Bis(per trifluoromethyl catecholato)silane: Extreme Lewis
Acidity Broadens the Catalytic Portfolio of Silicon

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1. Experimental Details

1.1. Materials and General Methods

All used reagents and solvents were purchased from commercial sources. Unless otherwise noted, all manipulations were carried out under a dry nitrogen or argon atmosphere. Solvents were degassed prior to use with four freeze-pump-thaw cycles and were stored in sealed Schlenk ampulla over activated molecular sieve (3 or 4 Å, respectively) under a dry argon atmosphere. Liquid reactants were degassed for at least 10 min with a constant stream of dry argon through the fluid phase and were dried by storage over activated molecular sieve (3 or 4 Å, respectively). Solid reagents were dried and purified if necessary either by the application of vacuum and elevated temperature, or by sublimation under reduced pressure at elevated temperature.

All reactions on preparative scale were carried out in flame-dried standard laboratory glassware under a dry argon atmosphere using Schlenk line techniques and were permanently magnetically stirred. Syringes, magnetic stirring bars, and needles were dried and/or flushed with argon prior to use. Reaction on the NMR sample scale were done in dry J. Young NMR tubes. Compounds sensitive to ambient conditions were handled and stored in a glove box filled with dry nitrogen gas. Removal of solvents in vacuo was performed using a Heidolph VV2000 rotary evaporator or a Schlenk line.

Literature-known compounds were synthesized following published procedures, which are cited (see below). Analytical data of known compounds were compared to data of the respective reference and were found to be consistent in all cases. Novel compounds were characterized to the reported structures to the best of our knowledge.

Nuclear magnetic resonance (NMR) spectra were collected with a Bruker BZH 200/52, a Bruker DPX 200, a Bruker Avance II 400, a Bruker Avance III 500 or a Bruker Avance III 600 spectrometer at 298 K unless otherwise noted. Measurements with the Bruker Avance spectrometers were carried out by the NMR facilities of the Institutes of Inorganic or Organic Chemistry of the University of Heidelberg. Chemical shifts δ are given in parts per million (ppm) relative to the tetramethylsilane resonance. Deuterated dichloromethane, chloroform and toluene were used as solvent, and the signal of CHDCI₂, CHCl₃ or C₆D₆CD₃H was used for calibration of the spectra (CD₃Cl): ¹H: 5.32 ppm, ¹³C: 53.84 ppm, CDCI₃: ¹H: 7.26 ppm, ¹³C: 77.16 ppm, toluene-d₈: ¹H: 2.08 ppm, ¹³C: 20.43 ppm). Spectra in ortho-dichlorobenzene (oDCB) were obtained after the addition of CD₃Cl₂ or without lock. The signals against the tetramethylsilane resonance served as reference for calibration (¹H: 7.26 (m), 7.00 (m) ppm; ¹³C: 132.57, 130.56, 127.81). ¹H and ¹⁹F NMR data is reported as follows: chemical shift δ [ppm], multiplicity (s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, and combinations), scalar spin-spin coupling constant [Hz] as JAB (X = number of chemical bonds between coupled nuclei; A, B = coupled nuclei), integration value. ¹³C, ²⁹Si and ³¹P NMR data is reported as follows: chemical shift δ [ppm], multiplicity (if apparent), scalar spin-spin coupling constant [Hz] as JAB. NMR spectra were processed and plotted with MestReNova 14.2.

High resolution mass spectrometry (HR-MS) was conducted with the electrospray ionization method (ESI), the direct analysis in real time method (DART) on a Bruker ApexQe hybrid 9.4 T FT-ICR or with electron impact ionization (EI) on a JEOL JMS-700 magnetic sector, carried out by the Mass Spectrometry Facility of the Institute of Organic Chemistry of the University of Heidelberg. Mass spectrometry data is reported as follows: m/z ratio (relative intensity) [assigned fragment] (for HR experiments: calculated exact mass).

Gas chromatography mass spectroscopy (GCMS) experiments were conducted utilizing helium as carrier gas on an Agilent Technologies 6890 Series gas chromatograph equipped with a HP-5MS-column (5% diphenyl/polydimethylsiloxane, 95% dimethylpolysiloxane) and an Agilent 5973 Mass Selective Detector. IR spectra were measured on a Bruker Alpha or an Agilent Cary 630 spectrometer equipped with diamond ATR units. IR spectra were processed and plotted OriginPro 2021 (9.8.0.200).
1.2.  Synthesis

1.2.1.  1,2,3,4-tetraiodo-5,6-dimethoxy-benzene (ver)

N-iodosuccinimide (NIS) (22.0 g, 97.1 mmol, 4.50 eq.) was added to a solution of veratrole (3.0 g, 21.7 mmol, 1.0 eq.) in chloroform (200 mL) in an argon-atmosphere and the suspension was cooled to 0 °C. At that temperature, trifluoromethanesulfonic acid (1.91 mL, 21.7 mmol, 1.0 eq.) was added dropwise. The reaction mixture was warmed to 65 °C and stirred for two hours at that temperature. After cooling briefly, an additional quantity of NIS (7.33 g, 32.6 mmol, 1.50 eq.) was added, and the heating was continued for two hours. The mixture was allowed to cool to room temperature, and water was added. The phases were separated, and the organic layer was washed with aqueous Na₂S₂O₃-solution (1 M) and brine. The organic phase was dried over sodium sulfate and concentrated in vacuo to a volume of approx. 100 mL. 900 mL ethanol were added, the mixture kept at −20 °C for 12 h and the formed cloudy precipitate was filtered off, washed with ethanol and dried in vacuo, to give a yellow solid (10.1 g, 15.74 mmol, 72%), that yielded thin, yellow needles after recrystallization from toluene.

\(^{1}H\) NMR (400 MHz, CDCl₃) \(\delta\) 3.82 (s, 6H).
\(^{13}C\) NMR (101 MHz, CDCl₃) \(\delta\) 152.43 (C₆O ≈ C\(^{1}\)), 115.46 (C\(^{6}\)), 108.38 (C\(^{5}\)), 60.47 (OCH₃).

HR-DART MS* \(m/z\) 668.5655 (100%) [M+OH]⁺ (calc. 668.5658), 641.6529 (42%) [M⁺]⁺ (calc. 641.6541).

1.2.2.  1,2-dimethoxy-3,4,5,6-tetra(trifluoromethyl)benzene (verCF₃)

The trifluoromethylation protocol was adapted from a literature known synthesis.\(^{[1]}\) Freshly purified copper(I) bromide (according to literature known procedure\(^{[2]}\)) (10.1 g, 70.1 mmol, 9.0 eq.) was suspended in DMF (47 mL) and (trifluoromethyl)trimethylsilane (8.64 mL, 58.4 mmol, 7.5 eq.) was added. The mixture was cooled to −5 °C and KF (3.39 g, 58.4 mmol, 7.5 eq.) was added in roughly three equal portions, so the temperature rose not above 0 °C. Subsequently DMI (12 ml) was added and the mixture stirred for 3 h at 0 °C. Then, 1,2,3,4-tetraiodo-5,6-dimethoxybenzene (5.00 g, 7.79 mmol, 1.0 eq.) was added in one portion followed by another 56 mL DMI. The mixture was stirred for 30 h, then water (50 mL) and diethyl ether (200 mL) were added and the phases separated. The organic phase was washed with water, half concentrated brine and brine, dried (Na₂SO₄) and afterwards concentrated in vacuo. The residue was purified using flash chromatography (silica – petroleum ether 19:1 ethyl acetate), to give a colorless solid (2.29 g, 5.58 mmol, 72%). Importantly and as noted before,\(^{[1]}\) yield and formation of the described product depends heavily on the purity of the applied CuBr (as pale green as possible or ideally colorless) and the content of water in solvents. The formation of the reactive copper reagent can be verified via \(^{19}F\) NMR spectroscopy.\(^{[1]}\)

Single crystals suitable for SCXRD developed from a saturated petroleum ether, ethyl acetate (19:1) solution at rt (details see section 7).

\(^{1}H\) NMR (400 MHz, CDCl₃) \(\delta\) 4.03 (s).
\(^{13}C\) NMR (101 MHz, CDCl₃) \(\delta\) 151.43 (C₆O ≈ C\(^{1}\)), 115.46 (C\(^{6}\)), 108.38 (C\(^{5}\)), 60.47 (OCH₃).

HR-DART MS* \(m/z\) 568.4337 (100%) [M+OH]⁺ (calc. 568.4338), 541.3209 (42%) [M⁺]⁺ (calc. 541.3211).

Elemental analysis 35.17% C (calc. 35.14%), 1.84% H (1.47%).

