

# Dihydrogen Activation with a Neutral, Intermolecular Silicon(IV)-Amine Frustrated Lewis Pair

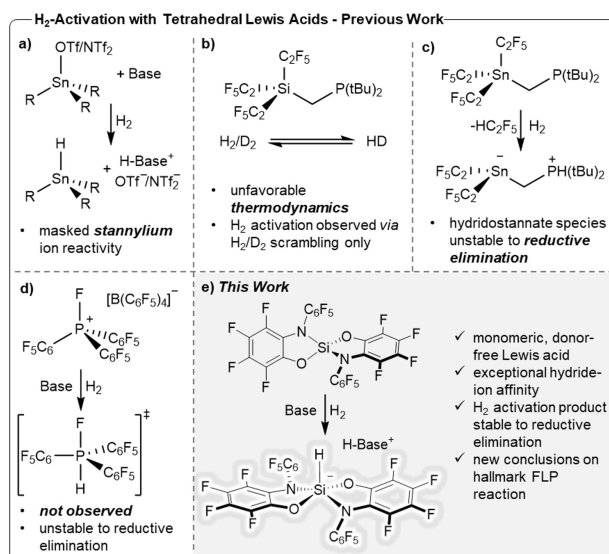
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**Abstract:** The heterolytic cleavage of dihydrogen constitutes the hallmark reaction of frustrated Lewis pairs (FLP). While being well-established for planar Lewis acids, such as boranes or silylium ions, the observation of the primary H<sub>2</sub> splitting products with non-planar Lewis acid FLPs remained elusive. In the present work, we report bis(perfluoro-*N*-phenyl-*ortho*-

amidophenolato)silane and its application in dihydrogen activation to a fully characterized hydridosilicate. The strict design of the Lewis acid, the limited selection of the Lewis base, and the distinct reaction conditions emphasize the narrow tolerance to achieve this fascinating process with a tetrahedral Lewis acid.

## Introduction

Frustrated Lewis pairs (FLPs) evoked considerable interest due to the conceptual generality and their broad applicability.<sup>[1]</sup> Numerous FLP bond activation reactions were achieved, but heterolytic H<sub>2</sub> cleavage remained the benchmark, provoked by the inert and nonpolar nature of the dihydrogen bond.<sup>[2]</sup> Whereas boranes, carbenium<sup>[3]</sup> or silylium ions,<sup>[4]</sup> planar Lewis acids with easily accessible acceptor orbitals were successfully employed, tetrahedral Lewis acids have been less effective in H<sub>2</sub> activation.<sup>[5]</sup> Intermolecular FLPs of neutral triflate silanes bind CO<sub>2</sub>, SO<sub>2</sub>—while the cleavage of dihydrogen was not realized.<sup>[6]</sup> The triflate-based nBu<sub>3</sub>SnOTf was found inactive for H<sub>2</sub>-activation,<sup>[6a]</sup> but the more bulky iPr<sub>3</sub>SnOTf or iPr<sub>3</sub>SnNTf<sub>2</sub> were needed for the process to proceed (Figure 1a).<sup>[7]</sup> Importantly, this behavior was attributed to the weakened Sn-OTf/NTf<sub>2</sub> bond, propelling the reactivity as a stannylum ion surrogate. Indeed, computational insights and the neutral stannane reaction products supported a stannylum ion character of the active Lewis acid.<sup>[8]</sup> Mitzel and coworkers prepared a series of geminal tetrel/phosphorus FLPs of the form (F<sub>5</sub>C<sub>2</sub>)<sub>3</sub>E-CH<sub>2</sub>-PtBu<sub>2</sub> (E=Si,<sup>[9]</sup> Ge,<sup>[10]</sup> Sn<sup>[11]</sup>). The silicon system binds CO<sub>2</sub> and SO<sub>2</sub>, while dihydrogen activation could be demonstrated only through H<sub>2</sub>/D<sub>2</sub> scrambling (Figure 1b).<sup>[9]</sup> The germanium derivative was



