

Si–F Bond Activation

Bis(perfluoropinacolato)silane: A Neutral Silane Lewis Superacid Activates Si–F Bonds

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Dedicated to Professor Holger Braunschweig on the occasion of his 60th birthday

Abstract: Despite the earth abundance and easy availability of silicon, only few examples of isolable neutral silicon centered Lewis superacids are precedent in the literature. To approach the general drawbacks of limited solubility and unselective deactivation pathways, we introduce a Lewis superacid, based on perfluorinated pinacol substituents. The compound is easily synthesized on a gram-scale as the corresponding acetonitrile mono-adduct **1** (MeCN) and was fully characterized, including single crystal X-ray diffraction analysis (SC-XRD) and state-of-the-art computations. Lewis acidity investigations by the Gutmann-Beckett method and fluoride abstraction experiments indicate a Lewis superacidic nature. The challenging Si–F bond activation of Et₃SiF is realized and promising catalytic properties are demonstrated, consolidating the potential applicability of silicon centered Lewis acids in synthetic catalysis.

The investigations of molecular main group element Lewis acids for bond activation and catalysis has drawn much attention.^[1] Especially cationic silylium ions and silyliumylidenes have demonstrated exceptional catalytic abilities including hydrosilylation^[2] or hydrodefluorination reactions,^[3] thus moving the second most abundant element of the earth's crust into the reach of industrial relevance.^[4] To overcome the poor functional group tolerance and mostly limited solubility of cationic silicon reagents, the use of neutral, silicon-centered Lewis acids is highly desirable. Initial reports inspired by the research of Denmark and co-workers revealed the suitability of SiCl₄ as a potent co-catalyst for specific reactivities including aldol additions^[5] and aza-

Michael additions.^[6] However, due to the easily cleaved Si–Cl bond, examples of SiCl₄-catalyzed reactions remained rather rare. To prevent bond cleavage and elimination reactions, neutral, silicon-centered Lewis acids were realized by the installation of strongly electron withdrawing, mostly aryl and alkyl, substituents.^[7] Using a perfluorinated catecholato ligand, Tilley and Bergmann et al. were able to isolate a strongly Lewis acidic silane that was successfully applied in the hydrosilylation catalysis of electron deficient aldehydes.^[8] By a slight variation of the catecholato system using less π -back donating chloride and bromide substituents, the isolation of the first Lewis superacidic silanes was achieved (Figure 1),^[9] which possess formal fluoride ion affinities (FIAs) exceeding that of SbF₅ (definition of Lewis superacidity).^[10] The very recently reported bis(pertrifluoromethylcatecholato)silane displayed an even stronger Lewis acidity and broadened the catalytic portfolio of Lewis acidic silanes by the reductive dialkyl ether formation, deoxygenation of several substrates and a carbonyl-olefin metathesis reaction.^[11b] Still, this compound class suffers from poor solubility. This issue was addressed by the hard and soft Lewis superacidic silicon tetrakis(trifluoromethanesulfonate).^[11a] Despite its remarkable reactivity and improved solubility, so far no catalytic but only stoichiometric reactions were reported for this compound, potentially caused by the rather labile Si–OTf bond nature.

To overcome undesired side reactions and to stabilize the highly electron deficient Si^{IV} center by steric protection, we investigated the incorporation of bulky as well as strongly electron-withdrawing perfluoropinacolato groups as suitable substituents for the synthesis of Lewis acids. In this regard, we present the straight-forward synthesis and characterization of a novel and easy to handle, neutral silicon-centered Lewis superacid, its exceptional catalytic activity, and its ability to

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<https://doi.org/10.1002/anie.202110980>.

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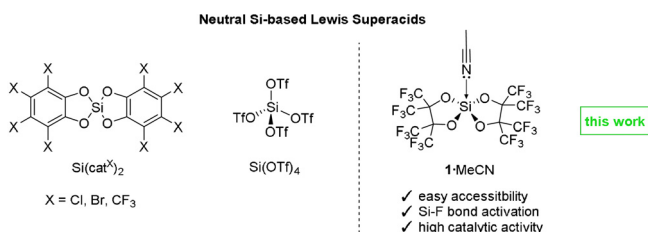


Figure 1. Literature known neutral, silicon-centered Lewis superacids (left)^[9,11] and the catalytically active Lewis superacid **1** (MeCN), presented in this work.

abstract fluorides even from neutral fluorosilanes. State-of-the-art computations support the experimental findings.

