Reactivity of the Bicyclic Amido-Substituted Silicon(I) Ring Compound \( \text{Si}_4\{\text{N(SiMe}_3\}_\text{Mes}\}_4 \) with FLP-Type Character

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Dedicated to Prof. Gerhard Erker on the occasion of his 75th birthday

Abstract: The bicyclic amido-substituted silicon(I) ring compound \( \text{Si}_4\{\text{N(SiMe}_3\}_\text{Mes}\}_4 \) (Mes = Mesityl = 2,4,6-Me\(_3\)C\(_6\)H\(_3\)) features enhanced zwitterionic character and different reactivity from the analogous compound \( \text{Si}_4\{\text{N(SiMe}_3\}_\text{Dipp}\}_4 \) \( \text{(Dipp} = 2,6-\text{Pr}_2\text{C}_6\text{H}_3\text{)} \) due to the smaller mesityl substituents. In a reaction with the N-heterocyclic carbene NHC\(_{\text{CMe}}\) (1,3,4,5-tetramethyl-imidazol-2-yldene), we observe adduct formation to give \( \text{Si}_4\{\text{N(SiMe}_3\}_\text{Mes}\}_4 \cdot \text{NHC}_{\text{CMe}}\) (3). This adduct reacts further with the Lewis acid BH\(_3\) to yield the Lewis acid–base complex \( \text{Si}_4\{\text{N(SiMe}_3\}_\text{Mes}\}_4 \cdot \text{NHC}_{\text{CMe}}\cdot \text{BH}_3\) (4). Coordination of AlBr\(_3\) to 2 leads to the adduct 5. Calculated proton affinities and fluoride ion affinities reveal highly Lewis basic and very weak Lewis acidic character of the low-valent silicon atoms in 1 and 2. This is confirmed by protonation of 1 and 2 with Brookharts acid yielding 6 and 7. Reaction with diphenylacetylene only occurs at 111°C with 2 in toluene and is accompanied by fragmentation of 2 to afford the silacyclopren and the trisilanoboradiene species 9.

Introduction

The concept of frustrated Lewis pair (FLP) chemistry has been shown to be widely used in chemistry, and the scope of the systems has been expanded from inorganic to other fields such as organic, bioinorganic chemistry and materials science. FLPs are effective in a number of unconventional stoichiometric reactions and are also able to catalyze hydrogenations.[1] A huge number of different systems have been developed, however, homoatomic silicon-based FLP systems are still rare. One such example represents an intermolecular FLP composed of a silylene and a silyl cation A that activates dihydrogen (Figure 1).[2]

![Figure 1. Silicon-based FLP system A and four-membered silicon ring compounds B-D. A similar compound to B with a different substituent is missing in Figure 1. A new Figure was generated and was sent together with this document. This also affects reference 3.](image)

A Lewis acidic and basic site is in principle also found in some unsaturated Si\(_4\)R\(_3\) silicon ring compounds. For instance, the EMind- and N(SiMe\(_3\))\(_2\)-substituted silicon-based cyclobuta-diene analogue B features a charge-separated electronic situation with alternating planar and pyramidal silicon atoms (Figure 1).[3] Furthermore, the amido-substituted silicon(i) ring compound 1 that contains a transannular bond was found to

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exhibit zwitterionic character at the two three-coordinate silicon atoms (Figure 1).[6] The Lewis acidic and basic site in B and 1 should allow to exploit these ring systems for FLP-type chemistry. Additionally, the amidino- and amido-substituted SiR ring compound features a planar SiR ring D with different polarization of the trigonal planar and four-coordinate silicon atoms however with a dominating electron delocalization of α-, π- and non-bonding electrons.[3]