**Figure 1.** FLP-type H<sub>2</sub> activation with tetrahedral Lewis acids. a) Tin triflates, reacting as masked stannylum ions. b) Geminal silane FLP, with limiting hydride ion affinity. c), d) Reductive elimination from putative hydride intermediates in tin(IV) or P(V) based FLP. e) Intermolecular, neutral silane FLP developed in this work.

inactive toward dihydrogen,<sup>[10]</sup> while the elusive reaction product of the tin analog suffered from following reductive elimination (Figure 1c).<sup>[12]</sup> Even the prominent [(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>PF]<sup>+</sup> based FLP could only induce H<sub>2</sub>/D<sub>2</sub> scrambling, while the observation of the hydridophosphorane was not reported (Figure 1d).<sup>[13]</sup> Computations challenged the stability of such intermediate due to the propensity towards reductive elimination of HF.<sup>[14]</sup> H<sub>2</sub> cleavage with naphthalene bridged dicationic diphosphonium FLP produced two equiv. of tBu<sub>3</sub>PH<sup>+</sup> and the two-electron reduced Lewis acid, but the hydrido-bound Lewis acid was not spotted.<sup>[15]</sup> Hence, all these results demonstrate that FLP dihydrogen cleavage is principally feasible with tetrahedral Lewis acids, but the primary hydridic reaction products remained elusive. While tin and phosphorus-based Lewis acids

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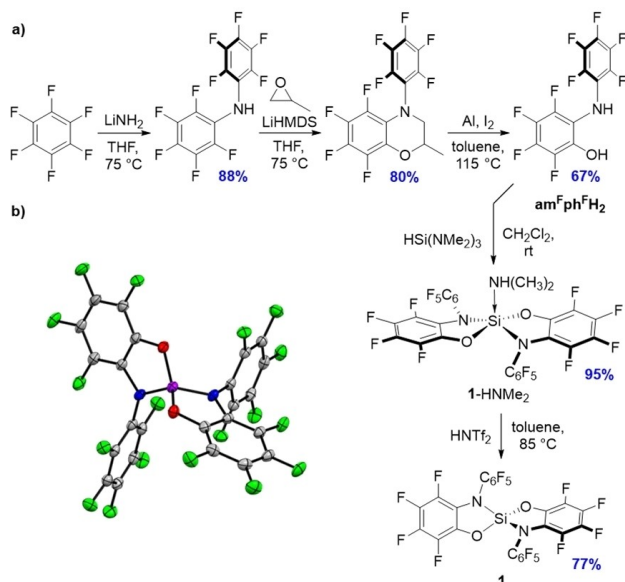
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are prone to reductive elimination, silanes lack sufficient hydride ion affinity. Enhancing the Lewis acidity of silanes was of considerable interest in recent years, launched with per-substituted *bis*(catecholato)silanes ( $\text{Si}(\text{cat}^X)_2$ ,  $X=\text{F}, \text{Cl}, \text{Br}, \text{CF}_3$ ),<sup>[16]</sup> *tetrakis*(trifluoromethanesulfonato)silane ( $\text{Si}(\text{OTf})_4$ )<sup>[17]</sup> and *bis*(perfluoropinacolato)silane ( $\text{Si}(\text{pin}^F)_2$ ).<sup>[18]</sup> Although these compounds should possess sufficient hydride ion affinity, FLP  $\text{H}_2$  activation was not achieved. Limitations emerged from poor solubility coupled with unstable hydridosilicates ( $\text{Si}(\text{cat}^X)_2$ ), necessary donor stabilization ( $\text{Si}(\text{cat}^X)_2$ ;  $\text{Si}(\text{pin}^F)_2$ ) or lability of ligand-silicon bonds ( $\text{SiOTf}_4$ ).<sup>[19]</sup> Hence, a strict design of a silicon(IV)-based Lewis acid appeared imperative—a strategy pursued and reported in the present work (Figure 1e).

The steric profile of a novel perfluorinated *ortho*-aminophenol ligand prohibits the oligomerization associated with the catechol-based silicon(IV) Lewis acids, while warranting for a sufficient hydride ion affinity. Combined with a fitting Lewis base and suitable reaction conditions, first evidence for  $\text{H}_2$  activation with a tetrahedral Lewis acid is obtained by the isolation of a rare hydridosilicate.