In a first reaction, perfluoro pinacol (H_2pin^F) was lithiated by deprotonation with $n\text{BuLi}$ to obtain the more nucleophilic lithium salt Li_2pin^F . For the introduction of the strongly electron withdrawing perfluoro pinacol moiety onto a Si^{IV} center, Li_2pin^F was reacted with SiCl_4 and HSiCl_3 , respectively, in acetonitrile solution. In both cases the precipitation of LiCl was observed shortly after the silane was added. The reaction mixtures were stirred at 85°C for three hours to ensure the complete formation of the monomeric reaction products. Subsequent filtration, and solvent removal in vacuo in both cases yielded colorless solids that could be assigned to the ionic compounds $\text{Li}[\mathbf{1}\text{-Cl}]$ (for SiCl_4) and $\text{Li}[\mathbf{1}\text{-H}]$ (for HSiCl_3), coordinated by residual acetonitrile.

The obtained pentavalent silicate species were characterized using NMR spectroscopic methods. The ^1H NMR spectrum of $\text{Li}[\mathbf{1}\text{-Cl}]\cdot(\text{MeCN})_2$ in CD_3CN gave a singlet at $\delta = 1.96$ ppm that was attributed to the coordinating non-deuterated solvent. Two multiplets in the ^{19}F NMR spectrum at $\delta = -69.0$ to -69.2 ppm and $\delta = -69.9$ to -70.2 ppm indicated the presence of diastereotopic CF_3 moieties, in line with the symmetry of a pentacoordinate state. The ^{29}Si NMR spectrum gave a singlet at $\delta = -93.26$ ppm matching chemical shifts of related pentavalent chloride-substituted silicate species, obtained by Greb and co-workers,^[9,11b] showing a distinct downfield-shift compared to penta-alkoxy substituted silicates given in the literature.^[12]

The ^1H NMR spectrum of $\text{Li}[\mathbf{1}\text{-H}]\cdot(\text{MeCN})_2$ gave an additional multiplet at $\delta = 4.52$ to 4.45 ppm that was attributed to the hydride substituent on the silicon center. The integral ratio between the acetonitrile proton and the hydride signal suggested a twofold coordination by the solvent. The ^{19}F NMR spectrum showed a similar but distinctively up-field shifted pattern, compared to $\text{Li}[\mathbf{1}\text{-Cl}]\cdot(\text{MeCN})_2$, by giving two multiplets at $\delta = -69.9$ to -70.2 ppm and $\delta = -70.7$ to -70.9 ppm. The singlet in the ^{29}Si NMR spectrum at $\delta = -90.19$ ppm was slightly shifted, but still within the expected range for pentavalent silicate species. Both structural motifs were supported by ^{29}Si NMR shift computations and ultimately confirmed by SC-XRD analysis. (see the supporting information). The formal activation of LiCl in $\text{Li}[\mathbf{1}\text{-Cl}]$, and LiH in $\text{Li}[\mathbf{1}\text{-H}]$, salts of high lattice energy, indicates a strong Lewis acidity of the targeted neutral bis(perfluoropinacolato)silane $\mathbf{1}$. In particular, the stability of $\text{Li}[\mathbf{1}\text{-H}]$ renders remarkable, in light of the instability of hydrosilicates based on the catecholate ligand.^[14]

By the sublimation of $\text{Li}[\mathbf{1}\text{-Cl}]\cdot(\text{MeCN})_2$ at elevated temperatures in fine vacuo, the neutral silane was released as the acetonitrile adduct $\mathbf{1}\cdot(\text{MeCN})$, which was isolated in moderate to good yields (Figure 2). Attempts to remove the residual coordinating solvent by additional sublimation or azeotropic distillation with less coordinating solvents, however, remained unsuccessful so far. The obtained $\mathbf{1}\cdot(\text{MeCN})$ was well soluble in CD_3CN and could be characterized using NMR spectroscopic methods. The ^1H NMR spectrum gave a singlet that was attributed to the solvent molecule. Further NMR experiments revealed two partially overlaying broad

