A Silyliumylidene Cation Stabilized by an Amidinate Ligand and 4-Dimethylaminopyridine

Hui-Xian Yeong,^[a] Hong-Wei Xi,^[b] Yongxin Li,^[a] Kok Hwa Lim,^[b] and Cheuk-Wai So^{*[a]}

Abstract: The synthesis and reactivity of a silyliumylidene cation stabilized by an amidinate ligand and 4-dimethylaminopyridine (DMAP) are described. The reaction of the amidinate silicon(I) dimer [LSi:]₂ (1; $L=PhC(NtBu)_2$) with one equivalent of *N*-trimethylsilyl-4-dimethylaminopyridinium triflate [4-NMe₂C₅H₄NSiMe₃]OTf and two equivalents of DMAP in THF afforded [LSi(DMAP)]OTf (2). The ambiphilic character of 2 is demonstrated from its reactivity. Treatment of 2 with 1 in THF afforded the disilylenylsilylium triflate $[L'_2(L)Si]OTf (3; L'=LSi:)$ with the dis-

Keywords: carbene homologues • cations • density functional calculations • N ligands • silicon

placement of DMAP. The reaction of **2** with $[K{HB(iBu)_3}]$ and elemental sulfur in THF afforded the silylsilylene $[LSiSi(H){(NtBu)_2C(H)Ph}]$ (**4**) and the base-stabilized silanethionium triflate [LSi(S)DMAP]OTf (**5**), respectively. Compounds **2**, **3**, and **5** have been characterized by X-ray crystallography.

Recently, the ability of amidinate ligands to stabilize a wide variety of low-valent silicon compounds has been demonstrated.^[4] They can also stabilize silylium moieties in

small ring compounds. Examples include a zwitterionic 2,4-

disila-1,3-diphosphacyclobutadiene,^[5] a germatrisilacyclobutadiene,^[6] a five-membered cationic CSi₃P ring,^[7] and a tet-

rasilacyclobutadiene dication.^[8] On the basis of these results,

it seems that amidinate ligands can stabilize a low-valent sil-

icon cation. However, in a recent communication on the

synthesis of the base-stabilized tetrasilacyclobutadiene dica-

tion,^[8] Driess et al. suggest that the amidinate silyliumylidene cation $[LSi:]^+$ (L=PhC(NtBu)₂) is highly electrophilic.

Moreover, the electron-deficient silicon atom cannot be

shielded from coordination to reactive nucleophilic inter-

mediates. As a result, it undergoes a disproportionation to

form the base-stabilized tetrasilacyclobutadiene dication.

The results show that the isolation of an amidinate silvliu-

should be a resonance hybrid of the canonical formulas I

and II (Scheme 1). The electronic-deficient low-valent sili-

con atoms could be stabilized by coordination to a Lewis base. Herein, we report the synthesis of the singlet silyliumylidene cation [LSi(DMAP)]OTf (2), which is stabilized by both an amidinate ligand and 4-dimethylaminopyridine

(DMAP). Additionally, its theoretical and reactivity studies

We anticipate that an amidinate silvliumylidene cation

mylidene cation is a formidable challenge.

Introduction

The silvliumylidene cation with the composition HSi:+ is the simplest form of polyatomic low-valent silicon moiety. Since it consists of two vacant orbitals and a lone pair of electrons on the low-valent silicon cation, it is Lewis ambiphilic and can possess both electrophilic and nucleophilic characters. By virtue of its diverse electronic structure, the silyliumylidene cation can serve as a useful building block for the synthesis of novel silicon compounds. However, it is highly reactive and can only be observed in the gas phase under mass spectrometric and astrophysical conditions.^[1] Since the discovery of an N-heterocyclic silvlene by West et al.,^[2] the concepts of thermodynamic and/or kinetic stabilization have been applied successfully in the isolation of stable lowvalent silicon compounds. Accordingly, stable derivatives of the silvliumylidene cation, which contain sterically hindered substituents with electron-donor moieties, were synthesized.^[3] However, the high synthetic potential of these cations is hampered by the particular stabilization effects of the substituents. In this context, the quest for isolating other types of stable silvliumylidene cation is still very demanding.

