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COMMUNICATION

A début for base stabilized monoalkylsilylenes†‡

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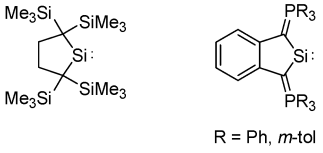
The first base stabilized monoalkylsilylenes LSi*t*Bu (2) and LSi[C(SiMe$_3$)$_3$] (3) (L = PhC(N*t*Bu)$_2$) were synthesized by the facile metathesis reactions of Li*t*Bu and KC(SiMe$_3$)$_3$ with LSiCl (1). The reaction of LSi*t*Bu (2) with N$_2$O afforded the dimer [LSi*t*Bu(μ-O)]$_2$ (4) which contains a four-membered Si$_2$O$_2$ ring.

Stabilization of highly reactive species under normal laboratory conditions has been an ever growing field of research in main group chemistry.[1] Among group 14 intermediates, carbenes and silylenes R$_2$E: (where R = alkyl, aryl, H, or halogen, E = C or Si) are highly reactive and attracted attention of theoreticians as well as experimentalists.[2–5] Their first stable analogues were isolated by Arduengo *et al.* (1991)[6] and West *et al.* (1994)[7] as N-heterocycles with a singlet ground state. Singlet carbenes have been used as ligands for main group and transition metals to stabilize unusual oxidation states and also find applications in activation of small molecules.[8,9] Gaseous dichlorosilylene Cl$_2$Si: has been known for many years.[10] However, it is unstable and readily condenses to polymeric (Cl$_2$Si)$_x$ or disproportionates to Si and SiCl$_4$. The properties of gaseous Cl$_2$Si: and polymeric (Cl$_2$Si)$_x$ have been studied early in the 1970s by Timms, Margrave and others.[10,11] In 2006, the first stable chlorosilylene was isolated as LSiCl (L = PhC(N*t*Bu)$_2$) (**1**) supported by an amidinato ligand in less than 10% yield using potassium as a reducing agent.[5d] After that it was possible to stabilize dichlorosilylene as NHC·Cl$_2$Si: (NHC = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene or 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene) in high yield by utilizing a new synthetic strategy comprising the reductive elimination of HCl from trichlorosilane in the presence of NHC under mild reaction conditions.[12] Subsequently a modified high yield method for **1** was also reported which further facilitates to explore its chemistry.[5e] We utilized silylenes as σ-donor ligands for transition metal complexes[13a–f] as well as for its oxidative addition reactions with organic substrates[14] and Lewis bases.[15] Recently, we were able to stabilize the fluorosilylenes as LSiF·M(CO)$_5$ (M = Cr, Mo, W) in the coordination sphere of transition metals.[13e] A literature survey revealed that so far two stable dialkylsilylenes **A** (by Kira *et al.* in 1999)[16] and **B** (Driess *et al.* in 2011)[17] are known (Chart 1), which were synthesized by KC$_8$ reduction of the corresponding dibromosilanes. A single-crystal X-ray analysis of **B** and its further derivatives have not been reported. In both **A** and **B**, sterically demanding groups such as SiMe$_3$ and PR$_3$ (R = Ph, *m*-tol) are present which provide protection at the low coordinate silicon atoms. Furthermore, **B** benefitted from neighbouring phosphorus ylide functionalities, which contribute electron density towards the silicon atom.

In continuation of our interest in developing safer and more convenient methods for the synthesis of silylenes, we report here a facile route to monoalkylsilylenes LSi*t*Bu (**2**) and LSi[C(SiMe$_3$)$_3$] (**3**) by metathesis reaction of Li*t*Bu and KC(SiMe$_3$)$_3$ with LSiCl (**1**).

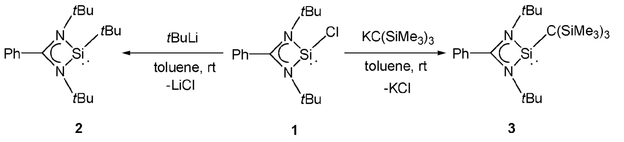
Compounds **2** and **3** were obtained as neat products by facile reactions of Li*t*Bu[18a] and KC(SiMe$_3$)$_3$ with **1** in a 1 : 1 ratio (Scheme 1). Compounds **2** and **3** are soluble in common organic solvents. They were fully characterized by spectroscopic techniques and by elemental analysis. Furthermore, the molecular structure of **3** was established unequivocally by single-crystal X-ray structural analysis. However, the reaction of **1** with MeLi or PhLi resulted in a mixture of uncharacterizable products.