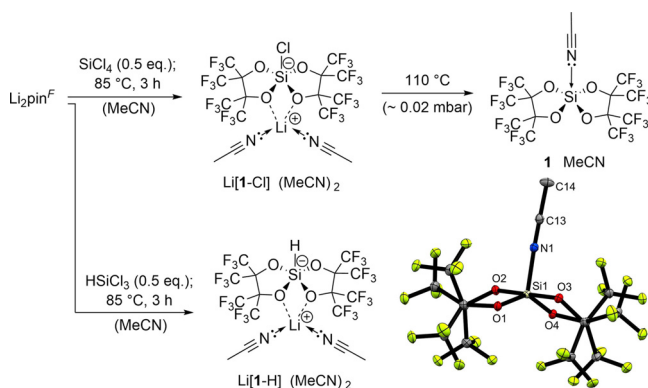


Figure 2. Left: Performed synthesis strategy yielding pentavalent silicate species $\text{Li}[\mathbf{1}\text{-Cl}]\cdot(\text{MeCN})_2$ and $\text{Li}[\mathbf{1}\text{-H}]\cdot(\text{MeCN})_2$ and the neutral Lewis superacidic silane $\mathbf{1}\cdot(\text{MeCN})$ as the acetonitrile mono-adduct. Right: Molecular structure of $\mathbf{1}\cdot(\text{MeCN})$ obtained by SC-XRD analysis (ellipsoids at 50% probability level). Selected bond lengths (Å): Si1–N1 1.8412(16), Si1–O1 1.6745(14), Si1–O2 1.7223(14), Si1–O3 1.7234(14), Si1–O4 1.6886(14).^[13]

multiplets at $\delta = -69.5$ to -70.6 ppm in the ^{19}F spectrum and a singlet at $\delta = -110.34$ ppm in the ^{29}Si spectrum.

The solid-state IR spectrum revealed two strongly overlapping signals at 2358 cm^{-1} and 2329 cm^{-1} that are assigned to the $\text{C}\equiv\text{N}$ stretching coupled to CH_3 -deformation vibrations of strongly coordinating acetonitrile. The coordinating CH_3CN was substituted with CD_3CN leading to only one sharp signal at 2352 cm^{-1} , that could be assigned to the blue-shifted $\text{C}\equiv\text{N}$ stretching vibration. The observed shift of 94 cm^{-1} with respect to the free CD_3CN (2258 cm^{-1})^[15] indicated an outstandingly high Lewis acidity, even exceeding literature known examples of acetonitrile adducts of Lewis superacids $\text{Si}(\text{cat}^F)_2$,^[9a] $\text{Al}(\text{OTeF}_5)_3$,^[15] and SbF_5 .^[16]

To further investigate the Lewis acidity by the Gutmann-Beckett method, $\mathbf{1}\cdot(\text{MeCN})$ was reacted with stoichiometric amounts of Et_3PO in non-polar solvent CD_2Cl_2 . Subsequent ^{31}P NMR analysis revealed the formation of the phosphine oxide monoadduct $\mathbf{1}\cdot\text{OPEt}_3$ with a ^{31}P shift of $\Delta\delta = 35.8$ ppm. This result is in good agreement with literature-known electron deficient silanes like $\text{Si}(\text{cat}^F)_2$ ($\Delta\delta = 36.1$ ppm) and even the Lewis superacidic $\text{Si}(\text{cat}^F)_2$ ($\Delta\delta = 36.7$ ppm).^[9b] In contrast to related silanes holding halogenated catechol derivatives or triflate substituents, no bis-adduct formation was observed in case of $\mathbf{1}\cdot(\text{MeCN})$,^[9,11] even when surplus Et_3PO amounts were added (up to 3.0 equiv.).

