Bis(pertrifluoromethylcatecholato)silane: Extreme Lewis Acidity Broadens the Catalytic Portfolio of Silicon

Thaddäus Thorwart,[a] Daniel Roth,[a] and Lutz Greb*[a]

Abstract: Given its earth abundance, silicon is ideal for constructing Lewis acids of use in catalysis or materials science. Neutral silanes were limited to moderate Lewis acidity, until halogenated catecholato ligands provoked a significant boost. However, catalytic applications of bis(perhalocatecholato)silanes were suffering from very poor solubility and unknown deactivation pathways. In this work, the novel per(trifluoromethyl)catechol, H_2cat^{CF3}, and adducts of its silicon complex $Si(cat^{CF3})_2$ (**1**) are described. According to the computed fluoride ion affinity, **1** ranks among the strongest neutral Lewis acids currently accessible in the condensed phase. The improved robustness and affinity of **1** enable deoxygenations of aldehydes, ketones, amides, or phosphine oxides, and a carbonyl-olefin metathesis. All those transformations have never been catalyzed by a neutral silane. Attempts to obtain donor-free **1** attest to the extreme Lewis acidity by stabilizing adducts with even the weakest donors, such as benzophenone or hexaethyl disiloxane.

Introduction

The Lewis acidity of common silanes is weak to moderate but reaches satisfying levels with electron-withdrawing ligands such as triflates, perfluoroalkyls, or by Lewis base or strain release activation.[1] If it comes to Lewis superacidity (fluoride ion affinity (FIA) $>500\ kJ\,mol^{-1}$), silicon was previously considered as a less appropriate central element.[2] Only through halogenated catecholato ligands (**$Si(cat^X)_2$**, $cat^x = O_2C_6X_4$, X = Cl, Br, Figure 1), neutral silanes were pushed into the ranks of Lewis superacids.[3] Experimental and computational studies on the Lewis acidity of **$Si(cat^X)_2$** revealed that the π-back bonding of the substituents **X** into the catecholates determines the electron deficiency at silicon.[4] The σ-Hammet parameter of **X** gave a reasonable correlation with the fluoride ion affinity (FIA) of the corresponding bis(perhalocatecholato)silane and disclosed **$Si(cat^{Br})_2$** as the top-edge FIA reachable with a neutral silane. Unfortunately, the application of the entire class of **$Si(cat^X)_2$** in catalysis was hampered by its very poor solubility and unidentified deactivation channels. Recent and ongoing studies on the structure of bis(catecholato)silanes suggest covalent oligomerization as the cause.[5] Thus, we considered addressing these issues by suitable substitution of the catecholates with sufficiently large yet electron-withdrawing groups.

According to its σ-Hammet parameter, a CF_3-substituted catecholate should furnish a Lewis acid even more potent than the perhalogenated derivatives.[6] Besides, the steric demand of $-CF_3$ might block oligomerization, thus hindering catalyst deactivation. Unfortunately, the synthesis of per(trifluoromethyl)catechol (**H_2cat^{CF3}**) or any precursor has never been reported. Herewith, we describe the synthesis of per(trifluoromethyl)catechol and its installation at silicon, yielding **$Si(cat^{CF3})_2$** (**1**) stabilized by weak donors at gram-scale. The experimental and computed features of **1** confirm a top-ranking Lewis acidity among all elements in the periodic table. The compound has improved robustness compared to the perhalogenated derivatives and substantially broadens the catalytic portfolio of the second most abundant element in the earth's crust.

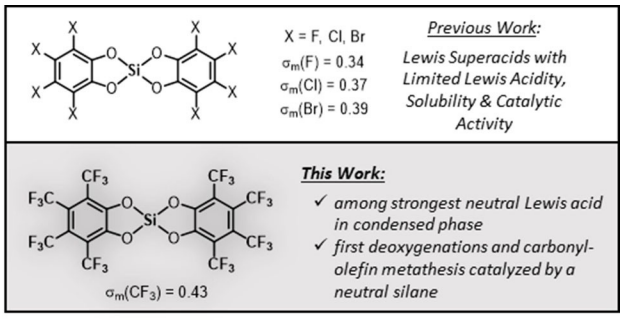

Figure 1. Previously described bis(perhalocatecholato)silanes **$Si(cat^X)_2$** with the σ-Hammet parameter of X,[6] and the per(trifluoromethyl) derivative described in this work.

