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A Zwitterionic Carbanion Frustrated by Boranes – Dihydrogen Cleavage with Weak Lewis Acids via an "Inverse" Frustrated Lewis Pair Approach

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S *Supporting Information*

ABSTRACT: The synthesis, structural characterization, and acid–base chemistry of $[C(SiMe_2OCH_2CH_2OMe)_3]Na$ (**2**), a sterically encumbered zwitterionic organosodium compound, is reported. **2** is a strong Brønsted base that forms frustrated Lewis pairs (FLPs) with a number of boron-containing Lewis acids ranging from weakly Lewis acidic aryl and alkyl boranes to various alkyl borates. These intermolecular FLPs readily cleave H_2, which confirms that even poor Lewis acids can engage in FLP-mediated H_2 cleavage provided that the present bulky base is of sufficiently high Brønsted basicity.

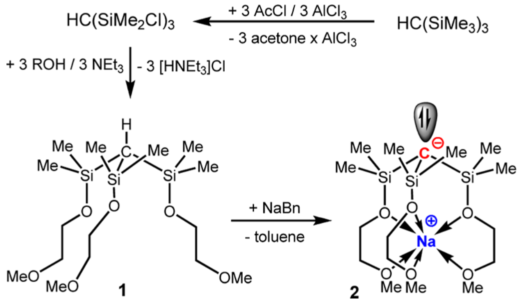
The transition-metal-free heterolytic cleavage of H_2 via frustrated Lewis pairs (FLPs), pioneered by Stephan,[1] represents an innovative concept in sustainable chemistry. It has the potential of replacing expensive, less abundant, and toxic precious metals in their classical domain, the catalytic hydrogenation of unsaturated organic species.[2] FLPs are sterically encumbered Lewis pairs unable to form classical Lewis acid–base complexes due to unfavorable repulsive interactions (frustration). Key to this unique mode of bond activation is the unquenched Lewis acidity and basicity of an FLP, which polarizes the H–H bond and facilitates its heterolytic cleavage.[3]

A number of Lewis bases ranging from amines, phosphines, to strongly basic carbenes[4] and phosphonium ylides[5] have been successfully utilized in FLP-induced H_2 cleavage. In contrast, the Lewis acidic component with a few exceptions[6] has been limited to expensive, highly fluorinated, but strongly Lewis acidic boranes such as $B(C_6F_5)_3$ and related systems. Even modest reductions in the Lewis acidity of the borane resulted in inactive FLPs with the commonly used base components.[7] Computational studies regarding the thermodynamic feasibility of FLP induced H_2 cleavage, however, suggested that weaker Lewis acids, most of them being cheaper and more readily available, might be active FLP components as well, provided a sufficiently strong base is used.[3c]

Zwitterionic carbanions, of which the carbanion is charge separated from the metal cation by internal donor bridges, are a rare class of strong Brønsted and Lewis bases.[8] As a result of charge separation the stereochemically active electron pair is largely localized at the "naked carbanion" and is accessible for Lewis acid–base chemistry.[9] Herein, we report on the synthesis, structural characterization, and "frustrated" Lewis acid–base chemistry of the first zwitterionic organosodium compound, $[C(SiMe_2OCH_2CH_2OMe)_3]Na$. We will demonstrate that this strongly basic and sterically encumbered zwitterion forms intermolecular FLPs with weak boron-containing Lewis acids capable of heterolytically cleaving H_2.

Our approach to enforce charge separation in carbanionic structures involves the incorporation of polydonor groups directly bound to the carbanion, a strategy that we already successfully applied to the construction of zwitterionic silyl anions.[10] The synthesis of the new carbanion **2** is outlined in Scheme 1 and involves the generation of $HC(SiMe_2Cl)_3$ via chlorodemethylation of $HC(SiMe_3)_3$ with $AlCl_3$/acetyl chloride, followed by treatment with excess $HOCH_2CH_2OMe/NEt_3$ to produce **1** in 94% yield. Deprotonation of **1** with benzylsodium cleanly generates zwitterionic carbanion **2**, which is an air- and moisture-sensitive colorless solid that dissolves in common organic solvents including hexanes, benzene, toluene, THF, and ethers.

