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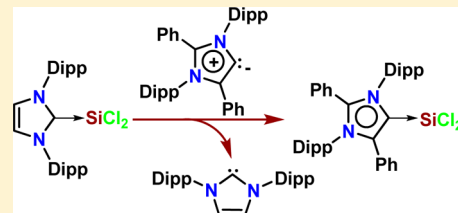
## Lewis Base Stabilized Group 14 Metalylenes

Amit Pratap Singh, Prinson P. Samuel, Kartik Chandra Mondal, Herbert W. Roesky,\* Navdeep S. Sidhu, and Birger Dittrich\*

Institut für Anorganische Chemie, Georg-August-Universität, Tammannstrasse 4, D-37077 Göttingen, Germany

## Supporting Information

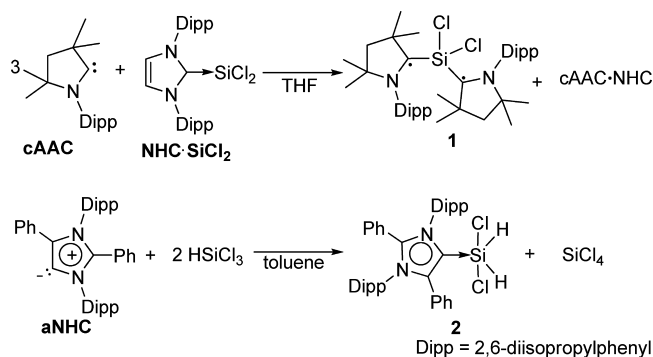
**ABSTRACT:** The chemistry of stable metalylenes (the heavier group 14 element analogues of carbenes) is an intriguing target of main group chemistry due to their synthetic potential and industrial application. In the present study, we report on the utilization of an abnormal N-heterocyclic carbene (aNHC) and a cyclic alkyl-amino carbene (cAAC) as a Lewis base for the syntheses of compounds aNHC·SiCl<sub>2</sub> (3), aNHC·SnCl<sub>2</sub> (4), and cAAC·SnCl<sub>2</sub> (5). The synthesis of silylene 3 involved the ligand-substitution reaction between NHC·SiCl<sub>2</sub> and an aNHC. However, compounds 4 and 5 were synthesized by the reactions of aNHC and cAAC with SnCl<sub>2</sub> in the molar ratio of 1:1. Compounds 3–5 are well-characterized with various spectroscopic methods and single-crystal X-ray structural analysis.



## INTRODUCTION

The chemistry of heavier group 14 elements has been developed due to the interest in comparative studies with the lighter congener carbon.<sup>1</sup> In recent years, the highly reactive metalylenes (heavier group 14 element analogues of carbene)<sup>2</sup> have attracted considerable attention due to their potential role in the development of advanced semiconductors, and in microelectronic engineering.<sup>3</sup> In 1994, West et al.<sup>4</sup> isolated the first divalent dicoordinate N-heterocyclic silylene, which is comparable to the N-heterocyclic carbene reported by Arduengo et al.<sup>5</sup> in 1991. The first monomeric stanylene was synthesized by Engelhardt et al.<sup>6</sup> in 1988. Since then, a number of stable silylenes and stanylenes have been synthesized and structurally characterized.<sup>7</sup> Stabilization of such metalylenes is highly dependent on the nature of the ligands. At this juncture, N-heterocyclic carbenes (NHCs) deserve special attention because of their excellent properties to stabilize species with the hitherto illusive and quite unusual low valency.<sup>8</sup> In this context, we synthesized and structurally characterized an NHC-stabilized dichlorosilylene (NHC·SiCl<sub>2</sub>)<sup>9</sup> by reductive elimination of HCl from HSiCl<sub>3</sub>. Many other highly reactive compounds containing NHCs with low-valent group 14 elements are also documented.<sup>10</sup> In searching to modify the NHC unit, chemists have adopted a series of strategies, such as changing the substituents on the nitrogen atoms, varying the backbone of the carbene, and also changing the position of the carbene carbon in the heterocyclic ring.<sup>11</sup> Recently, Bertrand et al. reported on stable cyclic alkyl-amino carbenes (cAACs)<sup>12</sup> and an abnormal N-heterocyclic carbene (aNHC).<sup>13</sup> Experimental data suggest that the aNHC is a strong nucleophile as well as an electrophile, and may be a better substitute for NHCs.<sup>13</sup> In line with this argument, we recently synthesized and structurally characterized a biradical silicon compound (cAAC)<sub>2</sub>·SiCl<sub>2</sub> (1)<sup>14</sup> by a ligand-substitution reaction of NHC·SiCl<sub>2</sub> with cAAC (Scheme 1). The Si–C bonds in 1 were found to be electron-sharing bonds instead of a