1.2.3.  2-methoxy-3,4,5,6-tetra(trifluoromethyl)phenol (guaCF₃)

1,2-dimethoxy-3,4,5,6-tetra(trifluoromethyl)benzene (1.60 g, 3.90 mmol, 1.0 eq.) was dissolved in dimethylacetamide (25 mL) in an argon-atmosphere. Potassium hydroxide (0.55 g, 9.75 mmol, 2.5 eq.) was added and the mixture stirred for 18 h at room temperature. The orange solution was cooled to 0 °C and quenched through slow addition of 15 mL water and 10 mL HCl(aq.) (1 M). The colorless precipitate was filtered off, washed with water, and taken up in diethyl ether. The filtrate was extracted once with diethyl ether and the combined organic phases were washed with water, half concentrated brine, and brine, dried (Na₂SO₄) and concentrated in vacuo. The residue was purified using flash chromatography (silica – petroleum ether 1:1 dichloromethane), to yield a colorless solid (1.35 g, 3.41 mmol, 87%), which can be recrystallized from n-heptane.

Single crystals suitable for SCXRD developed from a saturated dichloromethane solution at rt (see section 7).
1.2.4. 1-(sulfolane)

To a solution of gua$^{CF_3}$ (1.35 g, 3.41 mmol, 2.0 eq.) in a sulfolane, benzene mixture (12 mL, 97.3 V%) HSiCl$_3$ (195 µL, 1.93 mmol, 1.1 eq.) was added dropwise at rt. The reaction mixture was stirred for 15 min and then heated to 100 °C for 15 h. After cooling to rt, the colorless, crystalline solid (suitable for SCXRD, details see section 7) was filtered off and washed with benzene, dichloromethane, n-pentane and dried in vacuo (1.63 g, 1.58 mmol, 90%).

1$^H$ NMR (600 MHz, CDCl$_3$) δ 7.04 (s, 1H), 4.08 (s, 3H). Aromatic signals not detected due to limited solubility and high fluorine content (coupling).

1$^9$F NMR (188 MHz, CDCl$_3$) δ -51.21 – -52.20 (m, 12F), -56.45 – -56.98 (m, 12F).

1$^{13}$C NMR spectroscopy was prevented by limited solubility in common deuterated organic solvents.

IR (ATR-FTIR): δ [cm$^{-1}$] 3070 (m), 1644 (s), 1589 (s), 1462 (m), 1378 (s), 1354 (s), 1266 (s), 1148 (m), 973 (s).

HR-ESI MS+ m/z 818.9372 (59%) [Si(cat$^{CF_3}$)$_2$ + OH]$^+$ (calc. 818.9372), 804.9217 (27%) [Si(cat$^{CF_3}$)$_2$ + OH]' (calc. 804.9216), 583.9449 (6%) [Si(cat$^{CF_3}$)$_2$]' (calc. 583.9450).

Elemental analysis 31.99% C (calc. +0.5 CH$_2$Cl$_2$ 31.96%), 1.62% H (calc. +0.5 CH$_2$Cl$_2$ 1.60%).

1.2.5. 3,4,5,6-tetra(trifluoromethyl)catechol (H$_2$cat$^{CF_3}$)

Clean formation of the per(trifluoromethyl)catechol was observed upon addition of water to 1-(sulfolane)$_2$ in CH$_2$Cl$_2$. The suspension was filtered, and SCXRD analysis of suitable crystals formed from the filtrate revealed the molecular structure of H$_2$cat$^{CF_3}$ (see section 7). To obtain the compound without residues of sulfolane, donors in 1-(sulfolane)$_2$ (30.0 mg, 29.2 µmol, 1.0 eq.) were exchanged with acetonitrile in advance (as described in 1.2.7). Subsequent hydrolysis (1.31 µl, 72.9 µmol, 2.5 eq.) of a suspension in CH$_2$Cl$_2$ (1 mL), filtration and concentration of the filtrate in vacuo yielded per(trifluoromethyl)catechol as colorless solid, which develops a purple shade within a day on atmosphere. (17.0 mg, 44.5 µmol, 76%).

1$^H$ NMR (400 MHz, CD$_2$Cl$_2$) δ 7.12 (s).

1$^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) δ 147.39 (C$_4$OH), 122.84 (q, $^{13}$J$_{CF}$ = 276 Hz, C$_F$X), 122.30 (q, $^{13}$J$_{CF}$ = 277 Hz, C$_F$X), 118.94 (q, $^{13}$J$_{CF}$ = 33.2 Hz, C$_F$X).

1$^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) δ -51.43 – -52.12 (m, 6F), -56.15 (m, 6F).

HR-ESI MS+ m/z 381.9884 (14%) [M]$^+$ (calc. 384.9858), 362.9831 (42%) [M – F]$^+$ (calc. 362.9874), 313.9778 (90%) [M – CF$_3$ + H]$^+$ (calc. 313.9984).

1.2.6. [N(n-Bu)$_4$][1-F]

1-(sulfolane)$_2$ (20.0 mg, 19.5 µmol, 1.0 eq.) and tetra-n-butylammonium difluorotriphenylsilicate (7.2, 19.5 µmol, 1.0 eq.) were mixed in CH$_2$Cl$_2$ (0.2 mL). The solid reactants dissolved immediately to give a colorless solution. Addition of n-pentane led to the precipitation of a colorless solid which was separated from the solution, washed once with n-pentane, and dried in vacuo (18.7 mg, 17.8 µmol, 92%). Single crystals suitable for SCXRD developed from a saturated dichloromethane solution at rt confirmed the connectivity of the title species (for details see section 7).

1$^H$ NMR (400 MHz, CD$_2$Cl$_2$) δ 3.10 – 3.01 (m, 2H), 1.59 (quin, $^{3}$J$_{OH}$ = 8.2, 7.8 Hz, 2H), 1.40 (sext, $^{3}$J$_{OH}$ = 7.3 Hz, 2H), 1.00 (t, $^{3}$J$_{OH}$ = 7.3 Hz, 3H).
The compound was synthesized according to a literature-known procedure.\[3\]
2. Reactivity

2.1. Reactivity of gua$^{\text{CF}_3}$ with HSiCl$_3$ in acetonitrile

Synthesis of the bis-acetonitrile adduct of 1 was attempted via previously described procedures for related bis(perhalocatecholate)silanes.$^{[3-4]}$ A J.-Young type NMR tube was charged with 20 mg of gua$^{\text{CF}_3}$ dissolved in 0.5 mL CD$_3$CN. HSiCl$_3$ (0.5 eq.) was added to the solution dropwise, the reaction mixture was heated to 60 °C and monitored with $^1$H- and $^{19}$F-NMR spectroscopy. After 24 h, $^1$H NMR experiments revealed the formation of CH$_3$Cl and the decrease of the ligands OH and OCH$_3$ signals along with a 1:1:1 triplet at 6.35 ppm and further signals (Figure S1). $^{19}$F-NMR spectra showed symmetrization of the trifluoromethyl groups in the catechol motive. In contrast to the halo-derivatives, no precipitation occurred.$^{[3-4]}$ $^{29}$Si NMR spectrum showed a sharp signal at $-90.4$ ppm, indicating a pentacoordinated silicon species. The signal is in agreement with the calculated value of $-84.9$ ppm for the chloridosilicate [1-Cl]$^-$ (PBE0/def2-TZVP/PBEh-3c level of theory). When the reaction mixture is concentrated to a fifth of its volume and subsequenely refilled with CH$_2$Cl$_2$, crystals formed after several days for which SCXRD indicated the chloridosilicate anion, but the nature of the cation was not assignable (details see section 7). It proposedly originates from side reactivity of acetonitrile under the acidic conditions of the reaction mixture, such as oligomerization. After addition of one equivalent triethylamine to the reaction mixture, SCXRD analysis of formed, suitable colorless crystals confirmed the nature of the ion pair [Et$_3$N--H--NCCH$_3$][Cl-1] (see section 7).

Figure S1. $^1$H NMR (600 MHz, CD$_3$CN) of the reaction mixture of gua$^{\text{CF}_3}$ and HSiCl$_3$ in acetonitrile after full conversion.
**Figure S2.** $^{19}$F NMR (376 MHz, CD$_3$CN) of the reaction mixture of gua$^{29}$ and HSiCl$_3$ in acetonitrile after full conversion.

