Supporting Information

Synthesis and Characterization of Hypercoordinated Silicon Anions: Catching Intermediates of Lewis Base Catalysis

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Table of Contents

1. Experimental Procedures ........................................................................................................................................... 3
   a. Materials and General Methods ............................................................................................................................ 3
   b. Syntheses .................................................................................................................................................................. 4
2. Structural Details .......................................................................................................................................................... 9
   a. Overview of Structural Parameters .......................................................................................................................... 9
   b. Comparison of different [Y][TfO-1] compounds .................................................................................................. 11
3. Computational Details ............................................................................................................................................... 12
   a. Structure Optimization ........................................................................................................................................... 12
   b. CCSD(T)/CBS ......................................................................................................................................................... 12
   c. Single Point Energies with DLPNO-CCSD(T) ....................................................................................................... 13
   d. NMR Calculations .................................................................................................................................................. 15
   e. Natural Population Analysis (NPA) ...................................................................................................................... 15
4. X-Ray Diffraction ......................................................................................................................................................... 16
   a. General .................................................................................................................................................................. 16
5. NMR Spectra ............................................................................................................................................................... 28
6. IR Spectra ...................................................................................................................................................................... 52
6. References .................................................................................................................................................................. 58
1. Experimental Procedures

a. Materials and General Methods

All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (MBraun Labmaster dp, MB-20-G or a Sylatech Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). The argon was dried by passing over two columns of phosphorus pentoxide. Inorganic salts were dried at elevated temperatures (50 – 150 °C) in vacuo (10⁻² mbar) overnight prior to use. 18-crown-6 was dried over anhydrous phosphorous pentoxide for several days in vacuo and subsequently a solution of the crown-ether in DCM was stored over molecular sieves (4 Å) for three days before the crown ether was recrystallized. Tetrabutylammonium sulfate was purchased as a 50w% solution in water and the solvent was evaporated in vacuo to isolate this hygroscopic solid that was subsequently dissolved in DCM and stored over molecular sieves (4 Å) for three days before removal of the solvent yielded the dry salt. Other commercially available chemicals were used as received. Perchlorocatechol and bis(sulfolane)-bis(perchlorocatecholato)silane were synthesized according to literature known procedures.[1] All solution phase NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra (with the exception of ¹⁹F) were obtained with ¹H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ¹H and ¹³C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublet of doubles, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. ¹³C and ²⁹Si MAS NMR experiments were conducted on a Bruker Avance III 500 MHz NMR spectrometer equipped with a standard bore (54 mm room temperature bore) 11.7 T magnet. A double resonance magic angle sample spinning (MAS) probe was used for 4.0 mm spinners. The probe is doubly tuned to the frequency of the observe nucleus - ¹³C at 125.8 MHz and ²⁹Si at 99.4 MHz – and to the frequency of ¹H at 500.22 MHz. Chemical shift referencing was done by the substitution method following the IUPAC recommendations: ¹³C chemical shifts were calibrated setting the CH₂-signal position in adamantane to 38.4 ppm and calculating the ²⁹Si reference frequency using the tabulated values (19.867187 for ²⁹Si and 25.145020 for ¹³C). Following this procedure ²⁹Si chemical shifts refer to the IUPAC recommended standard Me₄Si (CDCl₃, ψ = 1 %). During the NMR measurements the rotor was spun at the magic angle (54.7°) at a rotation frequency of 10 kHz. The sample temperature was not regulated. NMR spectra were processed and plotted with TopSpin 4.0.8.[2] LIFDI-MS spectra were measured on a JEOL AccuTOF GCx instrument. IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with diamond ATR units inside a glovebox and processed using OriginPro 2020b.
Bis(perchlorocatecholato)silane [1]

To a solution of perchlorocatechol (2.00 g, 8.07 mmol, 2.00 eq) and dibutyl sulfone (611 mg, 3.43 mmol, 0.85 eq) in 30 ml dry DCM, trichlorosilane (489 μl, 4.64 mmol, 1.20 eq) was added neat. The flask was subsequently closed, and the resulting pale yellow reaction mixture was stirred at 50 °C for 20 h, which resulted in the precipitation of the target compound. After completion, the reaction mixture was condensed to dryness to remove excess silane. The residue was re-suspended in 30 ml DCM, filtered through a G4 frit and washed three times with DCM. After drying in vacuo, the target compound was isolated as a beige powder (1.78 g, 3.42 mmol, 85 %).

Solution phase NMR spectra of the compound could not be recorded, due to its poor solubility in non-donor solvents. $^{29}$Si MAS NMR (99.4 MHz): $\nu$ [cm$^{-1}$]: 1594 (w), 1432 (vs), 1388 (vs), 1207 (m), 1026 (vs), 892 (s), 857 (s), 755 (s), 666 (m). $^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 7.87 (m, 4H), 7.71 (td, $J$ = 7.6 Hz, $J$ = 3.6 Hz, 8H), 7.59 (m, 8H); $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 145.4 (s, C$_q$), 136.0 (d, $J$ = 3.0 Hz, CH), 134.8 (d, $J$ = 10.3 Hz, CH), 130.9 (d, $J$ = 12.9 Hz, CH), 121.7 (s, C$_q$), 117.8 (d, $J$ = 89.6 Hz, C$_q$), 115.0 (s, C$_q$); $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 23.2 (s); $^{29}$Si NMR (119 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = −90.5 (s).

$[\text{PPh}_4][\text{Cl}-]$ A suspension of bis(sulfolane)-bis(perchlorocatecholato)silane (30.0 mg, 39.5 μmol, 1.00 eq) and tetraphenylphosphonium chloride (13.3 mg, 35.5 μmol, 0.90 eq) in 0.5 ml CD$_2$Cl$_2$ was stirred at room temperature for 1 h. The resulting colorless solution was then characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the $^{13}$C and $^{29}$Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of $[\text{PPh}_4][\text{Cl}-]$ in CD$_2$Cl$_2$ at −40 °C.

$[\text{PPh}_4][\text{Br}-]$ A suspension of bis(perchlorocatecholato)silane (30.0 g, 57.7 μmol, 1.00 eq) and tetraphenyolphosphonium bromide (24.2 mg, 57.7 μmol, 1.00 eq) in 0.5 ml CD$_2$Cl$_2$ was stirred at room temperature for 3 h. The resulting solution was concentrated in vacuo. The target compound crystallized at −40 °C and was isolated through filtration. After three times of washing with cold DCM, the crystals were dried in vacuo to yield the compound, which was slightly contaminated with the respective chloride-adduct, formed through reaction of the target compound with the chlorinated solvent (26.0 mg, 27.7 μmol, 48 %). Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of $[\text{PPh}_4][\text{Br}-]$ in CD$_2$Cl$_2$ at room temperature.

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 7.88 (m, 4H), 7.72 (td, $J$ = 8.0 Hz, $J$ = 3.5 Hz, 8H), 7.59 (m, 8H); $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 145.2 (s, C$_q$), 136.1 (d, $J$ = 3.1 Hz, CH), 134.8 (d, $J$ = 10.3 Hz, CH), 130.9 (d, $J$ = 13.0 Hz, CH), 122.0 (s, C$_q$), 117.8 (d, $J$ = 89.9 Hz, C$_q$), 115.2 (s, C$_q$); $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = 23.3 (s); $^{29}$Si NMR (119 MHz, CD$_2$Cl$_2$, 295 K): $\delta$ = −96.0 (s); $^{77}$Br NMR: $\nu$ [br cm$^{-1}$]: 726 (s); $^{77}$Cl NMR: $\nu$ [cm$^{-1}$]: 374 (s); Crystallographic data [12] for C$_{34}$H$_{40}$BrCl$_2$O$_2$PSi: C, 46.04; H, 2.15 found; C, 45.18; H, 2.55.
SUPPORTING INFORMATION

[PPh₄][I-1]

A suspension of bis(sulfolane)-bis(perchloratechololate)silane (40.0 mg, 52.6 µmol, 1.00 eq) was suspended together with tetrabutylphosphonium iodide (24.5 mg, 52.6 µmol, 1.00 eq) in 0.5 ml CD₂Cl₂. The resulting off-white suspension was then characterized by NMR spectroscopy. Nearly quantitative adduct formation was indicated by the dissolution of the insoluble starting material and the formation of a single species in the ¹³C and ²⁹Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [PPh₄][I-1]in CD₂Cl₂ at room temperature.

¹H NMR (600 MHz, CD₂Cl₂, 295 K): δ = 7.89 (m, 4H), 7.73 (td, J = 8.2 Hz, J = 3.6 Hz, 8H), 7.60 (m, 8H); ¹³C[¹H] NMR (151 MHz, CD₂Cl₂, 295 K): δ = 146.3 (s, C₆), 122.1 (s, C₄), 115.1 (s, C₄), 59.0 (s, CH₂), 23.9 (s, CH₂), 19.9 (s, CH₂), 13.7 (s, CH₃); ²⁹Si NMR (119 MHz, CD₂Cl₂, 295 K): δ = -1.08 (s); ¹⁹F NMR (243 MHz, CD₂Cl₂, 295 K): δ = 23.2 (s); ²⁵Si NMR (119 MHz, CD₂Cl₂, 295 K): δ = -113.4 (s).

[NBu₄][N>1]

A suspension of bis(acetonitrile)-bis(perchloratechololate)silane (100 mg, 166 µmol, 1.00 eq.) and tetrabutylammonium azide (47.3 mg, 166 µmol, 1.00 eq.) in 1.5 ml oDCB was stirred at room temperature for 18 h. A clear colorless solution was obtained. The solution was filtered through a syringe filter to remove any fine insoluble solids (starting materials). The solvent was removed in vacuo and the product was obtained in quantitative yields as colorless solids. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a solution of oDCB at room temperature.

