A Stable N-Heterocyclic Silylene with a 1,1'-Ferrocenediyl Backbone

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Dedicated to Professor Peter Jutzi on the occasion of his 82nd birthday

Abstract: The N-heterocyclic silylene [Fe(η2-C5H4-NDipp)2]SiH (1DippSi, Dipp = 2,6-diisopropylphenyl) shows an excellent combination of pronounced thermal stability and high reactivity towards small molecules. It reacts readily with CO2 and N2O, respectively affording (CO2)Fe and (N2O)Fe, both with high reactivity towards small molecules. It reacts readily with H2O, NH3, and FcPH2, furnishing the respective oxidative addition products 1DippSi(OH)Fe, (NH)Fe, and (FcPH)Fe, respectively. The reaction with H3BNH3 affords the respective oxidative addition products 1DippSi(O)Fe-H3BNH2, which is sufficiently persistent at room temperature for detecting its NMR signals.

The N-heterocyclic silylene (NHSi) A· (Figure 1) is a heavier NHC analogue and represents the first stable compound containing divalent and dicoordinate silicon.[3] Backbone-saturated congeners are significantly more reactive. For example, whereas 1,3-bis(2,6-diisopropylphenyl)imidazolino-2-ylidene (IPr) is inert towards PPh3, the backbone-saturated congener SIPr readily inserts into an Si=P bond[4] and silylene B undergoes self-insertion into an Si–P bond during its tetramerisation.[5] The first isolable dialkylsilylene C· exhibits a more pronounced ambiphilicity than dianisosilylenes and rearranges to a SiIV compound.[6]

The rapid development of carbene chemistry has led to acyclic diamino carbenes (ADASi),[9] ring-expanded NHCs (reNHCs) with ring sizes > 5,[9] and cyclic (alkyl)-amino carbenes (CAACs),[10] which are all closely related to standard NHCs but exhibit a more pronounced ambiphilicity, and hence higher reactivity.[11] While more than a dozen silicon analogues of standard NHCs have been isolated,[12,13] only a single example each has been reported for stable silicon analogues of CAACs,[14] ADACs[15] and reNHCs, viz. silylenes D–F (Figure 1). The ambivalent reactivity of reNHSi F was rationalised by a significant contribution of N-ylic canonical structures summarised as F. We here report on the reNHSi [Fe(η2-C5H4-NDipp)2]SiH (1DippSi), which contains a six-membered FeC2N2Si ring. 1DippSi is an analogue of our stable ferrocene-based NHCs, whose ambiphilicity allowed for small-molecule activation reactions unprecedented for diamino carbenes.[16,17]

