The Si$_2$H radical supported by two N-heterocyclic carbenes†

Marius I. Arz,a Gregor Schnakenburg,a Andreas Meyer,b Olav Schiemannb and Alexander C. Filippou*a

Cyclic voltammetric studies of the hydridodisilicon(0,II) borate [(Idipp)(H)Si$_{11}$=Si$_{10}$][idipp][B(ArF)$_4$]$_2$ [1H][B(ArF)$_4$]$_2$, Idipp = C[N(C$_6$H$_5$-2,6-iPr)$_2$CH]$_2$, ArF = C$_6$H$_5$-3,5-(CF$_3$)$_2$ reveal a reversible one-electron reduction at a low redox potential (E$_{1/2}$ = −2.15 V vs. Fc$^+$/Fc). Chemical reduction of 1H[B(ArF)$_4$]$_2$ with KC$_8$ affords selectively the green, room-temperature stable mixed-valent disilicon(0,II) hydride Si$_2$(H)[idipp]$_2$ [1H], in which the highly reactive Si$_2$H molecule is trapped between two N-heterocyclic carbenes (NHCs). The molecular and electronic structure of 1H was investigated by a combination of experimental and theoretical methods and reveals the presence of a π-type radical featuring a terminal bonded H atom at a flattened trigonal pyramidal coordinated Si center, that is connected via a Si–Si bond to a bent two-coordinated Si center carrying a lone pair of electrons. The unpaired electron occupies the Si=Si π orbital leading to a formal Si–Si bond order of 1.5. Extensive delocalization of the spin density occurs via conjugation with the coplanar arranged NHC rings with the higher spin density lying on the site of the two-coordinated silicon atom.

1. Introduction

Open-shell silicon hydrides are of significant importance as transient intermediates in the chemical vapor deposition (CVD) of silicon or silicon-containing thin films, which are extensively used in the semiconductor industry.1 Fundamental species in the gas phase include the SiH$_x$ (x = 1–3) and Si$_2$H$_x$ (x = 1–5) molecules as well as higher aggregated Si$_n$H$_m$ clusters, which are formed from silane (SiH$_4$) or disilane (Si$_2$H$_6$) in a complex cascade of reactions.2 These species, which are also of interest in astrochemistry,3 are unstable under terrestrial conditions and can only be detected by spectroscopic or mass spectrometric techniques.4 One scarcely studied species in this context is the Si$_3$H$_4$ molecule, which was so far only detected by vibrationally-resolved photoelectron spectroscopy of Si$_2$H$_3$ anions.5 Quantum chemical calculations of Si$_3$H$_4$ suggest two almost iso-energetic, C$_{2v}$-symmetric H-bridged structures, in which the unpaired electron occupies either the Si–Si π-bonding orbital (3B$_1$ state) or a σ-type molecular orbital corresponding to the in-phase combination of the Si lone pair orbitals (3A$_2$ state).5

Recently, N-heterocyclic carbenes (NHCs) were found to be particularly suitable Lewis bases for the thermodynamic and kinetic stabilization of highly reactive, unsaturated, low-valent Si species, leading to the isolation of a series of novel compounds with intriguing synthetic potential.5,6 Several CAAC-stabilized open-shell silicon compounds (CAAC = cyclic alkyl(aminocarbene) were also reported, in which the unpaired electron is mainly located on the CAAC substituent.5 Trapping of SiH$_x$ by NHCs appeared therefore an achievable, albeit very challenging goal, given the fact that isolable molecular hydrides of silicon in an oxidation state <2 are very rare5,6 and open-shell congeners presently unknown. In comparison, three-coordinate Si$_{11}^{II}$ hydrides and four-coordinate Si$_{11}^{II}$ hydrides of the general formula [LB]SiH(X)[LA] (LB = neutral Lewis base; LA = neutral Lewis acid; X = singly bonded substituent) were meanwhile well documented.

