Supporting Information

**Bis(perchlorocatecholato)germane: Hard and Soft Lewis Superacid with Unlimited Water Stability**

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1. Experimental Procedures

a. Materials and General Methods

If stated, manipulations were carried out under a dry argon atmosphere by using standard Schlenk techniques to prevent oxidation and hydrolysis of sensitive compounds. In this case, all solvents were rigorously dried by applying standard procedures, freshly degassed and stored over molecular sieve (3 Å resp. 4 Å) prior to use. All glassware, syringes, magnetic stirring bars and needles were thoroughly dried. When necessary, glassware was silylated by immersion in a solution of Me₂SiCl₂ in toluene for 20 min, then immersed in methanol for 20 min and dried in an oven at 140 °C for several hours. Commercially available chemicals were used as received. Perchlorocatechol was prepared according to the literature procedure. Air or moisture sensitive compounds were stored in a glove box (MBraun Labmaster dp, MB-20-G or Sylatech Glovebox) under N₂ atmosphere. Purity and identity of the compounds were confirmed by high resolution multinuclear NMR spectroscopy, mass spectrometry, elemental analysis and where possible, X-ray diffraction analysis. ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded at 298 K with a Bruker DRX200, Bruker Advance II 400 or Bruker 2 Advance III 600 NMR spectrometer and referenced to the solvent in use. Chemical shifts are reported as dimensionless δ values in ppm, coupling constants J are given in Hertz (Hz). Electrospray ionization mass spectra were obtained with a Bruker ApexQe FT-ICR instrument. IR spectra were measured on a Bruker Alpha or an Agilent Cary 630 spectrometer equipped with diamond ATR units.
b. Syntheses

Bis(perchlorocatecholato)germane – water adduct (1-(H$_2$O)$_m$)

A suspension of GeO$_2$ (1.00 g, 9.61 mmol, 1 eq.) and perchlorocatechol (5.00 g, 20.2 mmol, 2.1 eq.) in water (80 mL) was heated to 60 °C and stirred for 4 h after which complete dissolution of the starting compounds occurred. The solvent was removed _in vacuo_ and the residue washed with dichloromethane and dried under high vacuum to give 1 as a colorless solid (5.72 g, 8.99 mmol, 94 %). Elemental analysis suggests that about four water molecules are bound per formula unit. The product can be recrystallized from water (suitable for X-ray diffraction) to give colorless crystals. After crystallization, six molecules water are bound per molecule, as supported by elemental and X-ray diffraction analysis.

$^{13}$C NMR (100 MHz, D$_2$O): δ = 145.7, 119.3, 115.1; HRMS (EI): [C$_{12}$Cl$_8$GeO$_4$]$^+$, calcd.: 561.6511, found: 561.6497; IR (ATR): 3594, 3501 (br), 2917 (br), 1631, 1578, 1431, 1390, 1290, 999, 972, 810, 708, 587, 508, 489 cm$^{-1}$; Anal. Calcd. for C$_{12}$H$_{12}$Cl$_8$GeO$_{10}$: C, 21.43; H, 1.80; found C, 21.36; H, 1.75.

Bis(perchlorocatecholato)germane – acetonitrile adduct (1-(CH$_3$CN)$_2$)

A suspension of 1 (500 mg, 1.57 mmol, 1 eq.) in a mixture of acetonitrile (1 mL) and CH$_2$Cl$_2$ (10 mL) was stored over molecular sieves (3 Å) for three days. Undissolved colorless solid was filtered off and physically separated from the molecular sieve. The filtrate was concentrated _in vacuo_ and CH$_2$Cl$_2$ (10 mL) added to promote further precipitation of a colorless solid, which was then filtered off. The solids were combined and dried _in vacuo_ to furnish a colorless solid (482 mg, 746 μmol, 95 %). $^1$H NMR spectroscopy in dry DMSO-$d_6$ and elemental analysis indicate the absence of water. Very slow displacement of acetonitrile by atmospheric water occurs under standard benchtop conditions.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ = 1.97; IR (ATR): 3004, 2934, 2324, 2293, 1671, 1579, 1437, 1391, 1358, 1289, 1033, 996; 979, 948, 810, 709, 672, 593, 510 cm$^{-1}$; Anal. Calcd. for C$_{16}$H$_6$Cl$_8$GeN$_2$O$_4$: C, 29.73; H, 0.94; N, 4.33 found C, 29.44; H, 1.01; N, 4.24.

Bis(perchlorocatecholato)germane – tributylphosphate adduct (1-(P(O)OBu)$_3$)$_2$)

To a suspension of 1-(H$_2$O)$_4$ (200 mg, 333 μmol, 1 eq.) in acetonitrile (7 mL) was added tributylphosphate (334 mg, 342 μL, 1.26 mmol, 4 eq.) and the mixture heated to reflux. After slowly cooling to room temperature, a crystalline precipitate formed (suitable for X-ray diffraction). The precipitate was collected by filtration, washed with cold acetonitrile and dried _in vacuo_ to give the product as a colorless, crystalline solid (266 mg, 242 μmol, 77 %).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ = 3.92 (q, J = 6.7 Hz, 12H), 1.44 (quint, J = 7.0 Hz, 12H), 1.20 (sext, J = 7.5 Hz, 12H), 0.85 (t, J = 7.4 Hz, 18H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): δ = 145.7, 120.6, 116.0, 70.6 (d, $^4$J$_{CP}$ = 6.8 Hz), 32.1 (d, $^2$J$_{CP}$ = 7.0 Hz), 18.7, 13.6; $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$): δ = -9.08; IR (ATR): 2960, 2932, 2873, 1576, 1438, 1386, 1292, 1245, 1237, 1160, 1030, 974, 911, 873, 809, 740, 704, 698, 584, 505, 486 cm$^{-1}$; Anal. Calcd. For C$_{36}$H$_{54}$Cl$_8$GeO$_{12}$P$_2$: C, 39.60; H, 4.96; found C, 39.60; H, 4.87.
Bis(perchlorocatecholato)germane – dimethylsulfoxide-d₆ adduct (1-(dmso-d₆)₂)

1-(H₂O)₄ was dissolved in DMSO-d₆ (0.5 mL). After standing at rt for 1 d, the product crystalized from the solution (suitable for X-ray diffraction).

