

## Silylenes | Hot Paper |

## An Isolable Bis(Silanone–Borane) Adduct

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**Abstract:** The reaction of bis(silylenyl)-substituted ferrocene **1** with two molar equivalents of BPh<sub>3</sub> yields the corresponding bis(silylene–borane) Lewis adduct **2**. The latter is capable to activate CO<sub>2</sub> to furnish the borane-stabilized bis(silanone) **3** through mono-oxygenation of the dative Si<sup>II</sup>→B silicon centers under release of CO. Removal of BPh<sub>3</sub> from **3** with PMe<sub>3</sub> affords the corresponding 1,3,2,4-cyclodisiloxane and the Me<sub>3</sub>P–BPh<sub>3</sub> adduct. All isolated new compounds were characterized and their molecular structures were determined by single-crystal X-ray diffraction analyses.

The activation of small molecules using non- and semi-metal-based compounds is an attractive field in main-group chemistry which led to the discovery of new activation modes and types of reactions.<sup>[1]</sup> In this context, the concept of frustrated Lewis pairs (FLPs) for cooperative activation of inert bonds employing Lewis acids and bases, firstly reported by Stephan, Erker and co-workers, is a landmark discovery.<sup>[2]</sup> Since then, the rapid expansion of FLP chemistry has paved the way to different inter- and intramolecular systems in which the majority is based on sterically encumbered phosphorus- and nitrogen-centered Lewis bases and organoboranes as Lewis acids.<sup>[3]</sup> Although divalent carbon species such as N-heterocyclic carbenes (NHCs) have also been successfully probed in FLP chemistry for the activation of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub>O, the use of analogous Lewis pairs-containing silylenes is less known.<sup>[4,5]</sup> The silicon(II) atom in silylenes exhibits an ambiphilic character due to its vacant 3p orbital (LUMO) and the 3s-centered lone pair (HOMO). Owing to their interesting property and reactivity, stable N-heterocyclic silylenes (NHSis), the heavier analogues of NHCs, have been utilized successfully for the metal-free activation of small molecules<sup>[6]</sup> and as powerful steering ligands in homogeneous catalysis.<sup>[7]</sup> After the first isolation of an N-heter-

ocyclic silylene in 1994 by Denk and West, the formation of a silylene–borane adduct was reported two years later, which, however, slowly rearranges to a silylborane through Si<sup>II</sup> insertion into the B–C bond of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[8]</sup> Since then, an increasing number of compounds containing a dative Si<sup>II</sup>→B<sup>III</sup> bond with four- and five-coordinate Si<sup>II</sup> centers have been isolated and structurally characterized.<sup>[9]</sup>

Due to a large polarization of the Si=O bond and the remarkably weak Si–O π bond (58.5 kJ mol<sup>-1</sup>) compared to the Si–O σ-bond strength (119.7 kJ mol<sup>-1</sup>), compounds with a Si=O bond are intrinsically susceptible to auto-oligomerization to the corresponding polysiloxanes.<sup>[10]</sup> Thus, introduction of an electron donor at the Si atom or/and an acceptor at the O atom are needed to disfavor head-to-tail oligomerization of the polar Si=O bond.<sup>[11]</sup> This led to the first Lewis acid-base supported silanone complex, the silaformamide–borane **A** (Scheme 1), which was reported by us in 2007, starting from a silylene and H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[12]</sup> Roesky et al. described in 2011 the isolation of the acid anhydride **B** generated from the reaction of a chlorosilylene with H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in the presence of NHC.<sup>[13]</sup> Similarly, Roesky et al. reported also the silaformyl chloride complex **C**, resulting from an NHC-stabilized silylene and H<sub>2</sub>O·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[14]</sup> In 2019, the isolation of the first donor–acceptor-supported silaaldehyde **D** was accomplished by the Inoue group.<sup>[15]</sup> Remarkably, Kippings dream of isolable genuine silanones was realized in 2014 with the isolation of the first metallosilanone by Filippou<sup>[16]</sup> and 2017 by the groups of Inoue and Rieger.<sup>[17]</sup> Very recently, a silicon analogue of a ketone with an unperturbed Si=O bond was synthesized by Iwamoto and co-workers.<sup>[18]</sup>