## Results and Discussion

Numerous *ortho*-aminophenols have been reported, but highly electron-deficient derivatives are unknown.<sup>[20]</sup> *Bis*(perfluorophenyl)amine, prepared on a multigram scale from  $\text{LiNH}_2$  and  $\text{C}_6\text{F}_6$  in excellent yields (Figure 2a),<sup>[21]</sup> served as an ideal precursor. The implementation of the oxygen in *ortho* position was achieved via lithiation of the amine followed by conversion with propylene oxide to yield a benzoxazine motive.



**Figure 2.** a) Synthesis of *N*-pentafluorophenyl-*ortho*-aminophenol ( $\text{am}^F\text{ph}^F\text{H}_2$ ). b) Molecular structure of **1** (shown at 50% probability, co-crystallized  $\text{CH}_2\text{Cl}_2$  molecule is omitted for clarity; selected bond lengths and angles:  $\text{Si}-\text{O}/\text{Si}-\text{O}' = 1.6465(13)$  Å,  $\text{Si}-\text{N} = 1.7138(15)$  Å,  $\text{Si}-\text{N}' = 1.7138(16)$  Å,  $\text{O}-\text{Si}-\text{O} = 118.44(10)^\circ$ ,  $\text{N}-\text{Si}-\text{N} = 119.73(11)^\circ$ ).

Subsequent  $\text{AlI}_3$  mediated ether cleavage gave the desired *ortho*-aminophenol  $\text{am}^F\text{ph}^F\text{H}_2$  (perfluoro(*N*-phenyl-*ortho*-aminophenol)) on a multigram scale. Rapid and clean complexation of silicon occurred by reacting  $\text{am}^F\text{ph}^F\text{H}_2$  with the commercially available precursor  $\text{HSi}(\text{NMe}_2)_3$ , yielding the dimethylamino-adduct of target compound **1**. Reacting **1**-HNMe<sub>2</sub> with  $\text{HNTf}_2$  in toluene at elevated temperatures and extraction with *n*-pentane yielded a colorless solid with excellent solubility in common organic solvents.

$^1\text{H}$  NMR spectroscopy confirmed the absence of protons and  $^{19}\text{F}/^{29}\text{Si}$  NMR suggested the formation of a single species. The experimental  $^{29}\text{Si}$  NMR resonance ( $-40.6$  ppm) agrees with the computed value for donor-free **1** ( $-41.6$  ppm, see Supporting Information). sXRD analysis of single crystals from a concentrated  $\text{CH}_2\text{Cl}_2$  solution confirmed the molecular structure (Figure 1b). The monomeric nature and the absence of stabilizing donors constitute the first critical requirements for a reactivity towards nonpolar substrates. The computed fluoride and hydride affinities (FIA ( $494$   $\text{kJ mol}^{-1}$ ) and HIA ( $449$   $\text{kJ mol}^{-1}$ ), DLPNO-CCSD(T)/aug-cc-pVQZ//PBE0-D3(BJ)/def2-TZVPP level of theory, see Supporting Information) of **1** range its *global* Lewis acidity between  $\text{Si}(\text{cat}^{\text{Cl}})_2$  and  $\text{Si}(\text{cat}^{\text{F}})_2$ .<sup>[16a]</sup> Experimental assessment of the *effective* Lewis acidity was performed via the Gutmann-Beckett method, resulting in a  $^{31}\text{P}$  NMR resonance of  $83.3$  ppm ( $\Delta^{31}\text{P} = 33$  ppm), well in the range of the  $\text{Si}(\text{cat}^X)_2$  derivatives.<sup>[22]</sup> Reacting trityl chloride with **1** led to the quantitative formation of the trityl cation, allowing the isolation of  $[\text{CPh}_3][\text{1-Cl}]$ . Remarkably, this was not possible with the first-generation catecholato-based Lewis superacids due to the presence of stabilizing donors that are incompatible with the trityl ion. The Lewis superacidity of **1** was proven by reaction with  $[\text{PPh}_3][\text{SbF}_6]$  in dichloromethane. Within seconds the reaction mixture took a deep blue color and  $^{19}\text{F}$  NMR spectroscopy revealed a multitude of signals, likely associated with the oxidative properties of  $\text{SbF}_5$  in conjunction with the redox-active nature of *ortho*-aminophenols.