## Scheme 1. Synthesis of Compounds 1 and 2



conventional coordinate bond (donor–acceptor bond) between the NHC carbene carbon atom and the silicon atom in NHC·SiCl<sub>2</sub>.<sup>9</sup> In another report, we have shown the dismutation of trichlorosilane in the presence of aNHC, resulting in the formation of aNHC·SiH<sub>2</sub>Cl<sub>2</sub> (2)<sup>15</sup> under the elimination of SiCl<sub>4</sub>. The unique synthesis and structural properties of 1 and 2 encourage us to explore the chemistry of both aNHC, and cAAC with other heavier group 14 elements.

Herein, we report the synthesis of compounds aNHC·SiCl<sub>2</sub> (3), aNHC·SnCl<sub>2</sub> (4), and cAAC·SnCl<sub>2</sub> (5) by using aNHC and cAAC as Lewis bases. Compound 3 was synthesized by the ligand-substitution reaction between aNHC and NHC·SiCl<sub>2</sub>. Because of the stronger nucleophilic nature of aNHC in comparison to that of NHC, aNHC selectively replaced NHC from NHC·SiCl<sub>2</sub> to afford compound 3 in toluene. However, compounds 4 and 5 were synthesized by the reactions of aNHC and cAAC each with SnCl<sub>2</sub> in a 1:1 molar ratio. Compounds 3–5 have been characterized with various

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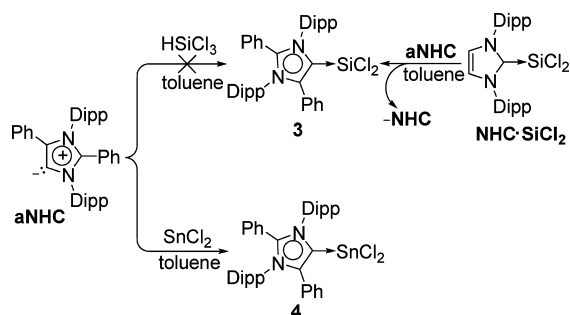
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spectroscopic methods and elemental analysis. The molecular structures of compounds **4** and **5** were confirmed by single-crystal X-ray analysis.

## RESULTS AND DISCUSSION

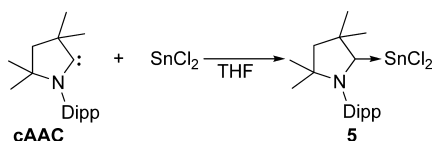
The reaction of abnormal N-heterocyclic carbene (aNHC) with trichlorosilane in toluene produces dichlorosilane aNHC·SiH<sub>2</sub>Cl<sub>2</sub> (**2**) instead of the expected dichlorosilylene aNHC·SiCl<sub>2</sub> (**3**) due to the dismutation reaction of trichlorosilane.<sup>15</sup> However, the synthesis of compound **1** where NHC was replaced by the cAAC encouraged us to react NHC·SiCl<sub>2</sub> with aNHC. In this reaction, aNHC selectively replaced NHC from the toluene solution of NHC·SiCl<sub>2</sub> to afford a mixture of compound **3** and NHC (Scheme 2). The NHC was removed from the crude solid by