**Figure S3.** $^{29}$Si(H) IG NMR (119 MHz, CD$_3$CN) of the reaction mixture of gua$^{29}$ and HSiCl$_3$ in acetonitrile.
2.2. Assessment of Lewis Acidity by the Gutmann-Beckett method

To a suspension of 1-(sulfolane)$_2$ (20.0 mg, 19.4 µmol, 1.0 eq.), triethylphosphine oxide (a. 2.61 mg, 19.4 µmol 1.0 eq.; b. 5.22 mg, 38.9 µmol 2.0 eq.) was added in roughly three equal portions. The colorless solid dissolved within seconds and $^1$H-, $^{19}$F-, $^{13}$C- and $^{31}$P-NMR spectroscopy revealed the formation of 1-OPE$_3$ (a.) and cis-1-(OPE)$_3$ (b.) in quantitative yields according to NMR spectroscopy, respectively. Crystallization by gas diffusion of n-pentane yielded single-crystals suitable for X-ray structural analysis for both compounds. Poor crystal quality and twinning of cis-1-(OPE)$_3$ prevented full structure refinement.

1-OPE$_3$:
$^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ 2.10 – 2.02 (dq, $^2$J$_{PH}$ = 11.5, 7.7 Hz, 6H), 1.15 (dt, $^3$J$_{PH}$ = 7.7 Hz, 9H).
$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) δ 150.67 ($^1$J$_{CF}$ = 275.74 Hz, C$_q$O), 122.08, 115.85 (q, $^2$J$_{CF}$ = 34.7 Hz, C$_q$CF$_3$), 17.00 (d, $^1$J$_{PC}$ = 62.5 Hz), 4.34 (d, $^3$J$_{PC}$ = 5.2 Hz).
$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -51.39 – -51.67 (m, 12F), -56.54 – -56.95 (m, 12F).
$^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) δ 89.37.

cis-1-(OPE)$_3$:
$^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ 2.11 (ddq, J = 15.4, 12.5, 7.7 Hz, 6H), 1.96 (ddq, J = 15.4, 11.8, 7.7 Hz, 6H), 1.11 (dt, $^3$J$_{PH}$ = 7.7 Hz, 18H).
$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) δ 154.35 (C$_q$O), 153.94 (C$_q$O), 124.62, 122.80, 122.48, 112.98, 17.22 (d, $^1$J$_{PC}$ = 66.2 Hz), 5.22 (d, $^3$J$_{PC}$ = 4.9 Hz).
$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -50.89 (sept, $^5$J$_{FF}$ = 14.9 Hz, 6F), -51.27 (sept, $^5$J$_{FF}$ = 15.3 Hz, 6F), -56.59 (q, $^5$J$_{FF}$ = 14.9 Hz, 6F), -56.59 (q, $^5$J$_{FF}$ = 15.3 Hz, 6F).
$^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) δ 74.70.

2.3. Reactivity against [PPh$_4$][SbF$_6$]

1-(sulfolane)$_2$ (20.0 mg, 19.4 µmol, 1.0 eq.) was suspended in CD$_2$Cl$_2$ (0.5 mL). Upon addition of [PPh$_4$][SbF$_6$] (11.2 mg, 19.4 µmol, 1.0 eq.) at rt the colorless solid dissolved immediately. Monitoring of the reaction using $^{19}$F-NMR spectroscopy revealed the immediate formation of the fluoridosilicate [1-F]$^-$ and SiF$_4$. 
2.4. Chloride-Abstraction from Trityl Chloride

To a solution of trityl chloride (6.8 mg, 24.3 μmol, 1.0 eq.) in CD$_2$Cl$_2$, 1-(sulfolane)$_2$ (25.0 mg, 24.3 μmol, 1.0 eq.) was added at rt. The solution turned immediately yellow to orange, indicating the formation of the tritylium cation along with the corresponding chloridosilicate [CPh$_3$][1-Cl]. After 24 h at rt, NMR spectroscopy revealed the absence of trityl chloride.

[CPh$_3$][1-Cl]:

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ 8.28 (t, $^3$J$_{HH}$ = 7.4 Hz, 3H, para-H), 7.89 (t, $^3$J$_{HH}$ = 7.4 Hz, 6H, ortho-H), 7.7 (t, $^3$J$_{HH}$ = 7.7 Hz, 6H, meta-H).

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) δ 211.28 (C$_{Ph}$), 152.08 (C$_{OSi}$), 144.06 (C$_{Ar$)-trityl}), 143.08 (C$_{Ar$)-trityl}), 140.33 (C$_{Ar$)-trityl}), 131.09 (C$_{Ar$)-trityl}), 122.80 (q, $^1$J$_{CF}$ = 276, CF$_3$), 115.41 (q, $^1$J$_{CF}$ = 34.0 Hz, C$_6$(CF$_3$)).

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -51.34 (m, 12F), -56.51 – -56.87 (m, 12F).

$^{29}$Si($^1$H) NMR (119 MHz, CD$_2$Cl$_2$) δ -89.65.
2.5. Reduction of 1-(Ph₂CO) with HSiEt₃

1-(OCPh₂) (35 mg, 36.1 μmol, 1.0 eq.) was dissolved in CH₂Cl₂ (1 mL) and cooled to −40 °C. Triethylsilane (12.1 μL, 75.7 μL, 2.1 eq.) was added in three portions, the reaction mixture kept at −40 °C for 12 h and was then allowed to warm to rt. Volatiles were removed in vacuo, and the residue taken up in CD₂Cl₂ (0.45 mL) and transferred to a J. Young type NMR tube. ¹H NMR of the red solution indicated quantitative formation of diphenylmethane whereas ³¹F NMR spectra indicated the formation of a newly formed species assigned with two resonances of the similar intensity. A ¹³C(¹⁹F) NMR supported the formation of a species containing one cat²³ unit. The ²⁹Si(¹⁹F) IG NMR spectrum showed two signals at 21.2 ppm and −78.4 ppm. The downfield signal assigned to the disiloxane was found to be significantly shifted to the free hexaethyl disiloxane (reference: 8.9 ppm)⁴⁵. In accordance, the methylene protons in the ¹H NMR spectrum were also more deshielded (0.63 ppm, reference 0.56 ppm)⁵⁰. Additionally, the calculated ²⁹Si NMR resonance for donor-free ¹ (~42.8 ppm, PBE0/def2-TZVP) differed from the signal found experimentally at −78.4 ppm. For an adduct 1-O(SiEt₃)_2, calculated ²⁹Si NMR references are 58.0 ppm (average for the two SiEt groups) and −101.8 ppm (PBE0/def2-TZVP, resp.). Experimental resonances are in line with an equilibrium for the formation of an adduct 1-O(SiEt₃)_2 resulting in averaged signals over free and bound states. For a ΔG value of approx. −1.0 kJ mol⁻¹ at 298K the equilibrium constant (e⁻ΔG/RT) indicates a proportion of 60.0% 1-O(SiEt₃)_2 and 40.0% of ¹ and hexaethyldisiloxane. When multiplied with the calculated NMR shifts of the compounds, combined signals of −78.2 ppm and 35.4 ppm are obtained, being in good agreement with the experimental resonances (Table 1, the significant off-set of the disiloxane entity is attributed to shortcomings in the computation method, cf. computed (1.6 ppm) vs. experimental (8.9 ppm) ²⁹Si NMR shift of free O(SiEt₃)_2. The calculated ΔG value of 19.8 kJ mol⁻¹ differs from the assumed value, but the deviation is within the borders of the accuracy of the used computational methods for the calculation of the thermodynamic properties (SMD(CH₂Cl₂) DSD-BLYP/def2-QZVPP//PBEh-3c) and the NMR resonances (SMD(CH₂Cl₂) PBE0/def2-TZVP//PBEh-3c).

\[
K = e^{\Delta G \over RT}
\]

Proportions [%]: \[1-O(SiEt₃)_2 = \frac{K}{1+K}\] and \[1], \[O(SiEt₃)_2 = \frac{1}{1+K}\]

Table 1. Rationalization of ²⁹Si NMR resonances in a mixture of ¹, O(SiEt₃)_2 and 1-O(SiEt₃)_2:

| Compound | Calculated ²⁹Si NMR Shifts (PBE0/def2-TZVP) | Proportion in Equilibrium for ΔG = −1.0 kJ mol⁻¹ | Averaged signals based on calculations | Experimental ²⁹Si resonances |
|----------|------------------------------------------|-----------------------------------------------|--------------------------------------|--------------------------|
| ¹       | −42.8 ppm                                |                                               |                                      |                          |
| (Et₃Si)₂O | 4.6 ppm                                   | 40.0%                                         | 35.4 ppm                            | 21.2 ppm                |
|         | −1.4 ppm                                  |                                                |                                      |                          |
| 1-O(SiEt₃)₂ | 58.6 ppm                                   | 60.0%                                         | −78.2 ppm                           | −78.4 ppm                |
|         | 57.4 ppm                                  |                                                |                                      |                          |

¹-O(SiEt₃)_2:

¹H NMR (600 MHz, CD₂Cl₂) δ 0.94 (t, Jdf = 8.0 Hz, 18H, -CH₂-), 0.63 (q, Jdf = 8.0 Hz, 12H, -CH₂-).

