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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b11137 • Publication Date (Web): 30 Nov 2018

Downloaded from http://pubs.acs.org on November 30, 2018

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Calix[4]pyrrole hydridosilicate: the elusive planar tetracoordinate silicon imparts striking stability to its anionic silicon hydride.

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Supporting Information Placeholder

ABSTRACT: Anionic hydridosilicates are highly reactive and strong hydride donors. In contrast, calix[4]pyrrole hydridosilicate is an entirely water-stable, anionic silicon hydride, which does not show hydridic reactivity. However, it still acts as an electron donor and enables the detection of a single electron transfer process in the reduction chemistry with hydridosilicates. Most important, these unusual properties are imparted by the unique planar structure of its elusive parent neutral silane – substantiating the effect of planar tetracoordinate silicon for the first time.

Anionic hypercoordinate silicon hydrides (hydridosilicates) are highly reactive species and powerful reducing agents.¹ The archetypal SiH5⁻ or SiH6²⁻ anions have only been observed under gas phase or high-pressure conditions, respectively.²⁻⁴ Recently, hydridosilicates were demonstrated to even react with Csp2-F bonds in hydrodefluorination reactions.⁵ Already neutral silanes turn into effective reductants upon transient coordination of neutral or anionic donors.^{2-3, 6-14} Besides being potent hydride donors, hydridosilicates are also involved in fundamentally different reactivity modes, like acting as strong bases,^{3, 15-17} electron or hydrogen atom donors,¹⁶⁻²⁰ making valuable dehydrogenative coupling processes feasible.²¹⁻²⁴ A reason for their high reactivity is the low hydride ion affinity of neutral silanes, which is indeed among the lowest known for neutral molecules, comparable with H₂O or benzene.^{2-3, 25-26} By consequence, the isolation of hydridosilicates needs special precautions, like the stabilization of the Si-H bonds by agostic interactions with transition metals.²⁷⁻³² However, also a small number of nontransition metal salts of [HSiR₄]⁻ or [H₂SiR₃]⁻ (R = Ar, OR, F) have been observed spectroscopically.^{1, 16-17, 20, 33-39} The first structural characterization of a hydridosilicate, H₂SiPh₃-, was achieved only in 2001,⁴⁰ followed by some related derivatives.⁴¹⁻⁴³ A general requirement were strict anhydrous conditions to prevent immediate hydrolysis of the activated and unstable Si-H bonds.

We herewith present the synthesis and characterization of an entirely water stable, anionic hydridosilicate [1-H⁻] (Figure 1). The hydridic reactivity of [1-H⁻] is suppressed, but it still undergoes single electron transfer, supporting such process as feasible reactivity mode of hydridosilicates. Most important, these features are caused by the unique planar conformation of its (so far elusive) parent neutral silane 1.



Figure 1: Highly reactive anionic hydridosilicates compared with the water stable silicon hydride of this work.



Scheme 1: Synthesis of different salts of [1-H-][M+].

The methyl-calix[4]pyrrole macrocyclic ligand, easily prepared in a one-step procedure,⁴⁴ was fully deprotonated with benzyl potassium in toluene at 120 °C (Scheme 1). Changing the solvent to acetonitrile and addition of HSiCl₃ at room temperature gave the potassium salt of methyl-calix[4]pyrrole hydridosilicate [1⁻][K⁺] in 50% isolated yield at mmol scale.⁴⁵ The respective lithium and tetraphenyl phosphonium salts [1-H⁻][Li⁺] and [1-H⁻][PPh₄⁺] were obtained by subsequent salt metathesis with LiCl or PPh₄Cl.

