Silylenes

An Isolable Bis(Silanone–Borane) Adduct

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Abstract: The reaction of bis(silylenyI)-substituted ferrocene 1 with two molar equivalents of BPh₃ yields the corresponding bis(silylene–borane) Lewis adduct 2. The latter is capable to activate CO₂ to furnish the borane-stabilized bis(silanone) 3 through mono-oxygenation of the dative Si≡Si II–Si bond under release of CO. Removal of BPh₃ from 3 with PMe₃ affords the corresponding 1,3,2,4-cyclosiloxane and the Me₅P–BPh₃ 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.[1] 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.[2] 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.[3] Although divalent carbon species such as N-heterocyclic carbene (NHCs) have also been successfully probed in FLP chemistry for the activation of CO₂, H₂ and N₂O, the use of analogous Lewis pairs-containing silylenes is less known.[4, 5] 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[6] and as powerful steering ligands in homogenous catalysis.[7] After the first isolation of an N-heterocyclic 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≡Si insertion into the B=C bond of B(CF₃)₂.[8] Since then, an increasing number of compounds containing a dative Si≡Si–B≡B bond with four- and five-coordinate Si II centers have been isolated and structurally characterized.[9]

Due to a large polarization of the Si=O bond and the remarkably weak Si=O π bond (119.7 kJ mol⁻¹) compared to the Si=O σ-bond strength (119.7 kJ mol⁻¹), compounds with a Si=O bond are intrinsically susceptible to auto-oligomerization to the corresponding polysiloxanes.[10] 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.[11] This led to the first Lewis acid-base supported silanone complex, the silaformaldehyde–borane A (Scheme 1), which was reported by us in 2007, starting from a silylene and H₂O·B(CF₃)₂.[12] Roeky et al. described in 2011 the isolation of the acid anhydride B generated from the reaction of a chlorosilylene with H₂O·B(CF₃)₂ in the presence of NHC.[13] Similarly, Roeky et al. reported also the silaformal chloride complex C, resulting from an NHC-stabilized silylene and H₂O·B(CF₃)₂.[14] In 2019, the isolation of the first donor-acceptor-supported silaalddehyde D was accomplished by the Inoue group.[15] Remarkably, Kippings dream of isolable genuine silanones was realized in 2014 with the isolation of the first metal-losilanone by Filippou[16] and 2017 by the groups of Inoue and Rieger.[17] Very recently, a silicon analogue of a ketone with an unperturbed Si=O bond was synthesized by Iwamoto and co-workers.[18]

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.[19] 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.[20] In 2017, our group reported the first intramolecular silylene–borane FLP which activates H₂, O₂, CO₂ and even dehydrogenates water yielding a borane-stabilized silanone E with a dative Si≡O–B bond.[19] Herein, we present the synthesis of the bis(silylene–borane) adduct 2 with the ferrocene spacer and its mild oxidation with CO₂ yielding the first borane-stabilized bis(silanone) adduct 3. Removal of BPh₃ from 3 by addition of PMe₃ leads to the corresponding 1,3,2,4-cyclosiloxane through intramolecular Si=O head-to-tail dimerization. Moreover, the reaction of 2 with elemental sulfur yields a bis(silanone) with two ‘borane-free’ Si–S moieties.

The reaction of the ferrocene-derived bis(silylene) with two molar equivalents of triphenylborane in toluene at room temperature affords the corresponding polysiloxanes.