Upon conversion of **1** with  $\text{LiAlH}_4$  in THF-*d*<sub>8</sub>, a singlet in the  $^1\text{H}$  NMR with  $^{29}\text{Si}$  coupling ( $^1J_{\text{SiH}} = 319$  Hz) was observed.  $^1\text{H}$ - $^{29}\text{Si}$ -HMBC and  $^{29}\text{Si}$ -DEPT experiments supported the formation of a silicon-bound hydrogen, and the experimental  $^{29}\text{Si}$  NMR resonance at  $-98.2$  ppm is in excellent agreement with the computed shift of  $-98.2$  ppm for  $[\text{1-H}]^-$ . The hydridosilicate was isolated after adding 12-crown-4 as  $[\text{Li@12-crown-4}][\text{1-H}]$ . The molecular structure of  $[\text{1-H}]^-$  was confirmed by sXRD of suitable crystals from an  $\text{Et}_2\text{O}/n$ -pentane solution (Figure S19). Notably, hydridosilicates of  $\text{Si}(\text{cat}^X)_2$  could never be isolated in our hands, but decomposition into  $\text{Si}(\text{cat}^X)_3^{2-}$  and  $\text{SiH}_4$  was indicated. Thus, this stability provided the second critical requirement for dihydrogen activation.

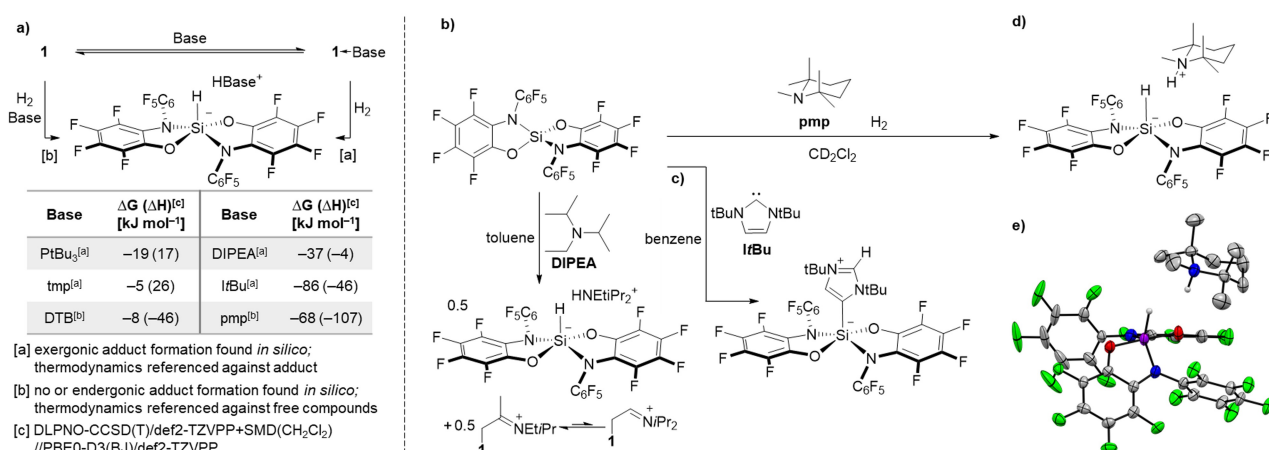
Hence, cleavage of dihydrogen was tested in presence of the Lewis bases tri(*tert*-butyl)phosphine ( $\text{PtBu}_3$ ), 2,2,6,6-tetramethylpiperidine (tmp), 2,6-ditertbutylpyridine (DTB), *N,N'*-diisopropyl-*N''*-ethylamine (DIPEA), the *N*-heterocyclic carbene (NHC) 1,3-di-*tert*-butyl-1,3-imidazol-2-ylidene (*ItBu*) and 1,2,2,6,6-pentamethylpiperidine (pmp). All experiments were accompanied by computation of the corresponding solution phase thermodynamics, and kinetics were evaluated for results