¹H NMR (600 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ = 2.71 (m, 8H), 1.30-1.24 (m, 8H), 1.11 (sext, J = 7.42 Hz, 8H), 0.75 (t, J = 7.30 Hz, 12H); ¹³C[¹H] NMR (151 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ = 146.3 (s, C₆), 122.1 (s, C₄), 115.1 (s, C₄), 59.0 (s, CH₂), 23.9 (s, CH₂), 19.9 (s, CH₂), 13.7 (s, CH₃); ²⁹Si NMR (119 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ = -99.9; ¹⁹F NMR (61 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ = 249.2 (Si-N=N=N'), 236.0 (Si-N=N=N'), 175.4 (Si-N=N=N'), IR (ATR): ν [cm⁻¹]: 2963 (m), 2934 (m), 2876 (m), 2137 (m), 1454 (vs), 1387 (s), 1315 (m), 1202 (m), 1124 (m), 1234 (m), 988 (vs), 833 (s), 811 (vs), 736 (m), 712 (m), 698 (m), 660 (m); Anal. Calcd. for C₅₆H₄₅Cl₄N₄O₂Si: C, 41.81; H, 4.51; N, 6.97 found: C, 42.05; H, 4.35; N, 7.02.

[NBu₄][(N₃)₂-1]

A solution of NBU₄N₃ (7.10 mg, 24.9 µmol, 1.00 eq.) and [N₃-1][NBu₄] (20.0 mg, 24.9 µmol, 1.00 eq.) in 0.5 ml oDCB was stirred at room temperature for 18 h. A clear colorless solution was obtained. The solvent was removed in vacuo and the product was obtained in quantitative yields as colorless solids. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a solution of oDCB at room temperature.

¹H NMR (600 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ [ppm] = 3.03 (m, 16H), 1.51-1.45 (m, 16H), 1.22 (sext, J = 7.5 Hz, 16H), 0.80 (t, J = 7.4 Hz, 24H); ¹³C[¹H] NMR (151 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ [ppm] = 149.5 (s, C₆), 118.2 (s, C₄), 112.9 (s, C₄), 59.0 (s, CH₂), 24.1 (s, CH₂), 20.1 (s, CH₂), 13.8 (s, CH₃); ²⁹Si NMR (119 MHz, oDCB:CD₂Cl₂ (50:1), 295 K): δ = -155.1; IR (ATR): ν [cm⁻¹]: 2961 (m), 2933 (w), 2875 (w), 2120 (s), 2086 (s), 1461 (s), 1379 (m), 1303 (m), 1243 (m), 988 (s), 881 (w), 815 (vs), 806 (vs), 739 (w), 712 (w), 687 (m), 655 (s); Anal. Calcd. for C₃₆H₃₆Cl₄N₆O₆Si: C, 48.54; H, 6.67; N, 10.29 found: C, 48.24; H, 6.46; N, 10.60.
A suspension of bis(perchlorocatecholato)silane (30.0 g, 57.7 μmol, 1.00 eq) and tetraphenylphosphonium thiocyanate (22.9 mg, 57.7 μmol, 1.00 eq) in 0.5 ml CD$_2$Cl$_2$ was stirred at room temperature for 16 h. The resulting pink solution was characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the $^{13}$C and $^{29}$Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [PPh$_4$][SCN-1] in CD$_2$Cl$_2$ at room temperature.

Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [NBu$_4$][SCN-1] in CD$_2$Cl$_2$ at room temperature, which was obtained by the same procedure.

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K): δ = 7.87 (m, 4H), 7.72 (td, J = 8.2 Hz, J = 3.6 Hz, 8H), 7.60 (m, 8H); $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K): δ = 145.5 (s, C$_6$), 136.0 (d, J = 3.0 Hz, C$_6$), 134.8 (d, J = 10.3 Hz, CH), 130.9 (d, J = 12.9 Hz, CH), 122.0 (s, C$_6$), 117.8 (d, J = 89.6 Hz, C$_6$), 115.1 (s, C$_6$); $^{31}$P($^1$H) NMR (243 MHz, CD$_2$Cl$_2$, 295 K): δ = 23.2 (s); $^{29}$Si NMR (119 MHz, CD$_2$Cl$_2$, 295 K): δ = −110.6 (br s). MS (LIFDI(-)):$^2$[C$_6$Cl$_7$NO$_2$SSi]; calcd.: 573.68, found: 573.72; IR (ATR): ν [cm$^{-1}$]: 3075 (w), 2081 (vs), 1587 (m), 1450 (vs), 1388 (s), 1300 (m), 1233 (m), 1108 (s), 988 (s), 952 (m), 820 (vs), 721 (vs).

$[\text{K@}(18\text{-c}-6)][\text{HCO}_2\text{-1}]$

A suspension of bis(sulfolane)-bis(perchlorocatecholato)silane (40.0 mg, 52.6 μmol, 1.00 eq), potassium formate (4.42 mg, 52.6 μmol, 1.00 eq) and 18-crown-6 (13.9 mg, 52.6 μmol, 1.00 eq) in 0.5 ml CD$_2$Cl$_2$ was stirred at room temperature for 18 h. The resulting colorless solution was characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the $^{13}$C and $^{29}$Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [K@(18-c-6)][HCO$_2$-1] in CD$_2$Cl$_2$ at −40°C.

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 295 K): δ = 8.22 (s, 1H), 3.53 (s, 24H); $^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 295 K): δ = 160.9 (br s, C$_6$), 145.7 (br s, C$_6$), 121.8 (br s, C$_6$), 114.9 (br s, C$_6$), 70.4 (s, CH$_2$); $^{29}$Si NMR (119 MHz, CD$_2$Cl$_2$, 295 K): δ = −107.9 (s); IR (ATR): ν [cm$^{-1}$]: 2888 (m), 1720 (m), 1453 (vs), 1389 (m), 1351 (m), 1300 (s), 1102 (vs), 988 (s), 960 (s), 817 (br, vs), 710 (br, s).

$[\text{K@}(18\text{-c}-6)][\text{H}_3\text{CCO}_2\text{-1}]$

A suspension of bis(perchlorocatecholato)silane (30.0 mg, 57.7 μmol, 1.00 eq), potassium acetate (5.66 mg, 57.7 μmol, 1.00 eq) and tetraphenylphosphonium thiocyanate (22.9 mg, 57.7 μmol, 1.00 eq) in 0.5 ml of a solvent mixture of o-DCB and C$_6$D$_6$ (50:1) was stirred at room temperature for 2 h. The resulting pink solution was characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the $^{13}$C and $^{29}$Si NMR spectra. Colorless crystals were obtained by gaseous diffusion of pentane into a saturated solution of [K@(18-c-6)][H$_3$CCO$_2$-1] in CD$_2$Cl$_2$ at −40°C.

$^1$H NMR (600 MHz, o-DCB:C$_6$D$_6$ (50:1), 295 K): δ = 3.26 (s, 24H), 1.82 (s, 3H); $^{13}$C($^1$H) NMR (151 MHz, o-DCB:C$_6$D$_6$ (50:1), 295 K): δ = 146.9 (br s, C$_6$), 121.3 (br s, C$_6$), 114.8 (br s, C$_6$), 70.2 (s, CH$_2$); $^{29}$Si NMR (119 MHz, o-DCB:C$_6$D$_6$ (50:1), 295 K δ = −107.6 (s); IR (ATR): ν [cm$^{-1}$]: 3068 (w), 1574 (m), 1456 (vs), 1435 (s), 1251 (m), 1126 (s), 1108 (m), 1034 (s), 745 (vs).
SUPPORTING INFORMATION

[Li@((12-c-4))2][TfO-1]

A suspension of bis(perchlorocatecholato)silane (35.0 mg, 67.3 μmol, 1.00 eq), lithium triflate (10.5 mg, 67.3 μmol, 1.00 eq) and 12-crown-4 (21.8 μl, 135 μmol, 2.00 eq) in 0.5 ml CD2Cl2 was stirred at room temperature for 90 min. The resulting brown suspension was filtered through a syringe filter and concentrated in vacuo. The target compound crystallized at −40°C and the resulting brown crystals were carefully washed with cold DCM before drying in vacuo to yield the target compound (17.0 mg, 20.0 μmol, 30 %). Colorless crystals were obtained by gaseous diffusion of pentane into a saturated solution of [Li@((12-c-4))2][TfO-1] in CD2Cl2 at room temperature.

1H NMR (600 MHz, CD2Cl2, 295 K): δ = 3.68 (s, 16H); 13C{1H} NMR (151 MHz, CD2Cl2, 295 K): δ = 145.2 (s, Cq), 122.5 (s, Cq), 115.4 (s, Cq), 67.7 (s, CH2); 7Li NMR (233 MHz, CD2Cl2, 295 K): δ = −0.7 (s); 19F NMR (376 MHz, CD2Cl2, 295 K): δ = −78.4 (s); 29Si NMR (119 MHz, CD2Cl2, 295 K): δ = −106.1.

[K@18-c-6][TfO-1]

A suspension of bis(perchlorocatecholato)silane (30.0 mg, 57.7 μmol, 1.00 eq), potassium triflate (10.9 mg, 57.7 μmol, 1.00 eq) and 18-crown-6 (15.3 mg, 57.7 μmol, 1.00 eq) in 0.5 ml CD2Cl2 was stirred at room temperature for 4 h. The resulting colorless suspension was characterized by NMR spectroscopy. Nearly quantitative adduct formation was indicated by the dissolution of the insoluble starting material and the formation of a single species in the 13C and 29Si NMR spectra. Colorless crystals were obtained by gaseous diffusion of pentane into a saturated solution of [K@18-c-6][TfO-1] in CD2Cl2 at −40°C.

1H NMR (600 MHz, CD2Cl2, 295 K): δ = 3.58 (s, 24H); 13C{1H} NMR (151 MHz, CD2Cl2, 295 K): δ = 145.2 (s, Cq), 122.5 (s, Cq), 119.4 (q, J = 319.0 Hz, Cq), 115.4 (s, Cq), 70.5 (s, CH2); 19F NMR (376 MHz, CD2Cl2, 295 K): δ = −77.7 (s); 29Si NMR (119 MHz, CD2Cl2, 295 K): δ = −105.9 (s).