[a] T. Thorwart, D. Roth, Dr. L. Greb
Anorganisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: greb@uni-heidelberg.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202101138

Results and Discussion

Literature unknown tetraiodoveratrole (**ver^{I}**) was synthesized by HOTf induced iodination of veratrole with N-iodo succinimide (NIS), and subsequently converted to per(trifluoromethyl) veratrole (**ver^{CF3}**) by using a copper-based protocol for trifluoromethylation (Figure 2a).[7] Lewis acid-mediated aryl ether cleavage failed to yield the corresponding catechol, but the addition of hydroxide or thiolates allowed a nucleophilic cleavage of one ether moiety at rt. Single-crystal X-ray diffraction analysis (SCXRD) of the tetrakis(trifluoromethyl) guaiacol (**gua^{CF3}**) showed strong bending of the CF_3-groups out the aryl-plane.

Neighboring substituents have torsion angles up to 25° (Figure 2b), similar to the pentakis(trifluoromethyl)phenyl group.[7] To a solution of **gua^{CF3}** in CD_3CN, 0.5 equiv. of $HSiCl_3$ was added, and the mixture was heated to 50 °C. ^{19}F NMR spectroscopic monitoring revealed the disappearance of the four signals of **gua^{CF3}** and the appearance of only two new signals with equivalent integrals within 24 h. In accordance, ^{1}H NMR spectra showed a decrease of the OH and OCH_3 peaks of **gua^{CF3}** along with chloromethane formation. However, in contrast to the reactions of bis(perhalocatecholato) silanes, no precipitation occurred in this case.[3b,4] Instead, ^{29}Si NMR spectroscopy revealed a signal at −90.4 ppm, in line with the computed value of a corresponding chlorido silicate [**1**-Cl]$^-$ (Figure 2c and Supporting Information). SCXRD analysis of several poor-quality crystals obtained from the reaction mixture verified the formation of [**1**-Cl]$^-$, while the nature of the cation remained unclear. An unexpected number of signals in ^{1}H NMR spectroscopy, including a characteristic 1:1:1 triplet at 6.35 ppm, indicated protonated nitriles and nitrilium ion follow products.[8] Further support was obtained by adding one equivalent of triethylamine to the fully converted reaction mixture, yielding single crystals of the chlorido silicate [**1**-Cl]$^-$ with a triethylammonium-acetonitrile counter cation. Although not yielding the desired compound, this observation revealed two vital points: 1) The guaiacol undergoes an unprecedented chlorosilane induced aryl methyl ether deprotection and can serve as a convenient precursor for Si–O bond formation. 2) The chlorido silicate [**1**-Cl]$^-$ is a WCA that is compatible with the highly Brønsted acidic conditions of protonated acetonitrile. Since a WCA's stability against Brønsted acids is connected to the strength of its underlying Lewis acid,[9] this observation promised beneficial features of the target compound.

To tackle the difficulties encountered with acetonitrile (DN[10] = 14.6), sulfolane was chosen as a similar weakly coordinating solvent (DN[11] = 14.8) more robust toward Brønsted acids.[12] After heating a solution of **gua^{CF3}** and $HSiCl_3$ or $SiCl_4$ in a sulfolane:benzene mixture (97:3 v%) to 100 °C for 15 h, colorless single-crystals developed in 90% yield (Figure 2d). SCXRD analysis verified the target compound as bis-sulfolane adduct, **1**-(sulfolane)$_2$ (Figure 3a). Identity and purity were confirmed by NMR-spectroscopy, elemental analysis, and mass spectrometry, and **1**-(sulfolane)$_2$ obtained at > 1.5 gram-scale as a robust precursor for all following experiments. For structural comparison, the bis-sulfolane adduct of **Si(cat^{Cl})$_2$** was prepared similarly (see Supporting Information). The Si–O3 bond length in **1**-(sulfolane)$_2$ (1.905(1) Å) is shortened compared to the one in the perchlorinated derivative (1.925(2) Å), giving indications for a more substantial electron deficiency on the silicon center in **1**. The donor-free Lewis acid **1** was not accessible by direct methods thus far, but approached by reduction of a ketone-adduct, as described in a later section. Hydrolysis of **1**-(sulfolane)$_2$ provided the free pertrifluoromethylcatechol, **H$_2$cat^{CF3}**, whose structure was verified by SCXRD (see Supporting Information).

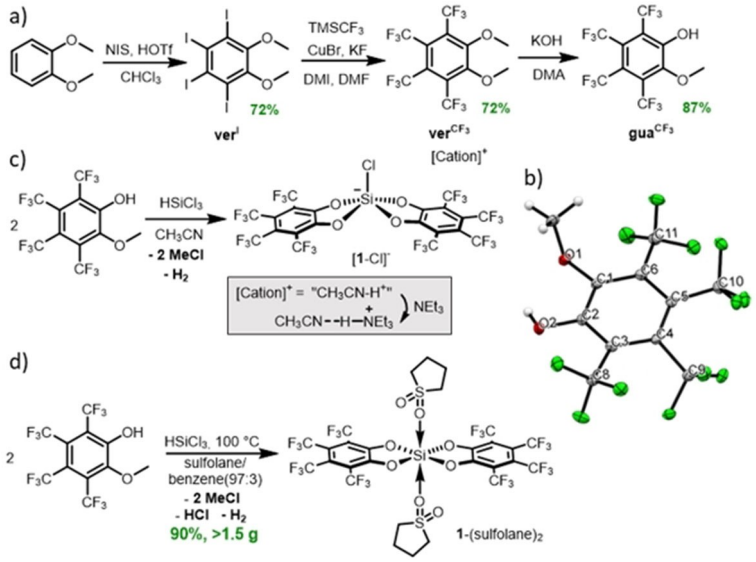

Figure 2. a) Synthesis of per(trifluoromethyl)guaiacol **gua^{CF3}**. b) Molecular structure of **gua^{CF3}** (selected bond length and angles: C1–O1 1.3672(16) Å, C2–O2 1.3468(15) Å; C4–C3–C2–C1 5.09(19)°, C10–C5–C4–C9 25.64(17)°). c) Formation of [**1**-Cl]$^-$ in acetonitrile. d) Synthesis of **1**-(sulfolane)$_2$.

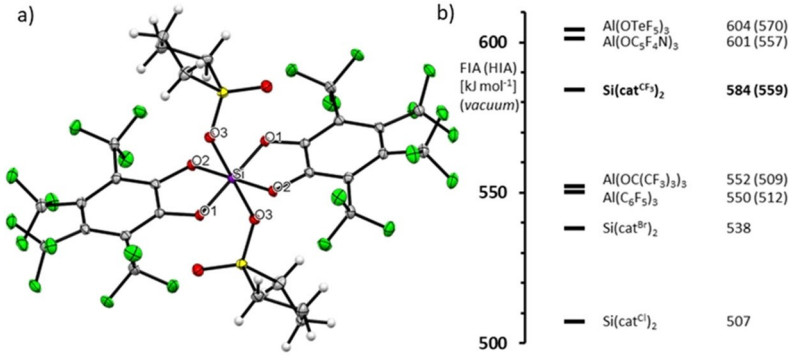

Figure 3. a) SCXRD-derived molecular structure of **1**-(sulfolane)$_2$, cocrystallized benzene molecule was omitted for clarity. Selected bond lengths and angles: Si–O1 1.7321(10) Å, Si–O2 1.7379(10) Å, Si–O3 1.9051(11) Å; O1–Si–O2 90.10(5)°, O1–Si–O3 92.75(5)°. b) Comparison of computed fluoride ion affinities (FIA) and hydride ion affinities (HIA) of **1** and the strongest fluoride ion acceptors currently accessible (for computational details see the Supporting Information).

As a global measure for Lewis acidity, the fluoride ion affinity (FIA) and the hydride ion affinity (HIA) were computed at the DLPNO-CCSD(T)/aug-cc-pVQZ//PW6B95-D3(BJ)/def2-TZVPP level of theory and anchored isodesmically to the TMS system.[13] An FIA of 584 kJ mol^{-1} and an HIA of 559 kJ mol^{-1} were obtained for **1**. Comparison with other Lewis acids disclosed **1** not only as a distinct new FIA-record holder for neutral silanes, but approaching even the strongest Lewis acids currently accessible in the condensed phase (Figure 3b).[4,13b] It is worth noting that those stronger aluminum-based Lewis acids require stabilization by weak donors or aggregation alike.[14] Further, the HIA of **1** significantly exceeds that of $B(C_6F_5)_3$ (471 kJ mol^{-1}), qualifying the compound as the first *soft* Lewis superacid based on silicon.[2] Experimental evaluation of the effective Lewis acidity of **1** was performed according to Gutmann-Beckett.[15] The addition of sub-stochiometric amounts of $OPEt_3$ to **1**-(sulfolane)$_2$ in CD_2Cl_2 led to immediate liberation of sulfolane, and the formation of the mono-adduct, as confirmed by SCXRD (Figure 4a). ^{31}P NMR spectroscopy showed an induced shift of $\Delta^{31}P = 39$ ppm, surpassing that of the hitherto strongest **Si(cat^{Br})$_2$** ($\Delta^{31}P = 37$ ppm). The addition of >1 equivalent of $OPEt_3$ provided the bis-adduct, with a shift ($\Delta^{31}P = 24.2$ ppm) also larger compared to that of **Si(cat^{Br})$_2$**–$(OPEt_3)_2$ ($\Delta^{31}P = 22.6$ ppm). In contrast to the halogenated bis(catecholato)silanes,[4] the bis-$OPEt_3$ adduct adopted *cis*-arrangement in solution (^{19}F NMR spectroscopy, see Supporting Information) and the solid-state (SCXRD, Figure 4a). This altered conformational preference might be associated with the distinguished catalytic efficiency, as discussed below.

Adding one equivalent $[PPh_4][SbF_6]$ to a suspension of **1**-(sulfolane)$_2$ in CD_2Cl_2 led to a prompt dissolution, and the fluoridosilicate [**1**-F]$^-$ was observed by ^{19}F NMR spectroscopy (matching shifts compared to [(*n*-Bu)$_4$N][**1**-F] prepared independently, Figure 4a). Opposed to the slow reactions observed with the poorly soluble acetonitrile-adducts of Lewis superacids **Si(cat^{X})$_2$** (X = Cl, Br, several hours), the fluoride abstraction from SbF_6^- with **1**-(sulfolane)$_2$ occurred within seconds.[4] Subsequent ligand scrambling/oxidation prevented the isolation of defined reaction products. Adding $ClCPh_3$ to a suspension of **1**-(sulfolane)$_2$ in CH_2Cl_2 led to the characteristic coloration, and

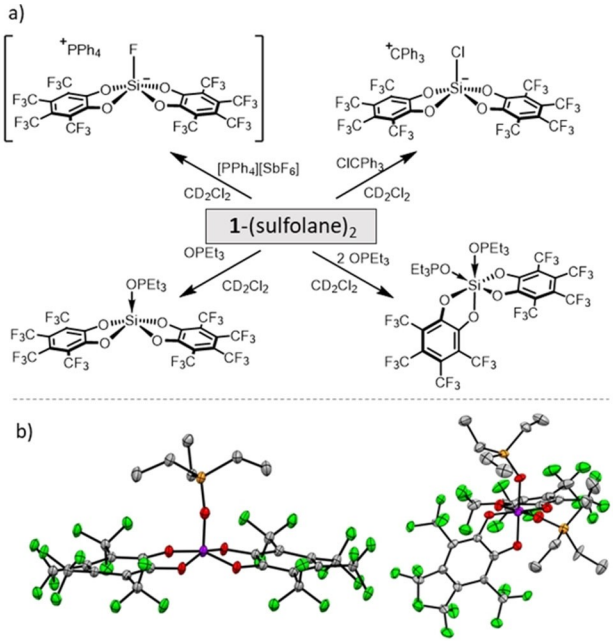

Figure 4. a) Formation of adducts and reactivities of **1**-(sulfolane)$_2$. b) Molecular structures of **1**-$OPEt_3$ (selected bond lengths: **1**-$OPEt_3$: Si–OP 1.6815(16) Å, Si–OC 1.7162(15) Å, 1.7293(15) Å, 1.7173(15) Å, 1.7293(16) Å) and **1**-$(OPEt_3)_2$ (connectivity).

^{1}H/^{13}C NMR revealed quantitative formation of the trityl cation. A sole ^{29}Si NMR signal at −89.7 ppm verified the formation of the chlorido silicate [**1**-Cl]$^-$ (matching signal with [Et_3N–H–$NCCH_3$][**1**-Cl]). This behavior gives further evidence for the distinguished Lewis acidity of **1** since the acetonitrile adducts of the bis(perhalocatecholato)silanes afforded the trityl cation in max. 83% equilibrium.[4]

Encouraged by the strong affinity of **1**-(sulfolane)$_2$, catalytic applications were addressed. Previously, the acetonitrile stabilized bis(perfluorocatecholato)silane (**Si(cat^{F})$_2$**) has been applied for catalytic hydrosilylation reactions (5 mol%), but the scope was limited to electron-deficient, aromatic aldehydes.[3a] Interestingly, reactions of aldehydes with triethylsilane in the

presence of 1 mol% of **1**-(sulfolane)$_2$ did not lead to the hydrosilylation products, but the formation of dialkyl ethers in excellent yields (Figure 5a).[16] Beyond activated electron-poor aldehydes, also electron-rich *p*-methylbenzaldehyde or an alkyl aldehyde were efficiently converted. With benzophenone as a substrate, the exclusive and quantitative formation of the deoxygenation product diphenylmethane was detected after 30 min at rt (Figure 5b). At 100 °C and $PhSiH_3$ as the reducing agent, the deoxygenation catalysis was successful also for acetophenone. For the dialkyl ketone cyclohexanone, deoxygenative olefine formation (cyclohexene) was observed in moderate yields (Figure 5b). Next, the catalyst was tested in conjunction with an amide and two phosphine oxides, as more challenging substrates (Figure 5c).[17] In toluene at 100 °C with 5 mol% of **1**-(sulfolane)$_2$ and $PhSiH_3$ as reducing agent, exhaustive deoxygenation proceeded with excellent conversion. Under the harsher reaction conditions and excess of $PhSiH_3$, even the deoxygenation of *p*-fluor benzaldehyde to *p*-fluorotoluene was effectuated (Figure 5a).

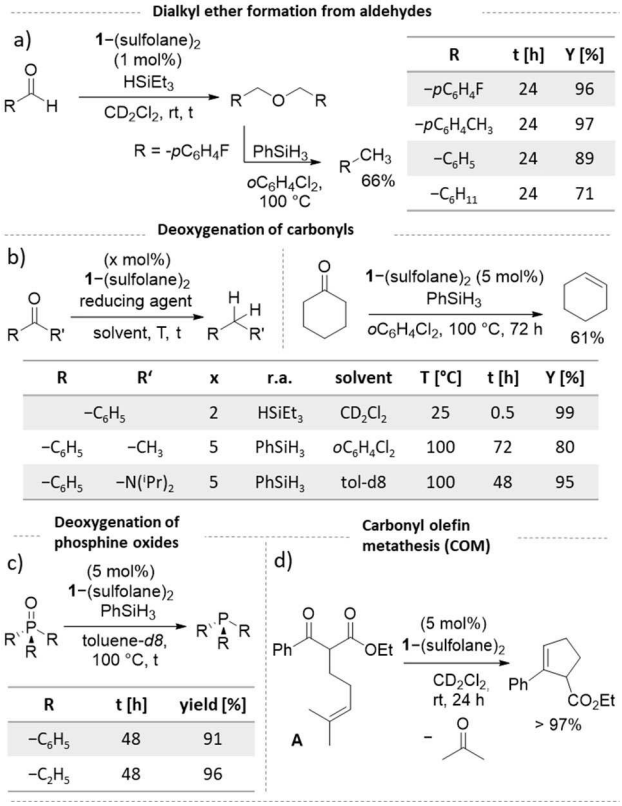

Figure 5. Catalytic applications of **1**-(sulfolane)$_2$ in a) the reduction of aldehydes to dialkyl ethers, b) the deoxygenation of ketones and amides, c) the deoxygenation of phosphine oxides, and d) the intramolecular carbonyl-olefin metathesis. Conversions were determined by ^{1}H NMR or ^{31}P NMR integration against an internal standard.

To probe a Lewis acid catalysis beyond reductions, and inspired by the fact, that the carbonyl-olefin metathesis (COM) critically depends on the strength of a Lewis acid,[18] the cyclization of **A** with 5 mol% of **1**-(sulfolane)$_2$ was attempted (Figure 5d). Indeed, the reaction went to completeness at rt during 24 h without any observable side reactions. In light of the previous restriction to metal halide catalysts for the COM (e.g., MCl_3, M = Fe, Al, Ga, Au),[18c,19] this is very promising as it ultimately allows to tackle selectivity by ligand design in future. Overall, the first deoxygenation reactions catalyzed by a neutral silane and the first silicon catalyzed carbonyl-olefin metathesis are realized, clearly broadening silicon's reach in homogeneous catalysis.