For a closer structural investigation, single crystals suitable for SC-XRD analysis were obtained by recrystallization from toluene.^[13] The obtained structure shows a pentavalent, square pyramidal coordination of Si1 by two pinacolato groups and a terminal acetonitrile molecule. The extreme close Si1–N1 bond length of $1.8412(16)\text{ Å}$ surpasses literature known acetonitrile adducts of aluminum-based Lewis superacid $\text{Al}(\text{OCa}^F)_3$ ($1.9431(11)\text{ Å}$)^[17] and matches bond lengths reported for silylium ion-MeCN adducts (1.864 to 1.847 Å).^[18] To our knowledge, this represents the first MeCN-adduct of a neutral silicon-based Lewis acid confirmed by SC-XRD. The steric protection of the pinacolato groups is demonstrated by a slightly bent geometry with

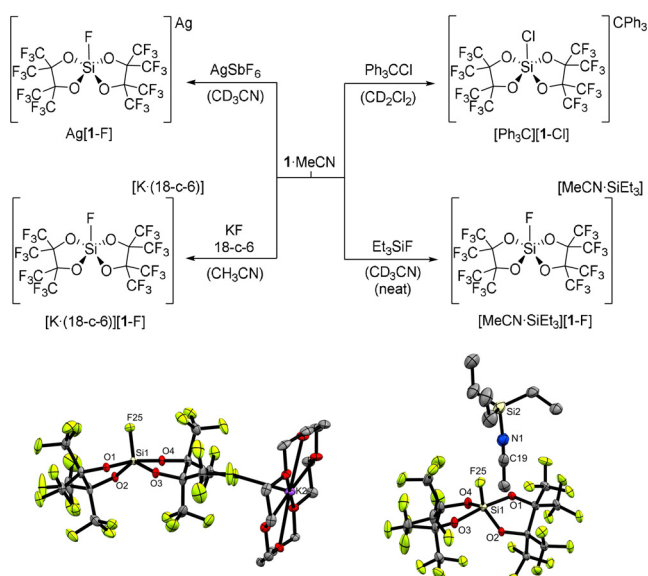


Figure 3. Top: Reactivity experiments of **1**·(MeCN) showing the successful fluoride abstraction from AgSbF₆ confirming formal Lewis superacidity. Halide abstraction was also observed for KF, Et₃SiF and trityl chloride. Bottom: Crystal structures (50% probability level) obtained by diffraction analysis of reaction products with KF and Et₃SiF.^[13]

diagonal bond angles O1-Si1-O4 and O2-Si1-O3 of 136.31(7)^o and 179.60(7)^o.

To investigate potential Lewis super acidity, **1**·(MeCN) was reacted with AgSbF₆ in acetonitrile solution (Figure 3 top). Already after 10 minutes at room temperature the ¹⁹F NMR spectrum showed nearly quantitatively consumption of the starting material. Instead, the formation of the pentavalent [**1-F**]⁻ anion was observed, thus confirming Lewis superacidity by experiment (FIA > SbF₅). The computed FIA (474 kJ mol⁻¹, DLPNO-CCSD(T)/aug-cc-pVQZ) did not exceed that of SbF₅, but suggested additional effects are supporting the thermodynamics of this reaction in experiment. Still, **1**·(MeCN) thus extends the rare class of experimentally confirmed neutral Si^{IV} Lewis superacids by a well-defined and well-soluble derivative. The pentavalent [**1-F**]⁻ silicate species was additionally synthesized by the reaction of **1**·(MeCN) with KF in the presence of the crown ether 18-c-6. The ¹⁹F NMR spectrum matched the pattern obtained from isolated Ag[**1-F**] showing two split multiplets at δ = -69.8 to -70.1 ppm and δ = -70.8 to -71.1 ppm for the CF₃ moieties as well as a smaller multiplet at δ = -138.6 to -138.9 ppm corresponding to the silicon bound fluoride. The ²⁹Si NMR spectrum gave a doublet at δ = -108.37 ppm with a silicon-fluoride coupling constant of ¹J_{Si,F} = 179.8 Hz. Single crystals suitable for SC-XRD analysis were obtained from a saturated solution in chloroform at -30 °C.^[13] The [**1-F**]⁻ anion shows a pentavalent square pyramidal structure of the central silicon atom by two perfluoropinacolato groups and one fluoride with bond lengths of 1.592(2) Å for the Si-F bond and 1.698 to 1.740 Å for the Si-O bonds. The pinacolato substituents are slightly bent towards each other with bond angles of 169.82(11)^o

(O1-Si1-O4) and 133.11(11)^o (O2-Si1-O3) in the *trans* position, respectively.