[HpyNMe2][TfO-1] and [HpyNMe2][OTf][TfO-1]

The reactions of bis(sulfolane)-bis(perchlorocatecholato)silane and 2-(dimethylamino)pyridine triflate in CD2Cl2 or oDCB lead to similar chemical shifts in the respective NMR spectra for the [TfO-1]- anion but were less selective. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [HpyNMe2][TfO-1] in CD2Cl2 at room temperature and by gaseous diffusion of pentane into a saturated solution of [HpyNMe2][TfO-1] in oDCB at room temperature whereby the latter conditions lead to the crystallization of [HpyNMe2][OTf][TfO-1].
A suspension of bis(sulfolane)-bis(perchlorocatecholate)ilane (40.0 mg, 52.6 \( \mu \)mol, 2.00 eq) and dibenzo-18-crown-6 (19.0 mg, 52.6 \( \mu \)mol, 2.00 eq) in 0.5 ml CD\(_2\)Cl\(_2\) or 0.5 ml of a mixture of oDCB and C\(_6\)D\(_6\) (50:1) was stirred at room temperature for 4 h. The resulting colorless solution was characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the \(^{13}\)C and \(^{29}\)Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of pentane into a saturated solution of [K@db-18-c-6][1-SO\(_4\)-1] in DCM at room temperature.

\[^{1}\text{H NMR}\ (600 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = 6.91 \) (m, 8H), 6.82 (m, 8H), 4.12 (m, 16H), 3.94 (m, 16H); \[^{13}\text{C}(^{1}\text{H})\text{NMR}\ (151 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = 151.3 \) (s, C\(_6\)), 149.9 (s, C\(_6\)), 126.4 (s, CH), 126.1 (s, C\(_6\)), 119.0 (s, C\(_6\)), 116.1 (s, CH), 73.9 (s, CH\(_2\)), 71.8 (s, CH\(_2\)); \[^{29}\text{Si NMR}\ (119 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = 108.0 \) (s).

\[^{1}\text{H NMR}\ (600 \text{ MHz}, \text{oDCB}:\text{C}_6\text{D}_6\ (50:1), 295 \text{ K})\]: \( \delta = 6.78 \) (m, 8H), 6.60 (m, 8H), 3.87 (m, 16H), 3.71 (m, 16H); \[^{13}\text{C}(^{1}\text{H})\text{NMR}\ (151 \text{ MHz}, \text{oDCB}:\text{C}_6\text{D}_6\ (50:1), 295 \text{ K})\]: \( \delta = 147.5 \) (s, C\(_6\)), 145.9 (s, C\(_6\)), 121.8 (s, CH), 121.6 (s, C\(_6\)), 114.7 (s, C\(_6\)), 111.9 (s, CH), 69.3 (s, CH\(_2\)), 67.6 (s, CH\(_2\)); \[^{29}\text{Si NMR}\ (119 \text{ MHz}, \text{oDCB}:\text{C}_6\text{D}_6\ (50:1), 295 \text{ K})\]: \( \delta = -107.4 \) (s); IR (ATR): \( \nu [\text{cm}^{-1}]\): 3068 (w), 1574 (w), 1456 (s), 1435 (s), 1251 (m), 1126 (s), 1034 (s), 745 (vs), 659 (s).

A suspension of bis(sulfolane)-bis(perchlorocatecholate)ilane (30.0 mg, 39.5 \( \mu \)mol, 2.00 eq) and tetrabutylammonium sulfate (11.5 mg, 19.7 \( \mu \)mol, 1.00 eq) in 0.5 ml CD\(_2\)Cl\(_2\) was stirred at room temperature for 1 h. The resulting colorless solution was characterized by NMR spectroscopy. Quantitative adduct formation was indicated by the dissolution of all the insoluble starting material and the formation of a single species in the \(^{13}\)C and \(^{29}\)Si NMR spectra. Colorless crystals suitable for SCXRD were obtained by gaseous diffusion of benzene into a saturated solution of [NBu\(_4\)][1-SO\(_4\)-1] in DCM at room temperature.

\[^{1}\text{H NMR}\ (600 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = 3.05 \) (m, 16H), 1.57 (quint, \( J = 7.8 \) Hz, 16H), 1.36 (sext, \( J = 7.5 \) Hz, 16H), 0.97 (t, \( J = 7.3 \) Hz, 24H); \[^{13}\text{C}(^{1}\text{H})\text{NMR}\ (151 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = 145.2 \) (br s, C\(_6\)), 122.4 (br s, C\(_6\)), 115.3 (br s, C\(_6\)), 59.3 (s, CH\(_2\)), 24.1 (s, CH\(_2\)), 20.0 (s, CH\(_2\)), 13.7 (s, CH\(_2\)); \[^{29}\text{Si NMR}\ (119 \text{ MHz}, \text{CD}_2\text{Cl}_2, 295 \text{ K})\]: \( \delta = -107.8 \) (s).

The reaction of bis(perchlorocatecholate)ilane with tetrabutylammonium sulfate resulted in similar NMR spectra but with hydrolysis species as impurities.


### 2. Structural Details

#### a. Overview of Structural Parameters

| Table S2.1: Selected structural parameters of halogenide adducts. Bond lengths (Å) and bond angles (°). |
|---------------------------------------------------------------|
| **Space group** | **[Cl⁻]** | **[Br⁻]** | **[I⁻]** |
| Z' | Z | Z | Z |
| TP | 0.267 | 0.002 | 0.027 |
| Si1–O(1–4) | 1.7371(15) | 1.7296(13) | 1.735(2) |
| Si1–X | 2.0867(8) | 2.2560(5) | 2.5297(9) |

| Table S2.2: Selected structural parameters of azide adducts. Bond lengths (Å) and bond angles (°). |
|---------------------------------------------------------------|
| **Space group** | **[NBu₄][N₃⁻]** | **[NBu₄][N₃]⁻** |
| Z' | Z | Z' | Z |
| TP | 0.519 | - | - |
| Si1–O(1–4) | 1.7370(11) | 1.7852(17) | 1.7852(17) |
| Si1–N1 | 1.7659(14) | 1.883(11) | 1.883(10) |
| Si1–N4 | - | 1.883(10) | - |
| N1–N2 | 1.2303(19) | 1.203(12) | 1.203(12) |
| N4–N5 | 1.206(11) | 1.159(9) | 1.159(9) |
| N2–N3 | 1.118(2) | 1.146(7) | 1.146(7) |
| N4–N6 | 1.159(9) | 1.159(9) | 1.159(9) |
| N1–N2–N3 | 174.54(17) | 176.5(17) | 176.5(17) |
| N4–N5–N6 | 176.5(8) | 176.5(8) | 176.5(8) |
| Si1–N1–N2 | 122.80(11) | 123.5(12) | 123.5(12) |
| Si1–N4–N5 | - | 120.9(9) | - |

| Table S2.3: Selected structural parameters of thiocyanate adducts. Bond lengths (Å) and bond angles (°). |
|---------------------------------------------------------------|
| **Space group** | **[NBu₄][SCN⁻]** | **[PPh₄][SCN⁻]** |
| Z' | Z | Z |
| TP | 0.430 | 0.079 |
| Si1–O(1–4) | 1.7371(15) | 1.7296(13) | 1.735(2) |
| Si1–X | 2.0867(8) | 2.2560(5) | 2.5297(9) |

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**NH**
**Table S2.4**: Selected structural parameters of carboxylate adducts. Bond lengths (Å) and bond angles (°).

|                  | [HCO\textsubscript{2}1\textsuperscript{−}] | [H\textsubscript{2}C\textsubscript{2}O\textsubscript{2}1\textsuperscript{−}] |
|------------------|---------------------------------------------|---------------------------------------------|
| Space group      | P\textbar\textbar                      | P\textbar\textbar                      |
| Z' | Z       | 1 | 2 | 1 | 2 |
| TP               | 0.362                                      | 0.274                                      |
| Si1−O5          | 1.6928(15)                                 | 1.690(3)                                  |
| O5−C13          | 1.322(2)                                   | 1.341(5)                                  |
| O6−C13          | 1.196(3)                                   | 1.215(5)                                  |
| O5−C13−O6      | 123.0(2)                                   | 123.3(4)                                  |

**Table S2.5**: Selected structural parameters of [1-SO\textsubscript{4}1\textsuperscript{2−}]\textsuperscript{2−}. Bond lengths (Å) and bond angles (°).

|                  | [1-SO\textsubscript{4}1\textsuperscript{2−}]\textsuperscript{2−} |
|------------------|---------------------------------------------------------------|
| Space group      | C2/c                                                          |
| Z' | Z       | 0.5 | 4 |
| TP               | 0.004                                                         |
| Si1−O5          | 1.702(3)                                                     |
| S1−O5           | 1.536(2)                                                     |
| S1−O6           | 1.414(3)                                                     |
b. Comparison of different [Y][TfO-1] compounds

We were able to obtain different crystal structures of [TIO-1]. Figure S1 shows the acquired structures and Table S2.6 gives an overview of selected structural parameters of them. They differ in counterion ([K@18-c-6]* for [TIO-1]a, Figure S1a, Table S2.6, col 2; Li’@12-c-4)2 for [TIO-1]b, Figure S1b, Table S2.6, col 3; Hpy-2-NMe2 for [TIO-1]c, Figure S1c and d, Table S2.6, col 4 and 5) as well as in the coordination environment. While structures A–C display a more “innocent” coordination of only the triflate, [TIO-1]b exhibits a hydrogen bond from the pyridinium cation to the O1-atom of one perchlorate moiety (Figure S1d). This results in a considerably longer Si–O1 bond (1.746(2) Å) compared to the average Si–O–bond lengths, which vary between 1.716(2) and 1.725(4) Å (see Table S2.6, last row). Other than that, the parameters of the different [TIO-1] structures do not change much. For example, all fivefold silicon coordination environments lie strongly on the sp side (TP between 0.003 and 0.095) and the Si1–O5 bond lengths (O5 is the coordinating triflate-O-atom) are all in between the range of 1.731(4) and 1.766(3) Å. Even the hydrogen bond in [TIO-1]b has no significant influence in the Si1–O5 bond length (1.743(10) Å).

The Si–O bond is significantly longer in the adducts [TfO–1]−Nils and [TfO–1]−Na061 compared to the average Si–O–bond lengths, which vary between 1.716(2) and 1.725(4) Å (see Table S2.6, last row). Other than that, the parameters of the different [TIO-1] structures do not change much. For example, all fivefold silicon coordination environments lie strongly on the sp side (TP between 0.003 and 0.095) and the Si1–O5 bond lengths (O5 is the coordinating triflate-O-atom) are all in between the range of 1.731(4) and 1.766(3) Å. Even the hydrogen bond in [TIO-1]b has no significant influence in the Si1–O5 bond length (1.743(10) Å).