A comparison was made with adducts of **Si(cat^{Cl})$_2$** to demarcate the advancement of **1**-(sulfolane)$_2$ against its perhalogenated predecessors (Table 1). The catalytic superiority of **1**-(sulfolane)$_2$ becomes apparent from the significantly higher conversion and the higher selectivity in the reductive dialkyl ether formation (Table 1, col2 vs. col3).

Whereas with **1**-(sulfolane)$_2$, the pristine formation of dialkyl ethers **P1** was observed, with **Si(cat^{Cl})$_2$**•(sulfolane)$_2$, the unselective formation of both **P1** and hydrosilylation product **P2** was encountered. The conversions with **Si(cat^{Cl})$_2$**·(sulfolane)$_2$ are higher than the ones for the corresponding bis-acetonitrile adduct, but the selectivity remains low (col3 vs. col4). In contrast to the previously reported **Si(cat^{X})$_2$**, which form their bis-adducts in *trans* orientation,[4] the *cisoid* binding mode, as observed for $OPEt_3$ with **1** (Figure 4), might preorganize two substrates for intramolecular ether formation. Beyond, the *cis-adduct* arranges the substrates *trans* with a catecholate, which might cause more efficient substrate activation. Indeed, a *cisoid* coordination was indicated for aldehydes by four peaks in the ^{19}F NMR spectra upon mixing **1**-(sulfolane)$_2$ with 10 equiv. of cyclohexanecarboxaldehyd (see Supporting Information).

Finally, benzophenone's deoxygenation in the coordination sphere of **1** was considered a promising route to donor-free **1**. Thus, the mono-benzophenone adduct **1**-($OCPh_2$) was prepared at a 200 mg scale and fully characterized (see Supporting Information for SCXRD). To the best of our knowledge, it represents the first Lewis adduct of a silane with a ketone, and it gives experimental evidence for the mode of carbonyl activation proposed during the catalytic hydrosilylation also with **Si(cat^{F})$_2$**·(acetonitrile)$_2$.[3a] Deoxygenation of benzophenone

Table 1. Comparison of catalytic activity of **1**-(donor)$_n$ and **Si(cat^{Cl})$_2$**-(donor)$_2$ in the reductive alkyl ether formation and the deoxygenation of benzophenone. **P1** dialkyl ether for aldehydes, and diphenylmethane for benzophenone, **P2** carbonyl hydrosilylation product. General conditions: 24 h, 150 μmol substrate, [a] 1 mol% catalyst and 225 μmol $HSiEt_3$ or [b] 2 mol% catalyst and 450 μmol $HSiEt_3$ in 0.5 mL CD_2Cl_2. Yields determined via ^{1}H NMR integration against an internal standard.

Catalyst/Substrate	Si(cat^{CF3})$_2$·(sulfolane)$_2$			Si(cat^{Cl})$_2$·(sulfolane)$_2$			Si(cat^{Cl})$_2$·(CH$_3$CN)$_2$			Si(cat^{CF3})$_2$·OCPh$_2$		
	Conv.	P1	P2	Conv.	P1	P2	Conv.	P1	P2	Conv.	P1	P2
*p*CH$_3$C$_6$H$_4$CHO[a]	98%	97%	< 0.5%	31%	27%	3%	7%	6%	< 0.5%	98%	97%	< 0.5%
*p*FC$_6$H$_4$CHO[a]	> 99%	96%	3%	26%	10%	16%	11%	5%	5%	82%	80%	2%
Ph$_2$CO[b]	> 99%	99%	–	25%	24%	–	16%	16%	–	78%	77%	–

with Et_3SiH occurred quantitatively, but donor-free **1** could not be separated from the reaction mixture. Instead, the formation of an adduct between **1** and the reaction product $Et_3SiOSiEt_3$ was observed (see section 2.5 in the Supporting Information). Although not isolable in the crystalline state, multinuclear NMR spectroscopy and computations strongly support such an adduct. To the best of our knowledge, this is the first example of a neutral Lewis acid pairing with a disiloxane, an extremely weak donor.[12,20] From a catalytic perspective, the monobenzophenone adduct **1**-($OCPh_2$) promised to serve as a precatalyst under reductive conditions. Thus, the representative set of catalytic silane reductions was performed with **1**-($OCPh_2$) and compared with **1**-(sulfolane)$_2$ (Table 1, col4 vs. col2). Interestingly, the catalytic activity of **1**-($OCPh_2$) turned out as inferior compared to **1**-(sulfolane)$_2$, particularly for the deoxygenation of benzophenone itself. This observation indicates that the donor-free Lewis acid **1** is a less effective catalyst, but sulfolane might take an active role in the catalytic cycle. Although further mechanistic studies are required, this handle offers exciting opportunities to control the activity and the selectivity within this class of Lewis superacids.