**Scheme 2. Synthesis of Compounds 3 and 4**



washing with *n*-hexane to afford pure colorless compound **3** in a quantitative yield. Compounds **4** and **5** were synthesized by the reactions of aNHC and cAAC with SnCl<sub>2</sub> in a 1:1 molar ratio (Schemes 2 and 3). Compounds **3**–**5** are highly soluble in

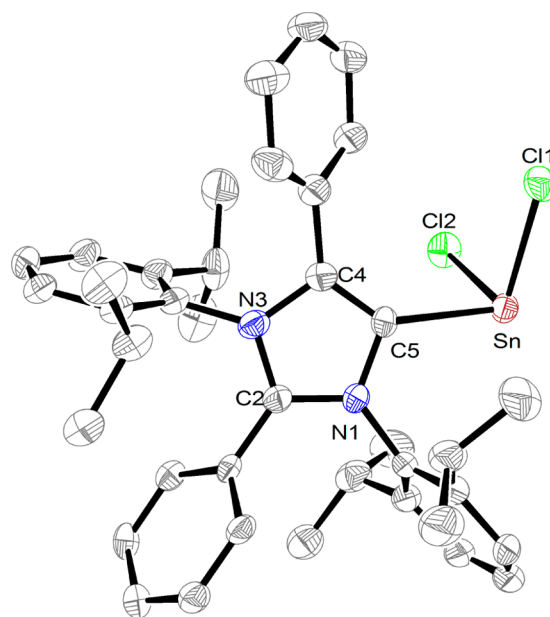
**Scheme 3. Synthesis of Compound 5**



tetrahydrofuran (THF) and less soluble in toluene and benzene. Compounds **3**–**5** have been characterized by their <sup>1</sup>H and <sup>13</sup>C NMR spectra and show resonances for the respective ligands. However, the positions of the resonances are shifted when compared with those of the uncoordinated ligands. For example, the CH proton of *i*Pr groups in the <sup>1</sup>H NMR spectrum of **3** resonates as two septets at significantly different positions ( $\delta$  2.85 and 2.71 ppm) when compared with those of the free ligand ( $\delta$  2.95 and 2.73 ppm). Furthermore, to investigate the electronic environments around the silicon (for **3**) and tin (for **4** and **5**) atoms, the <sup>29</sup>Si and <sup>119</sup>Sn NMR spectra were measured. The <sup>29</sup>Si NMR spectrum of compound **3** exhibits a resonance at  $\delta$  24.18 ppm, which is comparable to the reported value ( $\delta$  19.06 ppm)<sup>9</sup> for the analogous compound NHC·SiCl<sub>2</sub>. This suggests that both compounds (NHC·SiCl<sub>2</sub> and aNHC·SiCl<sub>2</sub>) have identical electronic environments around the silicon center. The <sup>119</sup>Sn NMR spectra of compounds **4** and **5** show resonances at  $\delta$  –60.01 and  $\delta$  –53.14 ppm, respectively. The molecular ions for **3**–**5** were observed in the EI-mass spectra at *m/z* 638.4, 730.2, and 475.1, respectively. The elemental analyses for compounds **3**–**5** are

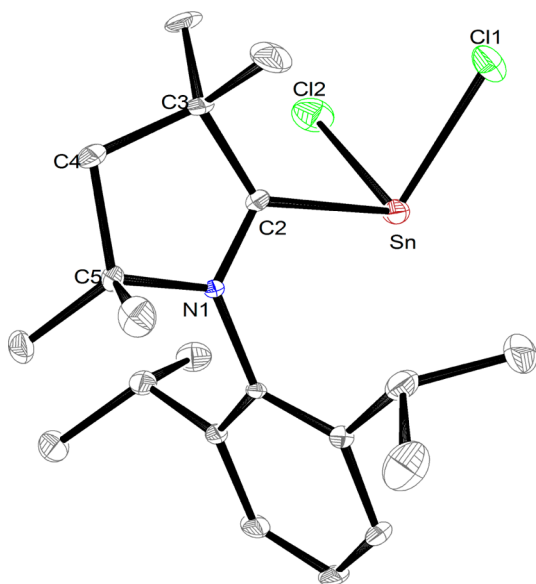
matching well with the theoretically calculated values, and hence prove the composition of the compounds.