¹³C(¹⁹F) (¹³COSi) (126 MHz, CD₂Cl₂) δ 150.60 (C₆OSi), 123.63 (CF₃), 122.46 (CF₃), 121.96 (CF₃), 118.53 (CF₃), 6.29 (-CH₂-), 5.88 (-CH₂-).

¹³C(¹⁹F) (¹³COSi) (151 MHz, CD₂Cl₂) δ 150.57 (C₆OSi), 123.66 (m), 122.44 (q, Jcf = 276 Hz, CF₃), 121.94 (q, Jcf = 279 Hz, CF₃), 118.49 (q, Jcf = 35.1 Hz, CF₃), 6.28 (-CH₂-), 5.86 (-CH₂-).

¹⁹F NMR (188 MHz, CD₂Cl₂) δ -51.73 (m, 12F), -57.18 (m, 12F).

²⁹Si(¹⁹F) IG NMR (119 MHz, CD₂Cl₂) δ 21.17, -78.35.
Figure S5. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) of the reaction mixture of 1-OCPh$_2$ and HSiEt$_3$.

Figure S6. $^{13}$C($^1$H, $^{19}$F) NMR (126 MHz, CD$_2$Cl$_2$) of the reaction mixture of 1-OCPh$_2$ and HSiEt$_3$. 

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Figure S7. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) of the reaction mixture of 1-OCPh$_2$ and HSiEt$_3$.

Figure S8. $^{29}$Si{[H]} NMR (119 MHz, CD$_2$Cl$_2$) of the reaction mixture of 1-OCPh$_2$ and HSiEt$_3$. 
2.6. Preferred conformation of the bis(cyclohexanecarboxaldehyde) adduct of 1

In order to investigate if the preferred cisoid conformation observed in 1-(OPEt$_3$)$_2$ is also present for aldehyde donors, 1-(sulfolane)$_2$ (10.0 mg, 9.72 µmol, 1.0 eq.) was suspended in 0.45 mL CD$_2$Cl$_2$. Cyclohexanecarboxaldehyde (11.8 µmol, 97.2 µmol, 10.0 eq.) was added, upon which a yellow homogeneous mixture was observed. $^{19}$F NMR spectroscopy revealed four signals, in line with the observation in 1-(OPEt$_3$)$_2$, advocating for a cis conformation. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) δ -50.82 – -51.45 (m, 6F), -51.61 (m, 6F), -55.60 – -56.66 (m, 6F), -56.68 – -57.16 (m, 6F).

Figure S9. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) of the mixture of 10.0 eq. cyclohexanecarboxaldehyde and 1.0 eq. 1-(sulfolane)$_2$. 
3. Catalysis

General procedure for reduction catalysis:
A J. Young type NMR tube was charged with x mol% catalyst, substrate (150 µmol, 1.0 eq.) and solvent (0.5 mL). The respective reducing agent (r.a.) was added and the reaction was conducted at the specified temperature (T) and monitored using GCMS, $^1$H or $^{31}$P NMR spectroscopy. Mesitylene, cyclooctane (75 µmol) or tri-n-butylphosphate were added as internal standard and conversion as well as yields were determined by integration. When non-deuterated solvent was used for the reaction, 50 µL CD$_2$Cl$_2$ were added prior to the final NMR measurement and the sample locked on CD$_2$Cl$_2$, to ensure sufficient resolution for yield determination by integration, if required.

Table 2. Conditions for reduction of aldehydes.

| Substrate                          | Catalyst          | x    | solvent | eq. r.a. | T [°C] | t [h] | Yield[a] [%] |
|------------------------------------|-------------------|------|---------|----------|--------|-------|--------------|
| benzaldehyde                       | 1-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 93           |
| p-fluorobenzaldehyde               | 1-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 96 (3°)      |
| p-methylbenzaldehyde               | 1-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 97 (<0.5°)   |
| cyclohexanecarboxaldehyde          | 1-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 71           |
| p-fluorobenzaldehyde               | 1-(Ph$_2$CO)     | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 80 (2°)      |
| p-methylbenzaldehyde               | 1-(Ph$_2$CO)     | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 97 (<0.5°)   |
| p-fluorobenzaldehyde               | Si(cat$^{[b]}_2$)-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 10 (16°)     |
| p-methylbenzaldehyde               | Si(cat$^{[b]}_2$)-(sulfolane)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 27 (3°)      |
| p-fluorobenzaldehyde               | Si(cat$^{[b]}_2$)-(CH$_2$CN)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 5 (6°)      |
| p-methylbenzaldehyde               | Si(cat$^{[b]}_2$)-(CH$_2$CN)$_2$ | 1    | CD$_2$Cl$_2$ | 1.5 HSiEt$_3$ | 25     | 24    | 6 (<0.5°)   |
| p-fluorobenzaldehyde               | 1-(sulfolane)$_2$, 5 oDCB | 6.0 PhSiH$_3$ | 100 | 168 | 66°          |

[a] yield for dialkyl ethers; [b] yield for hydrosilylation product – (methylene resonances in the reaction mixture at 4.70 ppm (p-FC$_6$H$_4$CH$_2$OSiEt$_3$, 4.69 ppm in CDCl$_2$[c]) and 4.69 ppm (p-CH$_3$C$_6$H$_4$CH$_2$OSiEt$_3$, 4.69 ppm in CDCl$_2$[c]) were found to be consistent with literature values; [c] yield for dihydrodeoxygenation (p-fluorotoluene).

Table 3. Conditions for the hydrodeoxygenation of carbonyls.

| Substrate                          | Catalyst          | x    | solvent | eq. r.a. | T [°C] | t [h] | Yield[a] [%] |
|------------------------------------|-------------------|------|---------|----------|--------|-------|--------------|
| benzoquinone                       | 1-(sulfolane)$_2$ | 2    | CD$_2$Cl$_2$ | 3.0 HSiEt$_3$ | 25     | 0.5   | 99           |
| acetylaldehyde                     | 1-(sulfolane)$_2$ | 5    | oDCB   | 3.0 PhSiH$_3$ | 100    | 72    | 80           |
| cyclohexanone                      | 1-(sulfolane)$_2$ | 5    | oDCB   | 3.0 PhSiH$_3$ | 100    | 72    | 61°          |
| N,N-disopropylbenzamide            | 1-(sulfolane)$_2$ | 5    | toluene-d$_8$ | 3.0 PhSiH$_3$ | 25     | 24    | 77           |
| benzenepoxide                      | 1-(sulfolane)$_2$ | 2    | CD$_2$Cl$_2$ | 3.0 HSiEt$_3$ | 25     | 24    | 24           |
| benzophenone                       | Si(cat$^{[b]}_2$)-(sulfolane)$_2$ | 2    | CD$_2$Cl$_2$ | 3.0 HSiEt$_3$ | 25     | 24    | 16           |

[a] yield for dihydrodeoxygenated product, [b] yield for cyclohexene, observed as main product.

Table 4. Conditions for the deoxygenation of phosphine oxides.

| Substrate                          | Catalyst          | x    | solvent | eq. r.a. | T [°C] | t [h] | Yield[a] [%] |
|------------------------------------|-------------------|------|---------|----------|--------|-------|--------------|
| triethylphosphine oxide            | 1-(sulfolane)$_2$ | 5    | toluene-d$_8$ | 3.0 PhSiH$_3$ | 100    | 48    | 96           |
| triphenylphosphine oxide           | 1-(sulfolane)$_2$ | 5    | toluene-d$_8$ | 3.0 PhSiH$_3$ | 100    | 48    | 91           |

[a] yield for phosphine product.

Exemplary NMR monitored reaction processes are shown in Figure S10 and Figure S11.
Figure S10. Monitored $^1$H NMR (200 MHz, CD$_2$Cl$_2$) spectra of the reaction of $p$-methylbenzaldehyde and triethylsilane catalyzed by 1 mol% of 1-(sulfolane)$_2$ at rt.

Figure S11. Monitored $^{31}$P NMR (81 MHz, toluene-d8) spectra of the reaction of triethylphosphine oxide and phenylsilane catalyzed by 5 mol% of 1-(sulfolane)$_2$ at 100 °C.
**SUPPORTING INFORMATION**

Bisbenzyl ether

1H NMR (200 MHz, CD2Cl2) δ 7.47 – 7.24 (m, 10H), 4.58 (s, 4H).