Further four-membered cyclic silicon ring compounds have attracted recent research activities because these compounds feature flexible electronic structures and interesting reactivity due to the presence of low-coordinate silicon atoms and the release of ring strain.[6] Recent investigations of such compounds revealed that the nature of the transannular bond can be modified upon introducing sterically rigid silacyclopentane substituents at the bridge position. This resulted in the formation of another SiR ring compound with an inverted Si–Si double bond (Figure 1) that can be transformed into a saturated tetrasilacyclobutane with a π-type single bond upon 1,2-di-iodination.[4,5]

Results and Discussion

Based on the unsaturated four-membered silicon ring compound Si4[N(SiMe3)Dipp]4, 1 with zwitterionic character (Figure 1),[4] we assumed that a similar compound with less sterically demanding substituents could display enhanced reactivity because the SiR ring is more accessible to the substrates. Therefore, we employed the amido substituent N(SiMe3)Mes with the sterically less bulky 2,4,6-trimethylphenyl (Mes) instead of the 2,6-disopropylphenyl group. The reductive debromination of the corresponding precursor (N(SiMe3)Mes)SiBr4 with commercially available Mg turnings as reducing agent provided access to the orange red bicyclo[1.1.0]tetrasilatetraamidodiSi(N(SiMe3)Mes)2, 2 in good yield of 53% with no solvent molecules in the crystal structure (Scheme 1 and Figure 2).

Using Rieke magnesium[10] affords 2 less selectively in contrast to the reductive debromination of the tribromosilane (N(SiMe3)Dipp)SiBr3[11] in 2, the Si2 atom is trigonal planar (\( \Sigma_6^z 355.8^\circ \)) and Si4 is trigonal pyramidal (\( \Sigma_6^z 287.3^\circ \)). For 1, in addition to our initial investigations and similarly to 2, we found that this compound can be crystallized from n-hexane with no solvent molecules in the crystal structure. In this case, the molecular structure represented in Figure S85 in the Supporting Information is very similar to that of 2 and that calculated in the gas phase and includes a trigonal-planar Si2 atom (\( \Sigma_6^z 353.13(3)^\circ \)) and a trigonal pyramidal threefold-coordinated Si4 atom (\( \Sigma_6^z 320.43(2)^\circ \)). This molecular structure of 1 allows to directly compare 1 and 2. The outcome from this structural comparison is, that the trigonal planar Si2 atoms have basically identical angle sums whereas the pyramidalization of Si4 in the novel bicyclic ring compound 2 increased by 32.7° upon using the smaller N(SiMe3)Mes substituent. This can be traced back to the more pronounced bending of the amido substituent at Si4, that is, the more acute N4-Si4 bond (1.7912(13) Å) at Si4 is longer than that at Si2 (1.7105(13) Å) and Si4 is trigonal pyramidal (\( \Sigma_6^z 131.18(10)^\circ \)). Furthermore, the Si–Si bond lengths in 2 around the pyramidal Si4 atom are in the range of single bonds and those around the trigonal planar Si2 atom are between single and double bonds. The bridgehead bond between Si1 and Si3 (2.523(5) Å) is somewhat longer than that of Si2 (2.418(2) Å) but still shorter than the longest observed Si–Si bond of 2.697 Å in RBu3Si–SiRBu3.[12] Similar to the Si–Si bonds, the Si4–N4 bond (1.7912(13) Å) at Si4 is longer than that at Si2 (Si2–N2 1.7105(13) Å).