To establish unambiguously the structural features of compounds **4** and **5**, single-crystal X-ray structural analyses were carried out. Suitable single crystals of both compounds were obtained from saturated THF solutions. Both compounds **4** and **5** crystallize in the monoclinic crystal system with space group *P*2<sub>1</sub>/*n* (Table S1, Supporting Information). The molecular structures of compounds **4** and **5** are shown in Figures 1 and 2, respectively. The molecular structure of **4**



**Figure 1.** ORTEP representation of the molecular structure of aNHC·SnCl<sub>2</sub> (**4**). ADPs are depicted at the 50% probability level. All C–H hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn–C(5) 2.308(9), Sn–Cl(1) 2.427(3), Sn–Cl(2) 2.460(3); C(5)–Sn–Cl(1) 96.9(2), C(5)–Sn–Cl(2) 89.8(2), Cl(1)–Sn–Cl(2) 94.24(10). The crystal structure of **4** is affected by the disorder at the tin site, with two split conformations of SnCl<sub>2</sub> attached to aNHC (see the Supporting Information).

reveals that an aNHC is coordinated to the tin atom through the carbene center C5, whereas in the case of compound **5**, cAAC is coordinated to tin through the carbene carbon C2. In both the compounds **4** and **5**, the tin atom is surrounded by one carbon (C5 for **4** and C2 for **5**) and two chlorine (Cl1 and Cl2) atoms, resulting in a distorted trigonal-pyramidal geometry around the tin center. Moreover, nearly the same bond lengths and angles were observed in compound **4** and **5**. The Sn–Cl1 and Sn–Cl2 bond lengths for compound **4** are 2.427(3) and 2.460(3) Å, respectively, while the Cl1–Sn–Cl2 bond angle is 94.24(10)°. The C5–Sn bond length is 2.308(9) Å, which is very similar to that of other reported analogous compounds.<sup>10c</sup> Both chlorine atoms Cl1 and Cl2 are nearly perpendicular to the C5–Sn bond. In compound **5**, the C2–Sn bond length is 2.358(3) Å, which is about 0.05 Å longer than the C5–Sn bond length found in **4**. The Sn–Cl1 and Sn–Cl2 bond lengths for compound **5** are 2.4617(9) and 2.4691(10) Å, respectively. The chlorine atoms Cl1 and Cl2 are showing an angle of 94.94(3)° with the tin center. Similar to compound **4**, the chlorine atoms Cl1 and Cl2 are nearly perpendicular (92–95°) to the C2–Sn bonds in compound **5**.



**Figure 2.** ORTEP representation of the molecular structure of  $\text{cAAC-SnCl}_2$  (**5**). ADPs are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn–C(2) 2.358(3), Sn–Cl(1) 2.4617(9), Sn–Cl(2) 2.4691(10); C(2)–Sn–Cl(1) 92.30(7), C(2)–Sn–Cl(2) 94.20(7), Cl(1)–Sn–Cl(2) 94.94(3).