Obtained signals matched the ones found in literature.[8]

GCMS EI+ m/z 107.0 (15%) [C6H5-CH2-O]+, 91.1 (100%) [C6H5-CH3]+, 91.1 (81%) [C6H5-CH2]+.

Bis(4-fluoro)benzyl ether

1H NMR (200 MHz, CD2Cl2) δ 7.44 – 7.27 (m, 4H), 7.17 – 6.96 (m, 4H), 4.57 – 4.48 (m, 4H).

Obtained signals matched the ones found in literature.[9]

GCMS EI+ m/z 234.1 (< 0.5%) [M]+, 125.0 (15%) [F-C6H4-CH2-O]+, 91.1 (81%) [F-C6H4-CH3]+.

Bis(4-methyl)benzyl ether

1H NMR (200 MHz, CD2Cl2) δ 7.27 (d, 3JHH = 8.2 Hz, 4H), 7.18 (d, 3JHH = 8.2 Hz, 4H), 4.51 (s, 4H), 2.37 (s, 6H).

Obtained signals matched the ones found in literature.[8]

GCMS EI+ m/z 226.1 (1%) [M]+, 121.1 (11%) [CH3-C6H4-CH2-O]+, 106.1 (100%) [CH3-C6H4-CH3]+, 91.1 (45%) [C6H5-CH2]+.

Bis(cyclohexyl)methyl ether

1H NMR (200 MHz, CD2Cl2) δ 3.17 (d, 3JHH = 6.4 Hz, 4H), 1.82-1.60 (m, 10H), 1.63-1.42 (m, 2H), 1.23 (tq, 4H), 1.15 (tq, 2H), 0.09 (dq, 4H).

Obtained signals matched the ones found in literature.[8]

GCMS EI+ m/z 210.2 (1%) [M]+, 97.1 (100%) [C6H11-CH2]+, 81.1 (31%) [C6H5]+.

Diphenylmethane

1H NMR (200 MHz, CD2Cl2) δ 7.42 – 7.14 (m, 10H), 4.01 (s, 2H).

Obtained signals matched the ones found in literature.[10]

GCMS EI+ m/z 168.1 (98%) [M]+, 167.1 (100%) [M – H]+, 91.1 (17%) [C6H5-CH2]+.

Ethylbenzene

1H NMR (600 MHz, oDCB) δ 2.57 (q, 3JHH = 7.7 Hz, 2H), 1.18 (t, 3JHH = 7.7, 3H).

Aromatic signals not resolved due to interference with solvent.

13C{1H} NMR (151 MHz, oDCB) δ 144.19, 128.48, 125.77, 29.14, 15.85.

GCMS EI+ m/z 106.1 (35%) [M]+, 91.0 (100%) [M – CH3]+, 77.0 (7%) [C6H5]+.

The identity of the product was additionally verified through matching signals in comparison with a spectrum of the commercially obtained chemical in the same solvent system that was used throughout the reaction.

Cyclohexene

1H NMR (600 MHz, oDCB) δ 5.61 (br, 2H), 1.92 (br, 4H), 1.53 (br, 4H).

Bad resolution originating from the use of non-deuterated solvent did not allow the assignment of coupling patterns.

13C{1H} NMR (151 MHz, oDCB) δ 127.25, 25.36, 22.85.

GCMS EI+ m/z 82.1 (44%) [M]+, 67.1 (100%) [M – CH3]+, 54.1 (60%) [M – C2H4]+.

The identity of the product was additionally verified through matching signals in comparison with a spectrum of the commercially obtained chemical in the same solvent system that was used throughout the reaction.
SUPPORTING INFORMATION

p-Fluorotoluene
$^1$H NMR (600 MHz, d6-DCB) δ 6.95 (m, 2H), (t, $^3$$J_{HH} = 8.7$ Hz, 2H), 2.15 (s, 3H).
$^{13}$C($^1$H) NMR (151 MHz, d6-DCB) δ 161.11 (d, $^1$$J_{CF} = 242$ Hz), 133.47 (d, $^2$$J_{CF} = 3.2$ Hz), 130.38 (d, $^2$$J_{CF} = 7.7$ Hz), 114.83 (d, $^2$$J_{CF} = 21.0$ Hz), 20.41.
$^{19}$F NMR (188 MHz, d6-DCB) –117.93.
The identity of the product was additionally verified through matching signals in comparison with a spectrum of the commercially obtained chemical in the same solvent system that was used throughout the reaction.

N,N-diisopropyl-N-benzylamine
$^1$H NMR (200 MHz, toluene-d8) δ 7.43 – 7.30 (m, 5H), 3.50 (s, 2H), 2.90 (sept, $^3$$J_{HH} = 6.6$ Hz, 2H), 0.92 (d, $^3$$J_{HH} = 6.6$ Hz, 12H).
$^1$H NMR (200 MHz, CDCl3) δ 7.44 – 7.27 (m, 5H), 3.20 (sept, $^3$$J_{HH} = 6.6$ Hz, 2H), 1.10 (d, $^3$$J_{HH} = 6.6$ Hz, 12H).
After the reaction the solvent was removed in vacuo, the residue washed with n-pentane and taken up in CDCl3, for which solution the $^1$H NMR spectrum matched the one found in literature.\(^{[11]}\)
GCMS EI+ m/z 191.2 (6%) [M]+, 176.1 (54%) [M – CH3]+, 91.0 (100%) [C6H5CH2]+.

Triethylphosphine
$^1$H NMR (200 MHz, toluene-d8) δ 1.32 – 1.09 (m, 6H), 1.08 – 0.80 (m, 9H).
$^{31}$P($^1$H) NMR (81 MHz, toluene-d8) δ -19.66 (s).
Obtained signal was found to be consistent with a literature spectrum.\(^{[12]}\)
GCMS EI+ m/z 118.1 (55%) [M]+, 90.1 (82%) [M – C2H4]+, 62.0 (100%) [M – 2 C2H4]+.

Triphenylphosphine
$^1$H NMR (200 MHz, toluene-d8) δ 7.43 – 7.20 (m, 6H), 7.16 – 6.92 (m, 9H).
$^{31}$P($^1$H) NMR (81 MHz, toluene-d8) δ -5.08 (s).
GCMS EI+ m/z 262.1 (100%) [M]+, 183.0 (75%) [M – C6H5 – 2 H]+, 108.0 (28%) [M – 2 C6H5]+.
The identity of the product was verified through matching signals in comparison with a spectrum of the commercially obtained chemical in the same solvent.

Hexaethyldisiloxane
$^1$H NMR (200 MHz, CDCl3) δ 0.95 (t, $^3$$J_{HH} = 7.9$ Hz, 18H), 0.56 (q, $^3$$J_{HH} = 7.9$ Hz, 12H).
Obtained signals matched the ones found in literature.\(^{[5]}\)
GCMS EI+ m/z 246.2 (< 0.5%) [M]+, 217.2 (100%) [M – C2H5]+.

Carbonyl-olefin metathesis:

\[
\text{A} \quad \overset{\text{1-(sulfolane)$_2$ (5 mol%)}}{\text{CD$_2$Cl$_2$, rt, 24 h}} \quad \overset{> 97\%}{\text{Ph}} \quad \overset{\text{CO$_2$Et}}{+} \quad \overset{\text{O}}{\text{EtOOH}}
\]

The metathesis substrate A was synthesized according to a literature procedure.\(^{[13]}\) To a solution of A (27.4 mg, 100 μmol, 1 eq.) in CD$_2$Cl$_2$ (0.5 mL) was added 1-(sulfolane)$_2$ (3.23 mg, 10.0 μmol, 0.05 eq.) and the reaction progress monitored via $^1$H NMR. After 24 h, full conversion of the starting material was observed. After the reaction was found to be complete the mixture was analyzed by GCMS.

Ethyl 2-phenylcyclopent-2-ene-1-carboxylate.
$^1$H NMR (600 MHz, CDCl3) δ 7.45 – 7.40 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 6.36 (td, $^4$$J_{HH} = 2.6$, 1.6 Hz, 1H), 4.13 – 4.00 (m, 2H), 3.96 (m, 1H), 2.68 (m, 1H), 2.60 – 2.50 (m, 1H), 2.36 (dtd, $^4$$J_{HH} = 13.0$, 9.2, 6.6 Hz, 1H), 2.25 – 2.15 (m, 2H), 1.15 (t, $^3$$J_{HH} = 7.1$ Hz, 3H).
Obtained shifts matched the ones found in literature.\(^{[14]}\)
GCMS EI+ m/z 216.1 (16%) [M]+, 142.1 (100%) [M – CO$_2$Et]+.