Characterization of 2 with NMR spectroscopy in [D8]toluene revealed one signal for the bridgehead Si1/Si3 atoms at 85.1 ppm. For the two threefold-coordinated silicon atoms (Si2/ Si4) one very broad signal was observed at ~27 ppm which is probably related to their dynamic configuration in solution similar to the case of 1.[4] Even at 220 K no sharp signals for these two silicon atoms were obtained. Instead line broadening of all signals occurs when cooling to this temperature and the signal for Si2 and Si4 disappears. 29Si NMR spectra at 360 K also show only one broad signal at ~27.4 ppm for Si2 and Si4 (Figures S13). But in the 1H NMR spectrum at 370 K only one set of signals for the four amido substituents starts to form (Figures S15) indicating that a second dynamic process takes place at this temperature similar to the case of 1.[4] To further analyze the chemical shifts of the SiR-ring in 2, we carried out solid state 29Si[1H] CP/MAS NMR spectroscopy which revealed four different signals for the silicon nuclei of the bicyclic ring. They appear at 82.6 and 88.8 ppm for the two fourfold-coordinated bridgehead Si1 and Si3 atoms, at 58.3 ppm for the trigonal planar Si2 atom and at ~118.7 ppm for the trigonal pyramidal Si4 atom (Figures S16 and S17). Although the isotropic 29Si chemical shifts in the solid-state show slight

![Scheme 1. Synthesis of 2 (R = Mesilyl = 2,4,6-Me3C6H3).](image1)

![Figure 2. Molecular structure of 2 (hydrogen atoms are omitted for clarity and thermal ellipsoids are set at a 50% probability level). Selected bond lengths/Å and angles/°: Si1–Si2 2.2375(6), Si2–Si3 2.2514(6), Si3–Si4 2.3617(6), Si1–Si4 2.3560(6), Si1–Si3 2.523(5), Si2–Si4 3.5633, Si1–N1 1.7267(13), Si2–N2 1.7105(13), Si3–N3 1.7221(12), Si4–N4 1.7912(13).](image2)
deviations from the calculated values, the $^{29}\text{Si}$ chemical shift anisotropies (CSAs) in terms of $\delta_a$ (reduced anisotropy)$^{11\text{[a]}}$ are in good agreement with those determined for the DFT-optimized structure of 2 (Tables S1 and S10). Note that molecular dynamics, corresponding to fast-limit angular fluctuations,$^{11\text{[b]}}$ may influence the experimentally determined $^{29}\text{Si}$ CSA parameters (recorded at ambient and higher temperatures). A clear example of such an effect can be observed for the SiMe$_3$ groups. Here, close to axial symmetric $^{29}\text{Si}$ CSA tensors (\(\eta_\text{q} \approx 0\)) are observed experimentally due to fast rotation of SiMe$_3$ groups around the Si–N axis. In contrast, the DFT calculations predict non-axial groups around the Si

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Chem. Eur. J.

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Chem. Eur. J.
sterically more demanding Dipp substituents. In contrast to this observation, the adduct 3 is actually the expected product from this reaction. The NHC is bound to the tetrahedrally coordinated Si2 atom with a Si2–C25 bond length of 1.943(2) Å. This is in the reported range of NHC-coordinated silicon ring compounds.23,26 The Si4 atom in 3 is less pyramidal (\( \Sigma \alpha = 311.6^\circ \)) compared to 2 (\( \Sigma \alpha = 287.3^\circ \)) which is noticeable by the decreased sum of the surrounding bond angles by 24.3°. Furthermore, the coordination of NHC\textsuperscript{Me} affects the transannular bond. The Si1–Si3 bond length (2.357(5) Å) in 3 (Figure 4) is 0.2 Å shorter than that of 2 (2.523(5) Å).

Multinuclear NMR spectroscopy of 3 showed that it coexists in toluene in an equilibrium with a minor component in a 4:1 ratio. The major component displays signals in the \( ^{29}\text{Si} \) NMR spectrum very similar to those calculated for the DFT-optimized structure of 3 (page S99). Analysis of the H,H correlated ROESY spectrum showed that in the minor component the NHC migrated to one of the bridgehead silicon atoms. We suggest that the minor component has the structure 3’ depicted in Figure S20. Upon coordination of NHC\textsuperscript{Me} to 2, the signals in the \( ^{29}\text{Si} \) NMR spectrum of the major component mainly appear at higher field when comparing \( ^{29}\text{Si}(\text{H}) \) CP/MAS NMR signals with those obtained in toluene for 3. This is demonstrated by the signals of the bridgehead Si1 and Si3 atoms that are up-field shifted by 62.8 ppm to a signal at \( \delta = 22.3 \) ppm. The signal for the Si2 atom (\( \delta = -53.1 \) ppm) is even shifted by 111.4 ppm to higher field upon the addition of NHC\textsuperscript{Me} to this atom. The signal for the trigonal pyramidal Si4 atom is less affected by the NHC-coordination and only shifts by 3.4 ppm to lower field to appear at \( \delta = -115.3 \) ppm.