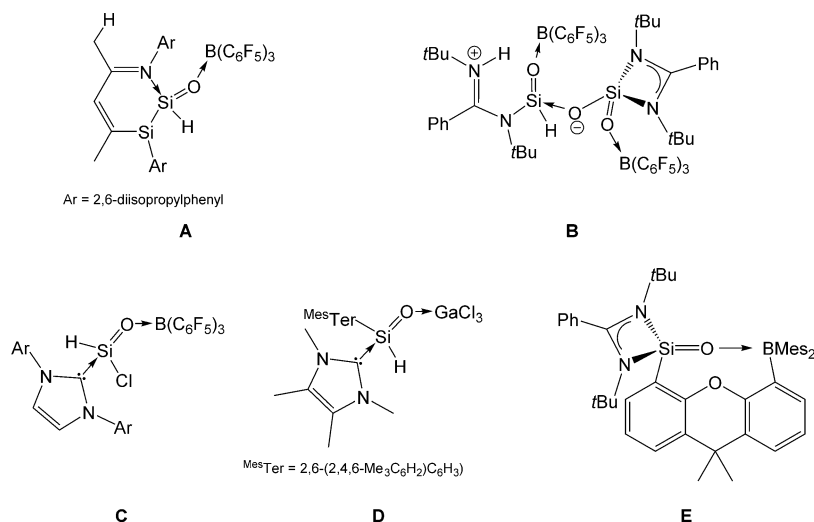
Starting from an in situ generated silylene–borane adduct, Teng et al. reported in 2016 on the activation of THF leading to the isolation of a corresponding ring-opening product.<sup>[20]</sup> Recently, Braun and co-workers used a silylene–borane Lewis adduct as a tool for trapping a single water molecule, affording a zwitterionic silanol stabilized by intramolecular hydrogen bonds.<sup>[23]</sup> In 2017, our group reported the first intramolecular silylene–borane FLP which activates H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and even dehydrogenates water yielding a borane-stabilized silanone **E** with a dative Si=O→B bond.<sup>[19]</sup> Herein, we present the synthesis of the bis(silylene–borane) adduct **2** with the ferrocene spacer and its mild oxidation with CO<sub>2</sub> yielding the first borane-stabilized bis(silanone) adduct **3**. Removal of BPh<sub>3</sub> from **3** by addition of PMe<sub>3</sub> leads to the corresponding 1,3,2,4-cyclodisiloxane through intramolecular Si=O head-to-tail dimerization. Moreover, the reaction of **2** with elemental sulfur yields a bis(sila-thione) with two ‘borane-free’ Si=S moieties.

The reaction of the ferrocene-derived bis(silylene)<sup>[24]</sup> **1** with two molar equivalents of triphenylborane in toluene at room

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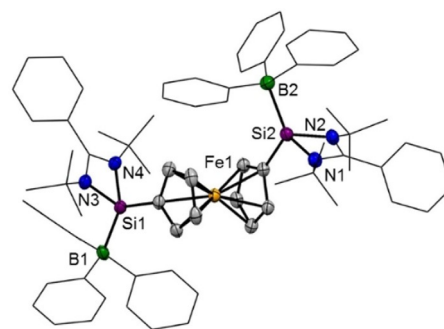
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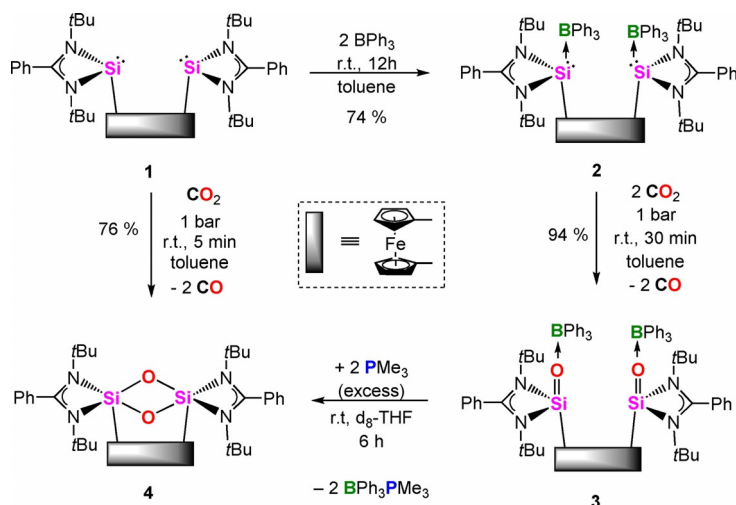
**Scheme 1.** Selected Lewis acid/base-supported Si=O compounds.

temperature leads to the formation of the bis(silylene-borane) adduct **2** which was isolated in 74% yields as a red crystalline solid (Scheme 2). The identity of **2** was proven by elemental analysis, single-crystal X-ray diffraction analysis and multinuclear NMR spectroscopy in the solid state and in solution. Crystals suitable for an X-ray diffraction analysis were obtained in a concentrated toluene solution of **2** at  $-30^{\circ}\text{C}$ , the crystals are a mixture of the two rotational conformers (Figure 1; see also the Supporting Information).

