Tin Compounds

International Edition: DOI: 10.1002/anie.201602178
German Edition: DOI: 10.1002/ange.201602178

A Tin Analogue of Carbenoid: Isolation and Reactivity of a Lithium Bis(imidazolin-2-imino)stannylenoid

*Tatsumi Ochiai, Daniel Franz, Xiao-Nan Wu, Elisabeth Irran, and Shigeyoshi Inoue**

Dedicated to Professor Herbert W. Roesky on the occasion of his 80th birthday

Abstract: *The lithium bis(imino)stannylenoid (NIPr)$_2$Sn(Li)Cl (**1**; NIPr = bis(2,6-diisopropylphenyl)imidazolin-2-imino) was prepared by the reaction of LiNIPr with 0.5 equiv of SnCl$_2$·diox (diox = 1,4-dioxane) and the ambiphilic character of the compound was demonstrated by investigations into its reactivity. Treatment of **1** with I$_2$ or MeI yielded the oxidative addition products (NIPr)$_2$SnI$_2$ and (NIPr)$_2$Sn(Me)I, respectively. In contrast, the reaction of **1** with one equivalent of Me$_3$SiCl resulted in the formation of Me$_3$SiNIPr and the chlorostannylene dimer [NIPrSnCl]$_2$. Moreover, the substitution reaction of compound **1** with MeLi led to the formation of the methyl-substituted stannate (NIPr)$_2$Sn(Li)Me.*

Carbenoids, which are α-functionalized organometallic compounds of general formula R$_2$CMX (Figure 1, **I**; M = metal, X = leaving group),[1] have attracted much attention not only for their unusual ambiphilic character, but also as carbene synthetic equivalents. Although numerous experimental and theoretical investigations on carbenoids have been carried out to date,[2] only a few stable crystalline carbenoids have been reported.[2,3] For example, the X-ray crystal structure of the pyridine adduct of dichloromethyllithium (Figure 1, **II**), one of the simplest carbenoids, was reported; however, it is persistent only at low temperature (−78 °C to −90 °C).[3d] In 2007, Le Floch and co-workers isolated the first room-temperature-stable carbenoid (Figure 1, **III**) by chlorination of the corresponding dianion.[4] Remarkably, **III** is stable up to 60 °C as a result of coordination of the lithium cation by the thiophosphinoyl ligands tethered to the carbenoid center and two molecules of diethylether, which prevents the elimination of lithium chloride. Since then, several isolable carbenoids have been reported by implementing a similar stabilization method.[5]

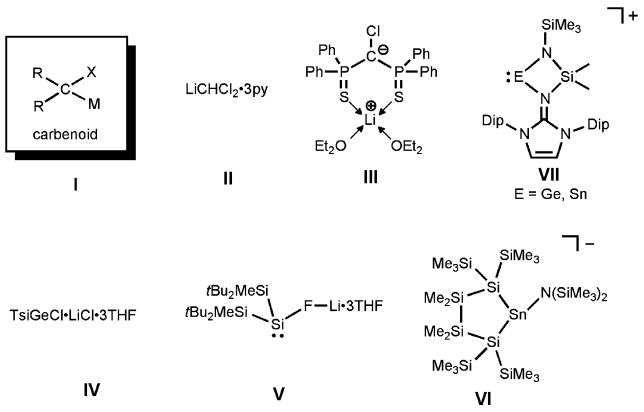


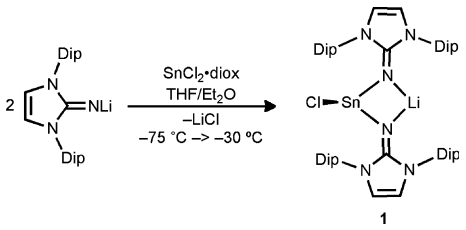
Figure 1. Carbenoid general formula **I** and the structures of selected carbenoid derivatives (**II**, **III**), as well as heavier carbenoid analogues (**IV**–**VI**). Imidazolin-2-iminato complexes of divalent germanium and tin (**VII**).