The adduct 3 cleanly reacts with the BH\textsubscript{3}\cdot(SMe\textsubscript{3}) complex under addition of BH\textsubscript{3} to the trigonal pyramidal Si4 atom to afford 4 (Scheme 3). In compound 4 (Figure 5), all silicon atoms in the butterfly-shaped four-membered ring are saturated which is reflected in the single bond character of the Si–Si and Si–N bonds. We note that upon coordination of BH\textsubscript{3} to Si4, the bonds around Si4 are slightly shorter than those of 2. Additionally, the resonances for Si2 and Si4 in the \( ^{29}\text{Si} \) NMR spectrum both appear in the high-field region (–41.4 and –79.5 ppm, respectively) due to their fourfold coordination in 4. The coordination of BH\textsubscript{3} to Si4 was confirmed by the high-field resonance at –32.0 ppm in the \( ^{11}\text{B} \) NMR spectrum compared to the signal at –19.6 ppm for BH\textsubscript{3}\cdot(SMe\textsubscript{3}) in C\textsubscript{6}D\textsubscript{6}. Furthermore, similar \( ^{11}\text{B} \) NMR signals (–32.9 and –36.3 ppm in C\textsubscript{6}D\textsubscript{6}) were observed in borane complexes of NHC-coordinated trisilacyclopolypropylenes.27

Adduct formation with 2 using only a Lewis acid was achieved with AlBr\textsubscript{3} to yield 5 (Scheme 4). Upon coordination of AlBr\textsubscript{3} to 2, the transannular distance between Si1 and Si3 increases to 2.691 Å and the bond lengths between Si1–Si2 and Si2–Si3 are slightly elongated to 2.247(9) Å and 2.268(9) Å with respect to 2, but indicate still partial Si–Si double bond character in these bonds. The distance between Si4 and Al1 (2.490 Å) is somewhat longer than in a normal Al–Si single bond (2.47 Å; Figure 6). \( ^{29}\text{Si} \) NMR spectroscopy of 5 revealed no signal for Si4 which is probably related to quadrupolar relaxation due to coupling to the coordinated Al1 atom. According to DFT-calculated signs for 5 a resonance at –88.5 ppm is expected for this pyramidal Si4 atom (page S100). The signals for Si1 and Si3 appear at 103.6 and that of Si2 resonates at 61.6 ppm. This is in line with the calculated \( ^{29}\text{Si} \) NMR chemical shifts and suggests that an allyl-type \( \pi \)-electron

Figure 4. Molecular structure of 3 (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 50% probability level). Selected bond lengths/Å and angles/°: Si1–Si2 2.3679(5), Si2–Si3 2.3567(5), Si1–Si4 2.3395(5), Si2···Si4 3.717(1), Si1–N1 1.7591(13), Si2–N2 1.7914(12), Si3–N3 1.7622(12), Si4–N4 1.8002(12), Si2–C25 1.943(2).

Figure 5. Molecular structure of 4 (hydrogen atoms are omitted for clarity, except those at B1, and thermal ellipsoids are set at the 50% probability level). Selected bond lengths/Å and angles/°: Si1–Si2 2.3324(5), Si2–Si3 2.3728(5), Si3–Si4 2.3316(5), Si1–N1 1.7576(13), Si1–N1 1.7576(13), Si2–N2 1.7914(12), Si3–N3 1.7622(12), Si4–N4 1.8002(12), Si2–C25 1.943(2).