[a] H.-X. Yeong, Dr. Y. Li, Dr. C.-W. So Division of Chemistry and Biological Chemistry Nanyang Technological University
21 Nanyang Link, Singapore 637371
Fax: (+65)6791-1961
E-mail: CWSo@ntu.edu.sg

 [b] Dr. H.-W. Xi, Prof. Dr. K. H. Lim Division of Chemical and Biomolecular Engineering Nanyang Technological University
 62 Nanyang Drive, Singapore 637459

11786

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300255.

WILEY CONLINE LIBRARY

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

are described.

Chem. Eur. J. 2013, 19, 11786-11790



Scheme 1. Canonical forms of an amidinate silyliumylidene cation.

Results and Discussion

The reaction of the amidinate Si^I dimer $[LSi:]_2$ (1)^[9] with one equivalent of *N*-trimethylsilyl-4-dimethylaminopyridinium triflate, [4-NMe₂C₅H₄NSiMe₃]OTf,^[10] and two equivalents of DMAP in THF at room temperature afforded [LSi-(DMAP)]OTf (2) in 54% yield (Scheme 2). The byproduct is Me₃Si–SiMe₃, the structure of which was confirmed by ²⁹Si and ¹H NMR spectroscopy and mass spectrometry.^[11] The reaction appears to proceed through the oxidation of 1 or the transient Si^I radical [LSi⁻] with [4-NMe₂C₅H₄NSiMe₃]OTf to form 2 and Me₃Si–SiMe₃.

Compound **2** is soluble in THF, CH₂Cl₂, and CHCl₃. It is stable in the solid state at room temperature under an inert atmosphere. Compound **2** has been characterized by NMR spectroscopy. The ¹H and ¹³C NMR spectra of **2** display resonances due to the amidinate and DMAP ligands. The ¹⁹F NMR spectrum of **2** shows a singlet at $\delta = -78.9$ ppm for



Scheme 2. Synthesis of compound 2.

the CF₃SO₃⁻ anion. The ²⁹Si NMR spectrum of **2** exhibits a singlet at $\delta = -82.3$ ppm, which shows an upfield shift relative to that of the three-coordinate amidinate-stabilized silylenes [LSiX] (X=Cl: δ =14.6 ppm; X=NMe₂: δ = -2.62 ppm).^[12] This can be explained by the strong donoracceptor interaction between the nitrogen atom of DMAP and the low-valent silicon cation, thus reducing the Lewis acidity of the latter. Interestingly, the reactivity studies show that DMAP can be released, hence 2 shows an ambiphilic character (see below). In addition, the ²⁹Si NMR spectroscopic signal is significantly shifted upfield relative to that of the three-coordinate bis(iminophosphorane) chelate ligandstabilized [SiCl]⁺ ($\delta = -3.3 \text{ ppm}$),^[3c] in which an extensive electronic delocalization is observed. It is also intermediate between that of $[HC(CMeNAr)_2Si]^+$ $(Ar=2,6-iPr_2C_6H_3;$ and $[\eta^{5}-Cp^{*}Si]^{+}$ (Cp*=Me₅C₅; $\delta = 69.3 \text{ ppm}$) $\delta =$ -400.2 ppm).^[3a,b] The results indicate that the nature of the silicon(II) cation is strongly influenced by the kinetic and electronic stabilization of the ligand.