In sharp contrast, heavier analogues of carbenoids, that is metallylenoids of type R$_2$EMX (E = Si, Ge, Sn, Pb), have been only marginally studied. When X is a good leaving group (for example, halides or alkoxides), metallylenoids exhibit high ambiphilic character, whereas when X is a poor leaving group (for example, organyls or amides) the compound behaves more like a typical metallyl anion. Similar to carbenoids, the characterization of metallylenoids is obviously hampered by their thermal instability leading to α-elimination of MX or self-condensation. In 1996, Ohtaki and Ando described the synthesis of a trisyl-substituted chlorogermylenoid (Figure 1, **IV**; Tsi = (Me$_3$Si)$_3$C),[6] however, the molecular structure of this compound in the solid state was not reported. In fact, the structural characterization of a halometallylenoid eluded synthetic chemists until 2006, when Apeloig and co-workers investigated fluorosilylenoid **V** (Figure 1) by X-ray diffraction analysis.[7] In this context, reactivity studies on silylenoids by Lee and co-workers have to be pointed out.[8] In contrast, the field of heavier Group 14 congeners (containing Sn or Pb) remains largely unexplored mainly as a result of the increased stability of the divalent Sn^{II} and Pb^{II} atoms in comparison to the lighter elements.[9] As a consequence, the elimination of the metalhalide from the high-coordinate tin or lead center is strongly favored. Notably, bis(silyl)aminostannide **VI** (Figure 1), which corresponds to the general formula R$_2$SnMX, was reported (with M = K(18-crown-6) and X = N(SiMe$_3$)$_2$).[10] However, a low degree of stannylenoid character would be expected for this compound because the amino substituent is a poor leaving group.

[*] T. Ochiai, Dr. X.-N. Wu, Dr. E. Irran, Prof. Dr. S. Inoue
Institut für Chemie, Anorganische Chemie
Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Dr. D. Franz, Prof. Dr. S. Inoue
Department of Chemistry
Catalysis Research Center and Institute of Silicon Chemistry
Technische Universität München
Lichtenbergstrasse 4, 85748 Garching (Germany)
E-mail: s.inoue@tum.de
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201602178.

Recently, we developed a simple route to novel four-membered-ring-containing metalliumylidenes (Figure 1, **VII**; E = Ge, Sn; counterion = $[MeB(C_6F_5)_3]^-$)[11] by taking advantage of the strongly electron-donating nature of the imidazolin-2-imino group.[12] Herein, we report a rare example of a lithium stannylenoid prepared by using an imidazolin-2-iminato ligand. Additionally, we verify the high stannylenoid character of this compound by demonstrating its ambiphilic reactivity.

The reaction of LiNIPr (NIPr = bis(2,6-(diisopropylphenyl)imidazolin-2-imino) with 0.5 equiv of $SnCl_2$·diox (diox = 1,4-dioxane) in a mixture of THF and Et_2O affords the bis(imino)stannylenoid **1** as confirmed by multinuclear NMR spectroscopy, high-resolution mass spectrometry, and single-crystal X-ray diffraction data (Scheme 1). Interestingly, stannylenoid **1** decomposed to give primarily HNIPr when the solution was warmed to 0 °C.



Scheme 1. Synthesis of the bis(imino)stannylenoid **1**. Dip = 2,6-diisopropylphenyl.

An X-ray crystallographic study revealed that **1** contains a four-membered LiN_2Sn ring, in which the two nitrogen atoms of the imino groups bridge in a μ_2-fashion between the tin and the lithium atom, generating a butterfly-shaped core (the sum of the internal bond angles amounts to 352°; Figure 2).[13] The Sn–N bond lengths in **1** are determined to Sn1–N1 = 2.143(5) Å and Sn1–N4 = 2.179(4) Å. These values are significantly elongated in comparison to the reported adduct of 4-dimethylaminopyridine with $(NIPr)SnN(SiMe_3)_2$ ($Sn–N_{imino}$ = 2.0588(13) Å), which represents an Sn–N single bond.[11a] However, they are shorter than the $Sn–N_{imino}$ distance in three-coordinated benzobisstannylenes (2.2056(14) Å, 2.206(2) Å) that mark an $Sn–N_{imino}$ dative bond.[14] Consequently, partial Sn–N dative bond character is ascribed to the tin–nitrogen interactions in **1**, similar to the structurally related $\{(NIPr)SnN_3\}_2$ which comprises a cyclic N_2Sn_2 core (Sn–N = 2.194(3) Å and 2.178(3) Å).[11a] Notably, high dative bond character was attributed to the $Sn–N_{imino}$ interaction in stannyliumylidene **VII** and the respective bond length had been determined to be 2.197(2) Å.[11a]