¹³C NMR (100 MHz, DMSO-d₆): δ = 148.1, 116.6, 113.1.

[Et₄N][Cl₂-Ge(catCl)₂] (5)

1-(H₂O)₄ (200 mg, 314 μmol, 1 eq.) was suspended in acetonitrile (3 mL) and Et₄NCl (104 mg, 629 μmol, 2 eq.) was added. After initial dissolution of the starting materials a colorless solid precipitated within a few minutes. The precipitate was filtered off and washed with pentane to give 5 as a colorless solid (155 mg, 173 μmol, 55 %). After recrystallization from acetonitrile, crystals suitable for X-ray diffraction analysis were obtained.

¹H NMR (400 MHz, DMSO-d₆): δ = 3.20 (q, J = 7.3 Hz, 16H), 1.16 (tt, J_HH = 7.2 Hz, J_HN = 1.18 Hz, 24H).

¹³C NMR (100 MHz, DMSO-d₆): δ = 146.7, 117.5, 113.8, 51.5 (t, J_CC = 3.0 Hz), 7.1;

IR (ATR): 2987, 1563, 1482, 1462, 1442, 1395, 1384, 1369, 1333, 1290, 1173, 1074, 1053, 995, 973, 911, 812, 805, 786, 698, 626, 583, 493, 471, 435, 420 cm⁻¹;

Anal. Calcd. for C₂₈H₃₈Cl₁₀GeN₂O₄: C, 37.63; H, 4.29; N, 3.13 found C, 37.50; H, 4.59; N, 3.06.

Bis(perchlorocatecholato)germane – acetone adduct (1-(acetone)₂)

1-(H₂O)₄ (310 mg, 487 mmol, 1 eq.) was dissolved in acetone (15 mL) and stored over molsieve 3 Å for 24 h at 40°C. The molsieve was filtered off, the solution concentrated to half volume and pentane (25 mL) added, leading to the precipitation of a colorless solid. The precipitate was collected by filtration, washed with pentane (10 mL) and dried in vacuo to give the product as a colorless solid (301 mg, 442 mmol, 91 %). The purity was confirmed by ¹H NMR spectroscopy in DMSO-d₆ or acetone-d₆.

¹H NMR (400 MHz, CD₂Cl₂): δ = 2.07 (s, 6H).

¹³C NMR (100 MHz, acetone-d₆): δ = 210.0, 205.8, 148.9, 118.4, 115.1, 30.6;

IR (ATR): 1709, 1696, 1569, 1472, 1441, 1385, 1360, 1293, 1237, 1090, 993, 975, 915, 813, 800, 699 cm⁻¹;
A suspension of 1-(CH<sub>3</sub>CN)<sub>2</sub> (20.0 mg, 30.9 μmol, 1 eq.) in CD<sub>2</sub>C<sub>2</sub> (0.5 mL) was treated with KF (1.80 mg, 30.9 μmol, 1 eq.) and 18-crown-6 (8.20 mg, 30.9 μmol, 1 eq.). After heating at 50 °C for 1.5 h a clear solution formed. The product was crystallized by gas phase diffusion of pentane into the solution at -40 °C (suitable for X-ray diffraction). After leaving the crystals under ambient conditions for several weeks, the water adduct [K@18-crown-6][F-Ge(catCl)<sub>2</sub>-OH<sub>2</sub>] formed (crystals still suitable for X-ray diffraction).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = 3.55 (s, 12H);
<sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = -141.8;
<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = 145.3, 121.2, 115.8, 70.5;
HRMS (ESI(−)): [C<sub>12</sub>Cl<sub>8</sub>FGeO<sub>4</sub>]<sup>−</sup>, calcd.: 580.6506, found: 580.6556.

To a suspension of 1-(H<sub>2</sub>O)<sub>4</sub> (100 mg, 157 μmol, 1 eq.) in 2 mL CH<sub>2</sub>C<sub>2</sub> was added Ph₄PCl (58.9 mg, 157 μmol, 1 eq.) which led to immediate dissolution of most of the starting materials. Undissolved solid was filtered off and the product precipitated with pentane (10 mL), collected and washed with pentane (3 x 4 mL) to give a colorless solid (120 mg, 128 μmol, 81 %).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = 7.89 – 7.86 (m, 1H), 7.74 – 7.69 (m, 2H), 7.61 – 7.56 (m, 2H);
<sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = 23.3;
<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>C<sub>2</sub>): δ = 145.3, 136.1 (d, J<sub>CP</sub> = 3.03 Hz), 134.8 (d, J<sub>CP</sub> = 10.3 Hz), 131.0 (d, J<sub>CP</sub> = 12.9 Hz), 121.1, 118.3, 117.4, 115.8; HRMS (ESI(−)): [C<sub>12</sub>Cl<sub>8</sub>GeO<sub>4</sub>]<sup>−</sup>, calcd.: 596.6211, found: 596.6210.

Bis(perchlorocatecholato)germane – ‘free’ Lewis acid

To a suspension of 1-(acetone)<sub>2</sub> (40.0 mg, 58.8 μmol, 1 eq.) in CD<sub>2</sub>C<sub>2</sub> (0.7 mL) was added 9-BBN (15.8 mg, 129 μmol, 2.2 eq.) and the mixture was stirred for 20 h at rt resulting in a suspension of a colorless solid in a colorless solution. NMR spectroscopy revealed full conversion for the hydroboration of acetone (fig. S1). The colorless solid was separated from the solution by centrifugation and washed with pentane (3 x 2 mL) to give a colorless solid (25.0 mg, 75 %). The solid dissolves in DMSO-d<sub>6</sub> to give an analytically pure spectrum with traces of CH<sub>2</sub>C<sub>2</sub> that could not be removed from the solid product even after prolonged exposure to high vacuum. This is also reflected in the elemental analysis.