Scheme 1. Synthesis of Zwitterion 2



2 was fully characterized by NMR spectroscopy, combustion and X-ray analysis (Figure 1). The X-ray data confirm a tripodal structure with the three bidentate donor groups of the podand coordinating in a chelate fashion to the sodium cation whose coordination sphere is best described as distorted octahedral. The central C6–Na distance with 3.22 Å is significantly longer than in other organo sodium compounds and suggests only weak if any bonding cation–anion interactions.

To have an estimate of the proton affinity of the "naked" carbanion, the p*K* of **1** (conjugate acid of zwitterion **2**) was

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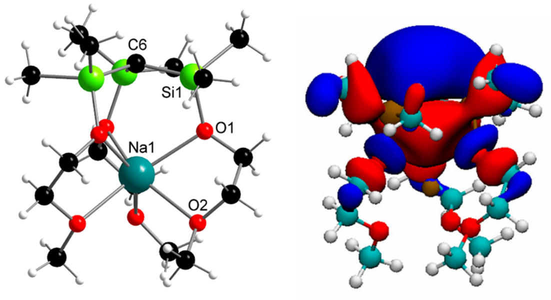
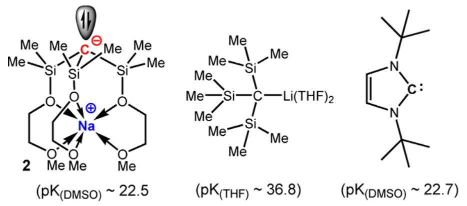


Figure 1. (Left) Solid-state structure of **2** (black = carbon, white = hydrogen); (Right) HOMO of **2**.

determined from acid–base reactions of **2** with substituted fluorenes using ^1H NMR spectroscopy (see Supporting Information). Evidently, **2** ($pK_{(DMSO)}$ of **1** = 22.5) is a considerably weaker base than $LiC(SiMe_3)_3$,[11] which is attributed to the presence of the alkoxide donors bound to silicon (Chart 1). These electron-withdrawing groups significantly reduce the electron density at the anionic carbon as reflected in the shorter C–Si bonds of **2** [av. 1.79 Å] relative to $LiC(SiMe_3)_3$ [av. 1.83–1.84 Å].[12] The notion that the reactive center is the "naked" carbanion is supported by electronic structure calculations, which revealed the HOMO of **2** to be largely located at the central anionic CSi_3 unit (Figure 1). It is of further note that the Brønsted basicitiy of **2** is similar to that of 1,3-di-*tert*-butylimidazol-2-ylidene[13] (Chart 1). This sterically encumbered carbene in combination with the strong Lewis acid $B(C_6F_5)_3$ forms a "metastable" frustrated Lewis pair (FLP) capable of cleaving H_2 irreversibly.[4a,b]