contradicting the experimental observations (Figure 3a). The Lewis bases tmp and PtBu<sub>3</sub> were calculated to form adducts with **1**, along with an endothermic H<sub>2</sub> activation. Accordingly, adduct formation was observed by NMR spectroscopy, and no H<sub>2</sub> activation was noticed up to 65 °C and 1 atm of H<sub>2</sub> pressure in dichloromethane experimentally. DTB seemed a more promising candidate, as no adduct formation with **1** and an exergonic activation process was predicted *in silico*.

No adduct formation between DTB and **1** was observed experimentally, but H<sub>2</sub> activation remained still unsuccessful under various conditions. We attribute this fact to the pronounced steric congestion of the Lewis base, excluding the formation of an active pocket in the encounter complex.<sup>[23]</sup> Hence, the shape of the Lewis base rendered as crucial, and had to be tuned. For the amine base DIPEA, calculations suggested only weak dative adduct formation and significant exergonic nature of the H<sub>2</sub> cleaving process. Upon adding an equimolar amount of DIPEA to a solution of **1** in toluene, NMR spectroscopic characterization showed the formation of the hydrosilicate already without exposure to dihydrogen. Dehydrogenation of DIPEA itself occurs, leading to 0.5 equiv. of the formal H<sub>2</sub> splitting product ion pair, and the formed enamine yielding an adduct with remaining **1** (Figure 3b). Similar findings were reported for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>[24]</sup> and calculations underpinned the proposed reactivity (see Supporting Information). No further conversion to [1-H]<sup>-</sup> was noted upon pressurizing with dihydrogen and heating. Next, the NHC ItBu was chosen, encouraged by successful reactivity with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and the computed highly favorable thermodynamics (Figure 3a).<sup>[25]</sup> However, similarly to the boron Lewis acid and as reported for a spirosilane,<sup>[26]</sup> the abnormal NHC adduct formed as a dead-end product (Figure 3c, verified by scXRD).

Lastly, the reactivity with pmp was explored. Calculated energies for the FLP pmp/**1** suggested the absence of adduct formation and a significant exergonic and exothermic dihydrogen activation process. A mixture of the Lewis pair gave a

<sup>29</sup>Si NMR signal assignable to unbound **1**, in line with the absence of a classical adduct, while NMR-signal broadening indicated tractable encounter complex formation. Still, experiments conducted at 1 atm H<sub>2</sub> and ambient temperature over several days revealed no indication of H<sub>2</sub> activation. Given the calculated highly exergonic thermodynamics, we suspected kinetic effects as the origin. Hence, equimolar amounts of **1** and pmp were dissolved in oDCB and the mixture was exposed to 1 atm H<sub>2</sub> and heated to 115 °C. Indeed, after 2 d, the cation [pmpH]<sup>+</sup> was formed to 45% (judged by internal integration) and a novel singlet at 6.14 ppm emerged in the <sup>1</sup>H NMR spectrum. After a total heating period of 8 d at 115 °C, the proportion of [pmpH]<sup>+</sup> compared to the free amine was 64%. The singlet of [1-H]<sup>-</sup> in the <sup>1</sup>H NMR spectrum was accompanied by <sup>29</sup>Si coupling (<sup>1</sup>J<sub>SiH</sub> = 313 Hz), and a resonance at -96.4 ppm in the <sup>29</sup>Si NMR. Since <sup>19</sup>F NMR spectra showed side products, a reactivity tuning towards milder reaction conditions was attempted. A tenfold excess of pmp to **1** allowed the formation of [1-H]<sup>-</sup> already at 65 °C under 1 atm H<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>. To our delight, the formation of the ammonium-hydrosilicate could be confirmed through scXRD analysis of suitable crystals grown by diffusion of *n*-pentane into the reaction mixture at -40 °C (Figure 3d). Contaminations in the solid-state products revealed the fluoro-adduct of **1**, potentially the product of hydro-defluorination of the perfluorinated aromatics by the hydrosilicate.<sup>[27]</sup> Raising the excess of Lewis base to 100 equivalents, again utilizing 1 atm H<sub>2</sub>, allowed the reaction to proceed after 20 h at rt to a conversion of 13%. When cautiously increasing the temperature to 40 °C, a continuous increase of the [1-H]<sup>-</sup> resonance was apparent, revealing a reaction progress to 71% after 7 d, with almost absent products from side reactions. The origin of both the proton and the hydride was verified using deuterium gas under the optimized conditions (see Supporting Information, section 2.4). Control experiments excluded an iminium Lewis acid (formed by hydride abstraction from pmp) as the active species. Computation of