2. Results and discussion

The hydridodisilicon(0,II) salt [(Idipp)(H)Si$_{11}$=Si$_{10}$][idipp][B(ArF)$_4$]$_2$ [1H][B(ArF)$_4$]$_2$, Idipp = C[N(C$_6$H$_5$-2,6-iPr)$_2$CH]$_2$, ArF = C$_6$H$_5$-3,5-(CF$_3$)$_2$, which was isolated recently in our group upon protonation of Si$_2$(Idipp)$_2$ (1)*, appeared to be a suitable starting material to tackle the problem of isolating an NHC-trapped Si$_2$H radical. Quantum chemical studies revealed the same sequence of frontier orbitals in 1H and its isolobal phosphorus counterpart [R$_2$P=PR]$,^7$ according to which the HOMO–1
corresponds to the lone-pair orbital at the two-coordinated E atom (E = Si, P), the HOMO is the E=E π-bonding orbital and the LUMO is the E=E π* orbital. This isobal interrelationship suggested that 1H* might be also reversibly reducible as the phosphonyldiphenylphosphonium cation [Mes*{(Me)P=PMe5*}] (Mes* = C6H5–C5Me5) in fact, cyclic voltammetric (CV) studies of 1H[B(ArF)4] in fluorobenzene at room temperature revealed a reversible one-electron reduction at a rather low half-wave potential (E1/2) of −1.63 V as well as an irreversible oxidation at +0.67 V versus the [Fe(η5-C5Me5)2]+1/0/0.1 M (Fc+/Fc) reference electrode (Fig. 1). The methyl analogue [(Idipp)(Me)SiII=Si0(Idipp)][B(ArF)4] (1MMe[B(ArF)4]) was found also to undergo a reversible one-electron reduction, albeit at a more negative potential (E1/2 = −1.85 V) than 1H[B(ArF)4]. Notably, reduction of 1H* and 1Me* occurs at much lower potentials than that of the cation [Mes*{(Me)P=PMe5*}] (E1/2 = −0.48 V). This marked difference in the redox potentials of the Si- and P-based cations can be rationalized with the large increase of the LUMO energy occurring upon replacement of the two Pmes* fragments by the much less electronegative isobal Si(Idipp) fragments as suggested by quantum chemical calculations.

The CV results prompted us to attempt a chemical one-electron reduction of 1H[B(ArF)4]. Indeed, vacuum transfer of THF to a 1 : 1 stoichiometric mixture of 1H[B(ArF)4] and KC8 at −196 °C followed by warming to −40 °C resulted in a distinct color change of the dark red solution of 1H[B(ArF)4] to give an intensely dark green solution, which after work-up and crystallization from n-hexane at −60 °C afforded Si2(H)(Idipp)2 (1H) as a dark green, almost black crystalline solid in 55% yield (Scheme 1) (see ESI†). Compound 1H is extremely air-sensitive and immediately decolorizes upon contact with air, but can be stored under an atmosphere of argon at −30 °C without any color change or signs of decomposition in its EPR spectrum. Thermal decomposition of 1H in a vacuum-sealed glass capillary was detected upon melting at 147 °C leading to a dark red mass. Analysis of the soluble part of the melting residue in C6D6 by 1H NMR spectroscopy revealed the presence of Idipp (95%) and 1 (5%).

