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(η5-C5H4-NDipp)]2Si)] (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 high reactivity towards small molecules. It reacts readily with H2O, NH3, and FcPH2 (Fc = ferrocenyl) furnishing the respective oxidative addition products 1DippSi(O)2C and 1DippSiO as follow-up products of the silanone 1DippSiO. Its reactions with H2O, NH3, and FcPH2 (Fc = ferrocenyl) furnish the respective oxidative addition products 1DippSiO-(H)X (X = OH, NH3, PH3). Its reaction with H2BNH2 unexpectedly results in B–H, instead of N–H, bond activation, affording 1DippSiH(BH2NH2). DFT results suggest that dramatically different mechanisms are operative for these H–X insertions.

The N-heterocyclic silylene (NHSi) A (Figure 1) is a heavier NHC analogue and represents the first stable compound containing divalent and dicoordinate silicon. Backbone-saturated congeners are significantly more reactive. For example, whereas 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr) is inert towards PH3, the backbone-saturated congener SiPr readily inserts into a P–H bond and silylene B undergoes self-insertion into an Si–N bond during its tetramerisation. The first isolable diarylsilylene C exhibits a more pronounced ambiphilicity than dianiminosilylenes and rearranges to a SiV compound.

The rapid development of carbene chemistry has led to acyclic diamino carbenes (ADACs), ring-expanded NHCs (reNHCs) with ring sizes > 5[9] and cyclic (alkyl)-(amino)carbenes (CAACs)[10] as analogues of 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[3,12] only a single example each has been reported for stable silicon analogues of CAACs[13] ADACs[14] and reNHCs[15] viz. silylenes D–F (Figure 1). The ambivalent reactivity of reNHSi F was rationalised by a significant contribution of N-ylidic canonical structures summarised as F. We here report on the reNHSi [{Fe(η5-C5H4-NDipp)]2Si]} (1DippSi), which contains a six-membered FeC5N2Si ring. 1DippSi is an analogue of our stable ferrocene-based NHCs, whose ambiphilicity allowed for small-molecule activation reactions unprecedented for diaminocarbenes.[16,17]

Our attempts to obtain reNHSi of the type 1RSi by reduction of corresponding SiV dihalides 1RSiX3 (X = Cl, Br) or by α-elimination of HCl from 1RSiHCl were unsuccessful.[18] An alternative approach, which was introduced for the acyclic diaminosilylene (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 77Si NMR signal (δ = 121.5 ppm), which is significantly downfield-shifted with respect to reNHSi F (δ = 88.4 ppm)[15] and NHSi A (78.3 ppm).[11] The signal of the SiII 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.

Figure 1. Silylenes A–F (Ad = 1-adamantyl, Dipp = 2,6-diisopropylphenyl, TMS = trimethylsilyl).

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Si(SiMe3)3, an acyclic (imino)(siloxy)- and (imino)silylene, 1DippSi reacts swiftly with CO2 under the same mild conditions, first reported for decamethylsilicocene (Cp*2Si).[22] Dialkyladdition with CO2 in a 2:1 ratio. When generated by reaction of ADASiE with (PhSe)2 in benzene solution at room temperature, this led to the precipitation of IPr(CO2).[14] This method was successful in our case, because, in contrast to E, 1DippSi reacts swiftly with CO2 under the same mild conditions, affording the orthocarbonate (1DippSiO)2C (Scheme 2; see the SI). The primary products are most likely CO and the silanone forms the expected dimer (1DippSiO)2 (Scheme 2; see Scheme 1). The Si bond angle (106.6°) lies in between the values determined for reNHSiE (99.3°)[15] and ADASiE (110.9°)[14] and is close to that reported for a heterocyclic silylene with a six-membered ring containing an NSiIIBP unit.[27] Silylenes whose dicoordinate SiII 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 FePH2, affording the corresponding derivatives of the type 1DippSi(H)X (Scheme 1, Figure 2; X = OH, NH2, PHFe; see the SI). The reaction of H2O with stable dicoordinate SiII compounds to the corresponding hydroxy-silanes 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 NHsIs cannot be employed for NH3 activation, although they are more Lewis acidic and have a smaller singlet-triplet gap compared to the corresponding NHCS.[34] Apart from [Cu(CO)5-Cr-Si(SiMe3)2]2[30] Dipp(Me2Si)N-Si-Si(SiMe3)2[25] and IPr–N-Si(OSiBu3)2[24a] we are not aware of any other stable silylene to undergo an oxidative addition of NH3. The reaction of NH3 with 1DippSi is remarkable for isolation (Scheme 1). IPr and 1DippSi could not be separated by crystallisation or sublimation. It was possible to remove IPr from ADASiE by stirring a hexane solution of the mixture at room temperature under an atmosphere of CO2, which led to the precipitation of IPr(CO2).[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 (1DippSiO)2C (Scheme 2; see the SI). The primary products are most likely CO and the silanone forms the expected dimer (1DippSiO)2 (Scheme 2; see Scheme 1). The Si bond angle (106.6°) lies in between the values determined for reNHSiE (99.3°)[15] and ADASiE (110.9°)[14] and is close to that reported for a heterocyclic silylene with a six-membered ring containing an NSiIIBP unit.[27] Silylenes whose dicoordinate SiII atom is part of a five-membered ring exhibit more acute Si bond angles close to 90°.[3,6,12,13,28]