The Li–N bond lengths of 1.946(9) Å and 2.004(9) Å in **1** are comparable to those in the iminolithium dimer $[LiNIPr]_2$ (1.841(6)–1.992(6) Å).[12d] In contrast to $[LiNIPr]_2$, compound **1** exhibits no contact between the lithium atom and one of the *ipso*-carbon atoms of the Dip groups. As is common for lithium stannates that bear nitrogen donor ligands,[15] no bonding interaction between the lithium and the tin atom is detected for **1**, as evidenced by the Sn···Li distance of 2.943(9) Å that is larger than the sum of the covalent radii

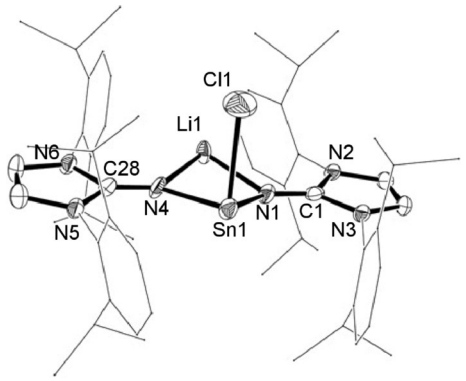
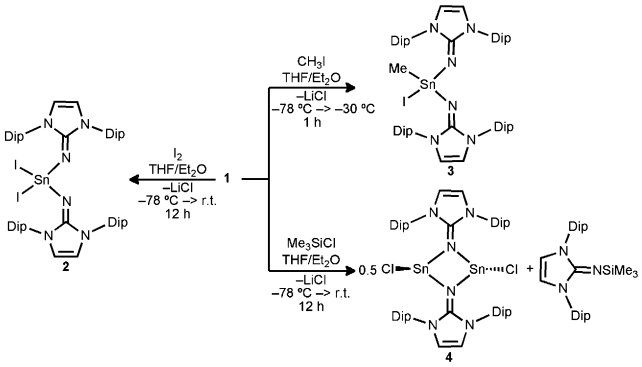


Figure 2. ORTEP representation of the molecular structure of **1** in the solid state.[13] Thermal ellipsoids are set at 40% probability. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.143(5), Sn1–N4 2.179(4), Sn1–Cl1 2.532(2), Li1–N1 2.004(9), Li1–N4 1.946(9), C1–N1 1.266(6), C1–N2 1.409(6), C1–N3 1.409(6), N4–C28 1.263(6), C28–N5 1.397(7), C28–N6 1.410(6); N1-Sn1-N4 80.68(17), N1-Li1-N4 90.2(4), Li1-N1-Sn1 90.3(3), Li1-N4-Sn1 90.9(3), N1-Sn1-Cl1 87.29(14), N4-Sn1-Cl1 87.75(14).

of these atoms (2.67 Å).[16] The $^{119}Sn\{^1H\}$ NMR spectrum of **1** in $[D_8]$THF displays a singlet at $\delta = -18$ ppm, which is significantly shifted to lower field as compared to monomeric trigonal-pyramidal coordinate tin chloride complexes of various 1,3-diketiminato-based ligands (for example (1,3-diketimino)SnCl: $\delta(^{119}Sn)$ in a range from −118 ppm to −337 ppm).[17] In fact, the chemical shift of the tin nucleus in **1** falls between the values reported by Gade and co-workers for lithium triamido stannates (δ = 11.9 ppm and −108.7 ppm, both in C_6D_6).[18]

To assess the stannylenoid character of **1** we were interested in its reactivity towards homopolar reagents, as well as electrophiles and nucleophiles. After the reaction of **1** with elemental iodine in a mixture of THF and Et_2O, diiodobis(imino)stannane **2** was isolated (36%; Scheme 2). Its formation can be reasoned by oxidative addition of diiodine to the Sn^{II} atom with subsequent extrusion of the chloro functionality to avoid an unfavorable high coordination number at the tin center. Presumably, the process is driven by the elimination of lithium chloride. The $^{119}Sn\{^1H\}$ NMR