Notably, the redox potential of 1H [E1/2 in C6H4F1 = −2.15 V vs. [Fe(η5-C5H5)2]+1/0/0.1 (Fc+/Fc) †] lies in-between that of the benzophenone radical anion (E1/2 in THF = −2.30 V vs. FeC+/Fe) and [Co(η5-C5H5)2] (E1/2 in MeCN = −1.91 V vs. FeC+/Fe), indicating that the radical 1H is a very strong one-electron reducing agent. Consequently, the radical 1H is selectively oxidized back to 1H[B(ArF)4] upon treatment with one equivalent of [Fe(η5-C5Me5)2][B(ArF)4] in THF-d8 (see ESI†). Thereby, the redox pair 1H+/1H provides a very rare example of a chemically reversible Si-based redox system. They are well soluble in n-hexane, benzene, diethyl ether or THF affording intensely dark-green solutions, even at low concentrations. The origin of this intense color was analyzed by UV-Vis-NIR spectroscopy of 1H in n-hexane (Fig. 2, left and ESI†), which revealed electronic absorptions in the whole spectral range from 220–1100 nm. Six absorption maxima were located at 254 (9970), 305 (8140), 436 (5170), 608 (7110), 704 (6860) and 958 (1440) nm, of which the intense absorptions were located at 254 (9970), 305 (8140), 436 (5170), 608 (7110), 704 (6860) and 958 (1440) nm, of which the intense absorptions at 608 and 704 nm are responsible for the green color of 1H (the values of the molar absorption coefficients ελ are given in brackets in L mol⁻¹ cm⁻¹). The UV-Vis-NIR spectrum was also analyzed by time-dependent density functional theory (TD-DFT) calculations (see ESI, Fig. S21†).

Magnetic susceptibility measurements of solid 1H from 300.0–1.9 K suggest the presence of a paramagnetic compound with one unpaired electron following Curie’s law. A plot of the reciprocal molar magnetic susceptibility (χm) against the absolute temperature (T) showed a linear correlation from which the effective magnetic moment μ eff was calculated after linear regression and found to be 1.68 μB (Fig. 2, right and ESI†). This value is slightly lower than the value derived from the spin-only formula for one unpaired electron (μeff = 1.73 μB).

The molecular structure of 1H was determined by single crystal X-ray crystallography. The radical features a crystallographically imposed inversion symmetry (space group: P21/c) in marked contrast to the C2-symmetric structure of 1H* in 1H[B(ArF)4]. The Si-bonded H atom was located in the difference Fourier map and anisotropically refined with a site occupancy of 1/2 at each Si atom. However, the exact position of this H atom could not be deduced by X-ray crystallography, since structural refinements with either a terminal (Si=H) or a bridging (Si–H=Si) position led to identical χR values. 1H features as 1H[B(ArF)4] and a trans-bent planar C5H5N-Si–Si=C5H5N core (Fig. 3). However, distinct structural differences became apparent upon comparing the three structures. For example, the Si-Si bond of...
**1H** (2.281(3) Å) is considerably longer than that in **1H[B(ArF)_4]** (2.1873(8) Å) or 1 (2.229(1) Å)\(^\text{a}\) (Table 1), and lies in-between that of a typical Si–Si double bond (2.20 Å)\(^\text{b}\) and a Si–Si single bond (e.g. 2.352 Å in α-Si).\(^\text{c}\) In comparison, the Si–C\(_{\text{NHC}}\) bonds in **1H** (1.873(4) Å) are shorter than the Si–C\(_{\text{NHC}}\) bonds of the dicoordinated Si atoms in **1H[B(ArF)_4]** (1.940(2) Å)\(^\text{a}\) and 1 (1.927(1) Å)\(^\text{a}\) (Table 1), and similar to that of the trigonal-planar coordinated Si atom in **1H[B(ArF)_4]** (1.882(2) Å).\(^\text{a}\) Reduction of **1H** results also in a distinct change of the conformation of the NHC substituents. Thus, both N-heterocyclic rings in **1H** are arranged coplanar with the trans-bent C\(_{\text{NHC}}\)-Si–Si–C\(_{\text{NHC}}\) core as evidenced by the dihedral angle \(\varphi_{\text{NHC}}\) of 3.3(2)° (Table 1), whereas in **1H** one of the two N-heterocyclic rings (bonded to the two-coordinated Si atom) adopts an almost orthogonal orientation (Table 1). All these structural changes can be rationalized by quantum theory (vide infra). Thus, reduction of **1H** leads to a population of the Si=Si \(\pi^*\) orbital with one electron, reducing thereby the formal Si–Si bond order from 2 in **1H** to 1.5 in **1H** as nicely reflected in the computed Si–Si Wiberg bond indexes (WBI; WBI(Si–Si) of **1H** = 1.70; WBI(Si–Si) of **1H** = 1.17) (see ESI, Tables S11 and S12†). The coplanar arrangement of the N-heterocyclic rings allows for an optimal in-phase interaction (\(\pi\)-conjugation) of the Si=Si \(\pi^*\) orbital with \(\pi^*(\text{CN}_2)\) orbitals of the NHC substituents in the SOMO of **1H** (Fig. 6), providing a rationale for the shortening of the Si–C\(_{\text{NHC}}\) bonds and the concomitant elongation of the C\(_{\text{NHC}}\)-N\(_{\text{NHC}}\) bonds of **1H** versus **1H** (Table 1).

