J|A|C|S
COMMUNICATIONS

Published on Web 07/06/2006

A New Type of N-Heterocyclic Silylene with Ambivalent Reactivity

Matthias Driess,*,† Shenglai Yao,† Markus Brym,† Christoph van Wüllen,† and Dieter Lentz‡

Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin, Strasse des 17. Juni 135, Sekr. C2, D-10623 Berlin, Germany, and Institute of Chemistry, Freie Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

Received April 27, 2006; E-mail: matthias.driess@tu-berlin.de

The synthesis of isolable silylene derivatives, that is, molecular compounds of divalent and dicoordinate silicon, represents one of the milestones in contemporary silicon chemistry.[1] This has been possible by taming their inherent high reactivity through sterically encumbering substituents and/or π-donor groups bonded to the divalent silicon atom. Therefore the presence of bulky π-donor substituents, such as the bis(trimethylsilyl)amido group, reduces the electrophilicity of the divalent silicon,[2] and this trend can be reinforced by involving the divalent silicon atom in a π-conjugated N-heterocyclic system, leading to nucleophilic silylenes as shown by the synthesis of silicon analogues[3] of the Arduengo N-heterocyclic carbenes.[4] Even more electronically variable, stable N-heterocyclic carbene congeners should be accessible by using the monoanionic, bidentate β-diketiminate ligand L$^-$, $\{HC[CMeN(aryl)]_2\}^-$ (aryl = 2,6-diisopropylphenyl).[5] In fact, this has been demonstrated for respective divalent germanium and tin compounds, LGeX and LSnX (X = halide, H), respectively,[6] but it appears surprising that nothing is known about β-diketiminate compounds of divalent silicon, presumably because of the lack of suitable sources for divalent silicon. To synthesize such a stable divalent silicon compound, we attempted to prepare a tribromosilyl complex $LSiBr_3$ as a suitable precursor for the desired divalent compound LSiBr, starting from [LiL] **1** and $SiBr_4$ in diethyl ether. Surprisingly, while the latter reaction leads to a mixture of insoluble products which could not be identified, the same reaction in the presence of TMEDA furnishes the unexpected dibromosilyl complex **2** as a colorless solid in 72% yield. The latter represents a dehydrobromination product of the hypothetical tribromosilyl precursor $LSiBr_3$. Although the mechanism is still unknown, it is evident that TMEDA bears two functions, forming a primary complex with $SiBr_4$ and serving as an auxiliary base for the dehydrobromination of the elusive tribromosilyl intermediate via monodeprotonation of a methyl group at the backbone of L. Apparently, the formation of the primary $SiBr_4$(tmeda) complex is crucial for the success since **2** is not accessible upon subsequent addition of TMEDA to the insoluble product mixture obtained from the reaction of **1** and $SiBr_4$.

Dehydrohalogenated β-diketiminato complexes have merely been reported for divalent germanium,[7] boron, and calcium.[8] The constitution of **2** has been confirmed by NMR spectroscopy (see Supporting Information) and additionally by an X-ray diffraction analysis (Figure 1). The six-membered SiN_2C_3 ring is puckered and possesses Si−N and Si−Br distances similar to those observed in related N-substituted bromosilanes.[9] The alternating endocyclic C−C and C═C distances indicate little π-conjugation.

Compound **2** appears as a promising precursor for the first heterofulvene-like stable silylene **3**. In fact, its debromination with C_8K in the molar ratio of 1:2.6 in THF at −60 °C furnishes the silylene **3** which can be isolated in the form of yellow crystals in 77% yield (Scheme 1). Its composition is proven by EI-MS (M = 444) and a correct combustion analysis.

