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Selective functionalization of a bis-silylene⁺

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Functionalization of N-heterocyclic carbenes (NHCs) has an important influence on their stability, Lewis donor, and acceptor properties. In this study, we report on the selective functionalization of a four-membered N-heterocyclic bis-silylene $(2,6-Ar_2C_6H_3NSi:)_2$ (1) $(Ar = 2,4,6-iPr_3C_6H_2)$ with mono-oxygen sources N₂O and Me₃NO. Treatment of 1 with N₂O results in the selective formation of mono-silylene $(2,6-Ar_2C_6H_3NSi(OH)_2)(2,6-Ar_2C_6H_3NSi:)$ (2) as a major product, along with a small amount of further oxidized product $(2,6-Ar_2C_6H_3NSi(OH)_2)_2$ (3). Compound 2 is the first fourmembered mono-silylene with a di-coordinate silicon atom.

Organosilicon compounds are valuable precursors in organic and organometallic synthesis, and materials science.¹ The availability of new stable compounds with low-valent silicon atoms (e.g., multiple bonded silicon compounds, silylenes and related species), which are otherwise only studied as short-lived reactive species, facilitates the preparation of new compounds which are difficult to isolate by traditional methods.^{2,3} The first stable silene and disilene were reported in 1981 by Brook et al. and West et al., respectively.4 The West group later succeeded in isolating an N-heterocyclic silylene (NHSi),⁵ a compound containing a di-valent di-coordinate silicon atom with a lone pair of electrons. This seminal publication sparked further interest in low-valent silicon chemistry and since then a number of silvlene compounds have been prepared using different stabilization concepts.⁶⁻⁸ Nevertheless, these stable silylenes are quite reactive and prone to oxidative addition reactions and lead to formation of Si(IV) compounds upon reaction with organic substrates such as alkenes, alkynes, amines, imines, ketones, thioketones, alcohols, and azides.6-16 Some of the interesting silicon compounds that are made available using silylene precursors include dimeric silaisonitrile,9 silaoxirane,10 silacyclopropene,¹¹ silaaziridine,¹² silacarbonyl compounds

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with a formal Si=O bond,¹³ and silaheterocycles.^{8,14} Also, functionalization of a NHC¹⁵ has been shown with IPr·SiCl₂ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).¹⁶

A few silicon compounds containing two silylene moieties in a single molecule have been prepared¹⁴ using Lewis-base stabilization and are known as bis-silylenes. Like silylenes, bis-silylenes react with different organic substrates to form silicon compounds in which both Si(π) centers transform into Si(π) centers.⁶⁻¹⁴ To the best of our knowledge, there is no report on the reaction of a bis-silylene, in which only one silylene moiety is oxidized to a Si(π) center, thereby maintaining the other silylene center. This is due to the high reactivity of these compounds.

Reactions of mono- and bis-silylenes with N_2O to form Si(w) compounds have been reported.^{7,8} Activation of small molecules by compounds containing low-valent main group elements that mimic transition metals has attracted attention during the last few years.¹⁷ Reactions of N_2O and compounds with low-valent main group elements are quite varied. Severin and co-workers have recently reported the formation of the NHC·N₂O adduct by the reaction of NHC with N₂O, which at higher temperature resulted in the formation of a ketone.¹⁸

Very recently, we have isolated the first dimeric silaisonitrile⁹ $(2,6-Ar_2C_6H_3NSi:)_2$ (1) (Ar = 2,4,6-iPr₃C₆H₂) (Scheme 1), which is stable at room temperature. Compound 1 features a fourmembered (Si₂N₂) ring with two di-valent di-coordinate silicon atoms, each bearing a lone pair of electrons. Thus, 1 is the first base-free stable bis-silylene. Theoretical studies suggest that 1 is a four π -electron antiaromate.⁹ Therefore, partial oxidation of 1 to a mono-silylene should be favoured due to the formation of a two π -electron aromate.¹⁴ Herein we report on such a species. Selective functionalization of a bis-silylene 1 with N₂O (Scheme 1) gives the mono-silylene (2,6-Ar₂C₆H₃NSi(OH)₂)-(2,6-Ar₂C₆H₃NSi:) (2).

Treatment of a toluene solution of 1 with N_2O yielded 2 as a major product (62%), whereas a further oxidized product, bissilanediol 3, was isolated as a minor product (8%). Reaction of 1 with Me_3NO afforded only compound 3. Moreover, 2 reacts

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further with Me_3NO to form 3. Compounds 2 and 3 were obtained as colorless crystals, soluble in common organic solvents and stable under an inert atmosphere.

The mechanism for the formation of 2 and 3 is at present unknown. Alkyne analogues of germanium and tin react with N₂O and yield respective metal(II) hydroxides,^{19,20} in which the hydrogen abstraction mechanism by radical type intermediates was suggested. Stable four-membered (E_2N_2) (E = Si, Ge, or Sn) cyclic biradical species are known.^{21,22} Their unusual stability is explained by the presence of heteroatoms in the ring. To ascertain the origin of hydrogen in products 2 and 3, reaction of 1 with N₂O in dry toluene-d₈ was carried out. Surprisingly, formation of compound 2 was again observed (as evident from similar NMR and IR spectral data), which was isolated in 56% yield.²³ No signal was observed in the deuterium NMR spectrum of 2 for OD (D = 2 H) groups, prepared in toluene-d₈. This excludes the involvement of radical type intermediates and hence hydrogen abstraction from the solvent molecules. Therefore, in the present study, we assume the initial formation of a silaketone (2') as an intermediate in the reaction of 1 with N₂O, (Scheme 1) which upon reaction with residual water²³ would afford compound 2. Similarly, further oxidation of 2 with N₂O would yield 3', which upon reaction with residual water would give 3.