IR spectroscopy proved to be a very useful method to determine unequivocally the position of the Si-bonded H atom. In fact, the ATR FT-IR spectrum of **1H** displayed a \(v(\text{Si–H})\) absorption band at 2089 cm\(^{-1}\), which is characteristic for stretching vibrations of terminal Si–H bonds (see ESI, Fig. S4†). In comparison, the \(v(\text{Si–H})\) band of Si\(_2\)H is predicted at significantly lower wavenumbers (1592 cm\(^{-1}\) (\(^2\)A\(_1\) state); 1491 cm\(^{-1}\) (\(^2\)B\(_\text{g}\) state)),\(^\text{a}\) and also the \(v(\text{Si–H})\) absorption bands of H-bridged silylum ions are shifted to much lower wavenumbers (ca. 1750–1950 cm\(^{-1}\); e.g. 1900 cm\(^{-1}\) in [Et\(_3\)Si–H]–[SiEt\(_3\)] [CH\(_3\)C\(_6\)H\(_4\)Me\(_2\)NH\(_3\)] compared with the \(v(\text{Si–H})\) bands of the corresponding silanes (ca. 2150 cm\(^{-1}\)).\(^\text{a}\) Notably, the \(v(\text{Si–H})\) absorption band of **1H** appears in-between that of **1H[B(ArF)_4]** containing a trigonal planar coordinated Si atom \((v(\text{Si–H}) = 2142 \text{ cm}^{-1})\),\(^\text{a}\) and the Si(\(\mu\)-hydride) \(\text{IMe}_4\text{SiH(Si}\text{Et}_3\)) containing a strongly pyramidal bonded Si atom \((v(\text{Si–H}) = 1984 \text{ cm}^{-1})\).\(^\text{a}\) Apparently, the \(v(\text{Si–H})\) frequency decreases with increasing pyramidalization of the Si atom, which according to the quantum chemical calculations can be traced back to the decreasing s-character of the Si hybrid orbital in the Si–H bond (see ESI, Tables S11 and S12†).

Further insight into the structure of **1H** was provided by continuous wave (cw) EPR spectroscopy at X-band frequencies. Spectra with a nicely resolved hyperfine coupling pattern could be obtained from samples of **1H** in \(n\)-hexane solution at 33 K (Fig. 4; see also ESI, Fig. S10† for EPR spectra at different temperatures). Notably, a similar EPR spectrum was obtained in diethyl ether solution at 298 K (see ESI, Fig. S12†), suggesting that solvent coordination effects are negligible. The EPR spectrum of **1H** displays a multiplet at a \(g_{zz}\) value of 2.00562, which could be well simulated assuming coupling of the unpaired electron to one \(^1\text{H}\) (I = 1/2) nucleus, two different \(^29\text{Si}\) (I = 1/2) and two pairs of two magnetically equivalent \(^14\text{N}\) (I = 1) nuclei, respectively (Fig. 4). These observations suggest that **1H** has

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**Fig. 2** Left: UV-Vis-NIR spectra of **1H** in \(n\)-hexane from 220–1100 nm at different concentrations (c) and path lengths (d). Right: Plot of the reciprocal molar magnetic susceptibility (\(\chi M^{-1}\)) against the absolute temperature (T) (dotted black line) and the corresponding line (red) and line equation obtained by linear regression.