Scheme 2. Reaction of the stannylenoid **1** with I_2 to form stannane **2**, with MeI to form stannane **3**, and with Me_3SiCl to form stannylene **4**.

spectrum of **2** in C_6D_6 revealed a signal at $\delta = -832$ ppm that marks a significant shift to higher field as compared to its precursor, probably as a result of the strong inductive effect imposed by the iodine nuclei bonded to the tin center. The molecular structure of $(NIPr)_2SnI_2$ (**2**) was also determined by single crystal X-ray diffraction analysis (see the Supporting Information).[13] The formation of **2** demonstrates the stannylene character of **1** with respect to the addition of homopolar reagents.

To probe the reactivity of **1** towards electrophiles, compound **1** was reacted with one equivalent of MeI in a mixture of THF and Et_2O. The reaction afforded the iodo(methyl)stannane **3** with the methyl iodide added to the tin center and lithium chloride expelled from the system (Scheme 2). In the $^{119}Sn\{^1H\}$ NMR spectrum, one sharp signal appears at $\delta = -263$ ppm (C_6D_6). This shift to lower field with respect to diiodostannane **2** reflects the decreased number of heavier halide atoms attached to the tin center. This behavior towards an electrophile underlines the role of the tin moiety as the active site in **1**.

Alternatively, the reaction of **1** with one equivalent of Me_3SiCl in a mixture of THF and Et_2O afforded dimeric $[NIPrSnCl]_2$ (**4**) along with $Me_3SiNIPr$ (Scheme 2). The formation of the latter is explained by a nucleophilic substitution at the silicon center through transfer of one iminato ligand from the tin atom to extrude lithium chloride. The remaining iminochlorostannylene fragment instantly dimerizes to form **4**, a molecule which bears a strong structural resemblance to its azide congener $[NIPrSnN_3]_2$.[11a] In this instance, stannylenoid **1** apparently behaves as an imino lithium reagent (nucleophilic at the N center) rather than a stannylenoid (nucleophilic at the Sn center). This may be reasoned by the steric congestion of a possible $(NIPr)_2Sn(SiMe_3)Cl$ intermediate. Moreover, according to Pearson's concept of hard and soft Lewis acids and bases, the stronger polarized SiCl bond renders the trimethylchlorosilane a harder electrophile in comparison to the softer methyliodide. Thus, the observed reactivity of **1** would account for a harder nucleophilic site at the imino nitrogen atom and a softer one at the tin center.

The single crystal X-ray diffraction analysis of **4** showed that the molecular structure in the solid state comprises a centrosymmetric dimer, with a planar and rhombic N_2Sn_2 ring (Figure 3).[13] The structural features are very similar to those seen in $[NIPrSnN_3]_2$ (see above) except for the slightly elongated Sn–N distances in **4**.[11a] In the $^{119}Sn\{^1H\}$ NMR spectrum, **4** gives rise to a resonance at $\delta = -125$ ppm ([D_8]THF), that is shifted downfield in comparison to $[NIPrSnN_3]_2$ ($\delta = -285$ ppm, [D_8]THF) presumably because the electron-donating capacity of the chloride is lower than that of the azido group.

Treatment of **1** with the strongly nucleophilic reagent methyllithium affords the methyl-substituted tin complex $(NIPr)_2Sn(Li)Me$ (**5**), and the NMR spectroscopic analysis of the reaction mixture prior to purification indicated circa 33% of HNIPr formed as a byproduct (Scheme 3). Attempts to obtain an analytically pure sample of **5** by recrystallization of the crude product were not successful. The formation of **5** demonstrates the electrophilicity of the tin(II) center in **1**. An