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.202000235.
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 °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 P121/c1 in which both silicon centers adopt a distorted tetrahedral geometry (Si1 = 356.72°, Si2 = 319.80°) 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).[9] Given the low solubility of 2 in deuterated benzene and THF, only a broad 29Si NMR signal of low intensity was observed at δ = 54.0 ppm which is low-field shifted compared to 1 (δ = 43.3 ppm). The solid-state 29Si NMR (VACP/MAS) spectrum of 2 shows a singlet at δ = 48.6 ppm (1: δ = 41.6 ppm). The isotropic 11B chemical shift was observed in [D8]THF solutions at δ = −7.8 ppm (Δν1/2 = 356 Hz) which is, as expected, low-field shifted due to its coordination to the SiII center (BPh3: δ11B = 55.2 ppm, C6D6).[9]

Compound 2 is inert towards H2 and CO but reacts with CO2 in C6D6 under ambient conditions (1 bar, 298 K), resulting in the simultaneous formation of a pale-yellow solid and CO as confirmed by an additional 13C-labeling experiment (See the Supporting Information, S11). Resolving the solid in [D8]THF and recording its multinuclear NMR spectra revealed the formation of a new species with a strongly high-field shifted 29Si NMR singlet resonance at δ = −44.7 ppm (2: δ = 454.1 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).
The silicon center in 3 adopts a distorted tetrahedral geometry with a short Si–O distance of 1.557(4) Å 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.[12–15,19,21–22] The Si–O distance is only slightly elongated when compared with recently reported genuine silanones (1.518–1.537 Å).[16–18] Bis(silanone) 3 is remarkable stable in solution ([D]THF) and no changes in the 1H 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 silaalddehyde through chloride–hydroxide substitution using K[HBEt3].[23] Addition of B(C6F5)3 to a cyclic amino(boranylide(silanone)) reported by Kato et al., increased the stability of the pre-formed free silanone.[24] 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(silanylene–borane) complex 3, trimethylphosphane (PMe3, 5 equiv) was added. This resulted in the clean formation of the corresponding Lewis pair Me3P–BPh3 (13P 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 CO2 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 Me3P–BPh3 was additionally confirmed by a single-crystal X-ray analysis obtained in the reaction mixture of 3 and PMe3 in THF solutions (see the Supporting Information).

As expected, the five-coordinate silicon centers in 4 show a drastically high-field shifted 29Si 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 elongated compared to those observed for 3 (1.557(4), 1.537(4) Å) in accordance with the presence of Si–O single bonds.[25] Reaction of 4 with an excess amount of BPh3 in toluene at room temperature does not regenerate 3.

Interestingly, reaction of the bis(silylene–borane) 2 with 10 equivalents of PMe3 led to the formation of a new species 2′ in the course of borane-deprotection of one SiI moiety in 2 (Scheme 3, see the Supporting Information). This process is reversible because removal of the solvent and PMe3 in vacuum and re-dissolving of the residue in C6D6 furnishes compound 2′ as shown by NMR spectroscopy.

In contrast to the oxygenation of 2 with CO2 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,[19] no Si=S–B interaction was observed. The structure of 5 (Figure 4) features two Si=S bonds with a low-field shifted singlet 29Si NMR signal at δ = 12.1 ppm. The Si=S distances of 1.9867(13) and 1.9858(13) Å are consistent with related silarithiones with four-coordinate sili-con atoms ([PhC(NiBu)],Si(SiCl)2(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).[19,26] Bis(silathione) 5 is stable in C6D6 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 SiI–BPh3 moieties in a single molecule was presented. Exposure of 2 to CO2 yields the corresponding
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]: S1–S2 1.9858(13). Selected bond angles [°]: C1-S1-S5 120.70(12).

borane-supported bis(siloxane) complex 3 featuring two Si=O—B units. Removal of the borane with PMe3 yields 1,3,2,4-cycloisoxolane 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.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany’s Excellence Strategy–EXC 2008/1–390540038 (Gefördert durch die Deutsche Forschungsgemeinschaft (DFG) im Rahmen der Exzellenzstrategie des Bundes und der Länder–EXC 2008/1–390540038) and with a PhD fellowship by the Einstein Foundation Berlin (M.-P.L.). We thank Paula Nixdorf for the assistance in the XRD measurements.

Conflict of interest

The authors declare no conflict of interest.

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

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