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ = 148.1, 116.6, 113.1; IR (ATR): 1570, 1432, 1386, 1362, 1322, 1295, 1237, 1221, 1001, 972, 911, 818, 800, 732, 700 cm<sup>−1</sup>; Anal. Calcd. for C<sub>10</sub>Cl<sub>8</sub>GeO<sub>4</sub>: C, 25.54; calcd. for C<sub>12</sub>Cl<sub>8</sub>GeO<sub>4</sub> x CH<sub>2</sub>C<sub>2</sub>: C, 23.97; H 0.62 found C, 23.83; H, 0.56.
c. Qualitative Assessment of Bronsted Acidity of 1-(H₂O)₄

A 0.1 mM solution of 1-(H₂O)₄ (6.36 mg, 10.0 μmol) in water (100 mL) was prepared and the pH value of the solution checked simply using pH paper to be around 4, which corresponds to the expected value for complete dissociation of 1-(H₂O)₄.
d. Assessment of Lewis Acidity by the Gutmann-Beckett Method

To a suspension of 1-(CH₃CN)₂ or 1-(H₂O)₄ in CD₂Cl₂, triethylphosphine oxide (OPEt₃) was successively added (0.3 eq. → 2 eq.) and the reaction monitored by ¹H and ³¹P NMR spectroscopy. Addition of only 0.3 eq. led to a broad signal (fig. S2) at 83.7 ppm, while 2 eq. lead to the appearance of two sharp signals at 75.1 and 70.6 ppm in a 1 : 1.3 ratio (fig. S3). The ¹H NMR spectrum suggests that the two signals correspond to a mixture of cis- and trans-bis-OPEt₃ substituted complexes. The chirality in the C₂ symmetric cis-adduct leads to strong diastereotopic splitting of the CH₂ signals (fig. S4).

Figure S2: ³¹P NMR spectrum of Ge(cat⁵)₃-(CH₃CN)₂ and 0.3 equiv OPEt₃ in CD₂Cl₂.

Figure S3: ³¹P NMR spectrum (CD₂Cl₂) of 1-(OPEt₃)₂ crystals, equilibrium of cis- and trans-adduct with 1:1.3 ratio.
Computed thermodynamics for the formation of 1-(OPEt)$_n$

The enthalpies for the formation of 1-(OPEt)$_n$ and 1-(OPEt)$_3$ were calculated at the PW6B95/def-TZVPP level of theory, showing the addition of the second unit of OPEt to 1 to be thermodynamically more favorable compared to the addition of the first unit, while the reverse is the case for silicon as central atom. For computational details, see section 4.

![Figure S5: Calculated enthalpies in kJ mol$^{-1}$ for the adduct formation of 1 with one and two equivalent of OPEt at the PW6B95/def2-TZVPP level of theory.](image)

2. Reactivity Studies

a. Fluoride Abstraction from [Ph,P][SbF$_6$]

1-(CH$_3$CN)$_2$ (20.0 mg, 30.94 μmol, 1 eq.) was suspended in CD$_2$Cl$_2$ in a J. Young NMR tube and [Ph,P][SbF$_6$] was added. ESI-MS(-) after two hours displayed a signal corresponding to the mono-fluoride adduct and various other reactions intermediates through ligand scrambling similar to the analogous reaction of bis(perchloratecholato)silane (Figure S8).[1] Concurrently, a signal at -142.1 ppm (-141.8 ppm for [K@18-c-6][F-Ge(cat$^3$)$_2$]) appeared in the $^{19}$F NMR spectrum alongside the signals in the expected shift range in the $^{13}$C NMR spectrum (figure S6 and 7).
Figure S6: $^{13}$C NMR spectrum in CD$_2$Cl$_2$ for the fluoride abstraction from SbF$_6$ (top) and for [K@18-c-6][F-Ge(cat$^3$)$_2$]. (*): Released ACN upon binding of F$^-$. 

Figure S7: $^{19}$F NMR spectra in CD$_2$Cl$_2$ for the fluoride abstraction from SbF$_6$ and for [K@18-c-6][F-Ge(cat$^3$)$_2$].
b. Hydride abstraction from $[^{[\text{Bu}_3\text{PH}]][\text{HB(C}_6\text{F}_5)_3]]$

$[^{[\text{Bu}_3\text{PH}]][\text{HB(C}_6\text{F}_5)_3]]$ was prepared according to the procedure described by STEPHAN et al.[2] $[^{[\text{Bu}_3\text{PH}]][\text{HB(C}_6\text{F}_5)_3]]$ was added to a suspension of $1-(\text{CH}_3\text{CN})_2$ in CD$_2$Cl$_2$ inside a J. Young NMR tube and the reaction monitored by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. After 3 hours, $^{19}\text{F}$ NMR revealed the formation of a BCF-acetonitrile adduct, with the signals in good agreement with the reference spectrum of a 1:1 mixture of BCF and acetonitrile in CD$_2$Cl$_2$ (fig. S9/10). The fate of a putative hydrido germanate remains unknown, but suggests a possible disproportionation into GeH$_4$ and Ge(catCl)$_2$.2.
**Figure S9**: $^{19}$F NMR spectra for the hydride abstraction from $\left[\text{tBu}_3\text{PH}\right]\left[\text{HB}(\text{C}_6\text{F}_5)_{3}\right]$ at rt in CD$_2$Cl$_2$. * denotes solvent signal.