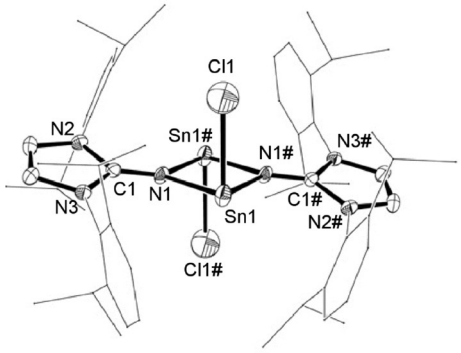
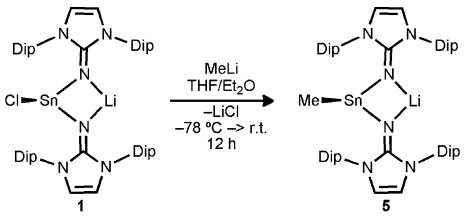


Figure 3. ORTEP representation of the molecular structure of **4** in the solid state.[13] Thermal ellipsoids are set at 40% probability. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.216(4), Sn1–N1# 2.179(5), Sn1–Cl1 2.525(3), C1–N1 1.286(7), C1–N2 1.384(8), C1–N3 1.399(7); N1-Sn1-N1# 78.18(18), Sn1-N1-Sn1# 101.82(18), N1-Sn1-Cl1 86.60(15), N1#-Sn1-Cl1 88.85(15).



Scheme 3. Reaction of the stannylenoid **1** with MeLi to **5**.

X-ray crystallographic study revealed that **5** features a planar four-membered LiN_2Sn ring (the internal bond angles add up to 359°; Figure 4) in contrast to the butterfly-shaped LiN_2Sn cycle in **1**.[13] However, the Sn–N and Li–N bond lengths in **1** and **5** differ only slightly and do not indicate that the structural deviation between the LiN_2Sn cores (butterfly

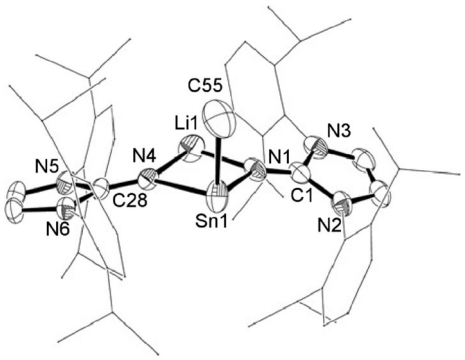
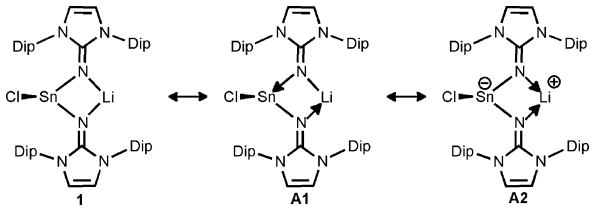


Figure 4. ORTEP representation of the molecular structure of **5** in the solid state.[13] Thermal ellipsoids are set at 40% probability. Dip groups are depicted as stick models. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.183(6), Sn1–N4 2.194(6), Sn1–C55 2.15(3), Li1–N1 1.921(16), Li1–N4 1.920(14), C1–N1 1.286(9), C1–N2 1.408(10), C1–N3 1.396(9), N4–C28 1.265(8), C28–N5 1.408(8), C28–N6 1.420(8); N1-Sn1-N4 81.1(3), N1-Li1-N4 95.5(6), Li1-N1-Sn1 91.1(4), Li1-N4-Sn1 90.8(5), N1-Sn1-C55 96.6(9), N4-Sn1-C55 96.4(8).

versus planar geometry) has a significant impact on the bonding situation.

As relevant resonance structures for chlorostannylenoid **1**, we conceived the imino-stabilized chlorostannylene formulation **A1** and the zwitterionic representation **A2**, featuring a chloro-substituted bis(imino)stannyl anion (Scheme 4).



Scheme 4. Selected resonance structures of **1**.