## SUMMARY

The synthesis and reactivity of compounds with heavier group 14 elements is a rapidly growing field in chemistry because of their extensive use in various applications. In the present study, we have shown that abnormal N-heterocyclic carbene (aNHC) easily replaces the N-heterocyclic carbene (NHC) molecule from a toluene solution of  $\text{NHC-SiCl}_2$  to afford compound **3**. This experiment proves the strong nucleophilic and electrophilic nature of aNHC in comparison to that of NHC. Compounds **4** and **5** were synthesized by the reactions of aNHC and cAAC with  $\text{SnCl}_2$  each in a 1:1 molar ratio. Compounds **3–5** were well-characterized with various spectroscopic methods and elemental analysis. The structural analysis of compounds **4** and **5** showed that tin is coordinated to the respective carbene, resulting in a distorted trigonal-pyramidal geometry. Compounds **3–5** might prove to be promising candidates for the synthesis of other potentially important derivatives with low-valent group 14 elements. Such types of investigations will be reported in due course from our laboratory.

## EXPERIMENTAL SECTION

All manipulations were performed in a dry and oxygen-free atmosphere ( $\text{N}_2$ ) using standard Schlenk-line techniques and inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . All solvents were dried by a MBraun solvent purification system prior to use. Compound  $\text{NHC-SiCl}_2$ , cyclic alkyl-amino carbene (cAAC) and abnormal N-heterocyclic carbene (aNHC) were synthesized by the reported procedures.<sup>9,12,13</sup> Other chemicals were purchased and used as received. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker Avance DRX instrument (300 or 500 MHz). The chemical shifts  $\delta$  are given in parts per million with tetramethylsilane as an external standard. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

**Synthesis of aNHC-SiCl<sub>2</sub> (3).** Compound **3** was synthesized by the reaction of aNHC (1.00 g, 1.85 mmol) in toluene with  $\text{NHC-SiCl}_2$

(0.81 g, 1.67 mmol) at  $-78^\circ\text{C}$  under a nitrogen atmosphere. The mixture was then warmed to room temperature and stirred for 3 h. All volatiles were removed under vacuum to afford a mixture of aNHC-SiCl<sub>2</sub> and NHC. The NHC was removed from the solid by washing with *n*-hexane ( $2 \times 50\text{ mL}$ ) to yield pure colorless **3** (yield: 0.89 g, 75%). mp  $265^\circ\text{C}$  (dec.). Elemental analysis (%) calcd for  $\text{C}_{39}\text{H}_{44}\text{Cl}_2\text{N}_2\text{Si}$  (638.27): C, 73.22; H, 6.93; N, 4.38. Found: C, 73.43; H, 7.02; N, 4.25.  $^1\text{H}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  7.77–7.75 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.53–7.43 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.34–7.14 (m, 8H,  $\text{CH}_{\text{ar}}$ ), 7.08–6.93 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 2.85 (sept, 2H,  $\text{Ar-CH}(\text{CH}_3)_2$ ), 2.71 (sept, 2H,  $\text{Ar-CH}(\text{CH}_3)_2$ ), 1.40 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.98 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.89 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.87 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  144.2, 143.2, 140.2, 139.9, 138.3, 136.4, 133.6, 130.8, 130.1, 129.6, 129.2, 128.5, 128.1, 127.9, 126.5, 126.2, 123.9, 29.5 ( $\text{CHCH}_3$ ), 29.1 ( $\text{CHCH}_3$ ), 25.9 ( $\text{CH}_3$ ), 24.5 ( $\text{CH}_3$ ), 24.0 ( $\text{CH}_3$ ), 22.5 ( $\text{CH}_3$ ) ppm.  $^{29}\text{Si}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  24.18 ppm. EI-MS:  $m/z$  638.4 ( $\text{M}^+$ ) (100%).