**Fig. 3** DIAMOND plot of the molecular structure of **1H** in the single crystal at 123(2) K. Thermal ellipsoids are set at 30% electronic probability. The Si-bonded H atom was omitted due to its uncertain position. Selected bond lengths [Å], bond angles [°] and torsion angles [°]: Si–Si# 2.281(3), Si–C1 1.873(4); C1–Si–Si# 109.5(1); C1–Si–Si#–C1# 180.0(3).
Table 1  Comparison of selected bonding parameters of $^{1}H$, $^{1}H[B(\text{Ar})_2]_4$ and $^{1}H$.

<table>
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<tr>
<th></th>
<th>Si–Si [Å]</th>
<th>Si–C$_{\text{NHC}}$ [Å]</th>
<th>C$<em>{\text{NHC}}$–N$</em>{\text{NHC}}$ [Å]</th>
<th>C$_{\text{NHC}}$–Si–Si [°]</th>
<th>$\phi_{\text{NHC}}$ [°]</th>
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<td>$^{1}H$</td>
<td>2.281(3)</td>
<td>1.873(4)</td>
<td>1.381(4), 1.402(4)</td>
<td>109.5(1)</td>
<td>3.3(2)</td>
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<td>$^{1}H[B(\text{Ar})_2]_4$</td>
<td>2.1873(8)</td>
<td>1.882(2) [Si1–C$_{\text{NHC}}$]</td>
<td>1.356(2), 1.358(2)</td>
<td>116.73(7) (C1–Si1–Si2)</td>
<td>8.60(6) ($\phi_{\text{NHC1}}$)</td>
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<td>$^{1}H$</td>
<td>2.229(1)</td>
<td>1.927(1)</td>
<td>1.356(2), 1.358(2)</td>
<td>95.34(6) (C28–Si2–Si1)</td>
<td>71.06(6) ($\phi_{\text{NHC2}}$)</td>
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$^a$ Data taken from ref. 9. Connectivity: [(NHC1)(H)Si1—Si2(NHC2)]$^-$.
$^b$ Data taken from ref. 19. $^c$ $\phi_{\text{NHC}}$ denotes the dihedral angles between the C$_{\text{NHC}}$–Si–Si–C$_{\text{NHC}}$ least-square plane and the respective N-heterocyclic ring least-square planes.

Fig. 4  Experimental (red curve) and simulated (green curve) X-band EPR spectra of $^{1}H$ in n-hexane at 336 K; the ordinate ($dA$/$dB$) is omitted for clarity. $g$$_{\text{iso}}$ = 2.00562, $a$(29Si) = 1.725 mT, $a$(14N1) = 0.246 mT, $a$(14N2) = 0.100 mT, $a$(H) = 0.605 mT.

Fig. 5  Calculated minimum structures ($^{1}H_{\text{calc}}$ and $^{1}H'_{\text{calc}}$) of $^{2}$SiH(Ldipp)$_2$ at the B97-D3/II level of theory. The relative energies are given in brackets. The H atoms, except the H atom bonded to Si1, and the iPr substituents are omitted for clarity.

a rigid structure and does not undergo a reversible 1,2-H-migration in solution in contrast to $^{1}H$.$^4$ Remarkably, two quite different $a$(29Si) hyperfine coupling constants (1.725 and 0.431 mT) were found, indicating an asymmetric spin density distribution over the Si atoms. Both values are smaller than those of other Si-based $\pi$ type radicals, such as the disilene $^{1}H$ or the disilene $^{1}H[B(\text{Ar})_2]_4$.

do not allow to clearly distinguish whether a flattened trigonal- or a trigonal-planar geometry of the $^{1}H$ is present in $^{1}H$, the theoretical studies suggest a flat energy hypersurface for the planarization of the three-coordinated Si atom.