**Figure S10**: $^1$H NMR spectra for the hydride abstraction from $\left[\text{tBu}_3\text{PH}\right]\left[\text{HB}(\text{C}_6\text{F}_5)_{3}\right]$ at rt in CD$_2$Cl$_2$. * denotes solvent signal.
3. Lewis acid catalysis

a. Hydrodefluorination of 1-fluoradamantane

In a J. Young NMR tube, 1-adamantylfluoride (15.4 mg, 0.10 mmol, 1 eq.), Et₃SiH (31.9 μL, 0.15 mmol, 1.5 eq.) and 1-(CH₃CN)₂ (0.05-0.0005 eq.) were suspended in CD₂Cl₂ (0.5 mL). Conversion was determined using ¹⁹F NMR by integration against C₆F₆ as internal standard. For the reaction with 0.05 mol% catalyst, 1-(CH₃CN)₂ was weighed outside the glove box.

Adamantane. ¹H NMR (CD₂Cl₂) δ [ppm] = 1.87 (s, 4H), 1.78 – 1.76 (m, 12H).

Figure S11: ¹H NMR in CD₂Cl₂ of the hydrodefluorination of 1-adamantylfluoride after 48h at 50°C employing 0.05 mol% catalyst.

Figure S12: ¹⁹F NMR in CD₂Cl₂ of the hydrodefluorination of 1-adamantylfluoride after 48h at 50°C employing 0.05 mol% catalyst.
Figure S13: $^{19}$F NMR spectrum (CD$_2$Cl$_2$) for the hydrodefluorination of 1-fluoroadamantane employing 3 mol% of 1-(CH$_3$CN)$_2$ after 15 min at rt.

Figure S13 shows the intermediary formation of a signal at -140.1 ppm corresponding to the formation of [1-F] as indicator for fluoride abstraction as reaction pathway and not Si-H bond activation. The signal is lost after standing of the reaction solution for several hours at room temperature.
b. Hydrosilylation of aldehydes

General Procedure:
A J. Young NMR tube was charged with aldehyde (0.10 mmol, 1 eq.), Et₃SiH (31.9 μL, 0.20 mmol, 2 eq.), 1-(CH₃CN)₂ (0.05 – 0.005 eq.) in dichloromethane-d₂ (0.5 mL). The reaction was followed by ¹H NMR and the conversion determined by integration against C₆(Me)₆ as an internal standard.

Triethyl((4-methylbenzyl)oxy)silane. ¹H NMR (CD₂Cl₂) δ [ppm] = 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.56 (q, J = 8.0 Hz, 6H).

Triethyl((4-fluorobenzyl)oxy)silane. ¹H NMR (CD₂Cl₂) δ [ppm] = 7.34 (dd, J = 8.9 Hz, 5.7 Hz, 2H), 7.06 (t, J = 8.8 Hz, 2H), 4.51 (s, 2H), 0.98 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H); ¹⁹F NMR (CD₂Cl₂) δ [ppm] = -115.6 (m, 1F).

(Cyclohexylmethoxy)triethylsilane. ¹H NMR (CD₂Cl₂) δ [ppm] = 3.17 (d, J = 6.5 Hz, 2H), 1.77 - 1.63 (m, 6H), 1.60 - 1.49 (m, 1H), 1.32 - 1.14 (m, 4H), 0.95 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H).

Figure S14: ¹H NMR spectrum for the hydrosilylation of cyclohexylcarboxaldehyde employing 0.5 mol% 1-(CH₃CN)₂ after 1 h at rt.
Figure S15: $^1$H NMR spectrum for the hydrosilylation of 4-methylbenzaldehyde employing 5 mol% 1-(CH$_3$CN)$_2$ after 20 h at rt.

Figure S16: $^1$H NMR spectrum for the hydrosilylation of 4-fluorobenzaldehyde employing 5 mol% 1-(CH$_3$CN)$_2$ after 20 h at rt.
c. Transfer hydrogenation of 1,1-diphenylethylene (1,1-DPE)

General Procedure:
A J. Young NMR tube was charged with 1,1-diphenylethylene (17.6 μL, 0.10 mmol, 1 eq.), 1,4-cyclohexadiene (28.8 μL, 0.20 mmol, 2 eq.) or Et₃SiH (31.9 μL, 0.20 mmol, 2 equiv) and 1-(CH₃CN)₂ or 1-(H₂O)₆ (0.01 mmol, 0.1 eq.) in CD₂Cl₂ (0.5 mL) and the reaction progress followed via 1H NMR. Conversion was determined by integration against C₆(Me)₆ as an internal standard.
To support the bound water in 1-(H₂O)₆ as proton source in the hydrogenation, a control reaction with Et₃SiH and D₂O as reagents was done. The resulting spectrum shows the expected product where one of the CH₃ protons of 1,1-diphenylethan is replaced by a deuterium atom, confirming initial protonation of 1,1-DPE and subsequent reaction of the generated carbocation with Et₃SiH as mechanism for this reaction.

Ethane-1,1-diyl dibenzene. 1H NMR (CD2Cl2) δ [ppm] = 7.32 – 7.23 (m, 8H), 7.21 – 7.16 (m, 2H), 4.17 (q, J = 7.3 Hz, 1H), 1.65 (d, J = 7.3 Hz, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H).

![Figure S17: 1H NMR spectrum of the reaction of 1,1-DPE with 10 mol% 1-(CH₃CN)₂ and Et₃SiH and D₂O after 24h at rt.](image-url)
d. Friedel-Crafts dimerization of 1,1-diphenylethylene
To a solution of 1,1-DPE (17.6 μL, 0.10 mmol, 1 eq.) in CD₂Cl₂ (0.5 mL) in a J. Young NMR tube was added 1-(CH₃CN)₂ (3.23 mg, 5.00 μmol, 0.05 equiv) and the mixture heated to 50 °C. Conversion was determined after 24 h at 50 °C by integration of ¹H NMR signals.

1-Methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene. ¹H NMR (CD₂Cl₂) δ [ppm] = 7.33 – 6.99 (m, 19H), 3.41 (d, J = 13.6 Hz, 1H), 3.14 (d, J = 13.6 Hz, 1H), 1.58 (s, 3H).