Silylenes and unsaturated silicon compounds are unstable in protic solvents and react immediately to form Si(rv) compounds. In view of this reactivity it seems unlikely to be able to isolate a silicon compound containing a silylene moiety together with an O–H functional group within the same molecule. The stability of silylene **2**, which bears two hydroxyl groups on the Si(rv) silicon, may be explained by steric protection of the silylene moiety by the bulky terphenyl groups. Further reactivity studies of **2** with various substrates will be performed in the future to explore its properties.

The ¹H and ¹³C NMR spectra of 2 and 3 show the resonances for the terphenyl groups on the nitrogen atoms. Formation of



Fig. 1 ORTEP-representation of the molecular structure of **2**; anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted and only *ipso*-carbons of 2,4,6-triisopropylphenyl groups are shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.6246(12), Si1–O2 1.6273(11), Si1–N1 1.7322(10), Si1–N2 1.7332(3), Si2–N1 1.7705(10), Si2–N2 1.7796(10); O1–Si1–O2 111.61(6), O1–Si1–N1 106.78(5), O1–Si1–N2 121.36(5), N1–Si1–N2 88.74(4), N1–Si2–N2 86.09(4).

mono-silylene was observed from the ^{29}Si NMR spectrum of 2, which shows two resonances at δ 111.16 and -62.42 ppm. The former resonance is characteristic of the silylene compounds 5,7 with di-coordinate silicon atoms, whereas the latter is consistent with those observed for Si(rv) compounds with tetra-coordinate silicon atoms. $^{7-14}$ The ^{29}Si NMR spectrum of 3 exhibits resonance at δ -68.26 ppm and is consistent with those of tetracoordinate silicon compounds. $^{7-14}$

The molecular structure of compound 2 is shown in Fig. 1. Compound 2 crystallizes in the monoclinic space group $P2_1/n$. Compound 2 features a four-membered Si2N2 ring with di- and tetra-coordinate silicon atoms. As observed for compound 1, a similar Si system with the Si₂N₂ core, compound 2 shows dynamic disorder.9 Two main occupancies for the Si₂N₂ core occurred and were included in our model.24 The Si2-N1 (1.7705(10) Å) and Si2-N2 (1.7796(10) Å) bond lengths are longer than the Si1-N1 (1.7322(10) Å) and Si1-N2 (1.7332(3) Å) ones. Similarly, the N1–Si2–N2 $(86.09(4)^{\circ})$ bond angle is smaller than that of N1-Si1-N2 (88.74(4)°). Compound 3 crystallizes in the triclinic space group $P\overline{1}$. Each of the silicon atoms is tetra-coordinate and features a distorted tetrahedral geometry (Fig. 2). The Si2-O3 1.586(10) and Si2-O4 1.598(11) bond lengths are shorter than those of Si1-O1 1.627(2) and Si1-O2 1.627(2).

Invariom refinements were performed for 2 and 3, taking into account non-spherical electron density in the aspherical scattering factors.²⁴ These refinements lead to improvements in the figures of merit, the physical significance of the anisotropic displacement parameters, and highlight un-modeled features in the residual electron density. The improvement of the structural model can be illustrated by comparing the residual electron density map from IAM (independent atom model) and invariom refinement.²⁴ This becomes most obvious for the phenyl ring as shown in Fig. 3.



Fig. 2 ORTEP-representation of the molecular structure of **3**; anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted and only *ipso*-carbons of 2,4,6-triisopropylphenyl groups are shown for clarity. Selected bond lengths [Å] and angles [°]: Si1–O1 1.627(2), Si1–O2 1.627(2), Si2–O3 1.586(10), Si2–O4 1.598(11), Si1–N1 1.733(2), Si1–N2 1.7431(19), Si2–N1 1.7743(19), Si2–N2 1.768(19); O1–Si1–O2 112.85(6), O1–Si1–N1 104.98(5), O1–Si1–N2 122.17(11), N1–Si1–N2 88.53(9), N1–Si2–N2 86.45(9).



Fig. 3 Part of the molecular structure of **2** with anisotropic displacement parameters depicted at 10% probability. (a) Shows the un-modelled bonding residual electron density remaining from IAM refinement, whereas (b) illustrates the reduction of residual density in the same region after invariom refinement.²⁴ Residual electron density features are shown at a level of 0.14 $eÅ^{-3}$.

In summary we have presented a convenient method for selective functionalization of a bis-silylene (1) with N₂O. The selective formation of mono-silylene (2) upon reaction of 1 with N₂O could be explained due to the formation of a two π -electron aromate. However, reaction of 1 with Me₃NO gave the further oxidized product diaminosilanol (3). Compound 2 features a silylene and two hydroxyl (OH) functionalities in a single molecule and may serve as a model for kinetic stability.

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- 24 See ESI[†].