A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201712155
Angew. Chem. 10.1002/ange.201712155

Link to VoR: http://dx.doi.org/10.1002/anie.201712155
http://dx.doi.org/10.1002/ange.201712155

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Bis(perchlorocatecholato)silane - A neutral silicon Lewis super acid

Rezisha Maskey, Marcel Schädler, Claudia Legler and Lutz Greb*[a]

Abstract: No neutral silicon Lewis super acids are known to date. We report on the synthesis of bis(perchlorocatecholato)silane and verify its Lewis super acidity by computation (DLPNO-CCSD(T)) and experiment (fluoride abstraction from SbF_6^-). The exceptional affinity towards donors is further demonstrated by e.g. the characterization of an unprecedented SiO_4F_2 dianion and applied in the first hydrodefluorination reaction catalyzed by a neutral silicon Lewis acid. Given the strength and convenient access to this new Lewis acid, versatile applications might be foreseen.

The success of molecular, main group element Lewis acids for the activation of inert bonds and catalysis evoked high research interests in recent years.[1] Especially the search for ever more powerful, yet bottleable and easy-to-handle, so-called *Lewis super acids* is an active field. The Lewis acidity is usually gauged by the fluoride ion affinity (FIA) and the threshold to Lewis super acidity was defined as the capability to abstract a fluoride ion from the monomeric SbF_6^- anion in the gas phase.[2] Unfortunately, most known Lewis super acids are not accessible in bulk quantities, hydrolyze under liberation of HF or are highly oxidizing. Several of these drawbacks have been overcome by the installation of fluorinated aryl, alkyl or pentafluoroorthotellurate substituents in boron,[3] aluminum,[2a, 4] arsenic[5] or phosphonium[6] species. Also for silicon(IV) as the central atom, strong neutral Lewis acids have been described (Figure 1). HOGE used pentafluoroethyl as electron-withdrawing substituents for the preparation of remarkably stable and strong silicon Lewis acids.[7] Bis(perfluorocatecholato)silane (*Si(cat^F)_2, cat^F* = *o*-$C_6F_4O_2$) was presented by TILLEY and applied in the catalytic hydrosilylation of aldehydes.[8] Yet, a neutral silicon Lewis super acid (FIA > SbF_5) is unprecedented so far. Herein, we describe a straightforward synthetic access to bis(perchlorocatecholato)silane **1** and verify its Lewis super acidity by experiment and quantum theory.

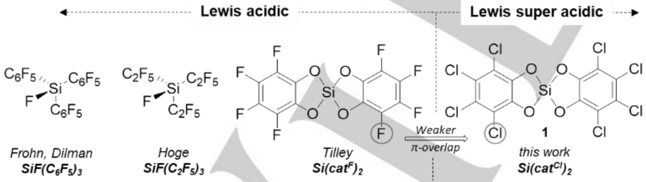

Figure 1. Previously studied strong neutral silicon Lewis acids and the herein presented Lewis super acid **1**.

More positive Hammett parameters denote more effective electron-withdrawal for substituents in aromatic systems. Although chlorine is not as electronegative as fluorine, its Hammett parameter ($\sigma_p^{Cl} = 0.227$) is much greater ($\sigma_p^{F} = 0.062$), as a result of weaker π-backbonding to the aromatic nucleus.[9] The aromatic *π*-electron density should be related to the electron deficiency at silicon in catecholato silanes, hence we expected the unknown bis(perchlorocatecholato)silane **1** to be more Lewis acidic than the perfluorinated derivative $Si(cat^F)_2$. Similar strategies led to very potent borane and antimony Lewis acids.[10] For an assessment of the impact of substituents on the Lewis acidity of neutral silicon(IV) species, the FIAs for strong silicon Lewis acids (Figure 1) and SiF_4 were determined computationally at the highly correlated and accurate DLPNO-CCSD(T)/aug-cc-pVQZ level of theory (see table 1, for all computational details, see SI).[11] Compared to SiF_4, (310 kJ mol^{-1}) the presence of perfluoroaryl ($SiF(C_6F_5)_3$, 361 kJ mol^{-1}) or perfluoroalkyl ($SiF(C_2F_5)_3$, 443 kJ mol^{-1}) groups increases the FIA significantly. The substitution with perhalogenated catechols ($Si(cat^F)_2$, 490 kJ mol^{-1}and **1**, 507 kJ mol^{-1}) boosts the FIA even more. However, only the aspired silane **1** exceeds the FIA of SbF_5, and thus qualifies it as a neutral silicon(IV) Lewis super acid. Not only the first FIA of **1** is remarkably high, but also its second FIA (71 kJ mol^{-1}), being 275 kJ mol^{-1} higher as for SiF_5^-. The theoretical results clearly revealed exceptional acceptor properties of **1** and prompted us for the experimental realization.

The CH_3CN adduct of **1** was readily accessible in a highly scalable 2-step procedure, starting from inexpensive bulk materials. Chlorination of catechol with H_2O_2/HCl according to literature[12] and the subsequent conversion with $HSiCl_3$ in CH_3CN led to the precipitation of **1**-$(CH_3CN)_2$ and the liberation of HCl and H_2 in a good overall yield (85%) at >3 g scale. Poor solubility in common organic solvents hampered solution phase analysis, but the formation of a *trans*-bisadduct **1**-$(CH_3CN)_2$ was strongly supported by elemental analysis, IR spectroscopy and DFT computations (see SI). The C≡N bond stretching mode in **1**-$(CH_3CN)_2$ (2335 cm^{-1}) is blue-shifted by 86 cm^{-1} with respect to free CH_3CN (2249 cm^{-1}), indicating high Lewis acidity.

Table 1. Computed 1st and 2nd fluoride ion affinities (FIAs) for selected neutral silicon(IV) Lewis acids and SbF_5.

Lewis Acid (LA)/LA-F$^-$/LA-F$_2^{2-}$	**FIA** (1st/2nd) [kJ mol^{-1}]^a
SiF_4 / SiF_5^- / SiF_6^{2-}	310/-204
$SiF(C_6F_5)_3$ / $SiF(C_6F_5)_3F^-$	361
$SiF(C_2F_5)_3$ / $SiF(C_2F_5)_3F^-$	443
$Si(cat^F)_2$ / $Si(cat^F)_2F^-$/ *cis*-$Si(cat^F)_2F_2^{2-}$	490/35
1 / **1**F$^-$ / *cis*-**1**F$_2^{2-}$	507/71
SbF_5 / SbF_6^-	501

[a] DLPNO-CCSD(T)/cc-aug-pVQZ//PW6B95-D3(BJ)/def2-TZVPP; for Sb atoms, the cc-aug-pwcVQZ-PP basis set was used. Enthalpies obtained by isodesmic reactions against G3/CBS anchor points (see SI).

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10.1002/anie.201712155

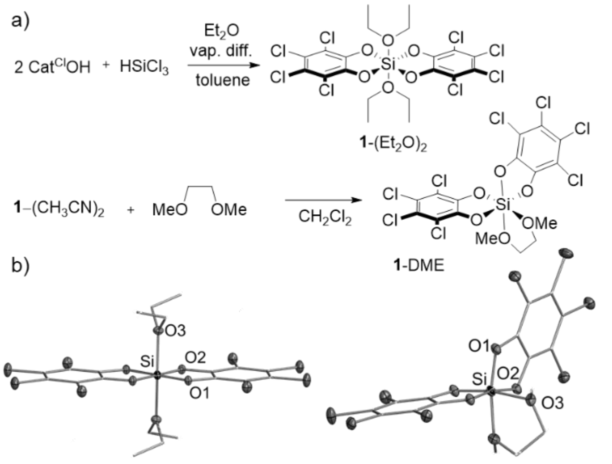

Figure 2. a) Formation of ether adducts of **1** together with b) the molecular structures obtained by X-ray diffraction (ellipsoids 50% probability, selected bond lengths [Å]) of **1**-$(Et_2O)_2$ (Si-O1 = 1.724(1), Si-O2 = 1.738(1), Si-O3 = 1.957(2)), **1**-(DME) (Si-O1 = 1.735(2), Si-O2 = 1.725(2), Si-O3 = 1.966(2)).