**Figure 3.** a) Computationally derived thermodynamic data for dihydrogen cleavage of **1** with different Lewis bases; for Lewis bases with favorable adduct formation, thermodynamic data is referenced against the adduct, for Lewis bases that form endergonic adducts, against the free compounds. b) Dehydrogenative enamine formation from DIPEA by **1**. c) Formation of an 'abnormal' adduct of **1** and ItBu. d) Dihydrogen cleavage through **1** and pmp, see main text for description of conditions. e) scXRD derived structure of the activation product (for details see Supporting Information, shown at 50% probability, carbon bound hydrogens omitted for clarity).

the reaction energy profile supports the experimental findings. Under standard conditions, an encounter complex of **1** and pmp forms with  $\Delta G_{\text{soliv}} = -10 \text{ kJ mol}^{-1}$ , which can be attributed to the very favorable attractive non-covalent interaction (see Figure S13 for NCI-plot). Against this structure as energetic reference point, the kinetic barrier for dihydrogen cleavage was calculated to be  $79 \text{ kJ mol}^{-1}$ . Interestingly, this barrier conflicts with the experimentally observed slow reaction rate, emphasizing critical effects of temperature, solvent, concentration, and entropy that computations do not reflect.

## Conclusion

The mechanism of  $\text{H}_2$  activation with *planar* Lewis acids has been studied in great detail in recent years.<sup>[28]</sup> The characteristics of the  $\text{H}_2$  activation found in the present work allows to judge the challenges imposed by the use of a *tetrahedral* Lewis acid. A first hurdle emerges from the necessity of deformation—a factor that is not encountered with planar Lewis acids. The substantial deformation energy of silanes<sup>[29]</sup> prohibits the formation of an encounter complex with an “active” cavity,<sup>[30]</sup> including the inability to span a sufficient electric field.<sup>[31]</sup> For a nominal termolecular reaction such as FLP-dihydrogen activation, this entropic penalty has been detrimental in earlier attempts. Second, the reaction conditions are decisive. Elevated temperatures are needed to surpass the  $\text{H}_2$ -splitting barrier, but simultaneously disfavor the formation of the weakly associated encounter complex. By consequence, the reaction features a very narrow temperature range for a successful transformation. Notably, an excess of the Lewis base has been found very favorable, which can be attributed to a higher concentration of the productive encounter complex. Overall, the obstacles that had to be addressed illustrate the fragile line for a successful  $\text{H}_2$  activation with a tetrahedral Lewis acid. Despite this success, numerous questions remain open until a structure-reactivity relation can be presented for this hallmark reaction, 16 years after its discovery.