Compared to the free triflate, there are mainly minor differences in the triflate moiety. For example shorter S–O distances: 1.440(3) Å in AgOTf or 1.440(3) Å in [BPh3(Me3)2][OTf]. Only the S1–O5 bond is significantly longer in the adducts [TIO-1]− (1.485(9) – 1.515(3) Å). Same sulfur-oxygen bond elongations are observable in (C6F5)2Si(OTf) (S1–O1 1.510(2), S1–O(2–3)av 1.433(3)).

Cocrystallized solvent molecules, carbon-bound hydrogen atoms and disorder are omitted for clarity. In b) and c) only one of two molecules is shown. Displacement ellipsoids are drawn with a probability of 50 %. For selected bond distances (Å) and bond angles (°) see Table S2.6.

Table S2.6: Selected structural parameters of triflate adducts. Bond lengths (Å) and bond angles (°).

| Space group | [TIO-1]a | [TIO-1]b | [TIO-1]c | [TIO-1]d |
|-------------|----------|----------|----------|----------|
| Z | 1 | 2 | 1 | 4 |
| TP | 0.029 | 1.721(13) | 1.720(4)(2) | 1.724(3)(1) |
| Si1–O(1–4)av | 1.740(17) | 1.731(4)(1) | 1.763(3)(1) | 1.743(10)(1) |
| Si1–O5 | 1.483(10)(1) | 1.474(4)(1) | 1.504(1)(1) | 1.490(4) |
| Si1–O6 | 1.423(6)(1) | 1.421(4)(1) | 1.423(5)(2) | 1.440(4) |
| Si1–O7 | 1.418(5)(1) | 1.394(4)(1) | 1.416(4)(2) | 1.422(4) |
| Si1–C13 | 1.812(7)(1) | 1.780(8)(1) | 1.826(6)(1) | 1.827(4) |

[a]average bond length of disordered OTf; [b]acceptor of H-bond; [c]cocrystallized with two molecules per asym. unit.

Figure S1: Molecular structures of a) [K@18-c-6][TIO-1]a, b) [Li@12-c-4][TIO-1]b, c) [Hpy-2-NMe2][TIO-1]c, d) [Hpy-2-NMe2][TIO-1]d. Cocrystallized solvent molecules, carbon-bound hydrogen atoms and disorder are omitted for clarity. In b) and c) only one of two molecules is shown. Displacement ellipsoids are drawn with a probability of 50 %. For selected bond distances (Å) and bond angles (°) see Table S2.6.
3. Computational Details

a. Structure Optimization

All computations have been performed with ORCA 4.2.1. Geometry optimizations were carried out with PBEh-3c/def2-mSVP, using grid5 settings. All obtained structures have been approved to be energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level. Structures with imaginary frequencies >10 cm$^{-1}$ have been reoptimized with grid6, TightOPT and VeryTightSCF settings. Unscaled ZPEs and thermal corrections at 298 K from the rigid-rotor harmonic oscillator (RRHO) approximation were carried over for enthalpy calculation. As starting geometries, VSEPR structures preoptimized with UFF were used.

Table S3.1: Comparison of experimental and computed (PBEh-3c) bond lengths.

| X | d(Si−X)$_{\text{comp}}$ | d(Si−X)$_{\text{exp}}$ | d(Si−O$_{\text{cat,av}}$)$_{\text{comp}}$ | d(Si−O$_{\text{cat,av}}$)$_{\text{exp}}$ |
|---|----------------|----------------|----------------|----------------|
| F | 1.6011 | 1.6057(13) | 1.7380 | 1.7366(14) |
| Cl | 2.0824 | 2.0867(8) | 1.7363 | 1.7371(15) |
| Br | 2.2548 | 2.2560(5) | 1.7474 | 1.7296(13) |
| I | 2.4974 | 2.5297(9) | 1.7450 | 1.735(2) |
| N$_5$ | 1.7635 | 1.7659(14) | 1.7505 | 1.7370(11) |
| HCO$_2$ | 1.6975 | 1.6928(15) | 1.7469 | 1.7333(14) |
| H$_3$CCO$_2$ | 1.6839 | 1.690(3) | 1.7493 | 1.742(3) |
| ACS | 1.7532 | 1.755(4) | 1.7438 | 1.732(3) |
| TFO | 1.7425 | 1.740(17) | 1.7353 | 1.721(13) |

b. CCSD(T)/CBS

For accurate treatment of the respective adduct affinity, we choose the respective TMS-system anchor enthalpies of Me$_3$Si$^+$ + X $\rightarrow$ [Me$_3$Si-X], computed on coupled cluster theory with single and double excitations and perturbative triples correction (CCSD(T)) as implemented before. The frozen core approximation was used with the default number of core electrons per element (see table 9.9 in ORCA 4.2.1 manual). The CCSD(T) total energies were extrapolated to the complete basis set limit (CBS) by using a two-point extrapolation scheme for the adjacent aug-cc-pVnZ level basis sets $n = T,Q$:

$$E_{CBS}(X,Y) = \frac{E_{\text{HF}}(X)e^{-\alpha X} - E_{\text{HF}}(Y)e^{-\alpha Y}}{e^{-\alpha X} - e^{-\alpha Y}} + \frac{\chi^\beta E_c(X) - \gamma^\beta E_c(Y)}{X^\beta - Y^\beta}$$

$\alpha = 5.79$ and $\beta = 3.05$ as calibrated in Ref$^{[12c]}$. For atoms up to bromine, the augmented correlation consistent basis sets aug-cc-pVnZ ($n = T,Q$) were used.$^{[13]}$ For heavier atoms (> bromine), ECP-based versions of correlation consistent basis sets with weighted core functions, aug-cc-pCVnZ-PP ($n = T,Q$)$^{[14]}$ were used in combination with the SK-MCDHF-RSC effective core potentials.$^{[15]}$
The single point electronic energies for the accurate calculation of the respective adduct affinity were calculated with the linear scaling version of domain based localized pair natural orbitals based coupled cluster theory (DLPNO-CCSD(T)), as implemented in ORCA 4.2.1. The NormalPNO and its threshold settings were used for the PNO localization. Like with canonical CCSD(T), for atoms up to boron, the correlation consistent basis sets aug-cc-pVQZ were used. For heavier atoms (> bromine), ECP-based versions of correlation consistent basis sets with weighted core functions, aug-cc-pwCVQZ-PP were used, including the SK-MCQDHF-RSC effective core potentials. To speed up the HF-part, the resolution of identity “chain of spheres” RIRUCOSX approximation (gridX6) was used with the respective auxiliary basis sets.

The absolute ion affinities were obtained by isodesmic computation: 1) compute ΔH for “Me₅Si⁺ + [1-X] → Me₅SiX + 1” at DLPNO-CCSD(T) level as described in the previous paragraph. 2) Subtract the CCSD(T)/CBS obtained anchor values for “Me₅Si⁺ + X → Me₅SiX”. For the solvation corrected values, the free energy of solution for [1-X] and X are added. For more details, see Ref S11. Numbers denoted with “-“ in column “Method” of Table S3.3 have been obtained non-isodesmically, e.g., ΔH for 1 + X → 1-X.

Table S3.3: Computed X-ion affinities (DLPNO-CCSD(T)/aug-cc-pVQZ in vacuum (Affinityᵥ) and in solution (COSMO-RO5(CH₃Cl₂)), Affinity𝑠𝑜𝑙.)