Our attempts to obtain reNHSis of the type 1RS by reduction of corresponding SiV dihalides 1RSiX2 (X = Cl, Br) or by α-elimination of HCl from 1RSi(H)Cl were unsuccessful.[18] An alternative approach, which was introduced for the acyclic diamino silylene (ADASi) E, is the reaction of [SiCl2-(IPr)] with the corresponding lithium amide.[14] This SiII precursor turned out to be the key to success. Its reaction with 1MesLi in C6D6 afforded the silylene 1MesSi together with IPr (Scheme 1). Although too unstable for isolation, 1MesSi was sufficiently persistent at room temperature for detecting its 29Si NMR signal (δ = 121.5 ppm), which is significantly downfield-shifted with respect to reNHSi F (δ = 88.4 ppm)[19] and NHSi A (78.3 ppm).[11] The signal of the SiIV atom in ADASi E was observed at even lower field (δ = 204.6 ppm).[19] Trapping of 1MesSi with (PhSe)2 at room temperature in benzene solution afforded 1MesSi(SePh)2; details are provided in the Supporting Information (SI). The bulkier homologue 1DippSi, obtained from [SiCl2(IPr)] and 1DippLi, in toluene at room temperature, is sufficiently stable...
Si(SiMe₃)₃, an acyclic (imino)(siloxy) and (imino)-1DippSi₁DippSi first reported for decamethylsilicocene (Cp*₂Si). [22] Dialkyl-addition with CO₂ in a 2:1 ratio. When generated by reaction E not successful in our case, because, in contrast to mixture at room temperature under an atmosphere of CO₂, it was possible to separated by crystallisation or sublimation. It was possible to for isolation (Scheme 1). IPr and 1DippSi could not be separated by crystallisation or sublimation. It was possible to remove IPr from ADASI E by stirring a hexane solution of the mixture at room temperature under an atmosphere of CO₂, which led to the precipitation of IPr(CO₂)₃. [14] This method was not successful in our case, because, in contrast to E, 1DippSi reacts swiftly with CO₂ under the same mild conditions, affording the orthocarbonate (1DippSiO₂)₂C (Scheme 2; see the SI). The primary products are most likely CO and the persistent Si₂N-Si-OSi[R]₈, which subsequently undergoes a cycloaddition with CO₂ in a 2:1 ratio. When generated by reaction of 1DippSi with N₂O in benzene at room temperature, this silanone forms the expected dimer (1DippSiO₂)₂C (Scheme 2; see the SI). [21] An analogous stepwise reaction with CO₂ was first reported for decamethylsilicocene (Cp*⁻(SiMe₃)₃) [22] Dialkyl-silylene C [23] as well as IPr = N-Si-OStBu₃ and IPr = N-Si-Si(SiMes)₃, an acyclic (imino)(siloxy)- and (imino)-(silyl)silylene, [24] are the only examples containing dicoordinate Si II in this context to date. [25] We found that IPr is easily removed by complexation with ZnCl₂, which is inert towards 1DippSi. In contrast to 1DippSi, [ZnCl₂(IPr)] [26] is insoluble in hexane.

The ²⁹Si NMR signal of 1DippSi is located at δ = 115.7 ppm, upfield-shifted by 6 ppm with respect to 1MesSi. 1DippSi was structurally characterised by X-ray diffraction (Scheme 1). The Si bond angle (106.6°) lies between the values determined for reNHSi F (99.3°) [23] and ADASI E (110.9°) [24] and is close to that reported for a heterocyclic silylene with a six-membered ring containing an NSiIBP unit. [27] Silylenes whose dicoordinate Si (H) atom is part of a five-membered ring exhibit more acute Si bond angles close to 90°. [3,6,12,13,28]

Similar to 1MesSi, 1DippSi undergoes an oxidative addition with (PhSe)₂ in benzene solution at room temperature to afford 1DippSi(SePh)₂ (see the SI). We next addressed the oxidative addition of strong H–X bonds of different polarities, which is of fundamental importance for chemical synthesis and catalysis. [29] While 1DippSi is inert towards H₂ under ambient conditions, it reacted readily with H₂O, NH₃ and FCPh₂, affording the corresponding derivatives of the type 1DippSi(H)X (Scheme 1, Figure 2; X = OH, NH₂, PHFc; see the SI). The reaction of H₂O with stable dicoordinate Si (H) compounds to the corresponding hydroxysilane has been reported only for the metallasilylene [Cp*(CO)₃Cr-Si-SIPr] [30] as well as for A [31] and F [32]. The hydroxysilanes A(H)OH and F(H)OH were not observed, but their intermediacy was merely inferred from the products isolated. In contrast, the analogous NH₂ addition product F(H)NH₂ was obtained in high yield from the reaction of F with NH₃, [33] F is the exception to the rule that five- and six-membered NHSi cannot be employed for NH₂ activation, although they are more Lewis acidic and have a smaller singlet-triplet gap compared to the corresponding NH₃C [34] Apart from [Cp*(CO)₂Cr-Si-SIPr] [30] Dipp(Me₃Si)N-Si-Si(SiMe₃) [35] and IPr = N-Si-OStBu₃, we are not aware of any other stable silylene to undergo an oxidative addition of NH₂. The reaction of NH₂ with 1DippSi is remarkable.