The calculated quasi-restricted orbitals (QROs) of $^{1}H_{\text{calc}}$ at the B3LYP/I level of theory and of $^{1}H_{\text{calc}}$ and $^{1}H'_{\text{calc}}$ at the B97-D3/II level of theory are almost identical (Fig. 6 and ESI, Fig. S17–S19†). The SOMO is the Si–$\pi^*$ orbital, confirming
that reduction of 1H⁺ leads to a population of the empty Si=Si π* orbital of 1H⁺ with one electron (see ESI, Fig. S16†). The SOMO reveals significant contributions of π* NHC orbitals due to π-conjugation. The two lower lying doubly occupied molecular orbitals (DOMOs) are the Si=Si π and the n(Si) lone pair orbital, respectively.

Notably, CASSCF(3,3)/def2-TZVP calculations of 1H_{calc} revealed that the overall wave function is described by a major ground state configuration of [2-1-0] of the DOMO, SOMO and LUMO with 96% contribution, suggesting that static correlation can be neglected in the electronic description of 1H (see ESI†).

The calculated spin densities of 1H_{calc} and 1H_{calc} at the B97-D3/II level of theory are depicted in Fig. 7. Mulliken analyses of the spin densities reveal that the highest spin density is located on the dicoordinated Si2 atom (37% in 1H_{calc}, 29% in 1H_{calc}), whereas the spin density at the Si1 atom is quite small (9% in 1H_{calc}, 6% in 1H_{calc}), which is in full agreement with the observation of one large and one small a\(^{29}\)Si hfcc in the experimental EPR spectrum of 1H (vide supra) (see ESI, Table S9f).\(^{26}\) Remarkably, a significant amount of the spin density is delocalized into the CNHC and NHC atoms of the Si1-bonded (17% in 1H_{calc}, 27% in 1H_{calc}) and Si2-bonded (29% in 1H_{calc}, 30% in 1H_{calc}) NHC substituents, which explains the EPR-spectroscopic detection of two a\(^{29}\)Si hfcc's. The calculated g_{iso} values of 1H_{calc} (2.00483) and 1H_{calc} (2.00454) agree well with the experimentally obtained g_{iso} value (2.00562).

Further insight into the electronic structure of 1H was provided by a natural bond orbital (NBO) analysis at the B3LYP/I level of theory (see ESI, Table S12f).\(^{28}\) The Si–Si σ bond is composed of a Si–Si σ bond and a Si=Si π bond with an occupancy of 1.95 and 0.82 electrons, respectively, which indicates indirectly a population of the Si=Si π* orbital with one electron leading thereby to a decrease of the formal Si–Si bond order from 2 in 1H\(^+\) to 1.5 in 1H (vide supra). The Si2 atom in 1H\(^+\) bears a lone pair of high s-character (72%) as similarly found for 1H\(^+\) (75%). Remarkably, both Si–C_{NHC} bonds in 1H_{calc} are composed of one doubly occupied Si–C_{NHC} σ NBO and one singly occupied Si–C_{NHC} π NBO, of which the latter is absent in 1H_{calc}. These additional Si–C_{NHC} π contributions rationalize the shortening and strengthening of the Si–C_{NHC} bonds in 1H, which is also reflected in the higher Si–C_{NHC} WBI indexes (1H: WBI(Si–C_{NHC}) = 1.01 and 0.95; 1H\(^+\): WBI(Si–C_{NHC}) = 0.86 and 0.74).

Comparative analyses of the charge by natural population analyses (NPA) of 1H_{calc} and 1H_{calc} at the B3LYP/I level of theory reveal that the positive partial charges at the Si atoms of 1H_{calc} (q(Si1) = 0.27e, q(Si2) = 0.21e) are decreased by the reduction (1H: q(Si1) = 0.14e, q(Si2) = 0.03e) (see ESI, Table S13t). Furthermore, the one-electron reduction leads to a significant decrease of the overall charges of the NHC substituents (1H_{calc}: q(NHC1) = 0.36e, q(NHC2) = 0.30e; 1H: q(NHC1) = 0.05e, q(NHC2) = −0.04e), whereas the hydridic character of the Si1-bonded H atom is retained (1H_{calc}: q(H) = −0.14e; 1H: q(H) = −0.18e).