Compound **2** has been characterized by X-ray crystallography (Figure 1). The SiNCN four-membered ring is puckered. The Si1 cation adopts a distorted trigonal-pyramidal geometry (sum of bond angles: 266.1°), which indicates that



Figure 1. ORTEP drawing of compound **2** (50% thermal ellipsoids). The hydrogen atoms and disorder in the triflate moiety are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–N1 1.8514(18), Si1–N2 1.8625(18), Si1–N3 1.8777(18), C5–N1 1.342(3), C5–N2 1.340(3); N1-Si1-N2 69.91(8), N1-Si1-N3 98.20(8), N2-Si1-N3 97.95(8).

it is almost nonhybridized and possesses lone-pair electrons with high s character. The shortest Si1…F (3.59 Å) distance is longer than the sum of van der Waals radii (3.57 Å), which suggests that the Si1 cation does not have any interaction with the CF₃SO₃⁻ coun-Si-N_{amidinate} teranion. The (1.8514(18),1.8625(18) Å) bond lengths are comparable with those in [LSiNMe₂] $(1.893(1), 1.905(1) \text{ Å}).^{[12b]}$ The Si1-N3 bond (1.8775(18) Å) is

FULL PAPER

longer than the Si– N_{amide} bond in [LSiNMe₂] (1.724(2) Å).^[12b] It is comparable with that in the DMAPstabilized silanone derivative [{HC(C{=CH₂}NAr)-(CMeNAr)}Si(DMAP)=O] (1.862(2) Å).^[13]

To understand the bonding nature of **2**, DFT calculations of $[LSi(DMAP)]^+$ (**2**⁺; Figure S1 in the Supporting Information) without a counteranion were performed (M06-2X/6-311+G(2d) for Si and 6-311+G(d,p) for H, C, and N).^[14] The calculated structural parameters are in good agreement with the crystallographic data of **2**. The lone-pair orbital at the Si1 atom can be illustrated in the HOMO (Figure S2a in the Supporting Information). Accordingly, the natural bond orbital (NBO)^[15] analysis (Table S1 in the Supporting Information) shows that the lone-pair orbital is high in s character (sp^{0.37}, electron occupancy: 1.94 e). Moreover, the natural population analysis (NPA) charges indicate that the silicon atom has a positive charge (+1.16).

The ambiphilic character of **2** can be demonstrated by its reactivity. The reaction of **2** with **1** in THF formed the disily-lenylsilylium triflate $[\mathbf{L}'_2(\mathbf{L})Si]OTf$ (**3**, $\mathbf{L}' = \mathbf{L}Si$; 23.3 % yield) with the displacement of DMAP (Scheme 3). The reaction appears to proceed through the oxidative addition of **2** with the Si^I-Si^I bond in **1**. Another possible mechanism is that

www.chemeurj.org



Scheme 3. Synthesis of compounds 3-5.

one of the Si^I atoms in **1** acts as a Lewis base to form an adduct with **2**. Compound **3** is the first example of a stable silylium cation that comprises low-valent silicon substituents, although the chemistry of stable silylium cations has been studied in recent decades.^[16]

Compound **3** is soluble in THF, DME, and pyridine. It is stable in the solid state at room temperature under an inert atmosphere. Compound **3** has been characterized by NMR spectroscopy. The ¹H and ¹³C NMR spectra of **3** display resonances due to the amidinate ligands. The ²⁹Si NMR spectrum of **3** exhibits two singlets at $\delta = 2.96$ and -0.53 ppm for the silylium cation and low-valent silicon atoms, respectively. The ²⁹Si NMR spectroscopic signals are intermediate between the silicon cations ($\delta = 53.4$ ppm) and the three-coordinate low-valent silicon atoms ($\delta = -128.7$ ppm) in the base-stabilized tetrasilacyclobutadiene dication.^[8]

Compound **3** was characterized by X-ray crystallography (Figure 2). The Si1 and Si3 atoms adopt a distorted trigonalpyramidal geometry (sum of bond angles of Si1: 281.9°; Si3: 281.2°), which indicates that they are almost nonhybridized and possess lone-pair electrons with high s character. The lone-pair electrons on these Si atoms have a gauche-bent conformation. The Si–Si bonds (2.441(3), 2.451(3) Å) are comparable to the Si^L–Si^I bond (2.413(2) Å) in **1**.^[9] They are longer than those in the base-stabilized tetrasilacyclobutadiene dication (2.321(2), 2.331(2) Å).^[8] The results indicate that the Si–Si bonds (1.819(6), 1.843(6) Å) are shortened relative to those in **2** because the oxidation state of the silicon cation increases from +II to +IV.