![Scheme 1. Synthesis of 1MesSi (persistent, Mes = mesityl) and 1DippSi (stable) and reactions of the latter with H₂O, NH₃, FePh₂ (Fc = ferroceny1), and H₂BNH₂ under ambient conditions in benzene or toluene. Selected bond lengths [Å] and angles [°] for 1DippSi: Si1-N1 1.7332(12), Si1-N2 1.7344(12), N1-Si1-N2 106.58(6); sum of angles (Σx) at N1 359.9, at N2 360.0.](image1)

![Scheme 2. Reactions of 1DippSi with CO₂ and N₂O under ambient conditions in benzene, respectively affording (1DippSiO₂)₂C and (1DippSiO₂)₃C via the silanone 1DippSiO as assumed intermediate.](image2)

![Figure 2. Molecular structures of 1DippSi(H)OH (left; selected bond lengths [Å] and angles [°]; Si1-N1 1.7197(16), Si1-N2 1.7199(16), Si1-O1 1.6071(16), N1-Si1-N2 111.49(8); Σx at N1 358.9, at N2 359.4, 1DippSi(H)NH₂ (middle; selected bond lengths [Å] and angles [°]; Si1-N1 1.691(4), Si1-N2 1.721(3), Si1-N3 1.730(3), N2-Si1-N3 111.72(14); Σx at N2 358.5, at N3 358.0 and 1DippSi(H)(BH₂NH₃) (right; selected bond lengths [Å] and angles [°]; Si1-N1 1.7571(14), Si1-N2 1.7694(14), Si1-B1 2.008(2), N3-B1 1.600(3), N1-Si2-N2 107.84(7), Si1-B1-N1 116.41(13); Σx at N1 358.3, at N2 356.6).](image3)
because NH$_3$ activation is a challenging target even for transition metal complexes$^{[36]}$—the potential of low-valent main-group element compounds in this context was uncovered only recently.$^{[25,37]}$ The reaction of 1DippSi with FCIP$_2$ afforded the oxidative addition product 1DippSi(H)(PHFc).

In view of the ability of 1DippSi for N-H activation, the activation of a P-H bond, which is weaker than an N-H bond by ca. 100 kJ mol$^{-1}$, is not unexpected.$^{[38]}$ reNH$_2$F is also capable of P-H activation.$^{[39]}$ We next addressed the reaction of 1DippSi with H$_3$BNH$_3$ (Scheme 1)$^{[40]}$ expecting the formation of 1DippSiH$_2$, most likely by transfer of a protic and a hydridic H atom$^{[41]}$ to the divalent atom, as was observed for 1,3-di-tert-butylimidazol-2-ylidine$^{[33]}$ and reNH$_2$F$^{[42]}$. Instead, the reaction furnished 1DippSiH(H)-(BH$_2$NH$_3$) (Figure 2), although the B-H bond is stronger than the N-H bond of H$_3$BNH$_3$.$^{[43]}$ First B-H bond activation reactions with SiH$_3$ compounds were reported only recently.$^{[44]}$ and the reaction of the (silyl)-(vinyl)silylene Me$_2$IPr = CH-Si-Si(SiMe$_3$)$_2$ ($^{[45]}$Me$_2$IPr = 1,3-bis(2,6-disopropylphenyl)-4,5-dime-thylimidazol-2-ylidine) with pinacolborane (HBPin), which affords Me$_2$IPr = CH-Si(Si)H-(Bpin)-Si(SiMe$_3$)$_2$, is the only example involving dicoordinate SiH$_3$.$^{[45]}$

We performed a DFT study on the electronic characteristics and the reactivity of 1, the full molecular model of 1DippSi$^{[46]}$. At the PBEh-3c level of DFT employed, the HOMO comprises the expected silylene lone pair together with significant contributions of the ferrocene moiety and the LUMO is dominated by the silylene p-orbital, with a substantial HOMO-LUMO energy separation of $\Delta E_{\text{SIL}} = 6.4$ eV. The unexpectedly low computed singlet-triplet energy difference of $\Delta E_{\text{ST}} = 0.4$ eV does not correlate with this value because the lowest triplet state arises from a local excitation within the ferrocene moiety and does not involve the silylene p-orbital (Figure 3).$^{[47]}$