The addition of Ph₃CCl to a CD₂Cl₂ solution of **1**·(MeCN) immediately led to the formation of a triphenyl carbenium ion, which was indicated by rapid color change yielding a luminous yellow solution. ¹⁹F and ²⁹Si NMR spectroscopic analyses of the reaction mixture after 24 hours revealed the quantitative formation of the pentavalent [**1-Cl**]⁻ species, matching the pattern of previously synthesized Li[**1-Cl**]⁻·(MeCN)₂.

The most remarkable testimonial of the high fluoride ion affinity was provided by the neat reaction of **1**·(MeCN) with stoichiometric Et₃SiF. After 10 minutes at room temperature complete conversion was observed in the ¹⁹F NMR spectrum showing quantitative formation of the [**1-F**]⁻ pattern. The ²⁹Si NMR analysis gave the characteristic doublet at δ = -108.37 ppm and an additional singlet at δ = +36.63 ppm that was assigned to the Et₃Si⁺ ion coordinated by acetonitrile.^[19] This observation was confirmed by SC-XRD analysis of single crystals obtained from saturated CH₂Cl₂ solution at -30 °C (Figure 3 bottom).^[13] The crystal structure reveals the presence of the [**1-F**]⁻ anion located directly next to a Et₃Si⁺ cation, that is coordinated by an acetonitrile molecule with a Si-N bond length of 1.826(3) Å. As already indicated by NMR, the anion showed the exact same pentavalent binding motif that was already observed for the potassium derivative [K-18-c-6][**1-F**]. The abstraction of the fluoride to form a silylium ion coordinated by acetonitrile confirms an exceptionally high Lewis acidity of **1**·(MeCN). Although the FIA of **1** is lower than those of silylium ions (see SI), the overall process is driven by the favorable thermodynamics of the binding of the silylium ion to acetonitrile, and the salt formation between [**1-F**]⁻ and [MeCN·SiEt₃]⁺. This was additionally confirmed by favorable solvation corrected DSD-BLYP-D3/def2-QZVPP computed thermodynamics for the reaction (see section 3 in the SI). Si-F bonds are among the most stable single bonds, and their activation

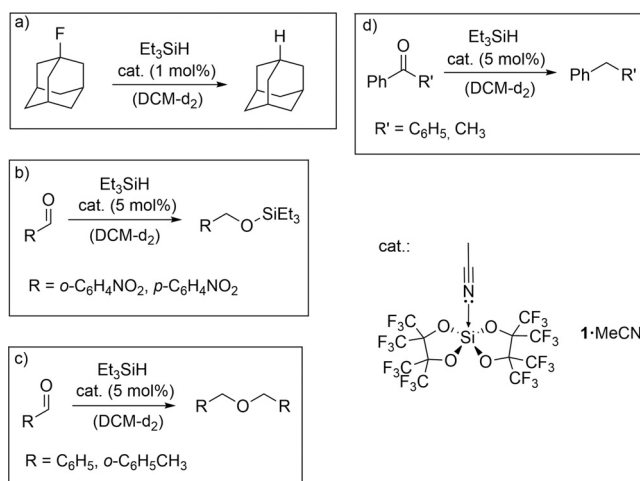


Figure 4. Reactivity investigations using **1**·(MeCN) as Lewis acid catalyst showing successful hydrodefluorination of 1-fluoroadamantane (a), hydrosilylation of *o*- and *p*-nitrobenzaldehyde (b), reductive dialkyl ether formation of benzaldehyde and *o*-methyl benzaldehyde (c) and deoxygenation of benzophenone and acetophenone (d).