In principle, compound 2 is highly electrophilic and can react with a wide range of nucleophilic reagents. As such, the reaction of 2 with $[K{HB(iBu)_3}]$ in THF was performed



Figure 2. ORTEP drawing of compound **3** (50% thermal ellipsoids). The hydrogen atoms and disorder in the triflate moiety are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.441(3), Si2–Si3 2.451(3), Si1–N1 1.852(6), Si1–N2 1.864(6), Si2–N3 1.843(6), Si2–N4 1.819(6), Si3–N5 1.865(6), Si3–N6 1.877(6); N1-Si1-N2 69.8(3), N1-Si1-Si2 105.6(2), N2-Si1-Si2 106.5(2), Si1-Si2-Si3 120.41(10), N3-Si2-N4 71.2(2), N5-Si3-N6 69.9(3), N5-Si3-Si2 107.2(2), N6-Si3-Si2 104.1(2).

to afford the silylsilylene [LSiSi(H){(NtBu)₂C(H)Ph]] (4)^[17] in 13.4% yield with the displacement of DMAP (Scheme 3). The reaction appears to proceed through the formation of the hydrosilylene intermediate [LSiH], which then reacts with the amidinate ligand of another [LSiH] molecule to form 4. We have also reported the synthesis of compound 4 by the reduction of [LSiHCl₂] with 4 equivalents of KC₈.^[17]

The existence of the lone-pair electrons in compound 2 can be illustrated by the reaction of 2 with elemental sulfur in THF to form the base-stabilized silanethionium triflate [LSi(S)(DMAP)]OTf (5) in 30.9% yield (Scheme 3). A similar compound supported by the bis(iminophosphorane) chelate ligand has been reported by Driess et al. very recently.^[3c] Compound **5** is soluble in THF, CH₂Cl₂, and CHCl₃. It is stable in the solid state at room temperature under an inert atmosphere. Compound 5 has been characterized by NMR spectroscopy. The ²⁹Si NMR spectrum of **5** exhibits one singlet at $\delta = -14.09$ ppm, which shows a downfield shift relative to that of 2. The ²⁹Si NMR spectroscopic signal of 5 is intermediate between the four-coordinate amidinate silanethione complexes [LSi(S)Cl] ($\delta = -17.5$ ppm) and [LSi(S)StBu] ($\delta = 1.57$ ppm).^[18a,b] It shows a downfield shift relative to that of the five-coordinate amidinate silanethione complex [L_2 SiS] ($\delta = -70.7 \text{ ppm}$).^[18c]

Compound **5** has been characterized by X-ray crystallography (Figure 3). The Si1 cation adopts a tetrahedral geometry. The Si1–S1 bond (1.969(10) Å) is comparable with that in the amidinate–silanethione complexes such as [LSi(S)St-Bu] (1.984(8) Å), [LSi(S)Cl] (2.079(6) Å), and [L₂SiS] (2.0193(9) Å).^[18] It is also comparable with those in base-stabilized silanethione complexes (2.006(1)–2013(3) Å).^[19] The results indicate that the Si1–S1 bond could have doublebond character or zwitterionic Si⁺–S⁻ bonding character. The Si–N_{amidinate} (1.800(2), 1.801(2) Å) bond lengths are

FULL PAPER



Figure 3. ORTEP drawing of compound **5** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–S1 1.9686(10), Si1–N1 1.801(2), Si1–N2 1.800(2), Si1–N3 1.794(2); N1-Si1-N2 73.03(11), N1-Si1-N3 104.46(11), N2-Si1-N3 106.30(11), N1-Si1-S1 124.65(9), N2-Si1-S1 124.91(9), N3-Si1-S1 115.49(8).

shorter than those in 2 because the oxidation state of the silicon cation increases from + II to + IV.