Surprisingly, direct oxidative addition of H$_2$O and NH$_3$ to 1 is precluded by high kinetic barriers for both substrates (35 and 42 kcal mol$^{-1}$, respectively), and two distinct alternative pathways were identified instead. The lowest-energy pathway for NH$_3$ activation commences with the formation of adduct 2 (Scheme 3, top). Proton transfer is facilitated by a second NH$_3$ molecule acting as a proton shuttle and the experimentally observed product 3 is formed in a strongly exergonic step with a moderate overall barrier of 20 kcal mol$^{-1}$. H$_2$O, in turn, does not form a dativebly bonded adduct with 1, but directly adds across an Si-N bond via TS2 to form hydroxysilylene 4 in an exergonic step (Scheme 3, bottom). From there on out, silanone 5 is formed through a water-assisted proton transfer,$^{[48]}$ the experimentally observed product 6 results in a strongly exergonic step after passage of a minute barrier in TS4.

The quantum-chemical evaluation discloses a concerted dehydrogenation of H$_3$BNH$_3$ by 1 as initial step along the lowest-energy pathway for ammonia-borane activation (Scheme 4). Alternative direct insertion of 1 into an N-H...
or B–H bond is precluded by high kinetic barriers (53 and 35 kcal mol⁻¹, respectively; see the SI). Whereas the resulting silane 7 forms as an unreactive side product, H₂BNH₃ is a highly reactive species that has been thoroughly studied in the thermal and catalytic dehydrogenation of H₂BNH₃ and is known to polymerize below −150°C.[50]

Obviously, B–H insertion of 1 in H₂BNH₃ competes efficiently with the polymerization of the latter, leading to the formation of 8 (Scheme 5). With a low barrier of 12 kcal mol⁻¹ 8 can dehydrogenate a second equivalent of H₂BNH₃ through intermediate 9 yielding the experimentally observed product 10 while regenerating H₂BNH₃. After initial formation of H₂BNH₃ from 1 and H₂BNH₃ the follow-up reaction cascade involving B–H insertion by 1 and subsequent dehydrogenation of H₂BNH₃ is kinetically favoured over the formation of 7.

In conclusion, we have described the synthesis and reactivity of the new stable reNHSi 1DippSi. 1DippSi reacts readily with N₂O and CO₂, which is in contrast to the inertness of F, the only other stable cyclic diaminosilylene featuring a ring-expanded structure known to date.[25a] Studies on the reactivity of 1DippSi towards H–X bonds of different strengths and polarities show parallels to previous reactivity studies on other silylenes. The reactions with NH₃ and H₂O both give the H–X insertion products. Mechanistically, however, they differ significantly. More particularly, the lowest-energy path of the reaction with H₂O involves the N-Si cooperative activation of an O–H bond. For H₂BNH₃ the reaction mechanism consists of two key elementary steps, the first one being the dehydrogenation of H₂BNH₃ to H₂BNH₂, which subsequently catalyses the conversion of 1DippSi to 1DippSi(H)(BH₂NH₃) with H₂BNH₂. In contrast to H₂BNH₃, H₂BNH₂ has a vacant p-orbital, which enables insertion of the silylene in a B–H bond in the second step. This silyborane can in turn dehydrogenate a second equivalent of H₂BNH₃ to give the final product 1DippSi(H)(BH₂NH₃).

Scheme 5. Computed reaction path for the formation of 10 from 1, H₂BNH₃ and H₂BNH₃ (ΔG° at 1 kcal mol⁻¹ relative to the separated reactants, activation barriers relative to the preceding minimum).

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Conflict of interest

The authors declare no conflict of interest.

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Recent examples for oxygenations of stable low-valent Si compounds with CO₂:


