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

Florian S. Tschernuth, Thaddäus Thorwart, Lutz Greb, Franziska Hanusch, and Shigeyoshi Inoue*

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. Especially cationic silylum ions and silyliumyldenes have demonstrated exceptional catalytic abilities including hydrolylation or hydrodefluorination reactions, thus moving the second most abundant element of the earth’s crust into the reach of industrial relevance. 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 investigated the incorporation of bulky as well as strongly electron-withdrawing perfluoropinacolato groups for the synthesis of Lewis acidic silanes by the reductive dialkyl ether formation, deoxygenation of several substrates and a carbonyl-olefin metathesis reaction. Still, this compound class suffers from poor solubility. This issue was addressed by the hard and soft 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. 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⁺⁺ 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 straightforward synthesis and characterization of a novel and easy to handle, neutral silicon-centered Lewis superacid, its exceptional catalytic activity, and its ability to activate Si–F bond nature.
abstract fluorides even from neutral fluorosilanes. State-of-the-art computations support the experimental findings.

In a first reaction, perfluoro pinacol (H(pin)\(^{2-}\)) was lithiated by deprotonation with \(\text{nBuLi}\) to obtain the more nucleophilic lithium salt Li(pin)\(^{2-}\). For the introduction of the strongly electron withdrawing perfluoro pinacol moiety onto a Si\(^{IV}\) center, Li(pin)\(^{2-}\) 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 Li[1-\(\text{Cl}\)] (for SiCl\(_4\)) and Li[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 Li[1-\(\text{Cl}\)](MeCN)\(_2\) in CD\(_3\)CN gave a singlet at \(\delta = 1.96\) ppm that was attributed to the coordinating non-deuterated solvent. Two multiplets in the \(^19F\) 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 \(^29Si\) 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.\(^{[10]}\)

The \(^1H\) NMR spectrum of Li[1-\(\text{H}\)](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 \(^19F\) NMR spectrum showed a similar but distinctively up-field shifted pattern, compared to Li[1-\(\text{Cl}\)](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 \(^29Si\) 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 \(^29Si\) NMR shift computations and ultimately confirmed by SC-XRD analysis. (see the supporting information). The formal activation of LiCl in Li[1-\(\text{Cl}\)], and LiH in Li[1-\(\text{H}\)], salts of high lattice energy, indicates a strong Lewis acidity of the targeted neutral bis(perfluoropinacolato)siylane \(\mathbf{1}\). In particular, the stability of Li[1-\(\text{H}\)] renders remarkable, in light of the instability of hydridosilicates based on the catecholate ligand.\(^{[14]}\)

By the sublimation of Li[1-\(\text{Cl}\)](MeCN)\(_2\) at elevated temperatures in fine vacuo, the neutral silane was released as the acetonitrile adduct I(\(\text{MeCN}\)), 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 I(\(\text{MeCN}\)) was well soluble in CD\(_3\)CN 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 multiplets at \(\delta = -69.5\) to \(-70.6\) ppm in the \(^19F\) spectrum and a singlet at \(\delta = -110.34\) ppm in the \(^29Si\) spectrum.

The solid-state IR spectrum revealed two strongly overlapping signals at 2358 \(\text{cm}^{-1}\) and 2329 \(\text{cm}^{-1}\) that are assigned to the \(\text{C} = \text{N}\) stretching coupled to \(\text{CH}_3\)-deformation vibrations of strongly coordinating acetonitrile. The coordinating CH\(_3\)CN was substituted with CD\(_3\)CN leading to only one sharp signal at 2352 \(\text{cm}^{-1}\), that could be assigned to the blue-shifted \(\text{C} = \text{N}\) stretching vibration. The observed shift of 94 \(\text{cm}^{-1}\) with respect to the free CD\(_3\)CN (2258 \(\text{cm}^{-1}\)) indicated an outstandingly high Lewis acidity, even exceeding literature known examples of acetonitrile adducts of Lewis superacids Si(cat\(^{2+}\))\(_2\),\(^{[9a]}\) Al(OTeF\(_5\))\(_3\),\(^{[15]}\) and SbF\(_5\).\(^{[16]}\)

To further investigate the Lewis acidity by the Gutmann-Beckett method, I(\(\text{MeCN}\)) was reacted with stoichiometric amounts of Et\(_3\)PO in non-polar solvent CD\(_3\)Cl. Subsequent \(^3P\) NMR analysis revealed the formation of the phosphine oxide monoadduct I(\(\text{OEP}\), with a \(\delta\) of 35.8 ppm. This result is in good agreement with literature-known electron deficient silanes like Si(cat\(^{2+}\))\(_2\) (\(\Delta\delta = 36.1\) ppm) and even the Lewis superacidic Si(cat\(^{2+}\))\(_2\) (\(\Delta\delta = 36.7\) ppm).\(^{[19]}\) In contrast to related silanes holding halogenated catechol derivatives or triflate substituents, no bis-adduct formation was observed in case of I(\(\text{MeCN}\)).\(^{[9,11]}\) even when surplus Et\(_3\)PO amounts were added (up to 3 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 SiI by two pinacolate groups and a terminal acetonitrile molecule. The extreme close Si1–N1 bond length of 1.8412(16) Á surpasses literature known acetonitrile adducts of aluminum-based Lewis superacid Al(OC\(_2\)Ar\(^{t}\))\(_3\) (1.9431(11) Á)\(^{[17]}\) and matches bond lengths reported for silylum ion-MeCN adducts (1.864 to 1.847 Á).\(^{[15]}\) 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 pinacolate groups is demonstrated by a slightly bent geometry with
(O1-Si1-O4) and 133.11(11)° (O2-Si1-O3) in the trans position, respectively.

The addition of Ph3CCI 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).[15] 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 [K18−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 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
hydrodefluorination of 1-fluoroadamantane, hydrosilylation of electron deficient tetravalent fluorosilanes remains a significant challenge, in the presence of acetonitrile. Si/C0 silicon-centered Lewis superacids by the straightforward conversion within 1 hour at room temperature. A catalyst loading of 5 mol% led to quantitative conversion was observed already after 2 hours at room temperature using only 1.5 equiv. of Et3SiH, no hydrosilylation could be observed at all (Figure 4d). In case of benzophenone nearly complete and selective conversion was detected in the 1H NMR spectrum after 2 hours at room temperature using only a catalyst loading of 1 mol %. For more challenging acetonitrile 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 SbF$_6^-$. The compound holds the rare ability to bind hydrides, granting access to the respective tetracoordinated hydroxidosilicate. Further experiments revealed the fluoride abstraction from stoichiometric Et$_3$SiF 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, hydrodefluorination 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.

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Conflict of Interest

The authors declare no conflict of interest.

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