Conclusion

The silyliumylidene cation [LSi(DMAP)]OTf (2), which is stabilized by both an amidinate ligand and DMAP, can be synthesized by a simple procedure. Its reactivity toward the amidinate silicon(I) dimer, [K{HB $(iBu)_3$ }], and sulfur demonstrates that it has both electrophilic and nucleophilic characters. Further reactivities of 2 are currently under investigation.

Experimental Section

General procedure: All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF, DME, and toluene were dried and distilled over Na/K alloy prior to use. [D₈]THF was dried and distilled over K metal prior to use. [D₁]Chloroform and [D₅]Pyr were dried and distilled over CAH₂ prior to use. Compound **1** and [4-NMe₂C₅H₄NSiMe₃]OTf were prepared as described in the literature.^[9,10] The ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were recorded using a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H, ¹³C, and ²⁹Si; and CFCl₃ for ¹⁹F. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of 2: A solution of $[4-NMe_2C_5H_4NSiMe_3]OTf$ (0.0735 g, 0.213 mmol) in THF (1 mL) was added to a stirring solution of 1 (0.108 g, 0.208 mmol) and DMAP (0.0518 g, 0.424 mmol) in THF (15 mL) at ambient temperature. The resulting dark red solution was stirred for 2 h. Volatiles were removed under vacuum, and the residue was extracted with toluene. After filtration and concentration of the filtrate, **2** was obtained as colorless crystals (0.060 g, 54.3%). M.p. 169.7°C (decomp); ¹H NMR

(400.2 MHz, $[D_8]$ THF, 24.8 °C): $\delta = 1.07$ (s, 18H; *t*Bu), 3.22 (s, 6H; NMe₂), 7.12–7.55 (m, 7H; Ph and DMAP), 8.37 ppm (d, ³*J*(H,H) = 6.44 Hz, 2H; DMAP); ¹³C NMR (100.6 MHz, $[D_8]$ THF, 24.7 °C): $\delta = 31.16$ (*CMe*₃), 39.61 (*NMe*₂), 54.64 (*CMe*₃), 108.84 (Ph), 121.72 (q, ¹*J*-(C,F)=321.7 Hz; *CF*₃), 126.16, 128.14, 128.71 (Ph), 128.95 (br; *meta-C*_{DMAP}), 129.48, 131.22, 132.46 (*C*NMe₂ and Ph), 146.02 (br; *ortho-C*_{DMAP}), 171.63 ppm (*NCN*); ²⁹Si[¹H] NMR (78.65 MHz, $[D_8]$ THF, 22.7 °C): $\delta = -82.27$ ppm; ¹⁹F[¹H] NMR (375.94 MHz, $[D_8]$ THF, 23.2 °C): $\delta = -78.90$ ppm; elemental analysis calcd (%) for C₂₃H₃₃F₃N₄O₃SSi: C 52.06, H 6.27, N 10.56; found: C 51.73, H 6.15, N 10.16.

Crystal data for **2**: $[C_{23}H_{33}F_{3}N_4O_3SSi]$; $M_r = 530.68$; monoclinic; space group *Cc*; a = 14.0577(6), b = 10.8815(4), c = 18.3062(8) Å; $\beta = 102.662(2)^\circ$; V = 2732.18(19) Å³; Z = 4; $\rho_{calcd} = 1.290$ mg m⁻³; 18381 measured reflections; 7566 independent reflections; 391 refined parameters; $R_1 = 0.0443$, $wR_2 = 0.0919$ ($I > 2\sigma(I)$).