Conclusion

The present contribution serves the advancement of Lewis acids in a two-fold sense. First, we introduce a neutral silicon-based Lewis acid that ranges among the strongest fluoride ion acceptors currently accessible in the condensed phase. This is a notable step for silicon, a central element that was associated with moderate Lewis acidity due to the lack of obvious acceptor orbitals. It allows stabilizing adducts with very weak donors, such as the first Lewis pair of a neutral Lewis acid with a disiloxane. Second, this Lewis acid allows expanding the catalytic portfolio of neutral silanes onto the first silicon catalyzed deoxygenation reactions of aldehydes, ketones, amides and phosphine oxides, as well as the carbonyl-olefin metathesis. The possibility of controlling the steric and electronic profile of Lewis acids by defined ligand-variations while maintaining their "*super*" aptitude to maneuver through high-energy reaction pathways will propel a transfer of Lewis superacids into synthetically relevant fields. Finally, the new compound $\mathbf{H_2cat^{CF3}}$ will stimulate other fields such as hydrogen bond donor catalysis,[21] redox-active ligands,[22] or weakly coordinating anions.[9b]

Experimental Section

Crystallographic data: Deposition numbers 2070464, 2070465, 2070466, 2070467, 2070468, and 2070469 contain 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.

Acknowledgements

We thank Prof. H.-J. Himmel for his constant support, and the DFG (GR5007/2-1) for financial support. Dr. Jürgen Graf and Prof. Markus Enders are thanked for their efforts with NMR spectroscopy. Dr. Marcel Schorpp is acknowledged for support in SCXRD structure refinement. The federal state Baden-Württemberg is acknowledged for providing computational resources (BWFor/BWUni). Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: catechol · deoxygenation · Lewis superacids · homogeneous catalysis · silicon