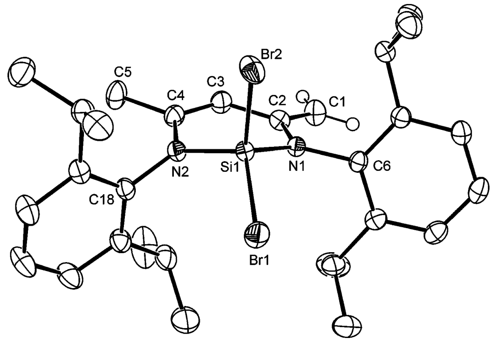
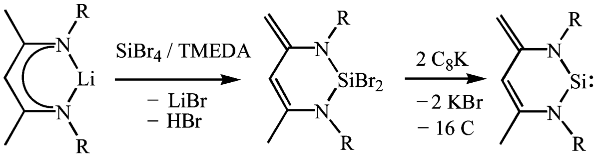


Figure 1. ORTEP view of **2** with thermal ellipsoids drawn at 50% probability level. The H atoms, except those at C1, are omitted for clarity. For selected distances and angles, see Supporting Information.

Scheme 1. Synthesis of the Silylene **3** from **2** and **1**



1: Li L **2** **3**: R = 2,6-^{i}Pr$_2$C$_6$H$_3$

The ^{29}Si NMR spectrum shows a singlet at δ = 88.4 ppm, indicating a similar electronic situation as observed in other N-heterocyclic, p_π−p_π-conjugated silylenes.[3] According to an single-crystal X-ray diffraction analysis (Figure 2), **3** consists of a planar six-membered SiN_2C_3 ring with slightly longer Si−N distances (173.4 and 173.5(1) pm) in comparison with those in **2** (170.4 and 171.1(1) pm). The geometric and electronic features of **3** are intriguing and resemble those of the germanium homologue which, however, results from the dehydrochlorination of the corresponding LGeCl compound.[7] The presence of conjugated C−C π-bonds in **3** is clearly indicated by the alternating endocyclic C−C distances of 140.2(2) (C2−C3) and 138.9(2) pm (C3−C4) and that of the exocyclic C2−C1 double bond (141.2(2) pm), respectively. Additionally, the remarkable short exocyclic C4−C5 single bond distance of 143.6(2) pm reflects that the C−C bond length equilibration in the framework and backbone is a shallow mode. This is confirmed by density functional theory (DFT, B3LYP/TZVP) calculations of the model compound **3′** in which the 2,6-diisopropylphenyl groups at nitrogen have been replaced by 2,6-dimethylphenyl substituents (see Supporting Information). The calculation of the ^{29}Si chemical shift of **3′** revealed a δ value at 111.6 ppm (IGLO B3LYP/IGLO-III, TMS referenced), about 23 ppm lower than the measured value of **3** due to typical overestimations of paramagnetic contributions to the chemical shielding in silylenes.[2] The calculations of magnetic properties of **3′** suggest a

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† Technische Universität Berlin.
‡ Freie Universität Berlin.

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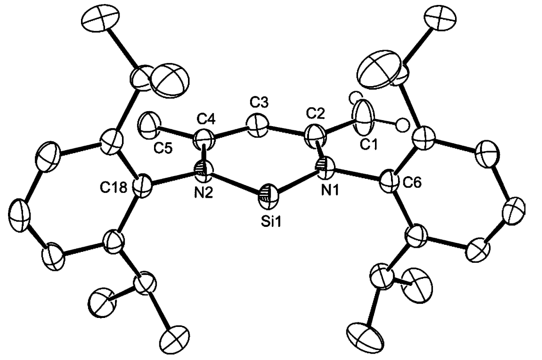
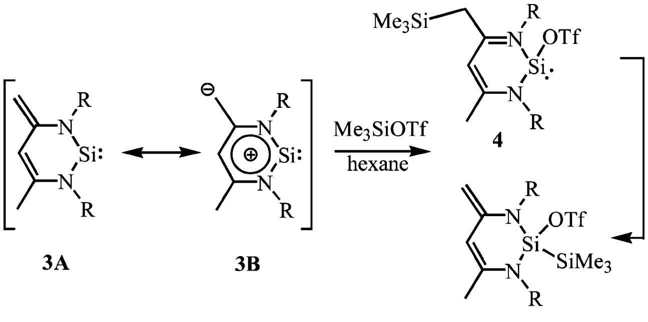


Figure 2. ORTEP view of **3** with thermal ellipsoids drawn at 50% probability level. The H atoms, except those at C1, are omitted for clarity. For selected distances and angles, see Supporting Information.