Synthesis of 3: A solution of 2 (0.107 g, 0.201 mmol) in THF (13.4 mL) was added dropwise to a stirring solution of 1 (0.104 g, 0.201 mmol) in THF (5 mL) at ambient temperature. The resulting dark red solution was stirred for 2 h. Volatiles were removed under vacuum, and the residue was extracted with DME. After filtration and concentration of the filtrate, 3 was obtained as yellow crystals (0.028 g, 22.6%). M.p. 270.1°C (decomp); ¹H NMR (399.5 MHz, [D₅]Pyr, 23.6 °C): $\delta = 1.20$ (s, 36H; *t*Bu), 1.32 (s, 18H; *t*Bu), 7.35–7.70 ppm (m, 15H; Ph); ¹³C NMR (100.5 MHz, $[D_5]$ Pyr, 24.1 °C): $\delta = 31.41$ (CMe₃), 31.73 (CMe₃), 53.59 (CMe₃), 55.91 (CMe₃), 128.21, 128.30, 128.78, 128.92, 129.20, 129.64, 130.85 (Ph), 132.09 (q, ${}^{1}J(C,F) = 301.0 \text{ Hz}$; CF₃) 133.11 (Ph), 165.76, 182.92 ppm (NCN); ²⁹Si{¹H} NMR (78.65 MHz, DME, 23.4 °C): $\delta =$ -0.534 (LSi:), 2.96 ppm (Si⁺); ¹⁹F{¹H} NMR (375.94 MHz, [D₅]Pyr, 23.7°C): $\delta = -77.09 \text{ ppm}$; elemental analysis calcd (%) for C46H69F3N6O3SSi3: C 59.58, H 7.51, N 9.07; found: C 59.31, H 7.24, N 8.75.

Crystal data for **3**: $[C_{46}H_{69}F_3N_6O_3SSi_3]$; $M_r=927.40$; monoclinic; space group *P21/n*; a=16.0420(13), b=17.2604(16), c=18.4942(15) Å; $\beta=90.112(6)^\circ$; V=5120.9(8) Å³; Z=4; $\rho_{calcd}=1.203$ mg m⁻³; 40958 measured reflections; 8788 independent reflections; 651 refined parameters; $R_1=0.0819$, $wR_2=0.1866$ ($I>2\sigma(I)$).

Synthesis of 4: $[K{HB(iBu)_3}]$ (0.22 mL, 1 M in THF) was added dropwise to a stirring solution of **2** (0.107 g, 0.201 mmol) in THF (13.4 mL) at -78 °C. The resulting orange solution was warmed to ambient temperature and stirred for an additional 2 h. Volatiles were removed under vacuum, and the residue was extracted with a mixture of toluene and THF. After filtration and concentration of the filtrate, **4** was obtained as colorless crystals (0.0071 g, 13.4 %). For spectroscopic data of **4**, see the literature.^[17]

Synthesis of 5: A solution of sulfur (0.0079 g, 0.246 mmol) in THF (1 mL) was added to a stirring solution of 2 (0.111 g, 0.208 mmol) in THF (13.8 mL) at -78 °C. The reaction mixture was warmed to ambient temperature and stirred for an additional 3 h. The insoluble precipitate was removed by filtration, and the filtrate was concentrated to obtain 5 as colorless crystals (0.036 g, 30.9%). M.p. 281.4°C (decomp); ¹H NMR (399.5 MHz, $[D_1]$ chloroform, 23.2 °C): $\delta = 1.13$ (s, 18H; *t*Bu), 3.02 (s, 6H; NMe_2), 6.52 (d, ${}^{3}J(H,H) = 6.39$ Hz, 1 H; ortho-CH of DMAP), 7.43 (d, ${}^{3}J$ -(H,H) = 7.31 Hz, 2H; ortho-CH of Ph), 7.56 (t, ${}^{3}J(H,H) = 7.79$ Hz, 2H; meta-CH of Ph), 7.66 (t, ³J(H,H)=7.53 Hz; para-CH of Ph), 8.21 (d, ³J-(H,H)=5.95 Hz, 1H; ortho-CH of DMAP), 8.68 ppm (br, 2H; meta-CH of DMAP); 13 C NMR (100.6 MHz, [D₁]chloroform, 24.2 °C): $\delta = 30.99$ (CMe₃), 39.34 (NMe₂), 57.06 (CMe₃), 106.83, 115.84 (Ph and DMAP), 120.60 (q, ${}^{1}J(C,F) = 319.14 \text{ Hz}$; CF₃), 127.08, 128.62, 129.74, 132.64, 149.19, 154.71 (Ph and DMAP), 166.83 ppm (NCN); ²⁹Si{¹H} NMR (79.49 MHz, [D₁]chloroform, 23.6 °C): $\delta = -14.09 \text{ ppm}$; ¹⁹F{¹H} NMR (372.5 MHz, [D₁]chloroform, 23.4 °C): $\delta = -79.16$ ppm; elemental analysis calcd (%) for C₂₃H₃₃F₃N₄O₃S₂Si: C 49.10, H 5.92, N 9.96; found: C 48.87, H 5.63, N 9.74.