Multinuclear NMR spectroscopy revealed noticeable spectroscopic features of [1-H⁻], being similar for the various cations. ¹H-NMR in thf-*d*₈ showed two doublets for the pyrrole hydrogen atoms and four different signals for the methyl groups, consistent with a $C_{2\nu}$ symmetry of [1-H⁻] in solution. The Si bound hydrogen resonated at $\delta = 6.60$ ppm with a coupling constant ¹*J*_{Si-H} = 270 Hz. The ²⁹Si chemical shift of -140 ppm rather lies in the range of hexacoordinate silicon.⁴⁶ In comparison to other hydridosilicates, the Si-H ¹H-NMR signal is shifted downfield and the ²⁹Si-NMR signal highfield, indicating an unusually deshielded hydrogen and a shielded silicon atom.^{16, 37, 47} The experimental values agree ideally with the computed NMR data of [1-H⁻] (ZORA-SO-PBE0(COSMO, CH₂Cl₂)/TZ2P), refuting any solvent coordination responsible for the observed strong shift.

IR spectroscopy for salts [1-H⁻][M⁺] showed distinct stretching modes of the Si-H bonds at 2176 cm⁻¹ [K+] or 2243 cm⁻¹ [PPh₄⁺]. Such values are much higher compared to other hydridosilicates $(1550 - 1970 \text{ cm}^{-1})$,^{4, 40, 43} but rather match with those of Si-H bonds in neutral silanes or aminosilanes $(2100 - 2200 \text{ cm}^{-1})$.^{41, 48-49} The IR-spectra thus indicate a remarkably strong Si-H bond in [1-H⁻].

Single crystals of [1-H⁻][K⁺] were obtained from dichloromethane and of [1-H⁻][Li⁺] from acetonitrile. [1-H⁻][K⁺] exists as a coordination polymeric structure in the solid state, wherein the cation bridges the anionic units *via* K^{...}π-pyrrole interactions. In [1-H⁻][Li⁺], the lithium cation is coordinated by four acetonitrile molecules, whereas the anion [1-H⁻] resides freely (Figure 2). In all previously reported hydridosilicates, the silicon was coordinated in a trigonal-bipyramidal fashion, with the hydrides being in the apical position.^{40-41, 43} In [1-H⁻], the coordination sphere around silicon is almost square-pyramidal, wherein the basal plane is generated by four nitrogen atoms (Si-N_{avg} = 1.86 Å, N-Si-N = 157°). The Si-H bond is rather short (1.36 Å) in comparison to the previously reported structures (1.50 – 1.60 Å).^{40-41, 43}



Figure 2: Molecular structure of $[1-H][Li^+(CH_3CN)_4]$ obtained by X-ray diffraction. Only one of the two independent fragments in the unit cell is shown. Selected hydrogen atoms are omitted for clarity. Ellipsoids 50 % probability, selected bond lengths [Å] and angles [°]: Si-N_{avg} = 1.860(3) Å, Si-H1 = 1.36(3) Å, N1-Si-N3 = 158.5(2), N2-Si-N4 = 157.4(2).

The calix[4]pyrrole ligand adopts a *ruffled* conformation, with two opposite methyl groups being identical, in agreement with the $C_{2\nu}$ symmetry in solution as observed by ¹H-NMR spectroscopy. The methyl groups block the coordination side *trans* to the Si-H bond.

The water and air stability of the [1-H⁻] salts were tested by exposing solutions to air at room temperature. In contrast to the immediate hydrolysis of all previously reported hydridosilicates, the lithium and potassium salts are hydrolyzed only over the range of hours. The tetraphenylphosphonium salt of [1-H⁻] remained entirely intact under such conditions and even in a 1:1 mixture of CD₃CN/D₂O, no hydrolysis was detected after several weeks (see SI). Moreover, [1-H⁻] does neither react with *p*-methyl benzalde-hyde, benzyl chloride, benzyl bromide nor with the TEMPO radical. These findings are in strong contrast to the pronounced water sensibility, the strong hydride donor capabilities and the weak Si-H bond energy of all previously described hydridosilicates.

But how can the stability and lack of reactivity be rationalized? To answer this question, the neutral silane 1 that results from hydride abstraction of [1-H⁻] was analyzed by quantum-theoretical tools, and compared with the related but structurally unrestricted Si(pyrrole)₄ (2) (Figure 3). For the neutral silane 1, irrespective of the used method (wavefunction or various density functionals) and starting geometry, a planar conformation at silicon is obtained (e.g. N-Si-N = 178.3° with B3LYP-D3(BJ)/def2-TZVPP). The neutral silane 2 has a common tetrahedral geometry. The LUMO energy in 1 (-2.3 eV) is reduced dramatically in comparison to 2 (-0.1 eV), and reveals almost pure *pz*-type character at silicon (Figure 3). The computed (DLPNO-CCSD(T)/cc-pVQZ, isodesmic) hydride ion affinity (HIA) of 1 is exceptionally high (517 kJ mol⁻¹, cf. for 2 HIA = 343 kJ mol⁻¹), as a consequence of the geometrical strain.