Compound **2** crystallizes in the monoclinic space group  $P12_1/c1$  in which both silicon centers adopt a distorted tetrahedral geometry ( $\Sigma\text{Si}1 = 356.72^{\circ}$ ,  $\Sigma\text{B}1 = 319.80^{\circ}$ ) with Si–B distances of 2.089(2) and 2.077(2) Å, similar to those of related silicon(II)–boranes adducts (1.9624(5)–2.108(2) Å).<sup>[9]</sup> Given the low solubility of **2** in deuterated benzene and THF, only a broad  $^{29}\text{Si}$  NMR signal of low intensity was observed at  $\delta = 54.0$  ppm which is low-field shifted compared to **1** ( $\delta = 43.3$  ppm). The



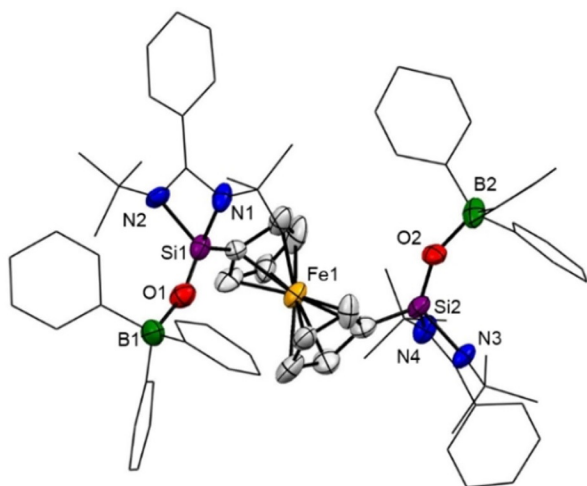
**Figure 1.** Molecular structure of **2** (only one of the two rotational conformers) with thermal ellipsoids drawn at the 50% probability level. Hydrogen and solvent atoms are omitted for clarity. Selected bond lengths [Å]: Si1–B1 2.089(2), Si2–B2 2.077(2). Selected bond angles [°]: C2–Si1–B1 130.74(9), C9–Si2–B2 130.63(9).



**Scheme 2.** Synthesis of the bis(silylene-borane) adduct **2** from **1** and its reactivity towards  $\text{CO}_2$  to give **4** and **3**, respectively.

solid-state  $^{29}\text{Si}$  NMR (VACP/MAS) spectrum of **2** shows a singlet at  $\delta = 48.6$  ppm (**1**:  $\delta = 41.6$  ppm). The isotropic  $^{11}\text{B}$  chemical shift was observed in  $[\text{D}_8]\text{THF}$  solutions at  $\delta = -7.8$  ppm ( $\Delta\nu_{1/2} = 356$  Hz) which is, as expected, low-field shifted due to its coordination to the  $\text{Si}^{\text{II}}$  center ( $\text{BPh}_3$ :  $\delta(^{11}\text{B}) = 55.2$  ppm,  $\text{C}_6\text{D}_6$ ).<sup>[9]</sup>

Compound **2** is inert towards  $\text{H}_2$  and  $\text{CO}$  but reacts with  $\text{CO}_2$  in  $\text{C}_6\text{D}_6$  under ambient conditions (1 bar, 298 K), resulting in the simultaneous formation of a pale-yellow solid and  $\text{CO}$  as confirmed by an additional  $^{13}\text{C}$ -labeling experiment (See the Supporting Information, S11). Resolving the solid in  $[\text{D}_8]\text{THF}$  and recording its multinuclear NMR spectra revealed the formation of a new species with a strongly high-field shifted  $^{29}\text{Si}$  NMR singlet resonance at  $\delta = -44.7$  ppm (**2**:  $\delta = +54.1$  ppm). An X-ray diffraction analysis of single crystals revealed the formation of the borane-stabilized bis(silanone) **3**, was isolated in 94% yields (Figure 2).