To shed light on the validity of these resonance structures, theoretical calculations for **1**, **4**, and **5** were carried out at the B3LYP level (see the Supporting Information). A direct comparison between **1** and **4** is useful to elucidate the bonding situation because each tin center in these compounds is attached to two nitrogen atoms, as well as to one chloro substituent. The Wiberg bond indices (WBI) of the $Sn{-}N_{imino}$ bonds in **1** were both calculated to be 0.43, which suggests significantly enhanced Sn–N interactions in comparison to the chlorostannylene dimer **4** (0.24, 0.24). Thus, although the X-ray structural analysis implied comparable Sn–N dative bond character for **1** and **4**, the WBI of **1** is more similar to the 0.58 that we reported for an $Sn{-}N_{imino}$ single bond.[11a] Moreover, the calculated NPA (natural population analysis) charge of the tin atom in **1** is +1.22, whereas the tin centers in **4** have a comparably higher charge of +1.42 each. These findings are in favor of the zwitterionic formulation **A2** and, thus, mitigate the relevance of chlorostannylene character (**A1**). As a result, non-negligible stannyl anion character is suggested for **1**. In contrast, upon comparison of the WBI values and the NPA charges of chlorostannyl anion **1** with the methyl derivative **5**, very similar $Sn{-}N_{imino}$ bond orders are observed (absolute deviation of 0.01), but the NPA charge at the tin atom in **5** amounts to +1.06 which is significantly less positive than calculated for **1**. This indicates that **5** is marked by higher stannyl anion character than **1** which corroborates the presumed stannylenoid nature of **1**. These findings agree with the commonly acknowledged correlation between the ambiphilicity of metallylenoids and the leaving group character of the metal-bonded substituents (methyl in **5** versus chloro in **1**).

In conclusion, we synthesized the bis(imino)stannylenoid **1** as a rare example of a heavier carbenoid congener from the reaction of LiNIPr with 0.5 equiv of $SnCl_2$·diox. Compound **1** reacts with I_2 or MeI to afford the diiodostannane **2** or iodomethylstannane **3**, respectively, with concomitant elimination of LiCl. The reaction of **1** with Me_3SiCl furnishes a tin(II) dimer (**4**), which features a chloro-functionalized N_2Sn_2 ring. The treatment of **1** with one equivalent of MeLi produces the methyl-substituted bis(imino)stannane **5**. These reactivity studies, as well as our DFT calculations, provide evidence for the stannylenoid nature of **1**. Future investigations will focus on differences between the chemistry of **1** and carbenoids.

Acknowledgements

Financial support from WACKER Chemie AG is gratefully acknowledged.

Keywords: carbenoids · imines · solid-state structures · stannylenes · tin

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 6983–6987
Angew. Chem. **2016**, *128*, 7097–7101

[1] IUPAC definition of carbenoid: "Complexed carbene-like entities that display the reactivity characteristics of carbenes, either directly or by acting as sources of carbenes".

[2] For reviews on carbenoids, see: a) G. Köbrich, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 41–52; *Angew. Chem.* **1967**, *79*, 15–27; b) G. Köbrich, *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 473–485; *Angew. Chem.* **1972**, *84*, 557–570; c) M. Braun, *Angew. Chem. Int. Ed.* **1998**, *37*, 430–451; *Angew. Chem.* **1998**, *110*, 444–465; d) G. Boche, J. C. W. Lohrenz, *Chem. Rev.* **2001**, *101*, 697–756.

[3] a) G. Boche, M. Marsch, A. Müller, K. Harms, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1032–1033; *Angew. Chem.* **1993**, *105*, 1081–1082; b) G. Boche, K. Harms, M. Marsch, A. Müller, *J. Chem. Soc. Chem. Commun.* **1994**, 1393–1394; c) E. Niecke, P. Becker, M. Nieger, D. Stalke, W. W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1849–1852; *Angew. Chem.* **1995**, *107*, 2012–2015; d) A. Müller, M. Marsch, K. Harms, J. C. W. Lohrenz, G. Boche, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1518–1520; *Angew. Chem.* **1996**, *108*, 1639–1640; e) M. Yoshifuji, S. Ito, *Top. Curr. Chem.* **2003**, *223*, 67–89.

[4] T. Cantat, X. Jacques, L. Ricard, X. F. Le Goff, N. Mézailles, P. Le Floch, *Angew. Chem. Int. Ed.* **2007**, *46*, 5947–5950; *Angew. Chem.* **2007**, *119*, 6051–6054.