**Synthesis of aNHC-SnCl<sub>2</sub> (4).** For the synthesis of compound **4**, the toluene solution of aNHC (1.00 g, 1.85 mmol) was treated with solid  $\text{SnCl}_2$  (0.36 g, 1.86 mmol) under a nitrogen atmosphere at  $-78^\circ\text{C}$ . The mixture was then warmed to room temperature and stirred for 6 h. All volatiles were removed under vacuum to afford a colorless crude product. The crude product was dissolved in a minimum amount of THF and filtered through a pad of Celite of a medium porosity frit. The filtrate was stored for 2 days at room temperature to give colorless crystals of **4** suitable for single-crystal X-ray structural analysis (yield: 1.10 g, 81%). mp  $278^\circ\text{C}$  (dec.). Elemental analysis (%) calcd for  $\text{C}_{39}\text{H}_{44}\text{Cl}_2\text{N}_2\text{Sn}$  (730.19): C, 64.13; H, 6.07; N, 3.84. Found: C, 64.45; H, 5.95; N, 3.97.  $^1\text{H}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  7.61–7.57 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.53–7.44 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.39–7.20 (m, 8H,  $\text{CH}_{\text{ar}}$ ), 7.16–7.01 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 2.91–2.62 (m, 4H,  $\text{Ar-CH}(\text{CH}_3)_2$ ), 1.45 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 1.03 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.99 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 0.93 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  155.8, 140.4, 138.2, 135.4, 133.2, 130.1, 129.6, 125.2, 123.3, 120.1, 118.4, 115.4, 113.8, 110.2, 109.2, 106.3, 103.1, 101.4, 29.7 ( $\text{CHCH}_3$ ), 29.5 ( $\text{CHCH}_3$ ), 25.2 ( $\text{CH}_3$ ), 24.3 ( $\text{CH}_3$ ), 24.1 ( $\text{CH}_3$ ), 23.9 ( $\text{CH}_3$ ) ppm.  $^{119}\text{Sn}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  –60.01 ppm. EI-MS:  $m/z$  730.2 ( $\text{M}^+$ ) (100%).

**Synthesis of cAAC-SnCl<sub>2</sub> (5).** For the synthesis of compound **5**, the solvent THF (40 mL) was added to a mixture of cAAC (1.00 g, 3.50 mmol) and solid  $\text{SnCl}_2$  (0.67 g, 3.50 mmol) under a nitrogen atmosphere at  $-78^\circ\text{C}$ . The mixture was then warmed to room temperature and stirred for 3 h. The reaction mixture was filtered through a pad of Celite of a medium porosity frit. The volume of filtrate was reduced up to 50% of the original volume and then stored for 2 days at  $-32^\circ\text{C}$  to give the colorless crystals of **5** suitable for single-crystal X-ray structural analysis (yield: 1.20 g, 72%). mp  $255^\circ\text{C}$  (dec.). Elemental analysis (%) calcd for  $\text{C}_{20}\text{H}_{31}\text{Cl}_2\text{NSn}$  (475.09): C, 50.65; H, 6.58; N, 2.95. Found: C, 50.55; H, 6.79; N, 3.05.  $^1\text{H}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  7.55–7.39 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 2.95–2.84 (sept, 2H,  $\text{Ar-CH}(\text{CH}_3)_2$ ), 2.19 (s, 2H,  $\text{CH}_2$ ), 1.87 (s, 6H,  $\text{CH}_3$ ), 1.50 (s, 6H,  $\text{CH}_3$ ), 1.37 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ), 1.29 (d,  $J = 6.8\text{ Hz}$ , 6H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  145.8, 132.7, 127.9, 123.6, 119.2, 85.5, 49.1, 30.4, 28.4, 26.5, 24.4 ppm.  $^{119}\text{Sn}$  NMR (500 MHz, THF-*d*<sub>8</sub>, TMS,  $25^\circ\text{C}$ ):  $\delta$  –53.14 ppm. EI-MS:  $m/z$  475.1 (65%) ( $\text{M}^+$ ), 405.4 ( $\text{M}^+ - 2\text{Cl}$ ) (100%).

## ASSOCIATED CONTENT

### Supporting Information

CCDC Nos. 896601 (**4**) and 896602 (**5**) and crystal structure determination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: hroesky@gwdg.de (H.W.R.), bdittri@gwdg.de (B.D.).



## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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## ■ DEDICATION

This paper is dedicated to Professor Heinz-Dieter Fenske on the occasion of his 70th birthday.

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