![Figure S20: ¹H NMR spectrum (CD₂Cl₂) of the reaction mixture for the Friedel-Crafts dimerization of 1,1-DPE mediated by 5 mol% 1-(CH₃CN)₂ (50 °C, 24 h).](image)

e. Carbonyl-olefin metathesis

The metathesis substrate A was synthesized according to the literature procedure described by Catti et al.[3] To a solution of A (27.4 mg, 100 μmol, 1 eq.) in CD₂Cl₂ (0.5 mL) was added 1-(CH₃CN)₂ (3.23 mg, 10.0 μmol, 0.05 eq.) and the reaction progress monitored via ¹H NMR. After 24 h, full conversion of the starting material was observed. The same reaction with either 20 mol% of 1-(H₂O)₂ or 10 mol% of 1-(acetone)₂ did not show consumption of the substrate even after heating for 24 h at 60 °C, suggesting that once two molecules of acetone are bound to 1, the catalytic activity is drastically decreased.

The reaction with 5 mol% of 1-(CH₃CN)₂ in the presence of excess acetone (10 eq.) proceeded in similar manner (full conversion of substrate within 24 h at rt) to the reaction without the excess acetone, further demonstrating that 1-(CH₃CN)₂ in the presence of acetone is still an active catalyst but the species 1-(acetone)₂ is somehow not.

No significant differences in reaction times and conversions were also observed between the reaction under inert conditions and non-inert conditions (use of ‘wet’ solvent under ambient atmosphere).

Ethyl 2-phenylcyclopent-2-ene-1-carboxylate. ¹H NMR (CD₂Cl₂) δ [ppm] = 7.43 – 7.40 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 6.35 (td, J = 2.6, 1.7 Hz, 1H), 4.09 - 4.02 (m, 2H), 3.98 (2.71 – 2.64 (m, 1H), 2.57 – 2.51 (m, 1H), 2.38 – 2.32 (m, 1H), 2.21 (ddt, J = 13.1, 8.7, 4.4 Hz; 1H), 1.15 (t, J = 7.0 Hz, 3H).
Figure S21: $^1$H NMR (CD$_2$Cl$_2$) of the reaction of A after 20 h at rt with 5 mol% 1-(CH$_2$CN)$_2$. 
f. Tests for hidden Brønsted acid catalysis

As traces of water in the acetonitrile adduct may lead to hidden Brønsted catalysis, investigations were made using the proton scavengers 2,6-di-tert-butylpyridine or trimesitylphosphine, which were selectively added to the reactions to inhibit any such pathways. Stoichiometric addition of either DTBP or PMes3 led to complete suppression of reactivity in the hydrosilylation and hydrodefluorination reactions and were coupled with the observation of large amounts of protonated base. However, for substoichiometric amounts of base (relative to 1-(CH2CN)2), the reactions still proceeded in the expected manners, hence, excluding trace protons from residual water as possible catalyst. In addition, the observed Brønsted base quenching was also observed in test reactions using 1-(CH2CN)2 that was prepared in a "water-free" method (Ge-metal + ortho-chloroquinone), thus conditions under which traces amounts of water can be excluded. Moreover, during the control reactions with only Ge(catCl)2-(CH2CN)2 and sterically hindered base, slow protonation of the was observed over time, suggesting only the base may provoke proton release and inhibit the reaction this way, which has been observed previously as well. Furthermore, excess amounts of non-nucleophilic proton traps such as Me3PhSi in the reaction solution did not suppress or slow down catalytic activity of 1-(CH2CN)2. These results generally suggest Lewis acid over Bronsted acid catalysis.

General Procedure:
To a solution of either 1-fluoroadamantane (Ad-F) (15.4 mg, 0.10 mmol, 1 eq.) or 4-fluorobenzaldehyde (10.7 μL, 0.10 mmol, 1 eq.), Et3SiH (31.9 μL, 0.20 mmol, 2eq) and 2,6-di-tert-butylpyridine (1.12 - 2.25 μL, 5 – 10 μmol, 0.05 – 0.1 eq.) or trimesitylphosphine (1.95 - 3.89 mg, 5 – 10 μmol, 0.05 – 0.1 eq.) in CD2Cl2 was added 1-(CH2CN)2. NMR spectra were measured before the addition of 1-(CH2CN)2 and after specific time intervals after the addition to follow the progress of the reaction. Control reaction were also done without substrate and Et3SiH.

Addition of stoichiometric amounts of base (relative to the catalyst) to the reactions led to complete inhibition of either hydrodefluorination of 1-fluoroadamantane or hydrosilylation of ρ-fluorobenzaldehyde. Large amounts of protonated base were observed (40 – 60 %, fig. S22), suggesting the proton source can’t be residual traces of water as such amounts would have been visible in either IR, elemental analysis or NMR measurements of 1-(CH2CN)2.

Figure S22: Representative 1H NMR spectrum (CD2Cl2) of catalysis attempts with sterically hindered base, in this case the hydrodefluorination of Ad-F and stoichiometric amounts of 2,6-di-tert-butylpyridine (relative to 1-(CH2CN)2) after 1 h at rt.

Adding only 5 mol% sterically hindered base to the reaction employing 10 mol% catalyst resulted in the expected catalytic hydrodefluorination or hydrosilylation of the respective substrates (fig. S23), although increased formation of a side product was observed (signal at 4.69 ppm). The result hinted at the base provoking the formation of protons, rather than excluding proton catalysis. Indeed, monitoring a 1:1 mixture of 1-(CH2CN)2 and sterically hindered base, a slow, but steady increase in the fraction of protonated base can be observed. The protonation rate may be increased by heating or the addition of Et3SiH. Large amounts of protonated base were observed (40 – 60 %, fig. S22), suggesting the proton source can’t be residual traces of water as such amounts would have been visible in either IR, elemental analysis or NMR measurements of 1-(CH2CN)2.