represents a formidable challenge, even for transition metal complexes.^[20]

Inspired by the strong fluoride affinity, compound **1**·(MeCN) was investigated as potential catalyst for the stoichiometric hydrodefluorination (HDF) of 1-fluoroadamantane with Et₃SiH using low catalyst loadings of 1 mol % (Figure 4a). After two hours at room temperature quantitative conversion was observed in the ¹⁹F NMR spectrum by the absence of the fluoroadamantane signal and the selective formation of Et₃SiF. While this reaction is well known for silylium cations,^[3,21] examples for neutral Lewis acidic silanes as a catalyst are rare. To our knowledge, only the perhalogenated Lewis superacids Si(cat^X)₂ (X = Cl, Br) show a comparable reactivity, but with longer reaction periods required.^[9] The observed reactivity prompted us to further investigate the HDF reactivity by using the terminal 1-fluoropentane as a substrate. In this case, however, fluoride abstraction led to dehydrodefluorination indicated by immediate hydrogen evolution. Subsequent isomerization led to an unselective mixture of pentene isomers and unreacted starting material. No HDF could be observed, as it was also reported for Si(cat^{Cl})₂.^[9a]

In analogy to previously reported Si(cat^F)₂, **1**·(MeCN) was investigated as catalyst (5 mol %) for the hydrosilylation of electron deficient *p*- and *o*-nitrobenzaldehyde using Et₃SiH (Figure 4b). In both cases complete silane conversion was observed already after 20 minutes at room temperature in CD₂Cl₂, selectively yielding the respective hydrosilylation products. After longer reaction periods, a subsequent reaction occurred, partially turning the hydrosilylation products into the respective dialkyl ethers.^[22] As the side product hexaethylidisiloxane was liberated during this reaction.

When using non-electron-deficient benzaldehyde and *o*-methylbenzaldehyde in the same experimental setup but with 1.5 equiv. of Et₃SiH, no hydrosilylation could be observed at all (Figure 4c). Instead, the immediate selective formation of the respective dialkyl ethers was favored. A similar reactivity was observed for the recently published Si(cat^{CF₃})₂.^[11b]

Reaction with benzophenone and even acetophenone rapidly yielded deoxygenation products when 3.0 equiv. of Et₃SiH and 5 mol % of catalyst **1**·(MeCN) were used (Figure 4d). In case of benzophenone nearly complete and selective conversion was detected in the ¹H NMR spectrum already after 2 hours at room temperature using only a catalyst loading of 1 mol %. For more challenging acetophenone a catalyst loading of 5 mol % led to quantitative conversion within 1 hour at room temperature.

In summary, we have extended the exclusive club of silicon-centered Lewis superacids by the straightforward synthesis of **1**·(MeCN), which was successfully tested for the fluoride abstraction from SbF₆⁻. The compound holds the rare ability to bind hydrides, granting access to the respective tetraoxy-substituted hydridosilicate. Further experiments revealed the fluoride abstraction from stoichiometric Et₃SiF in the presence of acetonitrile. Si–F bond activation in tetravalent fluorosilanes remains a significant challenge, ironically now achieved with a silicon-based Lewis acid. Finally, **1**·(MeCN) was successfully tested in the catalytic hydrodefluorination of 1-fluoroadamantane, hydrosilylation

of electron deficient aldehydes, reductive dialkyl ether formation of benzaldehydes and deoxygenation of ketones. With its easy accessibility and catalytic versatility **1**·(MeCN) represents a highly promising reagent that once again contributes to the overall aim of transition metal-free catalysis for a more ecologic future.

Acknowledgements

We are exceptionally grateful to the WACKER Chemie AG for the idealistic and financial support, as well as contributions in guidance and discussions, which enabled us to carry out this research project. We also thank Lena Staiger (Prof. R. A. Fischer) for conducting IR measurements. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: main-group catalysis · perfluoropinacol · Si-F activation · silicon Lewis superacid · silicon mediated catalysis

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Manuscript received: September 24, 2021

Accepted manuscript online: September 27, 2021

Version of record online: November 5, 2021