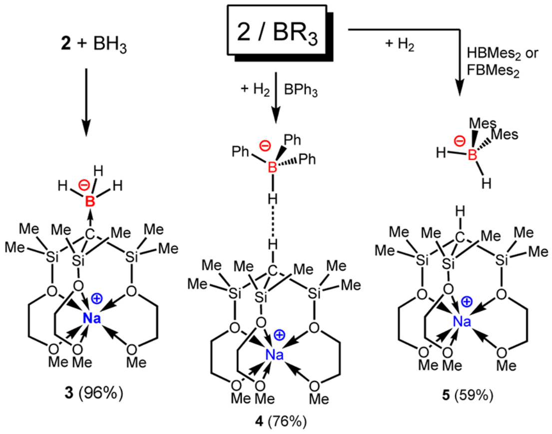
Chart 1



The favorable properties of **2**, high Brønsted basicity combined with the efficient steric protection of the "naked" carbanion, prompted us to develop novel carbanion-based FLP systems with simple boranes and to test their potential as H_2 cleaving FLPs. First, **2** was treated with excess BH_3 and the classical Lewis acid–base adduct **3** was isolated as a crystalline material in 96% yield. When BPh_3, $FBMes_2$, $HBMes_2$, $BMes_3$, and $B(OMe)_3$ were treated, respectively, with **2**, no Lewis acid–base adducts were obtained as a result of steric frustration. Benzene solutions of these FLPs are stable over prolonged periods of time. Astonishingly, the FLPs **2**/BPh_3, **2**/$HBMes_2$, and **2**/$FBMes_2$ engage in heterolytic cleavage of H_2, while **2**/$BMes_3$ and **2**/$B(OMe)_3$ were inactive in C_6D_6 solutions, presumably due to extensive repulsive interactions. Note that as single components neither **2** nor the employed boranes react with H_2 even after longer periods of time and higher pressures (4 atm).

Upon adding H_2 to **2**/BPh_3 and **2**/$HBMes_2$, respectively, crystalline solids were isolated from solution and characterized by NMR spectroscopy as the borate salts **4** and **5** (Scheme 2). The cationic parts of **4** and **5** exhibit ^{23}Na resonances at 0.3 and 3.1 ppm and ^1H resonances at −0.58 and 0.31 pm for the $H–CSi_3$ units, respectively. The anions, $HBPh_3^-$ and $H_2BMes_2^-$, give rise to ^{11}B resonances at −8.5 ppm and −25.8 ppm with B–H coupling constants of ~79 Hz (doublet) and ~74 Hz (triplet), respectively. Note that also the FLP **2**/$FBMes_2$ (2:1 molar ratio) heterolytically cleaves H_2 to cleanly generate salt **5**. We assume that in the first step of this FLP-mediated double hydrogenation reaction $[HFBMes_2][HC(SiMe_2OCH_2CH_2OMe)_3Na]$ is formed, which then readily decays into **1**, NaF, and $HBMes_2$. The latter borane in combination with **2** cleaves H_2 to finally generate **5**.

Scheme 2. Reaction of 2/BR_3 with H_2



The structures of **4** and **5** were further confirmed by X-ray analysis (Figures 2 and 3). The structural parameters are in full agreement with tetrahedral $HBPh_3^-$ and $H_2BMes_2^-$ anions with av. C–B–C angles of 114° and 110° and B–H bond lengths of 1.1 and 1.13 Å, respectively. Notably, the cation and anion in **4**

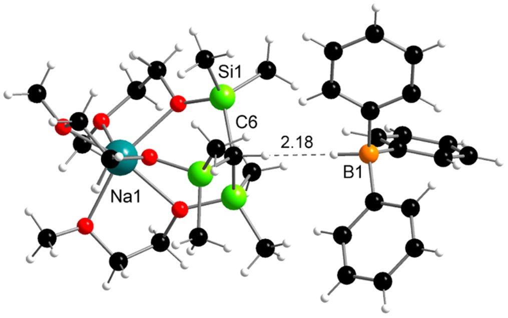


Figure 2. Solid-state structure of **4** (black = carbon, red = oxygen, white = hydrogen; minor disordered form has been omitted).

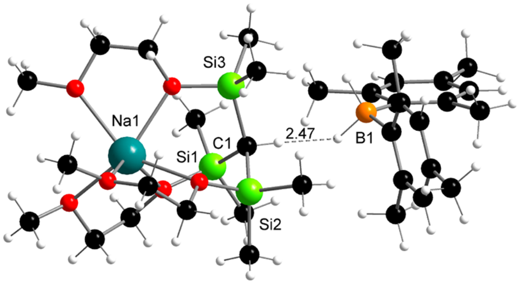


Figure 3. Solid-state structure of **5** (black = cabon, red = oxygen, white = hydrogen; toluene has been omitted for clarity).

pack such that the CH and BH units are oriented toward each other with a C−H···H−B distance of ca. 2.18 Å, significantly shorter than that found in **6** (2.47 and 2.98 Å) and the salts $[Bu^t_3PH\cdots HB(C_6F_5)_3]$[1b] with 2.75 Å and $[Bu^t_3PH\cdots HB(c\text{-}hexyl)(C_6F_5)_2]$[14] with 2.63 Å. Indeed, diffusion experiments (^1H DOSY NMR) in C_6D_6 show that the structure of **4** is retained in solution nondissociated, while in THF dissociation into the cation and anion occurs.