A similar blue-shift (86 cm^{-1}) was reported for the nitrile stretching mode in the $CH_3CN \rightarrow SbF_5$ adduct.[13] Further measurement of the Lewis acidity provided the ^{31}P-NMR shift difference (Δ^{31}P) upon complexation of $OPEt_3$ according to Gutmann-Beckett.[14] The addition of $OPEt_3$ to a suspension of **1**-$(CH_3CN)_2$ in CD_2Cl_2 led to a prompt dissolution of **1**-$(CH_3CN)_2$ and the liberation of 2 eq. of CH_3CN. ^{31}P- and ^{1}H-NMR spectroscopy, as well as ESI-MS(+) indicated a dynamic mixture of the three compounds **1**-$OPEt_3$, **1**-$(OPEt_3)_2$ and **1**$_2$-$(OPEt_3)_3$.[15] The monoadduct **1**-$OPEt_3$ revealed Δ^{31}P = 35 ppm, lying in accordance with the shift observed for $Si(cat)_2{}^F$ (36 ppm), and significantly above $B(C_6F_5)_3$ (26 ppm), whereas the shift in the bisadduct **1**-$(OPEt_3)_2$ indicated expectedly weaker acceptor ability (Δ^{31}P = 23 ppm). The nature of the bisadduct was proven by X-ray structural analysis, showing a hexacoordinated silicon with *trans* arranged phosphine oxides (see SI). Interestingly, these findings not only underline a strong Lewis acidity of **1**, but indicate also a stronger tendency towards hexacoordination compared to $Si(cat)_2$ and $Si(cat^F)_2$, for which only phosphine oxide monoadducts were observed.[8, 16]

Reaction of $HSiCl_3$ and perchlorocatechol in presence of Et_2O or displacement of acetonitrile from **1**-$(CH_3CN)_2$ with dimethoxyethane yielded ether adducts of **1** with hexacoordinate silicon (Figure 2a). The strong affinity towards such donors is remarkable for a neutral silicon(IV) species. The measured Si-O bond lengths indicate dative bonding for the ether oxygens towards silicon (1.957 Å in **1**-$(Et_2O)_2$, 1.966 Å in **1**-DME, Figure 2b). These distances are significantly shorter than in the two only known adducts of an acyclic ether with neutral silanes (e.g. 2.27 Å in H_3SiCl-Me_2O, stable only in the crystalline state at <100 K),[17] and rather bear resemblance to ether adducts of silylium cations.[18]

The ability of **1**-$(CH_3CN)_2$ to bind halide ions was further examined. Addition of one equivalent KF/18-crown-6 led to the formation of the fluorosilicate [**1**F][K@18-crown-6] (Figure 3a). Pentacoordination at silicon was supported by a doublet ($^{1}J_{SiF}$ = 196 Hz) at -105 ppm in the ^{29}Si-NMR spectrum and by X-ray diffraction. The Si-F bond length (1.606 Å) is analogous to the fluoride adduct of $Si(cat^F)_2$.[8] Addition of 2 eq. tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) led to the immediate formation of the bisfluorido(biscatecholato)silicate dianion [**1**F_2][$S(NMe_2)_3$]$_2$ (see Figure 3b), showing a triplet ($^{1}J_{SiF}$ = 152 Hz) at -155 ppm in the ^{29}Si-NMR spectrum. The number of peaks in the ^{13}C-NMR spectrum indicated a *cis*-arrangement of the fluoride substituents, in agreement with a computed lower energy relative to the *trans* isomer (see SI). The solid-state structural analysis revealed a *trans*-arrangement of the fluorides instead, with Si-F bond lengths of 1.686 Å. (*cf*. Na_2SiF_6 1.695 Å).[19] It stands thus in contrast to $Si(cat^F)_2$ and to the non-halogenated $Si(cat)_2$, where only the monoanions are accessible,[8, 20] and agrees with the computed high 2nd FIA for **1**. The solution and solid-state characterization of [**1**F_2][$S(NMe_2)_3$]$_2$ represent the first description of a dianionic SiO_4F_2 species to our knowledge and underlines the potential of the perchlorocatechol substituents to stabilize negative charge.