The ^{29}Si NMR spectrum of **2** shows a single resonance at δ 61.5, which is downfield shifted compared to LSiCl (δ 14.6).[5e] The *t*Bu protons attached to the nitrogen atom of compound **2** in



A **B**

Chart 1 Stable dialkylsilylenes **A** and **B**.



Scheme 1 Synthesis of monoalkylsilylenes **2** and **3**.

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its ^{1}H NMR spectrum appear as a singlet (δ 1.11), which is downfield shifted compared to that of LSiCl (δ 1.08).[5e] The *t*Bu protons on the silicon atom resonate at δ 1.30. Moreover, **2** shows its molecular ion for [M$^+$] in its mass spectrum at *m*/*z* 316.

Compound **3** exhibits two resonances at δ 72.7 and δ −0.4 for the silylene *Si*C(SiMe$_3$)$_3$ and silyl SiC(*Si*Me$_3$)$_3$ moieties, respectively, in its ^{29}Si NMR spectrum. In the ^{1}H NMR spectrum, the *t*Bu protons attached to the silicon atom exhibit a singlet at δ 0.57. The *t*Bu protons on the nitrogen atom resonate at δ 1.23. The molecular structure of **3** is shown in Fig. 1. Compound **3** crystallizes in the monoclinic space group $P2_1/n$. The silicon atom is three-coordinate and features a trigonal pyramidal geometry, with the lone pair of electrons residing on the apex. The coordination environment of silicon is derived from two nitrogen atoms of the amidinato ligand and one tertiary carbon atom of the alkyl group. The Si(1)–C(16) bond length in **3** is 2.0173(11) Å. This is longer than the value of 1.9075 (2) Å in compound **A** (Chart 1), presumably due to the higher coordination number of silicon in **3**. The bond length between the chelating nitrogen atoms and the silicon is nearly similar (Si1–N1, 1.9145(11) Å and Si1–N2, 1.9387(10) Å). The bite angle of N1–Si1–N2 is 68.30(4)°. The Si atom is shifted out of the plane defined by N1–C1–N2 by 0.3329(0.0003) Å.

In order to compare the reactivity of monoalkylsilylene with chlorosilylene, we carried out a reaction of **2** with N$_2$O, which yielded the dimer [LSi*t*Bu(μ-O)]$_2$ (**4**) (Scheme 2). It is interesting to mention that N$_2$O has been considered as an ideal source of atomic oxygen, which proceeds under elimination of dinitrogen as the single side product. Recently we reported on the reaction of LSiCl (**1**) with N$_2$O, which resulted in the formation of the trimer [LSi(μ-O)Cl]$_3$, which contains a Si$_3$O$_3$ six-membered ring.[15b] Driess *et al.* prepared the NHC-supported silanone upon reaction of N$_2$O with the adduct of NHC-silylene.[18b] In contrast, Severin *et al.* isolated a covalent bonded nitrous oxide of NHC.[19] Obviously the affinity of silicon to oxygen is much higher than that of carbon. From the above reactivity studies with N$_2$O, we presume that the formation of a dimer might be due to the presence of a bulkier *t*Bu group on the silicon atom.

Compound **4** is soluble in common organic solvents and it is stable both in the solid state and in solution for a long time without any decomposition under an inert gas atmosphere. The ^{29}Si NMR spectrum of **4** exhibits a single resonance at δ −74.3 consistent with the compounds containing five coordinate silicon. In the ^{1}H NMR spectrum of **4**, the *t*Bu protons attached to the nitrogen atoms show a single resonance at δ 1.35 and the *t*Bu protons on the silicon atom resonate at δ 1.68. In its mass spectrum, compound **4** exhibits its molecular ion at *m*/*z* 665 [M$^+$].

Compound **4** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **4** is shown in Fig. 2. In **4** the silicon atom is five-coordinate and arranged in a distorted trigonal bipyramidal geometry with a τ value[20] (τ = 1 for perfect trigonal bipyramidal; τ = 0 for perfect square based pyramid) of 0.64 (Si1), comprising two nitrogen atoms from the supporting amidinato ligand, one carbon and two oxygen atoms. The four-membered Si$_2$O$_2$ ring in **4** is slightly distorted from planarity.[21] There are two types of Si–N (amidinato ligand) bond lengths present, one being shorter (Si(1)–N(1) 1.8342(10) Å) and one longer (Si–N(2) 2.0579(10) Å). Similarly, two types of Si–O bond lengths are present; the shorter bond length is 1.6752(9) Å and the longer one is 1.7245(9) Å. These shorter and longer bond lengths correspond to the equatorial and axial positions. The Si–O–Si and O–Si–O bond angles are 94.79(5)° and 85.21(5)°.