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because NH₃ 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 FCPh₂ 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] reNHSi F is also capable of P-H activation.[39] We next addressed the reaction of 1DippSi with H₂BNH₃ (Scheme 1),[40] expecting the formation of 1DippSiH₂, 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-butylidazol-2-ylidene[33] and reNHSi F.[42] Instead, the reaction furnished 1DippSiH(H)-(BH₂NH₃) (Figure 2), although the B-H bond is stronger than the N-H bond of H₂BNH₃.[43] First B-H bond activation reactions with SiH₃ compounds were reported only recently,[44] and the reaction of the (silyl)-(vinyl)silylene MeIPr = CH-Si-Si(SiMe₃)₃ (MeIPr = 1,3-bis(2,6-dimethylphenyl)-4,5-dimethylimidazol-2-ylidene) with pinacolborane (HBPin), which affords MeIPr = CH-Si-(H)-(Bpin)-Si(SiMe₃)₃, is the only example involving dicoordinate SiII.[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 ΔE₁₁ = 6.4 eV. The unexpectedly low computed singlet-triplet energy difference of ΔE₀₋₁ = 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 H₂O and NH₃ 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 NH₃ activation commences with the formation of adduct 2 (Scheme 3, top). Proton transfer is facilitated by a second NH₃ 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. H₂O, in turn, does not form a datively 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,[39] 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 H₂BNH₃ 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

![Figure 3. Frontier molecular orbitals and triplet spin-density distribution](image)

**Scheme 3.** Computed lowest-energy reaction pathway for the formal H-X oxidative addition to 1 with NH₃ (top) and H₂O (bottom, ΔG° in kcal mol⁻¹). Bonds formed or broken in transition states are dashed, unreactive H atoms are omitted and the orientation of the Dipp substituents in the transition state is indicated by showing the respective Cipso atom only.

**Scheme 4.** Computed reaction path for the formation of 7 from 1 and H₂BNH₃; ΔG° in kcal mol⁻¹.
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, ⁴⁰ H₂BNH₂ is a highly reactive species that has been thoroughly studied in the thermal and catalytic dehydrogenation of H₂BNH₂ and is known to polymerize below −150 °C.⁵⁰

Obviously, B–H insertion of 1 in H₂BNH₂ 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 H₂BNH₂ through intermediate 9 yielding the experimentally observed product 10 while regenerating H₂BNH₂. After initial formation of H₂BNH₂ from 1 and H₂BNH₂ the follow-up reaction cascade involving B–H insertion by 1 and subsequent dehydrogenation of H₂BNH₂ 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. ⁴⁰ 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 H₂BNH₂ the reaction mechanism consists of two key elementary steps, the first one being the dehydrogenation of H₂BNH₂ to H₂BNH⁺ which subsequently catalyses the conversion of 1DippSi to 1DippSi(H)(BH₂NH₂) with H₂BNH₂. In contrast to H₂BNH₂, H₂BNH⁺ has a vacant p-orbital, which enables insertion of the silylene in a B–H bond in the second step. This silylborane can in turn dehydrogenate a second equivalent of H₂BNH₂ to give the final product 1DippSi(H)(BH₂NH₂).

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Conflict of interest

The authors declare no conflict of interest.