Addition of 1 eq. of bis(triphenylphosphine)iminium chloride ([PPN]Cl) to **1**-$(CH_3CN)_2$ led to the chloridosilicate [**1**Cl][PPN], a substance class made only recently accessible for the first time (Figure 3c).[21] A singlet at -90.4 ppm in the ^{29}Si-NMR spectrum and X-ray diffraction revealed pentacoordination at silicon.[22] More intriguingly, the addition of >1 eq. [PPN]Cl revealed the partial formation of an elusive dichlorosilicate dianion, as was visible by ^{13}C-NMR spectroscopy.[23] The chloride ion affinity was further shown by reaction of **1**-$(CH_3CN)_2$ with trityl chloride (Scheme 3d) causing immediate strong coloration of the solution to deep orange upon mixing. ^{1}H- and ^{13}C-NMR spectra unequivocally showed the partial (23%) formation of a trityl carbenium ion and at the same time, ^{29}Si- and ^{13}C-NMR spectra showed signals identical to the silicate anion in [**1**Cl][PPN].

The Lewis *super* acidity of **1** (as **1**-$(CH_3CN)_2$) was finally verified by reaction with either [NEt_4][SbF_6] or [PPh_4][SbF_6] at rt. In both cases, the initial formation of a silicate monofluoride was

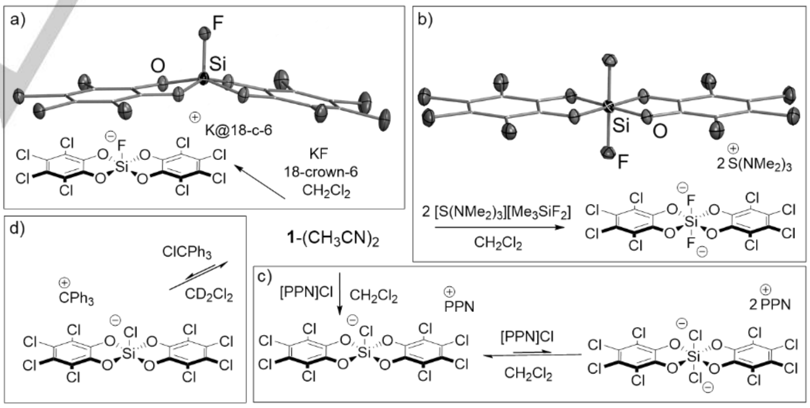

Figure 3: a,b) Fluoride ion additions **1**-$(CH_3CN)_2$ with molecular structures obtained by X-ray diffraction for [**1**F][K@18-crown-6] (Si-O = 1.738(1), Si-F = 1.606(1)) and [**1**F_2][$S(NMe_2)_3$]$_2$ (Si-O = 1.790(1), Si-F = 1.686(1), ellipsoids 50% probability, cations and solvent molecules are omitted for clarity) c) chloride ion additions to **1**-$(CH_3CN)_2$, d) chloride abstraction with **1**-$(CH_3CN)_2$ from tritylchloride.

observed (Figure 4a, $^{19}F/^{29}Si/^{13}C$-NMR spectra identical to [**1**-F][$S(NMe_2)_3$] and a strong signal of [**1**-F^-] in ESI-MS(-)). Due to ligand scrambling between silicon and antimony, the isolation of the intermediate species was not successful. However, and similar to reactions with PF_6^- salts (see SI for details), the finally identified product contained the tris(perchlorocatecholato)antimonate anion (see SI for X-ray diffraction), likely driven by the release of SiF_4 (for a proposed reaction scheme and the identification of all observed intermediates by ^{19}F-NMR/ESI-MS, see SI). Clearly, the neutral silicon Lewis acid **1** abstracts a fluoride ion from SbF_6^-, as the first necessary elementary step in the observed reaction cascade, serving as the experimental proof of its Lewis super acidity.[24] Importantly, in agreement with our computational results, no fluoride abstraction from [PPh_4][SbF_6] occurred with the weaker Lewis acid Si(cat^F)$_2$.