[5] a) J. Konu, T. Chivers, *Chem. Commun.* **2008**, 4995–4997; b) H. Heuclin, S. Y.-F. Ho, X. F. Le Goff, C.-W. So, N. Mézailles, *J. Am. Chem. Soc.* **2013**, *135*, 8774–8777; c) J. Becker, V. H. Gessner, *Dalton Trans.* **2014**, *43*, 4320–4325; d) S. Y.-F. Ho, C.-W. So, N. Saffon-Merceron, N. Mézailles, *Chem. Commun.* **2015**, *51*, 2107–2110.

[6] a) T. Ohtaki, W. Ando, *Organometallics* **1996**, *15*, 3103–3105. For synthetic application of Ando's germylenoid, see: b) A. C. Filippou, K. W. Stumpf, O. Chernov, G. Schnakenburg, *Organometallics* **2012**, *31*, 748–755. For further examples of germylenoids, see: c) A. Sekiguchi, V. Y. Lee, *Chem. Rev.* **2003**, *103*, 1429–1448; d) T. Tajima, T. Sasamori, N. Takeda, N. Tokitoh, K. Yoshida, M. Nakahara, *Organometallics* **2006**, *25*, 230–235; e) T. Sasamori, N. Tokitoh, *Organometallics* **2006**, *25*, 3522–3532.

[7] a) G. Molev, D. Bravo-Zhivotovskii, M. Karni, B. Tumanskii, M. Botoshansky, Y. Apeloig, *J. Am. Chem. Soc.* **2006**, *128*, 2784–2785. For further examples of silylenoids, see: b) K. Tamao, A. Kawachi, Y. Ito, *J. Am. Chem. Soc.* **1992**, *114*, 3989–3990; c) K. Tamao, A. Kawachi, Y. Tanaka, H. Ohtani, Y. Ito, *Tetrahedron* **1996**, *52*, 5765–5772; d) A. Kawachi, K. Tamao, *J. Am. Chem. Soc.* **2000**, *122*, 1919–1926; e) M. E. Lee, H. M. Cho, Y. M. Lim, J. K. Choi, C. H. Park, S. E. Jeong, U. Lee, *Chem. Eur. J.* **2004**, *10*, 377–381; f) A. Kawachi, Y. Oishi, T. Kataoka, K. Tamao, *Organometallics* **2004**, *23*, 2949–2955; g) P. R. Likhar, M. Zirngast, J. Baumgartner, C. Marschner, *Chem. Commun.* **2004**, 1764–1765.

[8] a) Y. M. Lim, H. M. Cho, M. E. Lee, K. K. Baeck, *Organometallics* **2006**, *25*, 4960–4964; b) H. M. Cho, Y. M. Lim, M. E.

Lee, *Dalton Trans.* **2010**, *39*, 9232 – 9234; c) H. M. Cho, Y. M. Lim, B. W. Lee, S. J. Park, M. E. Lee, *J. Organomet. Chem.* **2011**, *696*, 2665 – 2668.

[9] a) R. S. Drago, *J. Phys. Chem.* **1958**, *62*, 353 – 357; b) P. Schwerdtfeger, G. A. Heath, M. Dolg, M. A. Bennett, *J. Am. Chem. Soc.* **1992**, *114*, 7518 – 7527; c) M. Seth, K. Faegri, P. Schwerdtfeger, *Angew. Chem. Int. Ed.* **1998**, *37*, 2493 – 2496; *Angew. Chem.* **1998**, *110*, 2669 – 2672; d) K. S. Thanthiriwatte, M. Vasiliu, S. R. Battey, Q. Lu, K. A. Peterson, L. Andrews, D. A. Dixon, *J. Phys. Chem. A* **2015**, *119*, 5790 – 5803.

[10] H. Arp, J. Baumgartner, C. Marschner, T. Müller, *J. Am. Chem. Soc.* **2011**, *133*, 5632 – 5635.

[11] a) T. Ochiai, D. Franz, E. Irran, S. Inoue, *Chem. Eur. J.* **2015**, *21*, 6704 – 6707; b) T. Ochiai, D. Franz, X.-N. Wu, S. Inoue, *Dalton Trans.* **2015**, *44*, 10952 – 10956; c) T. Ochiai, S. Inoue, *Phosphorus Sulfur Silicon Relat. Elem.* **2015**, DOI: 10.1080/10426507.2015.1128920.