Scheme 3. Synthesis of 4 (R = Mesityl).

Scheme 4. Synthesis of 5 (R = Mesityl).
that of many common main group element bases and is comparable to that of donor-stabilized silylenes. These investigations show that 2 has intramolecular frustrated Lewis pair (FLP) character although it is solely composed of the element silicon. This is in contrast to FLPs reported in the literature that mostly consist of group 13 and group 15 elements\(^{33}\) or of group 14 and group 15 elements.\(^{34}\) Moreover, with the weak Lewis acidic site and the strong Lewis basic site, 2 belongs to the rare class of so-called “inverse” frustrated Lewis pairs.\(^ {35}\)

To experimentally confirm the high basicity at Si4, we performed reactions of 1 and 2 with Brookharts acid [H-(\text{OE}t)\_2]_2[B(3,5-(CF\_3)\_2C\(\text{H}\)_3)]\(^{36}\) (Scheme 5). Both 1 and 2 selectively react with Brookharts acid to 6 and 7 in 86 and 92% yield, respectively.

In the cations of 6 and 7, as expected, addition of the proton to the pyramidal Si4 atom occurs. Due to positional disorder in the Si4 ring in 6, only the cation in 7 is discussed here and shown in Figure 7. In the cation of 7 an elongation of the transannular distance between Si1 and Si3 to 2.695(9) Å takes place. Furthermore, the Si1–Si2, Si1–Si3 bond lengths (2.413(10) and 2.2263(9) Å) and the Si2–N2 1.681(2) Å bond are in the range between single and double bonds and indicate π-electron delocalization between Si2 and the adjacent atoms although Si2 is not perfectly planar (\(\alpha = 352.36(2)^\circ\)). Compared to 5 the bond lengths around Si2 are somewhat shorter which can be explained by the cationic nature of 7.

In accordance with that, the chemical shift of Si2 in the \(^{29}\)Si NMR spectrum at 71.7 ppm in CDCl\(_3\) is shifted by 10.1 ppm to lower field with respect to the corresponding signal of Si2 in

![Figure 6. Molecular structure of 5 (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 50% probability level). Selected bond lengths Å and angles °: Si4–Al1 2.4899(10), Si1–Si2 2.4966(9), Si2–Si3 2.2678(9), Si3–Si4 2.3540(9), Si1–Si4 2.3690(9), Si1–N1 1.7102(2), Si2–N2 1.704(2), Si3–N3 1.710(2), Si4–N4 1.755(2), Si2–Si1–Si4 94.42(3), Si1–Si2–Si3 73.18(3), Si2–Si3–Si4 94.28(3), Si3–Si4–Si1 69.47(3).](image1)

![Figure 7. Molecular structure of the cation in 7 (hydrogen atoms, except H4 and the counter-anion, are omitted for clarity, and thermal ellipsoids are set at the 50% probability level). Selected bond lengths Å and angles °: Si1–Si2 2.2413(10), Si2–Si3 2.2263(9), Si1–Si4 2.2997(9), Si3–Si4 2.3161(10), Si1–Si3 2.695(9), Si1–N1 1.686(2), Si2–N2 1.681(2), Si3–N3 1.689(2), Si4–N4 1.714(2); Si3–Si2–Si1 74.20(3), Si2–Si1–Si4 91.72(3), Si3–Si2–Si3 91.67(3), Si1–Si4–Si3 71.44(3).](image2)

![Scheme 5. Synthesis of 6 (R = Dipp = 2,6-iPr\(_2\)C\(\text{H}\)_3) and 7 (R = Mesityl).](image3)