To demonstrate the utility of **1**-(CH_3CN)$_2$ in catalysis, C(*sp*^{3})-F bond activation for hydrodefluorination (HDF) was attempted – processes well performed by silylium cations, but with no precedence for neutral silicon species as a catalyst.[1c, 25] Indeed, the HDF of 1-adamantylfluoride proceeded cleanly to full conversion applying 10 mol% of **1**-(CH_3CN)$_2$ in tetrachloroethane in 15 h at rt, using Et_3SiH or even deactivated PMHS as reducing agent (Figure 4b). With a primary alkyl fluoride (1-pentylfluoride), no catalytic HDF was obtained, but a stoichiometric dehydrofluorination with subsequent isomerization of the terminal to an internal olefin (2-pentene) occurred.

Despite the simple preparation of **1**-(CH_3CN)$_2$ and its high reactivity, access to donor-free **1** would be finally desirable. Comparable synthetic procedures with $HSiCl_3$ or $SiCl_4$ in non-donor solvents were not successful. However, a B(C_6F_5)$_3$ catalyzed, dehydrogenative protocol relying on OESTREICH's SiH_4 surrogate tris(cyclohexadienyl)silane in CH_2Cl_2 granted access to free **1**, with H_2 and benzene as the only byproducts (Figure 4c).[26] The formation of **1** was proven by addition of $OPEt_3$ or KF/18-crown-6 to the insoluble product, affording identical NMR spectra and single crystals as those obtained from the same reactions with **1**-(CH_3CN)$_2$.

In conclusion, we identified and prepared bis(perchlorocatecholato)silane as the first neutral silicon(IV) Lewis super acid by a straightforward synthesis. Fluoride abstraction from SbF_6^- experimentally verified the Lewis super acidity. The characterization of a SiO_4F_2 silicate dianion and stable chloridosilicates, as well as the catalytic activity in a hydrodefluorination reaction exemplified the high affinity towards halides. Given the Lewis acidity and the ease of preparation of **1**-(CH_3CN)$_2$, we are expecting versatile applications in bond activation and other fields of research, where superior Lewis acidity is needed.

Acknowledgements

We gratefully thank Prof. H.-J. Himmel for his support, the FCI for financial support and the BWFor/BWUniCluster for computational resources. D. Arian is acknowledged for ESI-MS measurements.

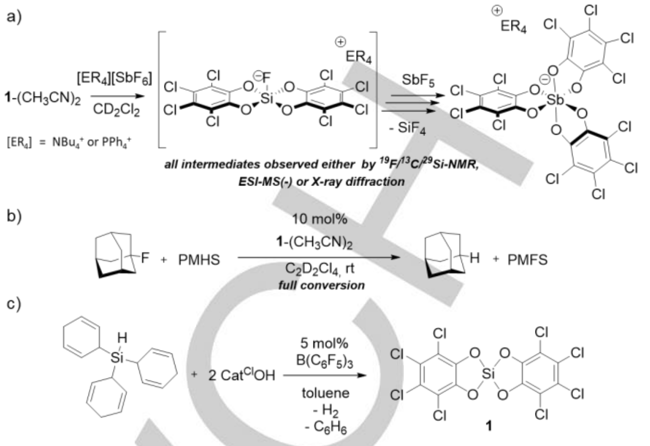

Figure 4: a) Fluoride abstraction from the SbF_6^- anion and following reactions, b) hydrodefluorination with polymethlyhydrosiloxane (PMHS) catalyzed by **1**-(CH_3CN)$_2$, c) synthesis of donor free **1** with Oestreich's SiH_4 surrogate.

Keywords: Lewis super acids • silanes • hydrodefluorination • main-group elements • catechol

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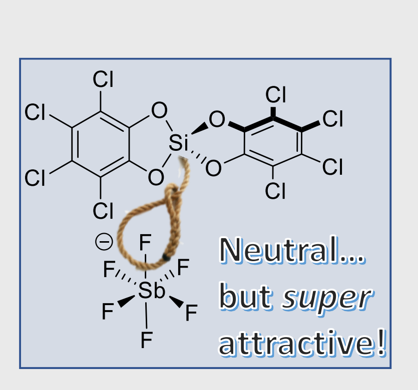
COMMUNICATION

Neutral, but *super* attractive: Bis(perchlorocatecholato)silane is presented as the first neutral silicon Lewis super acid. The Lewis acidity is exemplified by coordination of weak donors, halide abstractions and a catalytic hydrodefluorination reaction.



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