Aiming at the limit of FLP-mediated H_2-cleavage with **2** as the base component we employed even weaker Lewis acids such as BEt_3 and $B(OMe)_3$ (Table 1). Again, in both cases no Lewis acid−base adducts were obtained with **2**, presumably as a result of both steric and electronic frustration. Treating the FLP **2**/$B(OMe)_3$ with H_2 did not lead to H_2 cleavage even under forced conditions, due to the extremely poor Lewis acidity and low hydride affinity of $B(OMe)_3$. However, exposure of hexanes solutions of **2**/BEt_3 under an atmosphere of H_2 (2.5 atm, 25 °C) resulted after 1 h in the formation of a precipitate, which after one day was isolated from the solution and identified by NMR spectroscopy as the BEt_3-adduct **7**. In the ^{11}B NMR, the boron signal of **7** appears as a broad singlet for the $[Et_3B{-}H{-}BEt_3]$ unit, rather than as the expected doublet from scalar B−H coupling. The presence of a B−H bond in **7** was confirmed via hydride transfer to $HBMes_2$. Inspection of the reaction mixture by ^{11}B NMR revealed a doublet at ∼26 ppm with a coupling constant of 74 Hz arising from the $H_2BMes_2^-$ unit. The identity of **7** was further confirmed by its independent synthesis from the reaction of **1** with $Na[HBEt_3]$ followed by the addition of BEt_3 (Scheme 3). Interestingly, intermediate **6** could not be detected in none of the H_2 cleavage reactions.

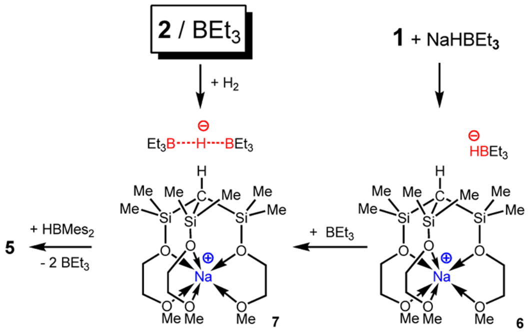
Table 1. Acceptor Numbers (ANs)[17] and Calculated Gas-Phase Hydride Affinities [ΔH_{HA}/kcal/mol] of Selected Boranes[18]

borane	AN[a]	$-\Delta H_{HA}$
$B(C_6F_5)_3$	78.2[19]	112.0[20]
BH_3	79.0	73.7[18]
BPh_3	65.6[19]	74.4
$HBMes_2$	37.3	74.7
$FBMes_2$	16.4	64.7
BEt_3	30.3	58.5
$B(OMe)_3$	13.2	38.2

[a] Measured in C_6D_6; molar ratio $BR_3/OPEt_3$ = 5:1.

Notably, examples of *intermolecular* FLP-mediated H_2 cleavage involving medium to weak Lewis acids such as $FBMes_2$, $HBMes_2$, and BEt_3 are without precedence. The only trialkyl borane able to engage in H_2 cleavage was reported recently by Labinger and Bercaw.[15] Even for BPh_3 only one example, the synthesis and isolation of $[Bu^t_3PH][HBPh_3]$, derived from the reaction of the intermolecular FLP Bu^t_3P/BPh_3 with H_2 and claimed to be stable at room temperature is reported.[1b] Its formation via H_2-cleavage has been questioned recently by the Papai group due to the insufficient Brønsted basicity of the Lewis base component PBu^t_3. DFT calculations of the Gibbs free energy for the overall reaction $BPh_3 + PBu^t_3 + H_2 \rightarrow [Bu^t_3PH][HBPh_3]$ in toluene as solvent (ΔG_R = +18.2 kcal/mol), indeed, disfavor formation of the product.[3c] Our results seem to be in line with Papai's calculations, as our base component, carbanion **2** ($pK_{(DMSO)} \approx 22.5$), is a considerably stronger base than PBu^t_3 ($pK_{(H_2O)} = 11.4$).[16]