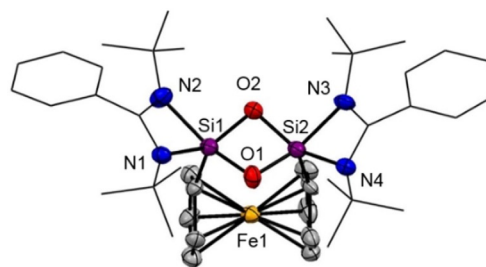


**Figure 2.** Molecular structure of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å]: Si1–O1 1.557(4), Si2–O2 1.537(4), O1–B1 1.545(7), O2–B2 1.541(7); selected bond angles [°]: B1–O1–Si1 157.59, B2–O2–Si2 145.96, C9–Si2–B2 130.63(9).

The silicon center in **3** adopts a distorted tetrahedral geometry with a short Si–O distance of 1.557(4) and 1.537(4) Å in accordance with related four-coordinated Lewis acid stabilized silanones (1.531–1.579 Å) containing a Si=O double bond.<sup>[12–15, 19, 21–22]</sup> The Si–O distance is only slightly elongated when compared with recently reported genuine silanones (1.518–1.537 Å).<sup>[15–18]</sup> Bis(silanone) **3** is remarkable stable in solution ([D<sub>8</sub>]THF) and no changes in the <sup>1</sup>H NMR spectra were observed upon heating to 60 °C. Compound **3** represents a rare example of borane-stabilized silanones. Aldridge and co-workers achieved the isolation of a stabilized sila-aldehyde through chloride–hydride substitution using K[HBEt<sub>3</sub>].<sup>[21]</sup> Addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to a cyclic amino(bora-ylide(silanone)) reported by Kato et al., increased the stability of the pre-formed free silanone.<sup>[22]</sup> In the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, Roesky et al. accomplished the isolation of a donor–acceptor stabilized silaformyl chloride.<sup>[14]</sup> However, isolation of a borane-stabilized silanone starting from a silylene–borane system is not reported so far.

To remove the boranes from the bis(silanone–borane) complex **3**, trimethylphosphane (PMe<sub>3</sub>, 5 equiv) was added. This resulted in the clean formation of the corresponding Lewis pair Me<sub>3</sub>P→BPh<sub>3</sub> (<sup>31</sup>P NMR: –15.3 ppm) and the 1,3,2,4-cyclodisiloxane **4** (head-to-tail dimer of Si=O moieties). The latter is identical with the isolated product from the reaction of **1** with CO<sub>2</sub> in 76% yields (Scheme 2). Single crystals of **4** suitable for X-ray diffraction analysis were obtained from a concentrated solution in a 1:1 benzene/hexane mixture at room temperature (Figure 3). The formation of Me<sub>3</sub>P→BPh<sub>3</sub> was additionally confirmed by a single-crystal X-ray analysis obtained in the reaction mixture of **3** and PMe<sub>3</sub> in THF solutions (see the Supporting Information).

As expected, the five-coordinate silicon centers in **4** show a drastically high-field shifted <sup>29</sup>Si NMR chemical shift at δ = –92.1 ppm (**3**: δ = –44.7 ppm). The Si–O distance of 1.709(4) and 1.681(4) Å are elongat-



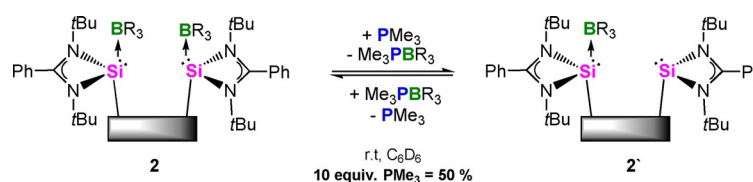
**Figure 3.** Molecular structure of **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å]: Si1–O1 1.709(4), Si2–O2 1.681(4). Selected bond angles [°]: Si1–O1–Si2 93.5(2), Si1–O2–Si2 93.9(2), O2–Si2–O1 84.4(2).

ed compared to those observed for **3** (1.557(4), 1.537(4) Å) in accordance with the presence of Si–O single bonds.<sup>[25]</sup> Reaction of **4** with an excess amount of BPh<sub>3</sub> in toluene at room temperature does not regenerate **3**.