| Compound     | E [a.u.] | Eₜhermal correction +k₀T [a.u.] | H [a.u.]       | Affinityᵥ [kJ/mol] | Affinity𝑠𝑜𝑙 [kJ/mol] | Method   |
|--------------|---------|---------------------------------|----------------|--------------------|----------------------|----------|
| Si(cal³)₂⁺   | -4724.4500 | 0.12945                         | -4724.3205    | -263               | -109                 | TMS-Br   |
| Br⁻          | -7297.4094 | 0.13198                         | -7297.2774    | -196               | -62                  | TMS-CN   |
| CN⁻          | -4817.3062 | 0.14021                         | -4817.1660    | -315               | -152                 | TMS-CN   |
| NC⁻          | -4817.3040 | 0.13995                         | -4817.1640    | -310               | -146                 | TMS-CN   |
| N₃⁻          | -4888.6037 | 0.14672                         | -4888.4570    | -304               | -155                 | TMS-N₃⁻  |
| NO₃⁻         | -5004.8329 | 0.15138                         | -5004.4816    | -255               | -105                 | TMS-NO₃⁻ |
| NCO⁻         | -4892.5097 | 0.14689                         | -4892.3628    | -330               | -178                 | TMS-NCO  |
| OCN⁻         | -4892.4842 | 0.14622                         | -4892.3380    | -265               | -120                 | TMS-NCO  |
| NCS           | -5215.1021 | 0.14646                         | -5214.9574    | -262               | -135                 | TMS-NCS  |
|          |       |       |       |       |       |          |
|----------|-------|-------|-------|-------|-------|----------|
| SCN⁻     | 5215.0745 | 0.14389 | 5214.9306 | -192 | -69 | TMS-NCS  |
| k¹-HCOO⁻ | 4913.5816 | 0.15782 | 4913.4238 | -327 | -178 | TMS-HCOO |
| k²-HCOO⁻ | 4913.5799 | 0.15795 | 4913.4219 | -322 | -178 | TMS-HCOO |
| k¹-H₂COO⁻ | 4952.8352 | 0.18006 | 4952.6471 | -316 | -173 | -       |
| k²-H₂COO⁻ | 4952.8407 | 0.18814 | 4952.6526 | -331 | -199 | -       |
| k¹-TIO⁻   | 5610.0231 | 0.16206 | 5609.8610 | -246 | -129 | -       |
| k²-TIO⁻   | 5610.0133 | 0.16176 | 5609.8515 | -221 | -110 | -       |
| k¹-SO₂⁻   | 5423.0068 | 0.15266 | 5422.8542 | -562 | -171 | -       |
| k²-SO₂⁻   | 5423.0263 | 0.15258 | 5422.8738 | -613 | -198 | -       |
| -SO₄²⁻    | -10147.5169 | 0.28459 | -10147.2323 | -713 | -163 | -       |
| SiCl₄     | -2128.3212 | 0.0150  | -2128.3062 | -     |     | -       |
| Br⁻       | -4701.2117 | 0.0173  | -4701.1943 | -82  | 15  | TMS-Br   |
| CN⁻       | -2221.1193 | 0.0256  | -2221.0936 | -163 | -53 | TMS-CN   |
| NC⁻       | -2221.1128 | 0.0253  | -2221.0875 | -147 | -36 | TMS-CN   |
| N₂⁺       | -2292.4149 | 0.0320  | -2292.3829 | -147 | -55 | TMS-N₂   |
| NO₃⁻      | -2408.4477 | 0.0366  | -2408.4111 | -107 | -11 | TMS-NO₃  |
| NCO⁻      | -2296.3164 | 0.0322  | -2296.2842 | -161 | -64 | TMS-NCO  |
| OCN⁻      | -2296.2996 | 0.0314  | -2296.2682 | -119 | -23 | TMS-NCO  |
| NCS⁻      | -2618.9116 | 0.0299  | -2618.8817 | -101 | -24 | TMS-NCS  |
| SCN⁻      | -2618.8939 | 0.0292  | -2618.8648 | -57  | 19  | TMS-NCS  |
| k¹-HCOO⁻  | -2317.3945 | 0.0431  | -2317.3514 | -175 | -77 | TMS-HCOO |
| k²-HCOO⁻  | -2317.3868 | 0.0432  | -2317.3436 | -154 | -80 | TMS-HCOO |
| k¹-H₂COO⁻ | -2356.6493 | 0.0733  | -2356.5760 | -167 | -79 | -       |
| k²-H₂COO⁻ | -2356.6515 | 0.0735  | -2356.5780 | -172 | -113 | -       |
| k¹-TIO⁻   | -3013.8418 | 0.0473  | -3013.7945 | -109 | -41 | -       |
| k²-TIO⁻   | -3013.8178 | 0.0469  | -3013.7708 | -49  | -2  | -       |
| k¹-SO₂⁻   | -2826.7885 | 0.0382  | -2826.7503 | -327 | -80 | -       |
| k²-SO₂⁻   | -2826.8016 | 0.0382  | -2826.7634 | -361 | -119 | -       |
| -SO₄²⁻    | -4955.1588 | 0.0550  | -4955.1039 | -451 | -69 | -       |
| SiMe₄      | -749.2602  | 0.1914  | -749.0688  | -     |     | -       |
| CN⁻       | -842.0117  | 0.2001  | -841.8116  | -46  | 38  | TMS-CN   |
| NC⁻       | -842.0069  | 0.1999  | -841.8070  | -34  | 51  | TMS-CN   |
| N₂⁺       | -913.3040  | 0.2066  | -913.0974  | -21  | 59  | TMS-N₂   |
| NO₂⁻      | -1029.3490 | 0.2116  | -1029.1374 | -12  | 64  | TMS-NO₂  |
| NCO⁻      | -917.2137  | 0.2069  | -917.0068  | -56  | 33  | TMS-NCO  |
| OCN⁻      | -917.1997  | 0.2065  | -916.9932  | -20  | 53  | TMS-NCO  |
| NCS⁻      | -1239.8179 | 0.2050  | -1239.6129 | -19  | 49  | TMS-NCS  |
| k¹-HCOO⁻  | -938.2850  | 0.2166  | -938.0864  | -55  | 28  | TMS-HCOO |
| k¹-H₂COO⁻ | -977.5438  | 0.2477  | -977.2961  | -56  | 22  | -       |
| k¹-SO₂⁻   | -1447.6724 | 0.2123  | -1447.4601 | -188 | 52  | -       |
| k²-SO₂⁻   | -1447.6628 | 0.2112  | -1447.4516 | -166 | 79  | -       |
| -SO₄²⁻    | -2196.9252 | 0.4045  | -2196.5208 | -167 | 201 | -       |
d. NMR Calculations

$^{29}$Si chemical shielding ($\sigma$)\cite{18} were computed in vacuum with the ADF 2019.30\cite{19} at PBE0\cite{20}/TZ2P\cite{21} level of theory, chemical shifts ($\delta$) were referenced to free Tetramethylsilane. The computations of NMR chemical shieldings were carried out without the frozen core approximation and with the scalar relativistic spin-orbit ZORA approximation\cite{22} to tackle HALA-effects.\cite{23}

| Compound | NMR shift [ppm] |
|----------|-----------------|
| Si(cat$^{3+}$)$_2$ | -37.9 |
| Br$^-$ | -89.2 |
| I$^-$ | -106.6 |
| CN$^-$ | -102.2 |
| NC$^-$ | -107.8 |
| N$_3^-$ | -96.7 |
| NCO$^-$ | -104.7 |
| OCN$^-$ | -100.3 |
| NCS$^-$ | -107.6 |
| SCN$^-$ | -81.3 |
| k$^1$-HCOO$^-$ | -100.6 |
| k$^2$-HCOO$^-$ | -125.7 |
| k$^1$-H$_2$CCOO$^-$ | -103.1 |
| k$^2$-H$_2$CCOO$^-$ | -132.6 |
| k$^1$-TfO$^-$ | -99.9 |
| k$^2$-TfO$^-$ | -134.5 |
| k$^1$-SO$_4^{2-}$ | -102.9 |
| k$^2$-SO$_4^{2-}$ | -157.4 |
| -SO$_4^{2-}$ | -103.9 |

Table S3.4: Calculated $^{29}$Si chemical shifts [ppm] at PBE0/TZ2P.

e. Natural Population Analysis (NPA)

Natural bond orbitals (NBO)\cite{24} analyze the electron density distribution. In recent work, it was shown that the hybrid PBE0 functional\cite{20a, 25} is among the best performing functionals for the accurate description of the electron density distribution, referenced against exact all-electron coupled-cluster singles and doubles densities.\cite{26} Hence, the wavefunction for the gas-phase optimized structures were recomputed with PBE0/def2-TZVPP at fine grid6 settings, with and without CPCM solvation correction (CH$_2$Cl$_2$, Orca 5.1) and analyzed with NBO 7.0\cite{27} The NPA charges at silicon can be found in Table S3.5.

| Compound | Natural charge | Natural charge (CPCM, CH$_2$Cl$_2$) |
|----------|----------------|----------------------------------|
| Si(cat$^{3+}$)$_2$ | 2.383 | 2.403 |
| F$^-$ | 2.316 | 2.322 |
| Cl$^-$ | 2.082 | 2.088 |
| Br$^-$ | 2.033 | 2.039 |
| I$^-$ | 1.997 | 1.999 |
| N$_3^-$ | 2.198 | 2.204 |
| NCS$^-$ | 2.231 | 2.238 |
| k$^1$-HCOO$^-$ | 2.288 | 2.297 |
| k$^1$-H$_2$CCOO$^-$ | 2.296 | 2.304 |
| k$^1$-TfO$^-$ | 2.292 | 2.300 |

Table S3.5: Calculated Si natural charges at PBE0/def2-TZVPP.
Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperatures with a Bruker D8 Venture diffractometer, dual source (Mo-K$_\alpha$ radiation, microfocus X-ray tube, Photon III detector, temperature 100 K). Data were processed with the standard standard Bruker (SAINT, APEX3) software package. Multiscan absorption correction was applied using the SADABS program. The structures were solved by intrinsic phasing and refined using the SHELXTL software package (Version 2014/6 and 2018/3). Graphical handling of the structural data during solution and refinement was performed with Olex2 and shelXle. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model.

For data visualization, Mercury 2020.3.0 was used. The thermal displacement ellipsoids are shown at the probability level of 50%. CCDC numbers (given in the respective tables) contain 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/.

Electron density attributed to solvent of crystallization (DCM), which could not be modelled was removed from the structures of [PPh$_4$][Cl-1], [PPh$_4$][Br-1], [PPh$_4$][I-1] and [K@18-c-6][HCO$_2$-1] with the BYPASS procedure as implemented in PLATON (squeeze/hybrid). Partial structure factors from the solvent masks were included in the refinement as separate contributions to $F_{\text{calc}}$. For [PPh$_4$][Cl-1] 121 electrons were found in a volume of 337 Å$^3$ in one void per unit cell. This is consistent with the presence of 3 DCM per unit cell which accounts for 126 electrons per unit cell. For [PPh$_4$][Br-1] 41 electrons were found in a volume of 115 Å$^3$ in one void per unit cell. This is consistent with the presence of 1 DCM per unit cell which accounts for 42 electrons per unit cell. For [PPh$_4$][I-1] 180 electrons were found in a volume of 399 Å$^3$ in two voids per unit cell. This is consistent with the presence of 4.5 DCM per unit cell which accounts for 189 electrons per unit cell. For [K@18-c-6][HCO$_2$-1] 74 electrons were found in a volume of 160 Å$^3$ in one void per unit cell. This is consistent with the presence of 2 DCM per unit cell which account for 84 electrons per unit cell.
| Compound | Identification code | Empirical formula | Formula weight | Temperature [K] | Crystal system | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Volume [Å³] | Z | ρcalc [g cm⁻³] | μ [mm⁻¹] | F (000) | Crystal size [mm³] | 2Θ range [°] | Index ranges | Reflections collected | Data/Restraints/Parameters | Final R indexes [I ≥ 2σ(I)] | Final R indexes [all data] | Largest peak/hole [e Å⁻³] |
|----------|---------------------|------------------|--------------|----------------|----------------|-------------|--------|--------|--------|-------|-------|-------|----------------|---|----------------|--------|--------|---------------------|----------------|--------------|------------------------|------------------------|-----------------------|---------------------|---------------------|
| [PPh₄][Cl⁻] | mo_na153_0m | C₆₀H₅₆Cl₀₄PSi | 979.55 | 100.00 | triclinic | P1 | 12.7627(8) | 13.2364(10) | 15.2799(11) | 104.429(3) | 96.533(2) | 114.486(2) | 2204.9(3) | 2 | 1.475 | 0.793 | 984.0 | 0.985 × 0.512 × 0.191 | 4.012 to 54.996 | -16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19 | 10072 [Rint = 0.0521, Rsigma = 0.0246] | 10072/10/487 | R₁ = 0.0381, wR₂ = 0.1018 | R₁ = 0.0395, wR₂ = 0.1029 | 0.73/-0.89 | 0.40/-0.38 |
| [C₈H₁₉N][Cl][Cl⁻] | mo_dh306_2802_0m | C₉₀H₇₆Cl₀₄N₂O₄Si | 851.21 | 100.0 | triclinic | P1 | 11.337(2) | 13.393(3) | 14.624(3) | 101.525(8) | 108.423(7) | 109.127(8) | 1872.9(7) | 2 | 1.509 | 0.812 | 876.0 | 0.201 × 0.154 × 0.094 | 3.77 to 50 | -13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17 | 6596 [Rint = 0.1032, Rsigma = 0.0485] | 6596/0/416 | R₁ = 0.0415, wR₂ = 0.0874 | R₁ = 0.0634, wR₂ = 0.0992 | 0.40/-0.38 | 0.40/-0.38 |
## Supporting Information