The use of the non-nucleophilic proton trap Me3PhSi either in stoichiometric amounts or in excess (20 eq. relative to 1-(CH2CN)2) did not impede the catalytic hydrosilylation of ρ-fluorobenzaldehyde in any measurable way and full conversion of the substrates were observed within the expected timeframes.
Figure S23: Representative $^1$H NMR spectrum (CD$_2$Cl$_2$) of the hydrosilylation of p-fluorobenzaldehyde employing 10 mol% 1-(CH$_3$CN)$_2$ and 5 mol% of PMes$_3$ after 20 h at rt.

Figure S24: $^1$H NMR spectrum (CD$_2$Cl$_2$) for the hydrodefluorination of p-fluorobenzaldehyde employing 100 mol% of Me$_3$SiPh and 5 mol% of 1-(CH$_3$CN)$_2$ after 6 h at rt.
4. Computational Details

All geometry optimizations and single point energies were calculated using the Orca 4.1.1 or 4.1.2 program package.\[5\] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.\[6\] 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.\[7\] 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.\[8\]

For the final anion affinities, single point energies were calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory.\[9\] Using the scheme 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 $\text{Me}_3\text{Si}^+ + X^- \rightarrow \text{Me}_3\text{SiX}$ from the column $\text{[B-A]}$ in the following tables.\[10\] Solvation free enthalpies for all molecular structures were determined using COSMO-RS, as implemented in the ADF program package and based on solute-solvent interactions calculated at the BP86-D3/TZP level of theory.\[11\] Summation over solvation enthalpies for Lewis acid, fluoride anion, fluoride adduct and the respective DLPNO-CCSD(T) vacuum enthalpies gave the corresponding solvation corrected anion affinities.

All structures shown were visualized using IboView v20150427.\[12\]
| Compound                  | E [a.u.] BP86 D3/def2-SVP | ΔE [kJ] | Thermal correction [kJ] | Electronic+Thermal [kJ] | LA + MeSiY (A) | MeSiY + LA-Y (B) | (B) – (A) | FIA/HIA/CIA [kJ/mol] |
|---------------------------|---------------------------|---------|-------------------------|-------------------------|----------------|-----------------|-----------|----------------------|
| Ge(catCl)$_2$             | -6515.5961                | -17106697.7 | 317.5                  | 317.5                  |                |                |           |                      |
| [F-Ge(catCl)$_2$]         | -6615.5475                | -17369119.9 | 326.6                  | -1729873.4             | -17421696.9   | 430.7           | 528       |                      |
| [H-Ge(catCl)$_2$]         | -6516.3324                | -17108630.7 | 337.8                  | -1718829.2             | -1815767.2    | 378.5           | 581       |                      |
| [Cl-Ge(catCl)$_2$]        | -6975.8918                | -18315204.0 | 325.1                  | -1831487.9             | -1938372.5    | 379.7           | 361       |                      |
| GeF$_4$                  | -2476.2087                | -6501286.0 | 42.3                   | -6501243.7             |                |                |           |                      |
| GeF$_5$                  | -2576.0926                | -6763531.0 | 50.4                   | -6763480.7             | -7837183.1    | -7836576.3     | 352       |                      |
| GeF+H$^+$                | -2476.8726                | -6503029.1 | 61.3                   | -6502967.7             | -8374401.6    | -8374228.2     |           |                      |
| GeF(CF$_3$)$_3$          | -3188.9815                | -8372671.0 | 156.5                  | -8372514.5             |                |                |           |                      |
| [F-GeF(CF$_3$)$_3$]       | -3288.8614                | -8634905.5 | 162.8                  | -8634742.7             | -9708454.0    | -9707838.4     | 343       |                      |
| [H-GeF(CF$_3$)$_3$]       | -3189.6407                | -8374401.6 | 173.4                  | -8374228.2             | -9447901.5    | -9447323.8     | 382       |                      |
| Ge(CF$_3$)$_4$           | -3426.5748                | -8996472.1 | 194.6                  | -8996277.5             |                |                |           |                      |
| [F-Ge(CF$_3$)$_4$]        | -3526.4461                | -9258684.3 | 200.1                  | -9258484.3             | -10332216.9   | -10331580.0    | 321       |                      |
| [H-Ge(CF$_3$)$_4$]        | -3427.2232                | -8998174.6 | 210.1                  | -8997964.5             | -10071664.5   | -10071060.2    | 355       |                      |
| Spirogerman              | -4115.0066                | -10803949.7 | 698.3                  | -10803251.5            |                |                |           |                      |
| [F-Spirogerman]          | -4214.8887                | -11066190.2 | 703.3                  | -11065486.8            | -12139190.9   | -12138582.5    | 350       |                      |
| [H-Spirogerman]          | -4115.6873                | -10805736.9 | 714.9                  | -10805022.1            | -11878638.4   | -11878117.7    | 439       |                      |
| B(CF)$_5$                | -2206.7527                | -5793829.3 | 473.8                  | -5793355.5             |                |                |           |                      |
| [F-B(CF)$_5$]            | -2306.6655                | -6056179.2 | 479.8                  | -6055699.4             | -7129295.0    | -7128795.1     | 458       |                      |
| [H-B(CF)$_5$]            | -2207.4540                | -5795670.5 | 494.5                  | -5795176.0             | -6868742.5    | -6868271.6     | 470       |                      |
| Si(catCl)$_2$            | -4728.0889                | -12413597.3 | 322.4                  | -12413274.9            |                |                |           |                      |
| [H-Si(catCl)$_2$]        | -4728.8027                | -12415471.6 | 343.4                  | -12415282.8            | -13488661.9   | -13488223.8    | 438.1     | 522                  |
Table 2: Computed energies for the calculation of anion affinities at the PW6B95-D3/def2-TZVPP level of theory.