![Table 1. Calculated proton affinities (PA) and fluoride ion affinities (FIA) of 1 and 2 in the gas phase and corrected with COSMO.](image4)
the neutral compound 5. The signal for Si2 in 7 is also shifted in the downfield region compared to the dicaticonic cyclobuta-
diene species [Si2L2(SiCl)4]2[2(ZrCl2(Cp*))]2 (L = PhC(NiBu)3, Cp* =
C6Me6) that displays a chemical shift at 53.4 ppm in CDCl3 for the
caticonic silicon centers. [35] But with respect to free aryl-
substituted silylium cations (216.2–244.7 ppm in CD2Cl2) [36] the
silyl cation character of 7 is low due to the partial double bond
character in the Si–Si and Si–N bonds and the electropositive
nature of the adjacent silicon atoms. Due to 29Si satellites
appearing in the 1H NMR spectrum in CDCl3, exact assignment
of the chemical shift to the core silicon atoms in 7 was possible.
The fourfold-coordinated Si4 atom has a signal at −90.8 ppm
with a 1J(Si,Si) coupling constant of 246 Hz. The adjacent Si1 and
Si3 atoms resonate at 74.4 ppm with 1J(Si,Si) coupling constant of
13 Hz. For Si2 a 1J(Si,Si) coupling constant of 53 Hz was
determined. The cation in 6 displays similar 29Si NMR chemical
shifts and coupling constants for Si4 (δ = −107.1 ppm, 1J(Si,Si) =
258 Hz), Si1/Si3 (δ = 61.5 ppm, 1J(Si,Si) = 24 Hz and δ = 61.9 ppm,
1J(Si,Si) = 10 Hz) and for Si2 (δ = 67.3 ppm, 1J(Si,Si) = 66 Hz). The allylic
character in 6 and 7 is reminiscent to that observed in a cyclotetrasilenium cation stabilized with [B(C6F5)4]− that was
obtained in a reaction of the silyl-substituted disilene
(SiMeBu2)Si=Si(SiMeBu2)2 with [Et3Si][BC(C6F5)4]. [37]

Furthermore, we investigated reactions of 2 with alkenes
and alkyenes. We note, that compound 1 did not show any
reactivity with these reagents. Even when the reactions were
carried out at elevated temperature compound 1 remained
unchanged. In contrast, compound 2 shows the formation of an
amido-substituted silacyclopentene 8 (Figure 8) upon exposure of
two equiv. of diphenylacetylene to 2 in refluxing toluene.
This was confirmed by a signal in the 29Si NMR spectrum at
−95.3 ppm which is in the expected range of silirenes. [40] This
product indicates that a fragmentation of 2 occurred at 111 °C
in toluene in the presence of the reagent. To identify the side
product from this reaction, we repeated the manipulation with an
excess of 10 equiv. of diphenylacetylene in toluene at 111 °C
for 18 h. 29Si NMR spectroscopy of the red solid residue of
the reaction showed signals of 8 besides signals of an unknown
product at 7.5, −47.7 and −67.8 ppm. Washing the red colored
residue with hexane allowed to remove 8, and compound 9
remained and can be crystallized from a saturated toluene
solution to afford pale yellow crystals of 9 with a trisilanorb-
nadiene scaffold (Scheme 6).

We note, that a fragmentation in solution upon reactions
with alkenes was also suggested for the isostructural analogue to
1 and 2, the bicyclic germanium(I) ring compound GeL2[N(Bu)2]
that also exhibits zwitterionic character. In this case, dissociation into two amidodigermanes, L2Ge[N(Bu)2]
molecules was proposed. This was elucidated upon reactions of GeL2[N(Bu)2], with ethene, cyclohexa-1,3-diene
and CO2 in solution that yield the corresponding cycloaddition/
insertion products of the digermene with the respective
reagent. [41]

For the formation of 8 and 9, we propose that 2 formally
dissociates into a bis(amiido)silylene and an amido-substituted
trisilacyclopentenylidene. The former can undergo a [2+1]
cycloaddition with diphenylacetylene to give 8 and the latter
can react in one [2+1] and one [2+2] cycloaddition to yield a housene intermediate, that probably isomerizes to a cyclo-
pentadiene species. This was observed in a reaction of a trisilacyclopentene with diphenylacetylene by Sekiguchi [42]
and Scheschkewitz. [43] The cyclopentadiene intermediate can under-
go a [4+2] cycloaddition to afford 9 (Scheme 7).