| Compound | CCDC number | [PPh₄][Br-1] | 2130729 |
|----------|-------------|--------------|---------|
| Identification code | mo_dhss12a_0ma |
| Empirical formula | C₃₇H₂₂BrClO₆Si |
| Formula weight | 1024.01 |
| Temperature [K] | 100.00 |
| Crystal system | triclinic |
| Space group | P̅1 |
| a [Å] | 13.1430(8) |
| b [Å] | 13.9325(9) |
| c [Å] | 13.9424(8) |
| α [°] | 61.557(2) |
| β [°] | 88.860(2) |
| γ [°] | 69.782(2) |
| Volume [Å³] | 2073.9(2) |
| Z | 2 |
| \( \rho_{\text{calc}} \) [g cm⁻³] | 1.640 |
| \( \mu \) [mm⁻¹] | 1.743 |
| \( F (000) \) | 1020.0 |
| Crystal size [mm³] | 0.406 × 0.295 × 0.181 |
| Radiation | Mo-Kα (\( \lambda = 0.71073 \) Å) |
| 2θ range [°] | 4.264 to 55.04 |
| Index ranges | h ≤ 17, k ≤ 18, l ≤ 18 |
| Reflections collected | 72238 |
| Independent reflections | 9459 [\( R_{\text{int}} = 0.0468, R_{\sigma} = 0.0262 \)] |
| Data/Restraints/Parameters | 9459/483/487 |
| Goodness-of-fit on \( F^2 \) | 1.070 |
| Final \( R \) indexes \([ I \geq 2\sigma(I) ]\) | \( R_1 = 0.0290, wR_2 = 0.0811 \) |
| Final \( R \) indexes \([ \text{all data} ]\) | \( R_1 = 0.0314, wR_2 = 0.0824 \) |
| Largest peak/hole \([ e \, \text{Å}^{-3} ]\) | 0.66/-0.80 |
| Compound | CCDC number | Identification code | Empirical formula | Formula weight | Temperature [K] | Crystal system | Space group | \( a \) [Å] | \( b \) [Å] | \( c \) [Å] | \( \alpha \) [°] | \( \beta \) [°] | \( \gamma \) [°] | Volume [Å³] | \( Z \) | \( \rho_{\text{calc}} \) [g cm⁻³] | \( \mu \) [mm⁻¹] | \( F(000) \) | Crystal size [mm³] | 2\( \Theta \) range [°] | Index ranges | Reflections collected | Data/Restraints/Parameters | Goodness-of-fit on \( F^2 \) | Final \( R \) indexes \([ I \geq 2\sigma(I) ]\) | Final \( R \) indexes \([ \text{all data} ]\) | Largest peak/hole [e Å⁻³] |
|-----------|-------------|---------------------|------------------|---------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| [PPh₄][I⁻] | 2130730     | mo_dh489b_0m_a_sq   | C₃₆H₂₀Cl₈IO₄PSi | 986.08        | 101.00         | monoclinic     | \( P2_1/n \) | 15.865(2)   | 16.610(2)   | 29.907(6)   | 90           | 99.801(9)   | 90           | 7766(2)       | 8             | 1.687          | 1.487          | 3888.0         | 0.218 x 0.18 x 0.08 | Mo-Kα \( (\lambda = 0.71073 \text{ Å} ) \) | 3.992 to 57.284 | -21 ≤ h ≤ 21, -22 ≤ k ≤ 22, -40 ≤ l ≤ 40 | 264223         | 19928/2884/020 | 1.120         | \( R_1 = 0.0434, \ wR_2 = 0.1015 \) | \( R_1 = 0.0519, \ wR_2 = 0.1067 \) | 0.86/-1.52     |
| Compound | Identification code | CCDC number | Empirical formula | Formula weight | Temperature [K] | Crystal system | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Volume [Å³] | Z | ρcalc [g cm⁻³] | μ [mm⁻¹] | F (000) | Crystal size [mm²] | Radiation | 2Θ range [°] | Index ranges | Reflections collected | Independent reflections | Data/Restraints/Parameters | Goodness-of-fit on $F^2$ | Final $R$ indexes [$I \geq 2\sigma(I)$] | Final $R$ indexes [all data] | Largest peak/hole [e Å⁻³] |
|-----------|---------------------|-------------|-------------------|----------------|----------------|---------------|-------------|-------|-------|-------|------|------|-------|---------------|---|--------------|--------|--------|-------------------|------------|-------------|-----------------|---------------------|---------------------------|------------------------|----------------------|------------------------|----------------------|------------------|
| [NBu₄][N₃⁻] | mo_dhss44_0m | 2130731 | C₂₈H₃₆Cl₈N₄O₄Si | 804.30 | 100.00 | triclinic | P̅ | 10.1657(6) | 11.4175(7) | 16.5825(10) | 93.933(2) | 98.196(2) | 111.561(2) | 1756.35(18) | 2 | 1.521 | 0.716 | 828.0 | 0.534 × 0.381 × 0.204 | Mo-Kα (λ = 0.71073 Å) | 4.324 to 57.504 | -13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22 | 72941 | 9083 [R_ex = 0.0506, R_factor = 0.0256] | 9083/314/410 | 1.075 | R₁ = 0.0313, wR₂ = 0.0741 | R₁ = 0.0346, wR₂ = 0.0760 | 0.43/-0.40 |
**Supporting Information**

| Compound | CCDC number | [NBu$_4$][(N$_3$)$_2$-1] | 2132184 |
|----------|-------------|--------------------------|----------|
| Identification code | P21c_a | | |
| Empirical formula | Cu$_4$H$_{2}$Cl$_3$N$_6$O$_2$Si | | |
| Formula weight | 1088.78 | | |
| Temperature [K] | 100.00 | | |
| Crystal system | monoclinic | | |
| Space group | P2$_1$/c | | |
| a [Å] | 9.8208(12) | | |
| b [Å] | 14.8040(15) | | |
| c [Å] | 36.978(5) | | |
| α [°] | 90 | | |
| β [°] | 94.199(4) | | |
| γ [°] | 90 | | |
| Volume [Å$^3$] | 5361.7(11) | | |
| Z | 4 | | |
| $\rho_{\text{calc}}$ [g cm$^{-3}$] | 1.349 | | |
| $\mu$ [mm$^{-1}$] | 0.490 | | |
| F (000) | 2296.0 | | |
| Crystal size [mm$^3$] | 0.3 × 0.15 × 0.08 | | |
| Radiation | Mo-K$_\lambda$ ($\lambda = 0.71073$ Å) | | |
| 2Θ range [°] | 4.158 to 54.618 | | |
| Index ranges | -12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -47 ≤ l ≤ 47 | | |
| Reflections collected | 211540 | | |
| Independent reflections | 11960 [R$_{int}$ = 0.0667, R$_{sigma}$ = 0.0272] | | |
| Data/Restraints/Parameters | 11960/387/671 | | |
| Goodness-of-fit on $F^2$ | 1.056 | | |
| Final R indexes [I ≥ 2σ(I)] | R$_1$ = 0.0463, wR$_2$ = 0.1043 | | |
| Final R indexes [all data] | R$_1$ = 0.0584, wR$_2$ = 0.1123 | | |
| Largest peak/hole [e Å$^{-3}$] | 0.92/-0.70 | | |
| Compound | CCDC number | Identification code | Empirical formula | Formula weight | Temperature [K] | Crystal system | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Volume [Å³] | Z | ρ calc [g cm⁻³] | μ [mm⁻¹] | F (000) | Crystal size [mm³] | Radiation | 2Θ range [°] | Index ranges | Reflections collected | Independent reflections | Data/Restraints/Parameters | Goodness-of-fit on F² | Final R indexes [I ≥ 2σ(I)] | Final R indexes [all data] | Largest peak/hole [e Å⁻³] |
|----------|-------------|---------------------|-------------------|---------------|---------------|---------------|-------------|--------|--------|--------|-------|-------|-------|---------------|--|---------------------|-------|-------|----------------------|------------|--------------|-------------|------------------|-------------------------|--------------------------|------------------------|
| [PPh₄][SCN⁻⁻] | 2130732 | mo_dhs52b_0m_a | C₃₇H₂₀Cl₈NO₄PSSi | 917.26 | 100.00 | orthorhombic | Pnba | 15.8039(4) | 21.3927(6) | 22.5090(6) | 90 | 90 | 90 | 7610.0(4) | 8 | 1.601 | 0.764 | 3696.0 | 0.531 × 0.478 × 0.228 | Mo-Kα (λ = 0.71073 Å) | 4.216 to 54.998 | -20 ≤ h ≤ 20, -26 ≤ k ≤ 27, -29 ≤ l ≤ 29 | 72747 | 7944 | 8743/0/478 | 1.036 | R₁ = 0.0302, wR₂ = 0.0689 | R₁ = 0.0576, wR₂ = 0.1651 | 0.34/-0.48 | 0.73/-0.56 |
| [NBu₄][SCN⁻⁻] | 2130733 | mo_dhs46b_210510_0m_4_a | C₂₉H₃₆Cl₈N₂O₄SSi | 820.35 | 100.00 | monoclinic | P2₁/n | 11.3166(7) | 15.7675(9) | 20.2801(14) | 97.016(3) | 90 | 90 | 90 | 3591.6(4) | 4 | 1.517 | 0.756 | 1688.0 | 0.398 × 0.256 × 0.249 | Mo-Kα (λ = 0.71073 Å) | 4.364 to 54.384 | -14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26 | 7944 | 7944 | 7944/0/410 | 1.203 | R₁ = 0.0638, wR₂ = 0.0183 | R₁ = 0.0623, wR₂ = 0.1674 | 0.73/-0.56 |
| Compound | CCDC number | [K@18-c-6][HCO₂-1] | 2130738 |
|-----------|-------------|---------------------|---------|
| Identification code | mo_na062_0m |  |  |
| Empirical formula | C₂₅H₂₅Cl₈KO₁₂Si |  |  |
| Formula weight | 868.24 |  |  |
| Temperature [K] | 100.00 |  |  |
| Crystal system | triclinic |  |  |
| Space group | P弛 |  |  |
| a [Å] | 10.2920(6) |  |  |
| b [Å] | 13.9464(9) |  |  |
| c [Å] | 15.1007(9) |  |  |
| α [°] | 114.341(2) |  |  |
| β [°] | 105.139(2) |  |  |
| γ [°] | 97.265(2) |  |  |
| Volume [Å³] | 1837.5(2) |  |  |
| Z | 2 |  |  |
| \(\rho_{\text{calc}}\) [g cm⁻³] | 1.569 |  |  |
| \(\mu\) [mm⁻¹] | 0.814 |  |  |
| \(F(000)\) | 880.0 |  |  |
| Crystal size [mm³] | 0.483 × 0.309 × 0.158 |  |  |
| Radiation | Mo-Kα (λ = 0.71073 Å) |  |  |
| 2Θ range [°] | 4.254 to 60.064 |  |  |
| Index ranges | \(-14 \leq h \leq 14, -19 \leq k \leq 19, -21 \leq l \leq 21\) |  |  |
| Reflections collected | 86832 |  |  |
| Independent reflections | 10750 | \(R_{\text{int}} = 0.0500, R_{\text{sigma}} = 0.0280\) |  |
| Data/Restraints/Parameters | 10750/0/427 |  |  |
| Goodness-of-fit on \(F^2\) | 1.053 |  |  |
| Final R indexes \([I \geq 2σ(I)]\) | \(R_I = 0.0376, wR_2 = 0.0949\) |  |  |
| Final R indexes \([\text{all data}]\) | \(R_I = 0.0433, wR_2 = 0.0994\) |  |  |
| Largest peak/hole [e Å⁻³] | 1.56/-0.49 |  |  |
| Compound | CCDC number |
|----------|-------------|
| [K@18-c-6][H$_2$CO$_2$-1] | 2143058 |