[1] a) A. G. Myers, S. E. Kephart, H. Chen, *J. Am. Chem. Soc.* **1992**, *114*, 7922–7923; b) H. Yamamoto, *Lewis acids in organic synthesis*, Wiley-VCH, Weinheim, **2002**; c) J. W. A. Kinnaird, P. Y. Ng, K. Kubota, X. Wang, J. L. Leighton, *J. Am. Chem. Soc.* **2002**, *124*, 7920–7921; d) A. D. Dilman, S. L. Ioffe, *Chem. Rev.* **2003**, *103*, 733–772; e) H. Yamamoto, K. Ishihara, *Acid catalysis in modern organic synthesis.*, Wiley-VCH, Weinheim, **2008**; f) S. E. Denmark, G. L. Beutner, *Angew. Chem. Int. Ed.* **2008**, *47*, 1560–1638; *Angew. Chem.* **2008**, *120*, 1584–1638; g) S. Steinhauer, J. Bader, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Angew. Chem. Int. Ed.* **2014**, *53*, 5206–5209; *Angew. Chem.* **2014**, *126*, 5307–5209; h) B. Waerder, M. Pieper, L. A. Körte, T. A. Kinder, A. Mix, B. Neumann, H.-G. Stammler, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2015**, *54*, 13416–13419; *Angew. Chem.* **2015**, *127*, 13614–13419; i) S. A. Weicker, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 13027–13034; j) M. Wiesemann, B. Hoge, *Chem. Eur. J.* **2018**, *24*, 16457–16471.
[2] L. Greb, *Chem. Eur. J.* **2018**, *24*, 17881–17896.
[3] a) A. L. Liberman-Martin, R. G. Bergman, T. D. Tilley, *J. Am. Chem. Soc.* **2015**, *137*, 5328–5331; b) R. Maskey, M. Schädler, C. Legler, L. Greb, *Angew. Chem. Int. Ed.* **2018**, *57*, 1717–1720; *Angew. Chem.* **2018**, *130*, 1733–1720.
[4] D. Hartmann, M. Schädler, L. Greb, *Chem. Sci.* **2019**, *10*, 7379–7388.
[5] D. Hartmann, L. Greb, *Angew. Chem. Int. Ed.* **2020**, *59*, 22510–22513; *Angew. Chem.* **2020**, *132*, 22699–22513.
[6] H. C. Brown, Y. Okamoto, *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987.
[7] A. Kütt, V. Movchun, T. Rodima, T. Dansauer, E. B. Rusanov, I. Leito, I. Kaljurand, J. Koppel, V. Pihl, I. Koppel, G. Ovsjannikov, L. Toom, M. Mishima, M. Medebielle, E. Lork, G.-V. Röschenthaler, I. A. Koppel, A. A. Kolomeitsev, *J. Org. Chem.* **2008**, *73*, 2607–2620.
[8] R. Haiges, A. F. Baxter, N. R. Goetz, J. A. Axhausen, T. Soltner, A. Kornath, K. O. Christe, *Dalton Trans.* **2016**, *45*, 8494–8499.
[9] a) I. Krossing, I. Raabe, *Chem. Eur. J.* **2004**, *10*, 5017–5030; b) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, *Angew. Chem. Int. Ed.* **2018**, *57*, 13982–14024; *Angew. Chem.* **2018**, *130*, 14178–14024.
[10] Y. Y. Lim, R. S. Drago, *Inorg. Chem.* **1972**, *11*, 202–204.
[11] V. Gutmann, A. Scherhaufer, *Monatsh. Chem.* **1968**, *99*, 335–339.
[12] C. Laurence, J.-F. o. Gal, *Lewis basicity and affinity scales : data and measurement*, John Wiley, Chichester, West Sussex, U. K., **2010**.
[13] a) H. Böhrer, N. Trapp, D. Himmel, M. Schleep, I. Krossing, *Dalton Trans.* **2015**, *44*, 7489–7499; b) P. Erdmann, J. Leitner, J. Schwarz, L. Greb, *ChemPhysChem* **2020**, *21*, 987–994.
[14] a) A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263–8266; *Angew. Chem.* **2017**, *129*, 8375–8266; b) I. M. Riddlestone, S. Keller, F. Kirschenmann, M. Schorpp, I. Krossing, *Eur. J. Inorg. Chem.* **2019**, 59–67.
[15] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235–1257; b) M. A. Beckett, G. C. Strickland, J. R. Holland, K. Sukumar Varma, *Polymer* **1996**, *37*, 4629–4631.
[16] M. B. Sassaman, K. D. Kotian, G. K. S. Prakash, G. A. Olah, *J. Org. Chem.* **1987**, *52*, 4314–4319.

[17] a) A. Volkov, F. Tinnis, T. Slagbrand, P. Trillo, H. Adolfsson, *Chem. Soc. Rev.* **2016**, *45*, 6685–6697; b) H. Fang, M. Oestreich, *Chem. Sci.* **2020**, *11*, 12604–12615.
[18] a) J. R. Ludwig, P. M. Zimmerman, J. B. Gianino, C. S. Schindler, *Nature* **2016**, *533*, 374–379; b) H. Albright, H. L. Vonesh, C. S. Schindler, *Org. Lett.* **2020**, *22*, 3155–3160; c) A. J. Davis, R. B. Watson, D. J. Nasrallah, J. L. Gomez-Lopez, C. S. Schindler, *Nat. Catal.* **2020**, *3*, 787–796.
[19] a) A. Djurovic, M. Vayer, Z. Li, R. Guillot, J.-P. Baltaze, V. Gandon, C. Bour, *Org. Lett.* **2019**, *21*, 8132–8137; b) R. Wang, Y. Chen, M. Shu, W. Zhao, M. Tao, C. Du, X. Fu, A. Li, Z. Lin, *Chem. Eur. J.* **2020**, *26*, 1941–1946.
[20] J. Pahl, H. Elsen, A. Friedrich, S. Harder, *Chem. Commun.* **2018**, *54*, 7846–7849.
[21] A. G. Doyle, E. N. Jacobsen, *Chem. Rev.* **2007**, *107*, 5713–5743.
[22] a) C. G. Pierpont, R. M. Buchanan, *Coord. Chem. Rev.* **1981**, *38*, 45–87; b) B. A. Vaughan, M. S. Webster-Gardiner, T. R. Cundari, T. B. Gunnoe, *Science* **2015**, *348*, 421–424; c) M. T. Huynh, C. W. Anson, A. C. Cavell, S. S. Stahl, S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2016**, *138*, 15903–15910.

Manuscript received: March 30, 2021
Accepted manuscript online: April 14, 2021
Version of record online: May 21, 2021