Only a few trisilanorbadiene species are reported in the
literature so far. One is obtained upon dimerization of a transient 9,10-disila-9,10-Dewar-anthracene. [44] A second example
was synthesized from a dianionic silyl-substituted silacyclo-
hexadiene upon reaction with Me3SiCl2. [45] In 9, the Si–Si
bond lengths (2.334(1) Å) are in the range of single bonds
(2.34 Å). The C=C bonds have lengths that are clearly in the
double bond range (1.34 Å; Figure 8).

As expected the Si2 atom in the silacyclopropene ring of 9
has a signal in the 29Si NMR spectrum at −67.8 ppm that is
more shielded than that of the other two silicon atoms (δ(Si)=
−47.7 ppm) in the six-membered Si3C4 heterocycle. We note,

Figure 8. Molecular structure of 8 and 9 (hydrogen atoms are omitted for clarity, and thermal ellipsoids are set at the 50% probability level). Selected bond lengths/Å and angles/° for 5: C1–C1 1.354(5), C1–C2 1.462(4), S1–N1 1.7135(2), S1–C1 1.8045(3), S2–N2 1.782(2), C1–C1–S1 67.97(8),
C1–S1–C1 44.064(17); for 6: S1–Si2 2.3339(12), S2–C1–1.887(3), S1–C8
1.889(3), C1–C8’ 1.359(4) S2–C15 1.816(3), S1–N1 1.724(3), S3–N1 1.758(3).
that the reaction of 2 with diphenylacetylene differs greatly from that observed with FLPs where the hydrocarbon unit usually connects the Lewis acidic and basic site in the final product. We assume that the different reactivity of 2 with the alkylene is related to the release of ring strain of the highly strained bicyclic ring system which is combined with the FLP-type character of 2.

Despite the enhanced zwitterionic character in 2 no reaction with dihydrogen occurs at room temperature. When the reaction temperature was increased to 60 °C, decomposition of 2 into the bisamido substituted silylene and an unknown side product was observed. By contrast, the isostructural Ge2[N(tBus)Dipp], analogue of 1 and 2 has been reported to react with H2 at 80 °C to give a cyclic tetrahydrodi-tetragermane.

Conclusion

In summary, we have reported a new bicyclic amido-substituted silicon(I) ring compound, 2, that features a greater difference in the polarization of the two three-coordinate silicon atoms than the analogous compound 1 with N(SiMe3)2Dipp substituents. This gives 2 more pronounced zwitterionic character and results in partially different reactivity that is mainly related to the sterically less demanding N(SiMe3)Mes substituent. The Lewis acidic and basic character of 2 was probed in a subsequent reaction with NHCl that resulted in the formation of 3. Adduct 3 serves as a donor to BH3, which supports the Lewis acid and Lewis base properties of the two threefold-coordinated silicon atoms in 2. Coordination of only one Lewis acid is possible when using AlBr3 and yields 5. Calculated fluoride ion and proton affinities showed that 1 and 2 have an extremely weak Lewis acidic site and a strong Lewis basic site. The high basicity of 1 and 2 was confirmed upon their reaction with Brookharts acid, which resulted in 6 and 7. Reaction of 2 with the alkylene diphenylacetylene only proceeds at elevated temperature and is accompanied by a formal fragmentation of 2 into a bis(amido)silylene and a trisilacycloprenylidene that were both trapped by cycloaddition to afford silacycloprenene 8 and trisilanorbornadiene 9. Further derivatization of 2 with other reagents such as chalcogens and Lewis acids are currently underway in our laboratory.

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Conflict of Interest

The authors declare no conflict of interest.

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