S17
Figure S12. Reaction progress monitored via $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectroscopy of the intramolecular carbonyl olefin metathesis catalyzed by 5 mol% 1-(sulfolane)$_2$ in CD$_2$Cl$_2$. 
4. Computational Details

All geometry optimizations and single point energies were calculated using the Orca 4.1.1, 4.1.2 or 4.2.1 program package.\[15\] As starting geometries, VSEPR structures preoptimized with UFF were used. For the calculation of anion affinities the same method was used as previously reported for bis catecholato silanes and germanes.\[3, 4, 14\] The hybrid functional PW6B95 was used with the Becke-Johnson damping function (BJ), Grimme’s semi-empirical dispersion correction (D3) and the def2-TZVPP basis set, as this was shown to be ideal for reproducing experimental solid-state structure parameters in previous benchmark studies.\[16\] The resolution-of-identity and “chain of spheres” approximation in the form of RIJCOSX was used in combination with matching auxiliary basis sets.\[17\] Calculated geometries were confirmed as energetic minima by frequency calculations at the BP86-D3 (BJ)/ def2-SVP level of theory. Enthalpies at 298 K were computed at the same level of theory using the rigid-rotor harmonic oscillator (RRHO) approximation.\[18\] For the final anion affinities, single point energies were calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory.\[19\] Using the protocol proposed by Krossing, anion affinities were determined by an isodesmic reaction scheme using G3 anchor points, thus by subtraction of the anchor enthalpies for the reaction $\text{Me}_3\text{Si}^+ + \text{X}^- \rightarrow \text{Me}_3\text{SiX}$ from the column [(B) − (A)] in Table 5.\[20\] Solvation correction ($\text{FIA}_{\text{calc}}$) was performed according to the COSMO-RS scheme described recently.\[21\] All other geometry optimizations were performed with PBEh-3c/def2-mSVP as implemented in ORCA, using grid5 settings.\[22\] Calculated geometries have been confirmed as energetic minima on the potential energy surface by the absence of negative frequencies in the analytical calculation of harmonic frequencies at the PBEh-3c level. Unscaled ZPEs and enthalpies at 298 K were obtained from the same level of theory by using the rigid-rotor harmonic oscillator (RRHO) approximation.\[18\] Calculation of $^{29}\text{Si}$ NMR resonances was conducted utilizing the PBE0 functional,\[23\] and the def2-TZVP basis set,\[16d\] as this combination was shown to be a reliable method in a recent benchmark.\[24\] Additionally, the auxiliary basis set def2/JK and grid4, finalgrid6 settings were applied.\[25\] Solvation effects were considered implicitly, using the Universal Solvent Model (SMD),\[26\] as implemented in the Orca program package. Resonances were referenced against tetramethylsilane, for which optimization and chemical shielding were calculated in the same manner.

Thermodynamic data for the formation of $\text{1-O(SiEt}_3\text{)}_2$ was guided by a method that has been shown to reliably resemble thermodynamic data for early main group Lewis acids.\[21\] described as follows. For the optimized structures single point energies were calculated with the double-hybrid functional DSD-BLYP,\[27\] the Becke-Johnson damping function (BJ),\[16c, 16d\] Grimme’s semi-empirical dispersion correction (D3),\[16c, 16d\] and the def2-QZVPP basis set.\[16e\] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.\[17b\] Solvation free enthalpies for molecular structures were determined implicitly using the Universal Solvent Model (SMD),\[26\] as implemented in the Orca program package.

Additional Fluoride and Hydride Ion Affinities displayed in Figure 3b

FIAs for the aluminum-based Lewis acids were taken from a recent benchmark study\[21\] (calculated at the PBE86/def2-QZVPP//PBEh-3c/def2-mSVP or DLPNO-CCSD(T)/aug-cc-pVQZ/PBEh-3c/def2-mSVP level of theory) but for consistency anchored to the G3 values.\[20\] The corresponding HIAs were calculated analogously as described for FIAs and will be published as part of an ongoing study.\[28\]
### Supporting Information

#### Table 5. Computed energies for the calculation of anion affinities.

**BP86-D3/def2-SVP level of theory**

| Compound   | $E$ [a.u.] | in kJ mol$^{-1}$ | Thermal correction [kcal mol$^{-1}$] | Electronic + Thermal [kJ mol$^{-1}$] | LA + Me$_2$SiY (A) | Me$_3$Si$^{+}$ + A-Y (B) | (B) - (A) | FIA / HIA |
|------------|-----------|-----------------|--------------------------------------|-----------------------------------|-------------------|-----------------|-------------|----------|
| Si(cat$^{+}$)$_2$ | -3746.4250 | -9836238.7       | 157.4                                | -9835578.4                       |                   |                  |             |          |
| [F-Si(cat$^{+}$)$_2$]$^-$ | -3846.4068 | -10098741.2      | 159.5                                | -10098071.8                       |                   |                  |             |          |
| [H-Si(cat$^{+}$)$_2$]$^-$ | -3747.1692 | -9838192.7       | 162.3                                | -9837511.8                       |                   |                  |             |          |

**PW6B95-D3/def2-TZVPP level of theory**

| Compound   | $E$ [a.u.] | in kJ mol$^{-1}$ | Thermal correction [kcal mol$^{-1}$] | Electronic + Thermal [kJ mol$^{-1}$] | LA + Me$_2$SiY (A) | Me$_3$Si$^{+}$ + A-Y (B) | (B) - (A) | FIA / HIA |
|------------|-----------|-----------------|--------------------------------------|-----------------------------------|-------------------|-----------------|-------------|----------|
| Si(cat$^{+}$)$_2$ | -3754.5723 | -9857629.5       |                                      | -9856969.2                       |                   |                  |             |          |
| [F-Si(cat$^{+}$)$_2$]$^-$ | -3854.7786 | -10120721.3      |                                      | -10120051.9                      |                   |                  |             |          |
| [H-Si(cat$^{+}$)$_2$]$^-$ | -3755.3071 | -9859558.8       |                                      | -9858877.9                       |                   |                  |             |          |

**DLPNO-CCSD(T)/aug-cc-pVQZ level of theory**

| Compound   | $E$ [a.u.] | in kJ mol$^{-1}$ | Thermal correction [kcal mol$^{-1}$] | Electronic + Thermal [kJ mol$^{-1}$] | LA + Me$_2$SiY (A) | Me$_3$Si$^{+}$ + A-Y (B) | (B) - (A) | FIA (exch) / HIA |
|------------|-----------|-----------------|--------------------------------------|-----------------------------------|-------------------|-----------------|-------------|----------------|
| Si(cat$^{+}$)$_2$ | -3745.3185 | -9833333.7      |                                      | -9832673.4                       |                   |                  |             |          |
| [F-Si(cat$^{+}$)$_2$]$^-$ | -3845.3158 | -10095876.8     |                                      | -10095207.4                      |                   |                  |             |          |
| [H-Si(cat$^{+}$)$_2$]$^-$ | -3746.0526 | -9835261.2      |                                      | -9834580.3                      |                   |                  |             |          |

#### Table 6. Computed energies for the calculation of thermodynamics of the formation of 1-O(SiEt$_3$)$_3$ from 1 and O(SiEt$_3$)$_3$. Concentration contribution from gas phase (1 atm) to solution phase (1 mol L$^{-1}$) for the solvation was additionally considered (7.9 kJ mol$^{-1}$ for 298K).