![Fig. 6] Quasi-restricted orbitals (QROs) of 1H_{calc} (B97-D3/RI-JCOSX/def2-TZVP) and their corresponding energy eigenvalues; isosurface value: 0.04 e bohr\(^{-3}\); DOMO = doubly occupied molecular orbital, SOMO = singly occupied molecular orbital, LUMO = lowest unoccupied molecular orbital.

![Fig. 7] Spin densities of the calculated minimum structures 1H_{calc} (left) and 1H_{calc} (right) at the B97-D3/RI-JCOSX/def2-TZVP level of theory. The N-bonded 2,6-disopropylphenyl substituents are omitted for clarity.

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<th>Table 2</th>
<th>Comparison of selected experimental and calculated bonding parameters of 1H, 1H_{calc} and 1H_{calc}</th>
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<td>Si1–Si2 [Å]</td>
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<tr>
<td>1H</td>
<td>2.281(3)</td>
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<td>1H_{calc} (^a)</td>
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<td>1H_{calc} (^b)</td>
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<td>1H_{calc} (^b)</td>
<td>2.289</td>
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\(^a\) Calculated at the B3LYP/6-311G**/6-31G* level of theory. \(^b\) Calculated at the B97-D3/RI-JCOSX/def2-TZVP level of theory. \(\sum_{Si}\) is the sum of angles around the Si1 atom. φ_{NHC1} and φ_{NHC2} denote the dihedral angles between the least-square plane of the atoms C1, Si1, Si2, C2 and the least square plane of the heterocyclic ring atoms of the NHC substituent bonded to Si1 and Si2, respectively.
3. Conclusions

The isolation and full characterization of NHC-trapped Si$_2$H ($\text{IH}$) can be considered as a major advance in low-valent silicon hydride chemistry, given the intermediacy of Si$_2$H in the chemical vapor deposition of amorphous hydrogenated silicon that is widely used in solar cell and thin film technologies. Whereas Si$_2$H features a C$_{2v}$-symmetric H-bridged ground state structure and is a $\sigma$-type radical with a symmetric distribution of the spin density over the two silicon atoms, its NHC-trapped counterpart Si$_2$(H)[Idipp]$_2$ ($\text{IH}$) features a terminal Si-H bond and is a $\pi$-type radical, in which the unpaired electron occupies the Si=Si $\pi^*$ orbital (SOMO), leading to a formal Si-Si bond order of 1.5. Significant delocalization of the spin density into the NHC substituents occurs via $\pi$-conjugation of the Si=Si $\pi^*$ orbital with the $\pi^*$ orbitals of the coplanar arranged N-heterocyclic rings leading to a stabilization of the radical, in which the spin density is higher at the leading to a formal Si bond order of 1.5. Significantly, the radical, in which the spin density is higher at the terminal Si

Acknowledgements

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Notes and references

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For comparison reasons, the half-wave potential of the \([\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]^{1/0}(\text{Fc}/\text{Fc})\) redox couple was determined in \(\text{C}_6\text{H}_2\text{F}\) under the same conditions and found to be +0.520 V versus the redox couple \([\text{Fe}(\eta^5-\text{C}_5\text{Me}_5)_2]^{1/0}\).


18 The TdDFT calculations suggest that the absorption bands of 1H centered at 608, 704 and 958 nm originate from several electronic transitions including those from the Si=Si \(\pi^*\) (HOMO(\(x\)) and Si=Si \(\pi\) (HOMO–1(\(x\))) orbitals into antibonding \(\pi^*\) orbitals of the N-bonded 2,6-disopropylphenyl substituents (for details see ESI†). The SOMO \(
\rightarrow\n\) LUMO transition is predicted to give rise to a band at 1295 nm.


28 The higher spin density at the Si2 atom in 1H can be rationalized considering the polarization of the Si=Si \(\pi\)-orbital in 1H* towards the Si1 atom due to the hydride substituent. This leads to a reversed polarization of the Si=Si \(\pi\)-orbital in 1H* with a higher contribution at the Si2 atom, which upon population with one electron gives rise to a higher spin density at Si2 in 1H.