 h. The precipitate was filtered off, and the solvent was partially reduced (ca. 20 mL). Storage of the remaining solutions in a freezer at −32 °C overnight afforded colorless crystals of **2** suitable for X-ray diffraction analyses. Yield: 0.490 g (80%). M.p. 206 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.02–7.17 (m, 6H, Ar-*H*), 5.11 (s, 1H, γ-C*H*), 3.99 (sept, 2H, C*H*(CH$_3$)$_2$), 3.11 (sept, 2H, C*H*(CH$_3$)$_2$), 1.61 (s, 6H, C*H*$_3$), 1.44 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (q, 12H, CH(C*H*$_3$)$_2$), 1.03 (d, 6H, CH(C*H*$_3$)$_2$) ppm. ^{119}Sn {^{1}H} NMR (186.50 Hz, C$_6$D$_6$): δ −180.47 ppm. EI-MS (70 eV): *m/z* (%): 616 (100) [M]$^+$. *Anal.* Calc. for C$_{29}$H$_{41}$BrN$_2$Sn (616.15): C, 56.52; H, 6.71; N, 4.55. Found: C, 55.58; H, 6.55; N, 4.42%.

4.3. Crystallographic studies

The data sets of **1** and **2** were collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics

Table 2
Crystallographic data for the structural analyses of compounds **1** and **2**.

	1	**2**
Empirical formula	$C_{29}H_{41}BrGeN_2$	$C_{29}H_{41}BrN_2Sn$
T (K)	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (pm)	1026.07(7)	1034.47(8)
b (pm)	1221.77(9)	1206.01(9)
c (pm)	1223.14(9)	1236.28(9)
α (°)	88.5760(10)	89.9690(10)
β (°)	69.8670(10)	72.4870(10)
γ (°)	72.0860(10)	71.0940(10)
V (nm^3)	1.36422(17)	1.38346(18)
Z	2	2
$D_{calc.}$ (Mg m^{-3})	1.388	1.479
μ (mm^{-1})	2.606	2.387
F(0 0 0)	592	628
θ range (°)	1.76–26.37	1.74–26.37
Reflections collected	32510	16293
Independent reflections	5574	5617
Data/restraints/parameters	5574/0/308	5617/0/308
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0213/0.0542	0.0170/0.0400
R_1/wR_2 (all data)[a]	0.0243/0.0557	0.0184/0.0405
Goodness-of-fit (GOF)	1.046	1.036
$\Delta\rho$(max), $\Delta\rho$(min) (e Å^{-3})	0.424, −0.287	0.363, −0.2860

[a] $R_1 = \sum \|F_o| - |F_c\| / \sum |F_o|$ and $wR_2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2 / \sum w\left(F_o^2\right)^2\right]^{0.5}$.

(Mo Kα $\lambda = 0.71073$ Å). The crystals were mounted in a shock-cooled oil drop at the tip of a fibre [16]. The data were integrated with Saint V7.23A [17] and an empirical absorption correction (Sadabs V2.10) was applied [18]. The structures were solved by direct methods (Shelxs) [19] and refined on F^2 using the full-matrix least-squares methods of Shelxl [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. Crystallographic data, details of data collection, and refinement are given in Table 2.

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Appendix A. Supplementary material

CCDC 743152 and 743153 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.051.

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