**PBEh-3c**

| Compound   | $E$ [a.u.] | in kJ  | Thermal correction [kJ] | Enthalpy $H$ [kJ] | Gibbs Free Energy $G^\circ$ (298K) [kJ] |
|------------|-----------|-------|-------------------------|------------------|---------------------------------------|
| O(SiEt$_3$)$_3$ | -1127.8183 | -2961086.9 | 1146.8                 | -2959937.6        | -2960132.7                             |
| Si(cat$^{+}$)$_2$ | -3741.7947 | -9624082.0 | 694.4                   | -9823385.1        | -9823668.3                             |
| Si(cat$^{+}$)$_2$-O(SiEt$_3$)$_3$ | -4869.6408 | -12785241.8 | 1854.7                 | -12783384.6       | -12783785.9                             |

**SMD(CH$_3$Cl)$_3$ D3-BLYP D3Bj/def2-QZVPP**

| Compound   | $E$ [a.u.] | in kJ  | Enthalpy $H$ [kJ] | Gibbs Free Energy $G^\circ$ (298K) [kJ] |
|------------|-----------|-------|------------------|---------------------------------------|
| O(SiEt$_3$)$_3$ | -1128.9337 | -2964015.4 |                     | -2962866.1                             |
| Si(cat$^{+}$)$_2$ | -3747.5693 | -9839243.2 |                     | -9838546.3                             |
| Si(cat$^{+}$)$_2$-O(SiEt$_3$)$_3$ | -4876.5259 | -12803318.8 |                     | -12801461.6                             |

\[ \Delta H = -57.2 \text{ kJ mol}^{-1} \]

\[ \Delta G = 19.6 \text{ kJ mol}^{-1} \]
## Table 7. Computed $^{29}\text{Si}$ NMR resonances.

| Compound | Isotropic Shielding | Solvent | Resonance $\delta$ [ppm] |
|----------|---------------------|---------|--------------------------|
| Si(CH$_3$)$_4$ | 332.132 | CH$_2$Cl$_2$ | 0.0 |
| Si(CH$_3$)$_3$ | 332.122 | CH$_2$CN | 0.0 |
| Si(catCF$_3$)$_2$ | 374.934 | CH$_2$Cl$_2$ | -42.8 |
| Si(catCF$_3$)$_2$-OCPh$_2$ | 436.154 | CH$_2$Cl$_2$ | -104.0 |
| [Si(catCF$_3$)$_2$-Cl]$^{-}$ | 416.983 | CH$_2$CN | -84.9 |
| Si(catCF$_3$)$_2$-O(SiEt$_3$)$_2$ | 433.946 | CH$_2$Cl$_2$ | -101.8 |
| | 273.535 | CH$_2$Cl$_2$ | 58.6 |
| | 274.703 | CH$_2$Cl$_2$ | 57.4 | $\varnothing$ 58.0 |
| (Et$_3$Si)$_2$O | 327.581 | CH$_2$Cl$_2$ | 4.6 |
| | 333.513 | CH$_2$Cl$_2$ | -1.4 | $\varnothing$ 1.6 |
5. NMR Spectra

Figure S13. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1,2,3,4-tetraiodo-5,6-dimethoxy-benzene (ver$^5$).

Figure S14. $^{13}$C{H} NMR (101 MHz, CDCl$_3$) spectrum of 1,2,3,4-tetraiodo-5,6-dimethoxy-benzene (ver$^6$).
Figure S15. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1,2-dimethoxy-3,4,5,6-tetra(trifluoromethyl)benzene (ver$_{CF_3}$).

Figure S16. $^{13}$C/$^1$H NMR (101 MHz, CDCl$_3$) spectrum of 1,2-dimethoxy-3,4,5,6-tetra(trifluoromethyl)benzene (ver$_{CF_3}$).
Figure S17. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1,2-dimethoxy-3,4,5,6-tetra(trifluoromethyl)benzene (ver$_{CF}$).

Figure S18. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of 2-methoxy-3,4,5,6-tetra(trifluoromethyl)phenol (gua$_{CF}$).
Figure S19. $^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$) spectrum of 2-methoxy-3,4,5,6-tetra(trifluoromethyl)phenol (gua$^{CF}$).

Figure S20. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2-methoxy-3,4,5,6-tetra(trifluoromethyl)phenol (gua$^{CF}$).
Figure S21. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 1-(sulfolane)$_2$.

Figure S22. $^{13}$C NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 1-(sulfolane)$_2$. 
Figure S23. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) spectrum of 1-(sulfolane)$_2$.

Figure S24. $^1$H NMR (200 MHz, CD$_2$Cl$_2$) spectrum of 3,4,5,6-tetra(trifluoromethyl)catechol (H$_2$cat(TF)).
Figure S25. $^{13}$C{($^1$H)} NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 3,4,5,6-tetra(trifluoromethyl)catechol (H$_2$catCF$_3$).

Figure S26. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) spectrum of 3,4,5,6-tetra(trifluoromethyl)catechol (H$_2$catCF$_3$).
Figure S27. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of [N(n-Bu)$_4$][1-F].

Figure S28. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of [N(n-Bu)$_4$][1-F].
Figure S29. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [N(n-Bu)$_4$][1-F].

Figure S30. $^{29}$Si($^1$H) IG NMR (119 MHz, CD$_2$Cl$_2$) spectrum of [N(n-Bu)$_4$][1-F].
Figure S31. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 1-(OCP)$_2$.

Figure S32. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 1-(OCP)$_2$. 
Figure S33. $^{19}$F NMR (188 MHz, CD$_2$Cl$_2$) spectrum of 1-(OCPh$_2$).

Figure S34. $^{29}$Si$[^1]$H NMR (119 MHz, CD$_2$Cl$_2$) spectrum of 1-(OCPh$_2$).
Figure S35. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of Si(cat$^{15}$Cl$_2$)(sulfolane)$_2$.

Figure S36. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of Si(cat$^{15}$Cl$_2$)(sulfolane)$_2$. 
Figure S37. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 1-OPEt$_3$.

Figure S38. $^{13}$C(1H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 1-OPEt$_3$. 
Figure S39. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of 1-OPEt$_3$.

Figure S40. $^{31}$P{H} NMR (243 MHz, CD$_2$Cl$_2$) spectrum of 1-OPEt$_3$. 
Figure S41. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of 1-(OPEt$_3$)$_2$.

Figure S42. $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) spectrum of 1-(OPEt$_3$)$_2$. 
Figure S43. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of $1$-(OPE$_3$)$_2$.
Figure S44. $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$) spectrum of 1-(OPEt)$_3$.

Figure S45. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of [CPh$_3$][1-Cl].
Figure S46. $^{13}$C{H} NMR (151 MHz, CD$_2$Cl$_2$) spectrum of [CPh$_3$][1-Cl].

Figure S47. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) spectrum of [CPh$_3$][1-Cl].
Figure S48. $^{29}$Si($^1$H) IG NMR (119 MHz, CD$_2$Cl$_2$) spectrum of [CPh$_3$][1-Cl].
6. IR Spectra

Figure S49. ATR-IR absorption spectrum of 1-(sulfolane)$_2$. The spectrum was manually base-line corrected after data acquisition.

Figure S50. ATR-IR absorption spectrum of 1-(OCPh)$_2$. The spectrum was manually base-line corrected after data acquisition.
7. X-Ray Diffraction

General
For SCXRD measurements, a suitable crystal was picked from the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a cryo loop. A Bruker APEX-III CCD diffractometer with a low-temperature unit using Mo-Kα radiation, chromated by mirror optics, was used for phi- and omega- scans. Data acquisition was done at 100.0 K. A strategy for data collection was calculated with Bruker’s APEX3 software. The same program was used for processing of collected data. Data reduction, scaling, and absorption corrections were done with SAINT. SA-DABS-2016/2 was used for multi-scan absorption correction. Structures were solved with dual methods as implemented in the ShelXT 2018 structure solution program. Structure refinement was carried out by full matrix least squares minimization on F2 using the 2018/3 version of ShelXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using a riding model. Handling of the structural data during solution and refinement was performed with the Olex2 v1.3 graphical interface.\(^{[29]}\)

For data visualization, Mercury 4.1.3 was used.\(^{[30]}\) The thermal displacement ellipsoids are shown at the probability level of 50%. CCDC 2070464-2070469 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre’s and FIZ Karlsruhe’s joint Access Service via https://www.ccdc.cam.ac.uk/structures/?.
Empirical formula: \( \text{C}_{11}\text{H}_4\text{F}_{12}\text{O}_2 \)

Formula weight: 396.14

Temperature/K: 100.0

Crystal system: triclinic

Space group: P-1

\( a/\text{Å} \) 5.9951(6)

\( b/\text{Å} \) 9.3385(11)

\( c/\text{Å} \) 11.6211(13)

\( \alpha/\text{°} \) 95.562(5)

\( \beta/\text{°} \) 98.690(4)

\( \gamma/\text{°} \) 106.298(4)

Volume/Å\(^3\): 610.60(12)

\( Z \): 2

\( \rho_{\text{calc}} \)/g/cm\(^3\): 2.155

\( \mu \)/mm\(^{-1}\): 0.266

F(000): 388.0

Crystal size/mm\(^3\): 0.14 \times 0.12 \times 0.11

Radiation: MoK\(\alpha \) (\( \lambda = 0.71073 \))

2\( \theta \) range for data collection/\( \text{°} \): 4.594 to 58

Index ranges: -8 \( \leq h \leq 8 \), -12 \( \leq k \leq 12 \), -15 \( \leq l \leq 15 \)