**Identification code**
mo_na46_b2_0m

**Empirical formula**
C$_{44}$H$_{60}$Cl$_2$K$_2$O$_2$Si$_2$

**Formula weight**
1979.76

**Temperature [K]**
100.00

**Crystal system**
triclinic

**Space group**
P1

| Parameter | Value |
|-----------|-------|
| $a$ [Å]   | 12.0484(18) |
| $b$ [Å]   | 13.2339(18) |
| $c$ [Å]   | 15.260(2)   |
| $\alpha$ [°] | 66.120(6)   |
| $\beta$ [°] | 73.502(6)   |
| $\gamma$ [°] | 73.431(6)   |

**Volume [Å$^3$]**
2092.5(5)

**Z**
1

| Parameter | Value |
|-----------|-------|
| $\rho_{calc}$ [g cm$^{-3}$] | 1.571 |
| $\mu$ [mm$^{-1}$] | 0.882 |
| $F(000)$ | 1002.0 |
| Crystal size [mm$^3$] | 0.631 x 0.393 x 0.202 |
| Radiation | Mo-K$_\alpha$ ($\lambda = 0.71073$ Å) |
| 2θ range [°] | 4.176 to 55 |
| Index ranges | -15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19 |
| Reflections collected | 82325 |
| Independent reflections | 9602 [$R_{int} = 0.0741, R_{factor} = 0.0391$] |
| Data/Restraints/Parameters | 9602/23/489 |
| Goodness-of-fit on $F^2$ | 1.143 |
| Final $R$ indexes [I > 2σ(I)] | $R_{1} = 0.0634$, $wR_{2} = 0.1508$ |
| Final $R$ indexes [all data] | $R_{1} = 0.0729$, $wR_{2} = 0.1565$ |
| Largest peak/hole [e Å$^{-3}$] | 0.89/-0.67 |
| Compound | CCDC number | Identification code | Empirical formula | Formula weight | Temperature [K] | Crystal system | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Volume [Å³] | Z | ρcalc [g cm⁻³] | μ [mm⁻¹] | F (000) | 2Θ range [°] | Index ranges | Reflections collected | Independent reflections | Data/Restraints/Parameters | Goodness-of-fit on F² | Final R indexes [/ I ≥2σ(I) ] | Final R indexes [all data] | Largest peak/hole [e Å⁻³] | Flack parameter |
|----------|-------------|---------------------|------------------|---------------|----------------|---------------|-------------|--------|--------|--------|-------|-------|-------|------------|----|----------------|-------------|-----------|----------------|----------------|-----------------------------|-------------------------|-----------------------------|--------------------------|--------------------------|-------------------------|----------------------|-------------------|-----------------|
| [K@18-c-6][TfO-1] | 2130734 | mo_na061_0m_pl | C₉₂H₂₅Cl₃F₂ KO₁₃SSi | 972.29 | 100.15 | triclinic | P1̅ | 10.7702(6) | 12.8220(6) | 14.9117(7) | 104.126(5) | 106.361(5) | 98.762(5) | 1861.24(17) | 2 | 1.735 | 0.881 | 980.0 | 4.058 to 60.068 | -15 ≤ h ≤ 15, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20 | 126400 | 10865 [Rint = 0.0552, Rsigma = 0.0326] | 10865/233/545 | 1.156 | 0.0426, wR2 = 0.0956 | R1 = 0.0441, wR2 = 0.0964 | 0.62/-1.08 | 0.038(18) |
| [Li@(12-c-4)] [TfO-1] | 2130735 | mo_dhss30a_0m | C₉₂H₂₅Cl₃F₂LiO₁₅SSi | 1028.23 | 100.00 | monoclinic | Cc | 14.2066(5) | 25.1955(8) | 22.6754(8) | 90 | 98.537(2) | 90 | 8026.6(5) | 8 | 1.702 | 0.724 | 4176.0 | 3.986 to 55.038 | -18 ≤ h ≤ 18, -32 ≤ k ≤ 32, -29 ≤ l ≤ 29 | 92277 | 17785 [Rint = 0.0541, Rsigma = 0.0368] | 17785/2357/1094 | 1.049 | 0.0445, wR2 = 0.1103 | R1 = 0.0504, wR2 = 0.1155 | 2.83/-1.04 |
| Compound | CCDC number | [HpyNMe$_2$][OTf][TfO-1] | 2130737 | [HpyNMe$_2$][TfO-1] | 2130736 |
|----------|-------------|--------------------------|---------|----------------------|---------|
| Identification code | mo_dhss31a_0ma | | | mo_dhss31b_0manuala | |
| Empirical formula | C$_{28}$H$_{22}$Cl$_8$F$_6$N$_4$O$_{10}$S$_2$Si | | | C$_{20}$H$_{11}$Cl$_8$F$_3$N$_2$O$_7$SSi | |
| Formula weight | 1064.30 | | | 792.06 | |
| Temperature [K] | 100.00 | | | 99.00 | |
| Crystal system | triclinic | | | monoclinic | |
| Space group | P$ar{1}$ | | | P$_2_1/n$ | |
| a [Å] | 14.0939(16) | | | 9.7810(5) | |
| b [Å] | 14.1137(16) | | | 28.8486(15) | |
| c [Å] | 20.489(2) | | | 10.3164(5) | |
| α [''] | 94.836(4) | | | 90 | |
| β [''] | 94.963(4) | | | 105.348(2) | |
| γ [''] | 93.510(5) | | | 90 | |
| Volume [Å$^3$] | 4036.3(8) | | | 2807.1(2) | |
| Z | 4 | | | 4 | |
| $\rho$calc [g cm$^{-3}$] | 1.751 | | | 1.874 | |
| $\mu$ [mm$^{-1}$] | 0.778 | | | 0.987 | |
| F (000) | 2136.0 | | | 1576.0 | |
| Crystal size [mm$^3$] | 0.196 x 0.171 x 0.166 | | | 0.256 x 0.132 x 0.078 | |
| Radiation | Mo-K$_\alpha$ ($\lambda = 0.71073$ Å) | | | Mo-K$_\alpha$ ($\lambda = 0.71073$ Å) | |
| 2$\Theta$ range [''] | 3.964 to 55.472 | | | 4.33 to 55.028 | |
| Index ranges | -18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -26 ≤ l ≤ 26 | | | -12 ≤ h ≤ 12, -37 ≤ k ≤ 37, -13 ≤ l ≤ 12 | |
| Reflections collected | 176528 | | | 46024 | |
| Independent reflections | 18773 [$R_{int} = 0.0885$, $R_{sigma} = 0.0478$] | | | 6456 [$R_{int} = 0.0713$, $R_{sigma} = 0.0368$] | |
| Data/Restraints/Parameters | 187730/1072 | | | 64562/259472 | |
| Goodness-of-fit on $F^2$ | 1.030 | | | 1.100 | |
| Final R indexes [$I \geq 2\sigma(I)$] | $R_I = 0.0508$, $wR_2 = 0.1202$ | | | $R_I = 0.0551$, $wR_2 = 0.1245$ | |
| Final R indexes [all data] | $R_I = 0.0641$, $wR_2 = 0.1309$ | | | $R_I = 0.0647$, $wR_2 = 0.1301$ | |
| Largest peak/hole [e Å$^{-3}$] | 0.69/-0.57 | | | 0.92/-0.95 | |
### Supporting Information

| Compound | CCDC number | [NBu₄]₂[1-SO₄-1] | 2156191 |
|----------|-------------|-------------------|---------|
| Identification code | mo_na174a_0m |                  |         |
| Empirical formula | C₆₂H₇₈Cl₁₆N₂O₁₂SSi₂ |                  |         |
| Formula weight | 1698.70 |                  |         |
| Temperature [K] | 100 |                  |         |
| Crystal system | monoclinic |                  |         |
| Space group | C2/c |                  |         |
| a [Å] | 22.75(3) |                  |         |
| b [Å] | 18.583(14) |                  |         |
| c [Å] | 18.043(15) |                  |         |
| α [°] | 90 |                  |         |
| β [°] | 107.56(5) |                  |         |
| γ [°] | 90 |                  |         |
| Volume [Å³] | 7272(12) |                  |         |
| Z | 4 |                  |         |
| μ [mm⁻¹] | 0.726 |                  |         |
| F (000) | 3504.0 |                  |         |
| Crystal size [mm³] | 0.289 × 0.217 × 0.148 | | |
| Radiation | Mo-Kα (λ = 0.71073 Å) | | |
| 2θ range [°] | 4.076 to 50 | | |
| Index ranges | -27 ≤ h ≤ 27, -22 ≤ k ≤ 22, -21 ≤ l ≤ 21 | | |
| Reflections collected | 89869 | | |
| Independent reflections | 6409 [R(int) = 0.1149, R(sigma) = 0.0503] | | |
| Data/Restraints/Parameters | 6409/222/482 | | |
| Goodness-of-fit on F² | 1.092 | | |
| Final R indexes ([I ≥ 2σ(I)]) | R₁ = 0.0563, wR₂ = 0.1393 | | |
| Final R indexes [all data] | R₁ = 0.0697, wR₂ = 0.1448 | | |
| Largest peak/hole [e Å⁻³] | 0.48/-1.25 | | |
Figure S2: $^{29}$Si MAS NMR spectrum (99.4 MHz) of 1 at 303 K.