[12] a) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876 – 877; b) S. Inoue, K. Leszczyńska, *Angew. Chem. Int. Ed.* **2012**, *51*, 8589 – 8593; *Angew. Chem.* **2012**, *124*, 8717 – 8721; c) X. Wu, M. Tamm, *Coord. Chem. Rev.* **2014**, *260*, 116 – 138; d) D. Franz, E. Irran, S. Inoue, *Dalton Trans.* **2014**, *43*, 4451 – 4461; e) D. Franz, S. Inoue, *Chem. Eur. J.* **2014**, *20*, 10645 – 10649; f) D. Franz, E. Irran, S. Inoue, *Angew. Chem. Int. Ed.* **2014**, *53*, 14264 – 14268; *Angew. Chem.* **2014**, *126*, 14489 – 14493; g) M. W. Lui, C. Merten, M. J. Ferguson, R. McDonald, Y. Xu, E. Rivard, *Inorg. Chem.* **2015**, *54*, 2040 – 2049; h) F. Dielmann, G. Bertrand, *Chem. Eur. J.* **2015**, *21*, 191 – 198; i) Y. K. Loh, C. Gurnani, R. Ganguly, D. Vidović, *Inorg. Chem.* **2015**, *54*, 3087 – 3089; j) T. Glöge, K. Jess, T. Bannenberg, P. G. Jones, N. Langenscheidt-Dabringhausen, A. Salzer, M. Tamm, *Dalton Trans.* **2015**, *44*, 11717 – 11724; k) D. Franz, T. Szilvási, E. Irran, S. Inoue, *Nat. Commun.* **2015**, *6*, 10037.

[13] CCDC 1438436 (**1**), 1438438 (**2**), 1452039 (**3**), 1438435 (**4**), and 1438437 (**5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[14] S. Krupski, J. V. Dickschat, A. Hepp, T. Pape, F. E. Hahn, *Organometallics* **2012**, *31*, 2078 – 2084.

[15] a) A. D. Bond, E. A. Harron, G. T. Lawson, M. E. G. Mosquera, M. McPartlin, D. S. Wright, *J. Chem. Soc. Dalton Trans.* **2002**, 3525 – 3528; b) T. Chivers, D. J. Eisler, *Angew. Chem. Int. Ed.* **2004**, *43*, 6686 – 6689; *Angew. Chem.* **2004**, *116*, 6854 – 6857; c) M. Kilian, H. Wadepohl, L. H. Gade, *Organometallics* **2008**, *27*, 524 – 533; d) S. Krupski, R. Pöttgen, I. Schellenberg, F. E. Hahn, *Dalton Trans.* **2014**, *43*, 173 – 181. A stannate with the lithium atom coordinated to the tin center was also reported: e) I. Haller, P. Renner, L. H. Gade, *Polyhedron* **2002**, *21*, 629 – 633.

[16] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832 – 2838.

[17] a) A. Akkari, J. J. Byrne, I. Saur, G. Rima, H. Gornitzka, J. Barrau, *J. Organomet. Chem.* **2001**, *622*, 190 – 198; b) Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, P. P. Power, *Organometallics* **2001**, *20*, 1190 – 1194; c) P. B. Hitchcock, J. Hu, M. F. Lappert, J. R. Severn, *Dalton Trans.* **2004**, 4193 – 4201; d) A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 9834 – 9843; e) S. L. Choong, C. Schenk, A. Stasch, D. Dange, C. Jones, *Chem. Commun.* **2012**, *48*, 2504 – 2506; f) R. Olejník, Z. Padělková, R. Mundil, J. Merna, A. Růžička, *Appl. Organometal. Chem.* **2014**, *28*, 405 – 412.

[18] a) M. Kilian, H. Wadepohl, L. H. Gade, *Organometallics* **2007**, *26*, 3076 – 3078; b) M. Kilian, H. Wadepohl, L. H. Gade, *Dalton Trans.* **2008**, 582 – 584.

Received: March 2, 2016
Published online: April 21, 2016