Reflections collected: 29542

Independent reflections: 3217 [\( R_{\text{int}} = 0.0780 \), \( R_{\text{sigma}} = 0.0372 \)]

Data/restraints/parameters: 3217/0/231

Goodness-of-fit on \( F^2 \): 1.158

Final R indexes [\( I \geq 2\sigma (I) \)]: \( R_1 = 0.0435 \), \( wR_2 = 0.1030 \)

Final R indexes [all data]: \( R_1 = 0.0528 \), \( wR_2 = 0.1074 \)

Largest diff. peak/hole / e Å\(^3\): 0.66/-0.59

CCDC: 2070465
SUPPORTING INFORMATION

Cocrystallized benzene molecule omitted for clarity.

| **Empirical formula** | C_{34}H_{22}F_{24}O_{8}S_{2}Si |
|-----------------------|---------------------------------|
| **Formula weight**    | 1106.72                         |
| **Temperature/K**     | 100                             |
| **Crystal system**    | triclinic                       |
| **Space group**       | P-1                             |
| **a/Å**               | 9.5386(12)                      |
| **b/Å**               | 9.8566(18)                      |
| **c/Å**               | 11.7258(17)                     |
| **α/°**               | 85.560(6)                       |
| **β/°**               | 68.090(4)                       |
| **γ/°**               | 69.683(6)                       |
| **Volume/Å³**         | 957.5(3)                        |
| **Z**                 | 1                               |
| **ρ_{calc}/g/cm³**    | 1.919                           |
| **μ/mm⁻¹**            | 0.342                           |
| **F(000)**            | 552.0                           |
| **Crystal size/mm³**  | 0.12 × 0.103 × 0.094            |
| **Radiation**         | MoKα (λ = 0.71073)              |
| **2θ range for data collection/°** | 4.414 to 54.248 |
| **Index ranges**      | -12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15 |
| **Reflections collected** | 45166                      |
| **Independent reflections** | 4230 [R_{int} = 0.0523, R_{sigma} = 0.0232] |
| **Data/restraints/parameters** | 4230/0/313                  |
| **Goodness-of-fit on F²** | 1.040                      |
| **Final R indexes [I>=2σ (I)]** | R₁ = 0.0275, wR₂ = 0.0642  |
| **Final R indexes [all data]** | R₁ = 0.0381, wR₂ = 0.0683  |
| **Largest diff. peak/hole / e Å⁻³** | 0.37/-0.41            |

CCDC 2070467
### Crystallographic Data

**Empirical formula** | \( \text{C}_{14}\text{O}_{4}\text{F}_{12}\text{SCI}_{10} \)  
---|---  
**Formula weight** | 502.28  
**Temperature/K** | 100(2)  
**Crystal system** | monoclinic  
**Space group** | C2/c  
**a/Å** | 18.1928(11)  
**b/Å** | 19.8514(10)  
**c/Å** | 20.0516(11)  
**α/°** | 90  
**β/°** | 107.826(2)  
**γ/°** | 90  
**Volume/Å\(^3\)** | 6894.0(7)  
**Z** | 16  
**ρ_{calc} g/cm\(^3\)** | 1.936  
**μ/mm\(^-1\)** | 0.336  
**F(000)** | 4000.0  
**Crystal size/mm\(^3\)** | 0.32 × 0.18 × 0.08  
**Radiation** | MoKα (λ = 0.71073)  
**2θ range for data collection/°** | 4.104 to 54.27  
**Reflections collected** | 7630  
**Independent reflections** | 7630 [R\(_{int}\) = 0.0468, R\(_{sigma}\) = 0.0119]  
**Data/restraints/parameters** | 7630/163/850  
**Goodness-of-fit on F\(^2\)** | 1.052  
**Final R indexes \([I>=2σ (I)]\)** | R\(_1\) = 0.0345, wR\(_2\) = 0.0891  
**Final R indexes \([all\ data]\)** | R\(_1\) = 0.0389, wR\(_2\) = 0.0929  
**Largest diff. peak/hole / e Å\(^-3\)** | 0.45/-0.39  
**CCDC** | 2070469
Empirical formula $\text{C}_{26}\text{H}_{15}\text{F}_{24}\text{O}_{5}\text{PSi}$
Formula weight 922.44
Temperature/K 100.0
Crystal system triclinic
Space group P-1
$a$/Å 10.9648(10)
$b$/Å 11.6048(10)
$c$/Å 14.5292(12)
$\alpha$/° 110.008(3)
$\beta$/° 107.408(3)
$\gamma$/° 97.525(4)
Volume/Å$^3$ 1600.5(2)
$Z$ 2
$\rho_{\text{calc}}$/g/cm$^3$ 1.914
$\mu$/mm$^{-1}$ 0.303
$F(000)$ 912.0
Crystal size/mm$^3$ 0.115 x 0.095 x 0.086
Reflections collected 50414
Independent reflections 6582 [R$_{\text{int}}$ = 0.0780, R$_{\sigma}$ = 0.0413]
Data/restraints/parameters 6582/0/517
Goodness-of-fit on $F^2$ 1.039
Final R indexes [$I>2\sigma(I)$] $R_1 = 0.0372$, $wR_2 = 0.0867$
Final R indexes [all data] $R_1 = 0.0593$, $wR_2 = 0.0952$
Largest diff. peak/hole / e Å$^{-3}$ 0.31/-0.38
CCDC 2070466
| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula             | C_{20}H_{16}Cl_{8}O_{8}S_{2}Si            |
| Formula weight                | 760.14                                     |
| Temperature/K                 | 100.0                                      |
| Crystal system                | triclinic                                  |
| Space group                   | P-1                                        |
| a/Å                           | 7.2278(6)                                  |
| b/Å                           | 9.2581(7)                                  |
| c/Å                           | 11.5754(9)                                 |
| α/°                           | 103.618(3)                                 |
| β/°                           | 105.853(3)                                 |
| γ/°                           | 105.889(3)                                 |
| Volume/Å³                     | 675.16(9)                                  |
| Z                             | 1                                          |
| ρ_{calc}/g/cm³                | 1.870                                      |
| μ/mm⁻¹                        | 1.081                                      |
| F(000)                        | 382.0                                      |
| Crystal size/mm³              | 0.103 x 0.088 x 0.065                      |
| Radiation                     | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/°| 3.882 to 55.052                            |
| Index ranges                  | -9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15   |
| Reflections collected         | 21585                                      |
| Independent reflections       | 3103 [R_{int} = 0.0701, R_{sigma} = 0.0407]|
| Data/restraints/parameters    | 3103/0/178                                 |
| Goodness-of-fit on F²         | 1.125                                      |
| Final R indexes [I>2σ (I)]    | R₁ = 0.0446, wR₂ = 0.1006                  |
| Final R indexes [all data]    | R₁ = 0.0561, wR₂ = 0.1059                  |
| Largest diff. peak/hole / e Å⁻³| 0.52/-0.44                                |
| CCDC                          | 2070464                                    |
### Empirical formula

**C$_{42}$H$_{19}$O$_5$F$_{24}$Si**

### Formula weight

1087.66

### Temperature/K

101(2)

### Crystal system

triclinic

### Space group

P-1

| Parameter          | Value                  |
|--------------------|------------------------|
| a/Å                | 12.0751(15)            |
| b/Å                | 13.7369(17)            |
| c/Å                | 14.1223(16)            |
| α/°                | 86.848(4)              |
| β/°                | 88.870(4)              |
| γ/°                | 65.183(4)              |
| Volume/Å$^3$       | 2123.0(4)              |
| Z                  | 2                      |
| ρ$_{calc}$ g/cm$^3$| 1.701                  |
| μ/mm$^{-1}$        | 0.208                  |
| F(000)             | 1082.0                 |
| Crystal size/mm$^3$| 0.24 × 0.12 × 0.1      |
| Radiation          | MoKα ($λ = 0.71073$)   |
| 2θ range for data collection/°| 4.474 to 56.564     |
| Index ranges       | -16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18 |
| Reflections collected| 48697               |
| Independent reflections| 10511 [R$_{int} = 0.0762$, R$_{sigma} = 0.0609$] |
| Data/restraints/parameters | 10511/3419/1108 |
| Goodness-of-fit on F$^2$ | 1.030               |
| Final R indexes [I>2σ (I)] | R$_1 = 0.0607$, wR$_2 = 0.1572$ |
| Final R indexes [all data] | R$_1 = 0.0982$, wR$_2 = 0.1813$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.72/-0.38 |

CCDC 2070468
[Et$_3$N-H-NCCCH$_3$][1-Cl]

1-(OPEt)$_3$


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