Figure S3: $^1$H NMR spectrum (600 MHz) of [PPh$_4$][Cl-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S4: $^{13}$C{H} NMR spectrum (151 MHz) of [PPh$_4$][Cl-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S5: $^{31}$P{H} NMR spectrum (243 MHz) of [PPh$_4$][Cl-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S6. $^{29}$Si NMR spectrum (119 MHz) of [PPh$_4$][Cl-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S7. $^1$H NMR spectrum (600 MHz) of [PPh$_4$][Br-1] in CD$_2$Cl$_2$ at 295 K.
Figure S8: $^{13}$C($^1$H) NMR spectrum (151 MHz) of [PPh$_4$][Br-1] in CD$_2$Cl$_2$ at 295 K.

Figure S9: $^{31}$P($^1$H) NMR spectrum (243 MHz) [PPh$_4$][Br-1] in CD$_2$Cl$_2$ at 295 K.
Figure S10: $^{29}$Si NMR spectrum (119 MHz) of $[\text{PPh}_4][\text{Br-1}]$ in CD$_2$Cl$_2$ at 295 K.

Figure S11: $^1$H NMR spectrum (600 MHz) of $[\text{PPh}_4][\text{I-1}]$ in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
**Figure S12**: $^{13}$C($^1$H) NMR spectrum (151 MHz) of [PPh$_4$][I-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

**Figure S13**: $^{31}$P($^1$H) NMR spectrum (243 MHz) of [PPh$_4$][I-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S14: $^{29}$Si NMR spectrum (119 MHz) of [PPh$_4$][I-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S15: $^1$H NMR spectrum (600 MHz) of [NBu$_4$][N$_3$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.
Figure S16: $^{13}$C{H$^1$} NMR spectrum (151 MHz) of [NBu$_4$][N$_3$-1] in oDCB:CsD$_6$ (50:1) at 295 K.

Figure S17: $^{15}$N NMR spectrum (61 MHz) of [NBu$_4$][N$_3$-1] in oDCB:CsD$_6$ (50:1) at 295 K.
Figure S18: $^{29}$Si NMR spectrum (119 MHz) of [NBu$_4$][N$_3$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.

Figure S19: $^1$H NMR spectrum (600 MHz) of [NBu$_4$][(N$_3$)$_2$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.
Figure S20: $^{13}$C-$^1$H NMR spectrum (151 MHz) of $[\text{NBu}_4]^2[\text{(N}_3)_2-1]$ in oDCB-$^6$D$_6$ (50:1) at 295 K.

Figure S21: $^{29}$Si NMR spectrum (119 MHz) of $[\text{NBu}_4]^2[\text{(N}_3)_2-1]$ in oDCB-$^6$D$_6$ (50:1) at 295 K.
Figure S22: $^1$H NMR spectrum (600 MHz) of [PPh$_4$][SCN-1] in CD$_2$Cl$_2$ at 295 K (contains small amounts of Bu$_2$SO$_2$).

Figure S23: $^{13}$C($^1$H) NMR spectrum (151 MHz) of [PPh$_4$][SCN-1] in CD$_2$Cl$_2$ at 295 K.
Figure S24: $^{31}$P($^1$H) NMR spectrum (243 MHz) of [PPh$_4$][SCN-1] in CD$_2$Cl$_2$ at 295 K.

Figure S25: $^{29}$Si NMR spectrum (119 MHz) of [PPh$_4$][SCN-1] in CD$_2$Cl$_2$ at 295 K.
Figure S26: $^1$H NMR spectrum (600 MHz) of [K@18-c-6][HCO$_2$-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S27: $^{13}$C($^1$H) NMR spectrum (151 MHz) of [K@18-c-6][HCO$_2$-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S28: $^{29}$Si NMR spectrum (119 MHz) of [K@18-c-6][HCO$_2$-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S29: $^1$H NMR spectrum (600 MHz) of [K@18-c-6][HCCO$_2$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.
Figure S30: $^{13}$C\{H\} NMR spectrum (151 MHz) of [K@18-c-6][H$_3$CCO$_2$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.

Figure S31: $^{29}$Si NMR spectrum (119 MHz) [K@18-c-6][H$_3$CCO$_2$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K.
Figure S32: $^1$H NMR spectrum (600 MHz) of [Li@(12-c-4)$_2$][TfO-1] in CD$_2$Cl$_2$ at 295 K.

Figure S33: $^{13}$C($^1$H) NMR spectrum (151 MHz) of [Li@(12-c-4)$_2$][TfO-1] in CD$_2$Cl$_2$ at 295 K.
Figure S34: $^7\text{Li}$ NMR spectrum (233 MHz) of $[\text{Li@}(12\text{-c-4})_2][\text{TfO-1}]$ in CD$_2$Cl$_2$ at 295 K.

Figure S35: $^{19}\text{F}$ NMR spectrum (376 MHz) of $[\text{Li@}(12\text{-c-4})_2][\text{TfO-1}]$ in CD$_2$Cl$_2$ at 295 K.
Figure S36: $^{29}$Si NMR spectrum (119 MHz) of [Li@(12-c-4)$_2$][TfO-1] in CD$_2$Cl$_2$ at 295 K.

Figure S37: $^1$H NMR spectrum (600 MHz) of [K@18-c-6][TfO-1] in CD$_2$Cl$_2$ at 295 K.
Figure S38: $^{13}\text{C}^1\text{H}$ NMR spectrum (151 MHz) of $[\text{K@18-c-6][TfO-1]}$ in CD$_2$Cl$_2$ at 295 K.

Figure S39: $^{19}\text{F}$ NMR spectrum (376 MHz) of $[\text{K@18-c-6][TfO-1]}$ in CD$_2$Cl$_2$ at 295 K.
Figure S40: $^{29}$Si NMR spectrum (119 MHz) of [K@18-c-6][TfO-1] in CD$_2$Cl$_2$ at 295 K.

Figure S41: $^1$H NMR spectrum (600 MHz) of [K@db18-c-6][1-SO$_4$-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S42: $^{13}$C{[$^1$H]} NMR spectrum (151 MHz) [K@db18-c-6][1-SO$_4$-1] in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S43: $^1$H NMR spectrum (600 MHz) of [K@db-18-c-6][1-SO$_4$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K (contains sulfolane).
Figure S44: $^{13}$C [$^1$H] NMR spectrum (151 MHz) of [K@db18-c-6]$_2$[1-SO$_4$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K (contains sulfolane).

Figure S45: $^{29}$Si NMR spectrum (119 MHz) of [K@db18-c-6]$_2$[1-SO$_4$-1] in oDCB:C$_6$D$_6$ (50:1) at 295 K (contains sulfolane).
Figure S46: $^1$H NMR spectrum (600 MHz) of $[\text{NBu}_4]^+\text{[1-SO}_4^-\text{]}$ in CD$_2$Cl$_2$ at 295 K (contains sulfolane).

Figure S47: $^{13}$C($^1$H) NMR spectrum (151 MHz) $[\text{NBu}_4]^+\text{[1-SO}_4^-\text{]}$ in CD$_2$Cl$_2$ at 295 K (contains sulfolane).
Figure S48: $^{29}$Si NMR spectrum (119 MHz) of $[\text{NBu}_4]^+\left[\text{1-SO}_4^{-}\right]$ in $\text{CD}_2\text{Cl}_2$ at 295 K (contains sulfolane).
Figure S49: IR (ATR) spectrum of [1]₄ under nitrogen atmosphere at 298 K.

Figure S50: IR (ATR) spectrum of [PPh₄][SCN-1] in CD₂Cl₂ under nitrogen atmosphere at 298 K.
Figure S51: IR (ATR) spectrum of [NBu₄][N₃₋₁] under nitrogen atmosphere at 298 K.

Figure S52: IR (ATR) spectrum of [NBu₄][N₃₋₂] under nitrogen atmosphere at 298 K.
Figure S53: IR (ATR) spectrum of \([\text{K@db}18\text{-c}-6]\text{[1-SO}_4\text{-1]}\) in \([\text{oDCB}\text{C}_6\text{D}_6\text{ (50:1)}]\) under nitrogen atmosphere at 298 K (contains sulfolane).

Figure S54: IR (ATR) spectrum of \([\text{K@18-c-6]}\text{[HCO}_2\text{-1]}\) in \([\text{CD}_2\text{Cl}_2]\) under nitrogen atmosphere at 298 K (contains sulfolane).
Figure S55: IR (ATR) spectrum of [K@18-c-6][H$_2$CCO$_2$-1] in oDCB:C$_6$D$_6$ (50:1) under nitrogen atmosphere at 298 K.

Figure S56: IR (ATR) spectrum of [PPh$_4$][SCN] under nitrogen atmosphere at 298 K.
Figure S57: IR (ATR) spectrum of $\text{K}_2\text{SO}_4$ under nitrogen atmosphere at 298 K.

Figure S58: IR (ATR) spectrum of $\text{KHCO}_2$ under nitrogen atmosphere at 298 K.
Figure S59: IR (ATR) spectrum of KOAc under nitrogen atmosphere at 298 K.
Supporting Information

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