## Experimental Section

**Synthesis of bis(perfluoro(*N*-phenyl-*ortho*-amidophenolato) silane (Si(am<sup>+</sup>ph<sup>-</sup>))<sub>2</sub>, **1**):** A solution of 1-HNMe<sub>2</sub> (765 mg, 1.0 equiv.) in toluene (10 mL) was heated to 85 °C. At this temperature, a solution of HNTf<sub>2</sub> in toluene (2 mL) was added dropwise over 15 min. The reaction mixture was further stirred for three hours at 85 °C and then cooled to room temperature. The solvent was removed *in vacuo* and *n*-pentane (10 mL) was added to the viscous residue. The mixture was rigorously stirred for 5 min and then filtered. This step was repeated two times. The combined *n*-pentane extracts were concentrated *in vacuo* to give a colorless solid (585 mg, 81%). Further purification was achieved through recrystallization from DCM (~2.5 mL) at -40 °C (repeated once) to yield a colorless, crystalline solid (557 mg, 77%). Colorless crystals suitable for scXRD developed from a saturated dichloromethane solution at ambient temperature. <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 145.2 (d, <sup>1</sup>J<sub>CF</sub> = 253 Hz, CF), 144.9 (d, <sup>1</sup>J<sub>CF</sub> = 253 Hz, CF), 141.9 (d, <sup>1</sup>J<sub>CF</sub> = 257 Hz, CF), 138.4 (d, <sup>1</sup>J<sub>CF</sub> = 253 Hz, CF), 138.2 (d, <sup>1</sup>J<sub>CF</sub> = 251 Hz, CF), 137.9 (d, <sup>1</sup>J<sub>CF</sub> = 251 Hz, CF), 137.3 (d, <sup>1</sup>J<sub>CF</sub> = 248 Hz, CF), 137.0 (d, <sup>1</sup>J<sub>CF</sub> = 249 Hz, CF), 136.6 (d,

<sup>1</sup>J<sub>CF</sub> = 249 Hz, CF), 129.6 (CO), 120.6 (CN), 111.7 (CN). <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -146.8 (d, <sup>3</sup>J<sub>FF</sub> = 22.7 Hz, 2F), -147.7 (m, 2F), -153.0 (t, <sup>3</sup>J<sub>FF</sub> = 21.4 Hz, 2F), -160.6 (td, <sup>3</sup>J<sub>FF</sub> = 22.0 Hz, <sup>4</sup>J<sub>FF</sub> = 4.2 Hz, 2F), -161.6 (dd, <sup>3</sup>J<sub>FF</sub> = 20.8 Hz, <sup>4</sup>J<sub>FF</sub> = 7.9 Hz, 2F), -161.8 (m, 2F), -164.8 (m, 4F), -165.9 (td, <sup>3</sup>J<sub>FF</sub> = 20.7 Hz, <sup>4</sup>J<sub>FF</sub> = 5.7 Hz, 2F). <sup>29</sup>Si NMR (119 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -40.6. HRMS EI+ (*m/z*) calc. for C<sub>15</sub>H<sub>6</sub>F<sub>9</sub>NO [M]<sup>+</sup>, 717.9436; found 717.9467 (9%), deviation 4.23 ppm; calc. for C<sub>12</sub>H<sub>2</sub>F<sub>9</sub>NO [am<sup>+</sup>ph<sup>-</sup>H<sub>2</sub>]<sup>+</sup>, 346.9987; found 346.9994 (100%), deviation 2.02 ppm. **Elemental analysis** calc. C 40.13%, N 3.90%. found C 39.56%, N 4.08%.

**General procedure for experiments with Dihydrogen:** Unless stated otherwise, in a N<sub>2</sub>-Glovebox, **1** and the corresponding Lewis base were dissolved in CD<sub>2</sub>Cl<sub>2</sub> in a *J. Young* NMR tube. The mixture was frozen in liquid nitrogen, the vessel evacuated and then charged with 1 atm H<sub>2</sub> (additionally dried over a column of P<sub>4</sub>O<sub>10</sub>) at 77 K before sealed and cautiously thawed.

**X-ray crystallography:** Deposition Number(s) 2181650 (for am<sup>+</sup>ph<sup>-</sup>C<sub>3</sub>H<sub>6</sub>), 2181653 (for 1-HNMe<sub>2</sub>), 2181652 (for 1·(CH<sub>2</sub>Cl<sub>2</sub>)), 2181651 (for 1-OPe<sub>3</sub>), 2181654 (for 1-ttBu<sup>isom</sup>), 2181656 (for [Li@12-crown-4][1-H]), 2181655 (for [pmpH][1-H(F)]) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** dihydrogen activation · frustrated Lewis pairs · Lewis superacid · reaction design · silicon

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