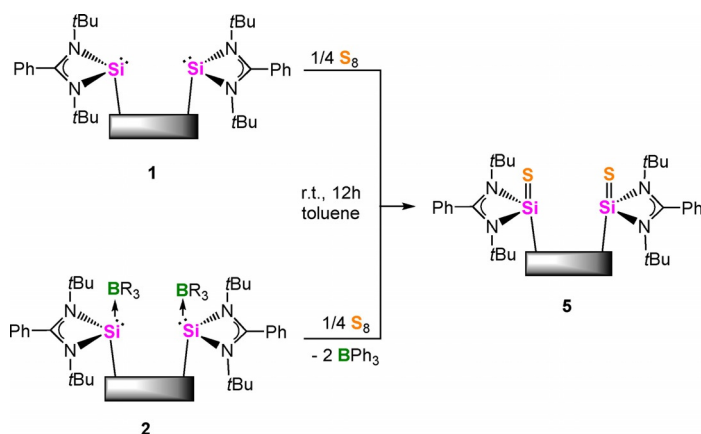
Interestingly, reaction of the bis(silylene–borane) **2** with 10 equivalents of PMe<sub>3</sub> led to the formation of a new species **2'** in the course of borane-deprotection of one Si<sup>II</sup> moiety in **2** (Scheme 3, see the Supporting Information). This process is reversible because removal of the solvent and PMe<sub>3</sub> in vacuum and re-dissolving of the residue in C<sub>6</sub>D<sub>6</sub> furnishes compound **2** as shown by NMR spectroscopy.

In contrast to the oxygenation of **2** with CO<sub>2</sub>, treatment of **2** with elemental sulfur in toluene at room temperature leads to the selective formation of the 'borane-free' bis(silathione) **5**. Compound **5** is identical with the product from the reaction of bis(silylene) **1** with elemental sulfur in toluene at room temperature, which was isolated in 54% yield (Scheme 4). Similar to the product of an intramolecular silylene–borane FLP with elemental sulfur reported by our group,<sup>[19]</sup> no Si=S→B interaction was observed. The structure of **5** (Figure 4) features two Si=S bonds with a low-field shifted singlet <sup>29</sup>Si NMR signal at δ = 12.1 ppm. The Si=S distances of 1.9867(13) and 1.9858(13) Å are consistent with related silathiones with four-coordinate silicon atoms [{PhC(NtBu)<sub>2</sub>}Si(S)Cl] (2.079(6) Å) and as reported for a Si=S product from sulfuration of an intramolecular silylene–borane FLP with elemental sulfur (1.9795(10) Å).<sup>[19, 26]</sup> Bis(silathione) **5** is stable in C<sub>6</sub>D<sub>6</sub> solutions over a period of several weeks which can be explained by a less polarized Si=S bond (ΔEN = 0.7) compared to the Si=O bond (ΔEN = 1.7) based on their electronegativities (EN).

In summary, the synthesis of bis(silylene–borane) Lewis adduct **2** containing two Si<sup>II</sup>–BPh<sub>3</sub> moieties in a single molecule was presented. Exposure of **2** to CO<sub>2</sub> yields the corresponding



**Scheme 3.** Reversible reaction of **2** with PMe<sub>3</sub> forming the monoborane adduct **2'**.



Scheme 4. Reaction of 1 or 2 with elemental sulfur affording 5.

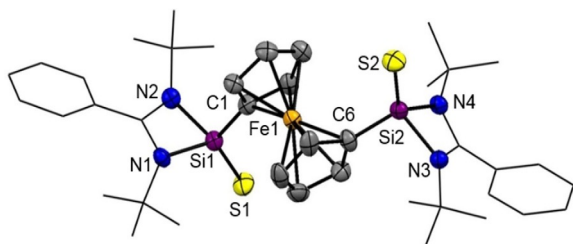


Figure 4. Molecular structure of 5 with thermal ellipsoids drawn at the 50% probability level. Hydrogen and solvent atoms are omitted for clarity. Selected bond lengths [Å]: Si1–S1 1.9867(13), Si1–S2 1.9858(13). Selected bond angles [°]: C1–Si1–S1 120.70(12).

borane-supported bis(silanone) complex 3 featuring two Si=O→B units. Removal of the borane with  $\text{PMe}_3$  yields 1,3,2,4-cyclodisiloxane 4 through intramolecular Si=O head-to-tail dimerization. In contrast, the reaction of 2 with elemental sulfur yields exclusively the borane-free bis(silathione) 5 which shows no tendency to undergo dimerization.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** FLP-chemistry · silanones · silylene · small-molecule activation

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