Crystal data for **5**: $[C_{23}H_{33}F_3N_4O_3S_2Si]$; $M_r = 562.74$; triclinic; space group $P\bar{1}$; a = 8.7357(12), b = 10.7468(12), c = 15.909(2) Å; a = 103.952(3), $\beta = 97.110(3)$, $\gamma = 100.141(6)^{\circ}$; V = 1405.0(3) Å³; Z = 2; $\rho_{calcd} = 1.330$ mgm⁻³; 22636 measured reflections; 7624 independent reflections; 333 refined parameters; $R_1 = 0.0652$, $wR_2 = 0.1647$ ($I > 2\sigma(I)$).

Chem. Eur. J. 2013, 19, 11786-11790

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

X-ray data collection and structural refinement: Intensity data for compounds **2**, **3**, and **5** were collected using a Bruker APEX II diffractometer. The crystals were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on $F^{2,[20]}$ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. The restraints and constraints for solving the disordering in the triflate moieties in compounds **2** and **3** are described in the Supporting Information.

CCDC-901880 (2), CCDC-901879 (3), and CCDC-901878 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the Academic Research Fund Tier 1 (RG 57/11).

- a) L. Wang, Y.-L. He, Int. J. Mass Spectrom. 2008, 276, 56-76; b) A. Nowek, J. Leszczyński, J. Phys. Chem. 1996, 100, 7361-7366; c) A. B. Sannigrahi, R. J. Buenker, G. Hirsch, J.-P. Gu, Chem. Phys. Lett. 1995, 237, 204-211; d) R. S. Grev, H. F. Schaefer, J. Chem. Phys. 1992, 97, 8389-8406; e) P. Botschwina, M. Oswald, P. Sebald, J. Mol. Spectrosc. 1992, 155, 360-364; f) R. H. Petrmichl, K. A. Peterson, R. C. Woods, J. Chem. Phys. 1988, 89, 5454-5459; g) N. Grevesse, A. Sauval, Astron. Astrophys. 1970, 9, 232-238; h) P. D. Singh, F. G. Vanlandingham, Astron. Astrophys. 1978, 66, 87-92; i) P. J. Bruna, S. D. Peyerimhoff, Bull. Soc. Chim. Belg. 1983, 92, 525-546.
- [2] M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Beljakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* 1994, 116, 2691–2692.
- [3] a) P. Jutzi, A. Mix, B. Rummel, W. W. Schoeller, B. Neumann, H.-G. Stammler, *Science* 2004, 305, 849–851; b) M. Driess, S. Yao, M. Brym, C. van Wüllen, Angew. Chem. 2006, 118, 6882–6885; Angew. Chem. Int. Ed. 2006, 45, 6730–6733; c) Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess, Angew. Chem. 2012, 124, 10221–10224; Angew. Chem. Int. Ed. 2012, 51, 10074–10077.
- [4] For reviews on amidinate-stabilized silylenes, see: a) S. S. Sen, S. Khan, P. P. Samuel, H. W. Roesky, *Chem. Sci.* 2012, *3*, 659–682;
 b) S. S. Sen, S. Khan, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* 2012, *45*, 578–587; c) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Organometallics* 2012, *31*, 4588–4592; d) R. Azhakar, R. S. Ghadwal, H. W. Roesky, H. Wolf, D. Stalke, *Chem. Commun.* 2012, *48*, 4561–4563.

- [5] a) S. S. Sen, S. Khan, H. W. Roesky, D. Kratzert, K. Meindl, J. Henn, D. Stalke, J.-P. Demers, A. Lange, *Angew. Chem.* 2011, *123*, 2370– 2373; *Angew. Chem. Int. Ed.* 2011, *50*, 2322–2325; b) S. Inoue, W. Wang, C. Präsang, M. Asay, E. Irran, M. Driess, *J. Am. Chem. Soc.* 2011, *133*, 2868–2871.
- [6] H.-X. Yeong, S.-H. Zhang, H.-W. Xi, J.-D. Guo, K. H. Lim, S. Nagase, C.-W. So, *Chem. Eur. J.* 2012, 18, 2685–2691.
- [7] S. S. Sen, J. Hey, M. Eckhardt, R. Herbst-Irmer, E. Maedl, R. A. Mata, H. W. Roesky, M. Scheer, D. Stalke, *Angew. Chem.* **2011**, *123*, 12718–12721; *Angew. Chem. Int. Ed.* **2011**, *50*, 12510–12513.
- [8] S. Inoue, J. D. Epping, E. Irran, M. Driess, J. Am. Chem. Soc. 2011, 133, 8514–8517.
- [9] S. S. Sen, A. Jana, H. W. Roesky, C. Schulzke, Angew. Chem. 2009, 121, 8688–8690; Angew. Chem. Int. Ed. 2009, 48, 8536–8538.
- [10] R. Weiss, N. J. Saloman, G. E. Miess, R. Roth, Angew. Chem. 1986, 98, 925–926; Angew. Chem. Int. Ed. Engl. 1986, 25, 917–919.
- [11] For ²⁹Si resonance of Me₃Si-SiMe₃, see: T. A. Blinka, B. J. Helmer, R. West, Adv. Organomet. Chem. **1984**, 23, 193–218.
- [12] a) C.-W. So, H. W. Roesky, J. Magull, R. B. Oswald, Angew. Chem.
 2006, 118, 4052–4054; Angew. Chem. Int. Ed. 2006, 45, 3948–3950;
 b) C.-W. So, H. W. Roesky, P. M. Gurubasavaraj, R. B. Oswald, M. T. Gamer, P. G. Jones, S. Blaurock, J. Am. Chem. Soc. 2007, 129, 12049–12054.
- [13] Y. Xiong, S. Yao, R. Müller, M. Kaupp, M. Driess, J. Am. Chem. Soc. 2010, 132, 6912–6913.
- [14] For the details of theoretical studies and respective references, see the Supporting Information.
- [15] F. Weinhold, C. R. Landis, Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective, Vol. 3, Cambridge University Press, 2005, pp. 215–275.
- [16] V. Y. Lee, A. Sekiguchi, Organometallic Compounds of Low-Coordinated Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds, Wiley, Chichester, 2010, Chapter 1.
- [17] S.-H. Zhang, H.-X. Yeong, H.-W. Xi, K. W. Lim, C.-W. So, Chem. Eur. J. 2010, 16, 10250–10254.
- [18] a) C.-W. So, H. W. Roesky, R. B. Oswald, A. Pal, P. G. Jones, *Dalton Trans.* 2007, 5241–5244; b) S.-H. Zhang, H.-X. Yeong, C.-W. So, *Chem. Eur. J.* 2011, *17*, 3490–3499; c) K. Junold, J. A. Baus, C. Burschka, D. Auerhammer, R. Tacke, *Chem. Eur. J.* 2012, *18*, 16288–16291.
- [19] a) S. Yao, Y. Xiong, M. Driess, *Chem. Eur. J.* 2010, *16*, 1281–1288;
 b) P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset,
 M. Perrot, C. Priou, *Angew. Chem.* 1989, *101*, 1069–1071; *Angew. Chem. Int. Ed. Engl.* 1989, *28*, 1016–1018; c) S. Yao, Y. Xiong, M. Brym, M. Driess, *Chem. Asian J.* 2008, *3*, 113–118.
- [20] G. M. Sheldrick, SHELXL-97; Universität Göttingen, Göttingen, Germany, 1997.

Received: January 23, 2013 Revised: May 28, 2013 Published online: July 12, 2013

11790 -