Herein, we report the base stabilized monoalkylsilylenes LSi*t*Bu (**2**) and LSi[C(SiMe$_3$)$_3$] (**3**). The formation of **2** and **3**

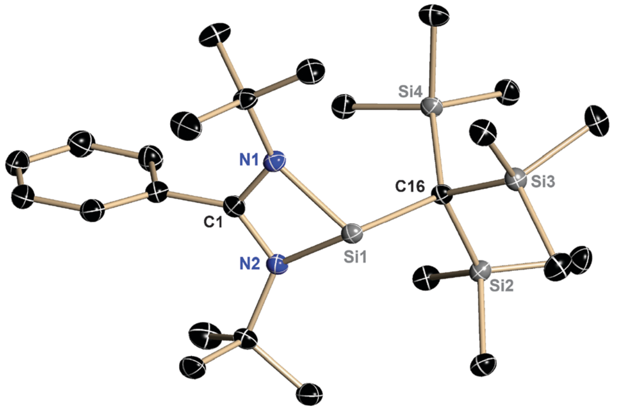
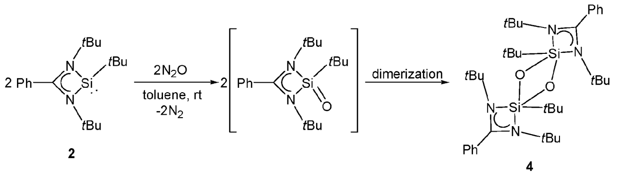


Fig. 1 Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si1–N1 1.9145(11), Si1–N2 1.9387(10), Si1–C16 2.0173(11), Si2–C16 1.9109(13), Si3–C16 1.9200(12), Si4–C16 1.9095(12); N1–Si1–N2 68.30(4), N1–Si1–C16 107.77(5), N2–Si1–C16 109.77(4).



Scheme 2 Synthesis of **4**.

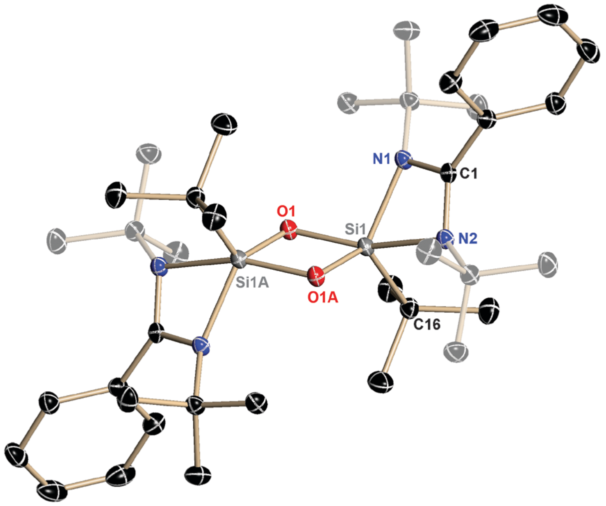


Fig. 2 Molecular structure of **4**. Hydrogen atoms are omitted for clarity. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si1–N2 2.0579(10), Si1–N1 1.8342(10), Si1–O1 1.6752(9), Si1–O1A 1.7245(9), Si1–C16 1.9209(13); O1–Si1–O1A 85.21(5), O1–Si1–N1 121.37(5), O1A–Si1–N1 100.54(5), O1–Si1–C16 121.44(5). O1A–Si1–C16 101.05(5), N1–Si1–N2 67.42(4), Si1–O1–Si1A 94.79(5).

was accomplished by the metathesis reactions of Li*t*Bu and $KC(SiMe_3)_3$ with LSiCl (**1**). This approach provided easy access to stable monoalkylsilylenes. Due to the presence of the bulky substituents, the reactivities of the monoalkylsilylene differ from other silylenes including monochlorosilylene. Interestingly, the reaction of LSi*t*Bu (**2**) with N_2O yielded the dimer $[LSi\textit{t}Bu](\mu\text{-}O)]_2$ (**4**), with a four-membered Si_2O_2 ring, which is in contrast to the trimer $[LSi(\mu\text{-}O)Cl]_3$ obtained from the reaction of LSiCl (**1**) with N_2O. The latter consists of a six-membered Si_3O_3 ring.

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