Scheme 2. Synthesis of **4** (kinetic product) and **5** (thermodynamic product) by Addition of Me_3SiOTf to **3**

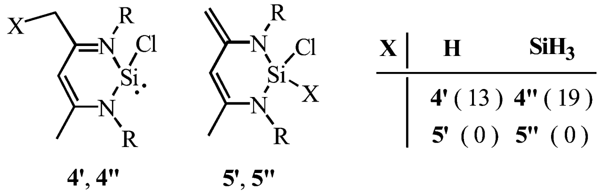


5: OTf = OSO_2CF_3

preference of the mesomeric form **3A** (SiN_2 allyl-like form) over **3B** (6π-heterofulvene ylide form) (Scheme 2) as indicated by the positive NICS values (NICS(O) = 3.6, NICS(1) = 1.4 ppm; see Supporting Information), akin to the behavior of the germanium homologue.[7]

Although the silylene **3** and the germanium homologue seem electronically very similar, their reactivity toward electrophiles is distinct from each other. This is exemplarily shown by the result of the reaction of **3** with Me_3SiOTf in hexane at ambient temperature (Scheme 2) which leads to **4** (1,4-adduct; ^1H NMR) as initial product. The latter represents the first diketiminato complex of divalent silicon. Interestingly, **4** is the kinetic product which slowly isomerizes at ambient temperature to form the thermodynamic product **5** (molar ratio of **4**:**5** is about 2:3 after 4 days). In contrast, the analogous addition of Me_3SiOTf to the germanium homologue of **3** furnishes solely the corresponding 1,4-adduct as final product.[7] The new silylene **4** and its isomer **5** have been characterized by means of NMR spectroscopy. Additionally, the structure of **5** has been confirmed by a single-crystal X-ray diffraction analysis (see Supporting Information). DFT calculations (B3LYP/TZVP) of the respective different model products formed by addition of H_3SiCl and HCl to the model compound **3′** showed a preference of the 1,1-adducts **5′** and **5″** (Chart 1) in both cases, in marked contrast to the analogous germanium compound, where the 1,4-adducts are strongly preferred. In the absence of a counterion (chloride in this case), electrophilic attack to the exocyclic C1═C2 double bond is preferred in all cases, which may contribute to the kinetic preference of **4**. The difference between the germanium and silicon compounds stems from the higher basicity of the silylene versus that of the germylene lone pair. For protonation at the C1═C2 bond, **3′** and its germanium analogue show a similar proton affinity. However, protonation at the divalent metal atom is disfavored by 149 kJ mol^{-1} for **3′** but strongly adversarial (by 258 kJ mol^{-1}) for the germanium congener (see Supporting Information). The higher proton affinity at divalent silicon thus is the most important contribution to the thermodynamic preference of **5′** over **4′**.

Chart 1. Relative Energies (kJ mol^{-1}) of the DFT-Calculated Pairs of Constitutional Isomers **4′**/**5′** and **4″**/**5″**; R = 2,6-Dimethylphenyl



In conclusion, we have reported the synthesis of the novel silylenes **3** and **4**, which represent two new types of metastable divalent silicon compounds with unique reactivity. The latter undergoes rearrangement to give the 1,1-adduct **5** in marked contrast to the reactivity of the germanium homologue. Accordingly, DFT calculations suggest a much higher basicity of the silylene versus that of germylene lone-pair electrons. Initial examination shows that the silylenes **3** and **4** are promising ligands for the synthesis of metal−silylene σ/π-complexes as catalysts for σ-metathesis reactions; these peculiar reactivity patterns will be the subject of further studies.

Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **2**, **3**, **4**, and **5** (PDF), crystallographic data for **2**, **3**, and **5** (CIF), and computational details for the model compounds **2′**−**5′** and **4″**, **5″** (PDF), respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA062928I