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Scheme 5. Computed reaction path for the formation of 10 from 1, H₂BNH₂ and H₂BNH₂ (ΔG° in kcal mol⁻¹ relative to the separated reactants, activation barriers relative to the preceding minimum).
Recent examples for oxygenations of stable low-valent Si compounds with CO₂: a) A. V. Protchenko, P. Vasko, D. Cao Huan Do, J. Hicks, M. Á. Fuentes, C. Jones, S. Aldridge, Angew. Chem. Int. Ed. 2019, 58, 1808–1812; Angew. Chem. 2019, 131, 1822–1826; b) A. Burchert, S. Yao, R. Müller, C. Schattenberg, Y. Xiong, M. Kaupp, M. Driess, Angew. Chem. Int. Ed. 2017, 56, 1894–1897; Angew. Chem. 2017, 129, 1920–1923; c) Y. Wang, M. Chen, Y. Xie, P. Wei, H. F. Schaefer III, G. H. Robinson, J. Am. Chem. Soc. 2015, 137, 8396–8399; d) F. M. Mück, J. A. Baus, M. Nutz, C. Burschka, J. Poater, F. M. Bickelhaupt, R. Tacke, Chem. Eur. J. 2015, 21, 16665–16672.

[35] A. V. Protchenko, J. I. Bates, L. M. A. Saleh, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, J. Am. Chem. Soc. 2016, 138, 4555–4564.
[36] J. Hooser, Science 2016, 354, 707–708.
[37] a) C. Westman, S. Inoue, ChemCatChem 2018, 10, 4213–4228; b) S. Yadav, S. Saha, S. S. Sen, ChemCatChem 2016, 8, 486–501; c) P. P. Power, Nature 2010, 463, 171–177.
[38] E–H bond dissociation energies for EH₄ and MeEH₂ are 450 and 425 kJ mol⁻¹, respectively, for E = N, but 351 and 322 kJ mol⁻¹, respectively, for E = P; see: Y. R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, FL, 2007.
[39] C. Präsang, M. Stoezl, S. Inoue, A. Meltzer, M. Driess, Angew. Chem. Int. Ed. 2010, 49, 10002–10005; Angew. Chem. 2010, 122, 10199–10202.
[40] a) U. B. Demirici, Int. J. Hydrogen Energy 2017, 42, 9978–10013; b) A. Staubitz, A. P. M. Robertson, I. Manners, Chem. Rev. 2010, 110, 4079–4124.
[41] D. H. A. Boom, A. R. Jupp, J. C. Skotterud, Chem. Eur. J. 2019, 25, 9133–9152.
[42] M. Stoezl, C. Präsang, S. Inoue, S. Enthaler, M. Driess, Angew. Chem. Int. Ed. 2012, 51, 399–403; Angew. Chem. 2012, 124, 411–415.
[43] a) M. H. Matus, D. J. Grant, M. Tho Nguyen, D. A. Dixon, J. Chem. Phys. 2009, 113, 16553–16560; b) P. R. Rablen, J. F. Hartwig, J. Am. Chem. Soc. 1996, 118, 4648–4653.
[44] a) V. S. V. S. N. Swamy, K. V. Raj, K. Vanka, S. S. Sen, H. W. Roesky, Chem. Commun. 2019, 55, 3536–3539; b) S. Khoo, Y. L. Shan, M.-C. Yang, Y. Li, M.-D. Su, C.-W. So, Inorg. Chem. 2018, 57, 5879–5887.
[45] M. M. D. Roy, M. J. Ferguson, R. McDonald, Y. Zhou, E. Rivard, Chem. Sci. 2019, 10, 6476–6481.

All calculations were performed with the PBEh-3c method implemented in ORCA 4.1.2. For a benchmark against F12 coupled cluster theory and further technical details see the SI.

As it is becoming commonplace to tentatively correlate characteristics evaluated at the PBEh-3c level for several silylenes published by others. In view of Singleton’s criticism, the corresponding alternative reaction paths identified are provided as SI. See: R. E. Plata, D. A. Singleton, J. Am. Chem. Soc. 2015, 137, 3811–3826.

The presence of traces of this silane in the crude product is indicated by a low-intensity ²⁷Si NMR signal at δ = −34.1 ppm (see Figure S44 in the SI), which was absent after recrystallization.

[50] C. T. Kwon, H. A. McGee, Jr., Inorg. Chem. 1970, 9, 2458–2461.