| Compound            | E [a.u.] PW6B95 D3/def2-TZVPP | In kJ | Electronic+ Thermal [kJ] | LA + MeSiY (A) | MeSiY⁺ + LA-Y⁻ (B) | (B) – (A) | FIA/HIA/CIA [kJ/mol] |
|---------------------|-------------------------------|-------|--------------------------|----------------|---------------------|-----------|----------------------|
| Ge(catCl₂)₂        | -6522.0611                    |       |                          |                |                     |           |                      |
| [F-Ge(catCl₂)₂]     | -6622.2374                    |       |                          |                |                     |           |                      |
| [H-Ge(catCl₂)₂]     | -6522.7918                    |       |                          |                |                     |           |                      |
| [Cl-Ge(catCl₂)₂]    | -6982.8191                    |       |                          |                |                     |           |                      |
| GeF₄                | -2478.1205                    |       |                          |                |                     |           |                      |
| GeF₅                | -2578.2457                    |       |                          |                |                     |           |                      |
| GeF₄⁺               | -2478.7969                    |       |                          |                |                     |           |                      |
| GeF(CF₃)₃          | -3192.4673                    |       |                          |                |                     |           |                      |
| [F-GeF(CF₃)₃]      | -3292.5942                    |       |                          |                |                     |           |                      |
| [H-GeF(CF₃)₃]      | -3193.1492                    |       |                          |                |                     |           |                      |
| Ge(CF₃)₄           | -3430.5878                    |       |                          |                |                     |           |                      |
| [F-Ge(CF₃)₄]       | -3530.7065                    |       |                          |                |                     |           |                      |
| [H-Ge(CF₃)₄]       | -3431.2596                    |       |                          |                |                     |           |                      |
| Spirogerman        | -4120.6115                    |       |                          |                |                     |           |                      |
| [F-Spirogerman]    | -4220.7233                    |       |                          |                |                     |           |                      |
| [H-Spirogerman]    | -4121.2942                    |       |                          |                |                     |           |                      |
| B(CF₃)₂            | -2211.7685                    |       |                          |                |                     |           |                      |
| [F-B(CF₃)₂]        | -2311.9255                    |       |                          |                |                     |           |                      |
| [H-B(CF₃)₂]        | -2212.4802                    |       |                          |                |                     |           |                      |
| Si(catCl₂)₂        | -4733.9182                    |       |                          |                |                     |           |                      |
| [H-Si(catCl₂)₂]    | -4734.6214                    |       |                          |                |                     |           |                      |
Table 3: Computed energies for the calculation of anion affinities at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory.

| Compound | E [a.u.] | DLPPNO-CCSD(T)/aug-cc-pVQZ In kJ | Electronic+ | LA + Me:SiY | Me:SiY + LA-Y | (B) – (A) | HIA/CIA/FIA [kJ/mol] |
|----------|----------|---------------------------------|-------------|-------------|---------------|-----------|----------------------|
| Ge(catCl)₂⁺ | -6510.9692 | -17094550.5 | -17094232.1 |             |               |           |                      |
| [F-Ge(catCl)₂]⁺ | -6610.9362 | -17357013.9 | -17356868.3 | -18429003.9 | -18428549.6 | 454.2     | 504.2                |
| [H-Ge(catCl)₂]⁻ | -6511.7018 | -17096473.1 | -18168403.3 | -18167998.7 |               | 404.6     | 555                  |
| GeF₄⁻ | -2474.9278 | -6497922.8 | -6497880.5 |             |               |           |                      |
| GeF₅⁻ | -2574.8394 | -6760240.9 | -7832652.3 | -7832053.9 |               | 598.5     | 360                  |
| GeF₄H⁻ | -2475.6037 | -6499697.6 | -7572051.8 | -7571499.7 |               | 552.1     | 407                  |
| GeF(CF₃)₃⁻ | -3187.5651 | -3287.4809 | -3831281.1 | -9703567.5 | -9702981.6 | 585.9     | 373                  |
| GeF(CF₃)₄⁻ | -3188.2515 | -3837054.3 | -9442966.9 | -9442444.3 |               | 522.7     | 437                  |
| Ge(CF₃)₄ | -3425.1160 | -8992642.0 | -8992444.7 |             |               |           |                      |
| Spirogerman | -4112.9739 | -4212.8696 | -11060185.9 | -12132049.2 |               | 637.3     | 321                  |
| [H-Spirogerman]⁻ | -4113.6682 | -10800435.8 | -11877088.0 | -11871584.3 |               | 501.6     | 458                  |
| B(C₆F₅)₃⁻ | -2206.0435 | -2305.9899 | -6053896.8 | -7126265.2 | -7125760.2 | 505.0     | 453                  |
| [H-B(C₆F₅)₃]⁻ | -2206.7612 | -5793351.5 | -6865864.8 | -6865220.4 |               | 444.2     | 515                  |
| Si(catCl)₂⁺ | -4724.4527 | -12404050 | -12403728.1 |             |               |           |                      |
| [H-Si(catCl)₂]⁻ | -4725.1611 | -12405910 | -13477899.3 | -13477430.4 |               | 468.9     | 491                  |
Table 4: Solvation corrected HIA and FIA values using DLPNO-CCSD(T)/aug-cc-pVQZ and COSMO-RS using dichloromethane as solvent.

| Compound                  | FIA/HIA (solvent corrected) [kJmol\(^{-1}\)] |
|---------------------------|---------------------------------------------|
| Ge(cat\(^{3+}\))\(_2\)       | 304/485                                     |
| GeF\(_4\)                   | 244/427                                     |
| GeF(CF\(_3\))\(_3\)         | 224/420                                     |
| Ge(CF\(_3\))\(_4\)          | 197/367                                     |
| Ge(C(CF\(_3\))\(_2\)OC\(_6\)H\(_4\))\(_2\) | 148/402                                     |
| B(CF\(_3\))\(_3\)           | 259/448                                     |
| Si(cat\(^{3+}\))\(_2\)       | 315/[1]/429                                 |

Gas Phase Acidity

The gas phase acidity of Ge(cat\(^{3+}\))\(_2\)-(H\(_2\)O)\(_2\) was determined as the difference in energy of Ge(cat\(^{3+}\))\(_2\)-(H\(_2\)O)\(_2\) and Ge(cat\(^{3+}\))\(_2\)-(H\(_2\)O)(OH)\(^-\). For better reference to previously obtained results, the energies were computed at the BP86/def2-TZVP level of theory. The resulting optimized structure of Ge(cat\(^{3+}\))\(_2\)-(H\(_2\)O)(OH)\(^-\) is shown below.