Scheme 3. Hydrogen Cleavage with the FLP 2/BEt_3



That strong bases are required to form stable products upon cleavage of molecular hydrogen with weak Lewis acids is further supported by calculations of the Gibbs free energies of the H_2-cleavage with the FLPs **2**/BPh_3, **2**/BEt_3, and **2**/$B(OMe)_3$. The results are shown in Table 2 for both the gas and solvent phase.

Table 2. Calculated Gibbs Free Energies[a] [ΔG_R in kcal/mol] for Heterolytic H_2 Cleavage with 2 and Selected Boranes {8 = $[(MeO)_3BH][HC(SiMe_2OCH_2CH_2OMe)_3Na]$}

reaction	ΔG_R (gas phase)	ΔG_R (hexane)	ΔG_R (benzene)
2 + H_2 + BPh_3 → **4**	6.7	5.1	1.0
2 + H_2 + BEt_3 → **6**	21.9	14.2	9.4
2 + H_2 + $B(OMe)_3$ → **8**	27.5	22.0	22.3

[a] DFT/B3LYP/SVP.

As expected, the thermodynamic feasibility of these reactions is in the order **4** > **6** > **8** and correlates well with the order in gas-phase hydride affinity (ΔH_{HA}) of the individual borane components that is $BPh_3 > BEt_3 > B(OMe)_3$ (Table 1). In line with our experimental results only **4** is predicted to form a stable product in the solvent phase. Salt **6** (not detected but independently synthesized) is at least thermally accessible, while **8** (not observed) is highly unstable. That **7**, the BEt_3 adduct of salt **6**, was isolated from the H_2 cleavage reaction with excess BEt_3 underlines the importance of bridging B−H−B interactions in stabilizing the borohydride of the final product via dispersion of the negative charge.[21]

The inability of **2** to engage in H_2 cleavage with the poor Lewis acid $B(OMe)_3$ encouraged us to employ $(Me_3Si)_3CLi(THF)_2$ as a base component, a more than 10 orders in magnitude stronger Brønsted base than **2**. Since $B(OMe)_3$ is known to react with $(Me_3Si)_3CLi(THF)_2$ to form $(Me_3Si)_3CB(OMe)_2$,[22] the electronically similar but bulkier borate $B(OPr^i)_3$ was chosen as a Lewis acid component. Indeed, THF solutions of the FLP $(Me_3Si)_3CLi/B(OPr^i)_3$ heterolytically cleave H_2 (pressure 2.5 atm) as confirmed by ^{11}B NMR spectroscopic studies, according to the following equation:

$$(Me_3Si)_3CLi + B(OPr^i)_3 + H_2$$
$$\rightarrow (Me_3Si)_3CH + Li[HB(OPr^i)_3]$$

In conclusion, we have synthesized and structurally characterized **2**, the first zwitterionic organosodium compound, and demonstrated its potential as a strong base component in the FLP-mediated cleavage of H_2. The experimental and computational results clearly show that even poor Lewis acids engage in H_2 cleavage provided that the present base is sterically encumbered and of sufficiently high Brønsted basicity. This FLP approach—weak Lewis acid combined with a strong base—is inverse to that pioneered and exhaustively studied by Stephan, Erker, and others,[1−5] with the latter utilizing FLPs composed of the exceptionally strong but expensive Lewis acid $B(C_6F_5)_3$ or $RB(C_6F_5)_2$ and weakly basic amines and phosphines. These systems have shown promise in FLP-mediated catalytic hydrogenations of unsaturated substrates. Studies regarding catalytic applications of "inverse" FLPs that contain strong and bulky organic bases are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, compound characterization data, and spectra for all new compounds, CIF file for compounds **2**, **4**, and **5** and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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