Figure 3: LUMO energies and HIA of planar 1 and Si(pyrrole)₄ 2 with computed structure of 1, including the isodensity plot of the Kohn-Sham LUMO.

Planar **1** has even a higher HIA than $B(C_6F_5)_3(512 \text{ kJ mol}^{-1})$, without bearing any electron withdrawing groups. NBO analysis of the Si-H bond in [**1**-H⁻] reveals a sp^{1.26} hybrid orbital at silicon. The high *s*-orbital character is in line with the strong bonding as well as with the large Si-H NMR coupling constant. Energy decomposition analysis (BP86-D3/TZ2P) further rationalized the much stronger hydride binding energy in [**1**-H⁻], in comparison to [**2**-H⁻]. The preorganization in **1** causes a strongly diminished deformation energy (96 kJ mol⁻¹) upon distortion to the structure in [**1**-H⁻], in comparison to **2** (281 kJ mol⁻¹). Moreover, the contribution of orbital interaction in the Si-H bond of [**1**-H⁻] (48 %) are more pronounced as in [**2**-H⁻] (45 %), in agreement with the very low LUMO energy in **1**.

The spectroscopic and theoretical results consistently identify the unusually strong silicon-hydride bond as responsible for the stability of [1-H⁻]. The weak steric demand of the methyl groups in the ligand refutes a strong kinetic effect, although the blocked position trans to the Si-H bond hinders associative processes, and could cause high reaction barriers. It is known for almost 40 years, that the planarization of silicon should significantly lower the LUMO energy of neutral silanes.⁵⁰⁻⁵¹ However, this effect has never been verified experimentally until now.

In contrast to the resistance of [1-H-] towards heterolytic Si-H bond cleavage (hydride donation), single electron transfer (SET) does readily occur. Upon mixing of [1-H-] with the electron acceptor *p*-chloranil, two independent short-lived radical species were detected by EPR spectroscopy, tentatively assigned as a neutral radical [1-H[•]] and the *p*-chloranil radical anion. Upon prolonged reaction time, the exhaustive reduction to *p*-perchlorohydroquinone was verified. Accordingly, reaction of [1-H-] with AgSbF₆ led to the formation of only one short-lived radical and elemental silver. The observation of radical intermediates during the reduction with a hydridosilicate is an important finding. Even though pentacoordinate hydridosilicates have been considered as electron transfer agents, respective intermediates were never detected.¹⁶⁻¹⁹ The metastability of the radical species again relies on the effect imparted by the underlying planar silane 1. Evidently, not only the HIA but also the electron affinity of **1** is larger as that of common neutral silanes - rendering the intermediate as metastable and enabling its observation.

The present contribution provides the first experimental proof for the effect of a planar tetracoordinate silicon, expressed by the taming of the reactive class of hydridosilicates. It furthermore supports SET steps in the reduction chemistry with hydridosilicates. Finally, it introduces the calix[4]pyrrole ligand as new, four fold anionic platform for the emerging field of geometrically constrained main-group element species.⁵²⁻⁵⁴

ASSOCIATED CONTENT

Supporting Information

The Supporting Information, containing all experimental and computational details, is available free of charge on the ACS Publications website.

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Notes

The authors declare no conflict of interest.

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ACKNOWLEDGMENT

We gratefully thank Prof. H.-J. Himmel for his support, H. Wadepohl for advice with X-ray structure solution, M. Enders for fruitful discussions, the FCI and DFG for financial support and the BWFor/BWUniCluster for computational resources. F.E. is grateful to the Foundation of German Business (sdw) for a fellowship.

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TOC:

high stability of

hydridosilicate



caused by planar silicon

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