Figure S25: Optimized gas phase structures of the bis-water adduct and the corresponding base.

Rationalizing the water stability of Ge(cat\(^{3+}\))\(_2\)

To assess the substantial stability of the bis(perchlorocatecholato)germane against hydrolysis, the thermodynamics for the different steps of hydrolysis were computed and compared against its silicon counterpart.

As seen in figure S10, steps involving the ring-opening of the pentacycle enclosed by the central atom and the catecholate ligands are significantly more exothermic for silicon. Even the steps without ring-opening are thermodynamically more favorable for silicon, likely the result of the higher bond polarity of the Si-O bonds compared to the Ge-O bonds. For the complete hydrolysis to M(OH)\(_4\) and four catechols, about double the energy is released for the silicon catecholate with respect to the germanium catecholate.

A full comparison of relevant bond lengths is given in figure S26.

As reference for the ‘ideal’ angle of the undisturbed catechol moiety, both angles for the parent perchlorocatechol and perchloroveratrole were considered. Since the bonding angles C\(_1\)C\(_2\)O (fig. S28) in perchlorocatechol vary greatly depending on the local environment due to its ability to form hydrogen bonds, comparisons (see main text) were referenced to the respective angles in perchloroveratrole, as this was considered to best represent the undisturbed catechol backbone (fig. S26, structure optimized at the PBEh-3c level of theory\(^{[13]}\)).

Figure S26: Optimized structure of perchloroveratrole
Figure S27: Thermodynamics (reaction enthalpies) for the different steps of hydrolysis of bis(catecholato)tetrelanes $M$($\text{cat}^2$)$_2$ ($M=$ Si, Ge) calculated at the PW6B95/def2-TZVPP level of theory in kJ mol$^{-1}$. 

$$M = \text{Si, Ge}$$

Figure S28: Comparison of crystal structures of Si($\text{cat}^2$)$_2$-(OPE)$_3$ and Ge($\text{cat}^2$)$_2$-(OPE)$_3$ and relevant bond lengths.
5. X-Ray Diffraction

General

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, covered with perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperature with a Bruker AXS D8 Venture diffractometer (Mo-Kα radiation, microfocus X-ray tube, multilayer mirror optics, Photon II detector) or an Agilent Technologies Supernova-E CCD diffractometer (Cu-Kα radiation, microfocus X-ray tubes, multilayer mirror optics). Detector frames (typically ω-, occasionally ϕ-scans, scan width 0.4...1°) were integrated by profile fitting.[14-16] Data were corrected for air and detector absorption, Lorentz and polarization effects[15,16] and scaled essentially by application of appropriate spherical harmonic functions.[17-19] Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling procedure) and augmented by a spherical correction.[17-19] The structures were solved by ab initio dual space methods (SHELXD, compound [Et₄N]₂[Cl₂-Ge(cat⁵Cl)₂])[20] or by intrinsic phasing (all other structures)[21] and refined by full-matrix least squares methods based on F² against all unique reflections.[22] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.[23] The water molecules of 1-(H₂O)₆ were refined as rigid groups, with the positions of the respective hydrogen atoms initially taken from difference Fourier syntheses.

Several datasets were collected from different batches of crystals of [Et₄N]₂[Cl₂-Ge(cat⁵Cl)₂]. Although the structures could be refined successfully to rather low R values, strong residual electron density features were still present in delta-F Fourier maps, notably a strong peak with the same x and y coordinates as the Ge atom (“Ge ghost peak”). In addition, the Flack asymmetry parameter did not refine to zero. Inspection of the total diffracted intensity pattern revealed diffuse features, regularly arranged among the sharp reflections used to solve and refine the structure. This pattern is characteristic of OD (oder-disorder) structures, possibly combined with allotwinning.[24] No attempt was made to model these effects. Upon careful scrutiny of the available crystals under a polarisation microscope a tiny platelet was eventually selected of which data were collected at 250 K with copper radiation. In this dataset, diffuse diffraction features were hardly recognizable. Indeed, refinement against these data resulted in a model with residual electron density only little above background noise and a satisfactory asymmetry index. Although even with this crystal some OD effects cannot be ruled out completely, we believe that the molecular structure of [Et₄N]₂[Cl₂-Ge(cat⁵Cl)₂] reported here is little if at all affected.

Graphical handling of the structural data during refinement was performed with OLEX2.[25] CCDC 2015935 – 2015941 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/?

Figure S29: Molecular structure of 1·(H₂O)₆ as ortep plot.

Empirical formula \( \text{C}_{24} \text{H}_{26} \text{Cl}_8 \text{GeK}_8 \)  
Formula weight 904.74  
Temperature 100.0 K  
Wavelength Mo K\( \alpha \), 0.71073 Å  
Crystal system Monoclinic  
Space group \( P \ c \)  
Unit cell dimensions  
\( a = 9.7518(10) \) Å  
\( b = 15.8621(15) \) Å  
\( c = 10.8766(11) \) Å  
Volume 1626.3(3) Å³  
\( Z \) 2  
Density (calculated) 1.848 Mg/m³  
Absorption coefficient 1.790 mm⁻¹  
\( F(000) \) 908  
Theta range for data collection 2.2 to 30.5°  
Index ranges \(-13 \leq h \leq 13, -22 \leq k \leq 22, -15 \leq l \leq 15\)  
Reflections collected 61517  
Independent reflections 9917 \( [R(\text{int}) = 0.0462] \)  
Completeness to theta 25.242° 99.9 %  
Data / restraints / parameters 9917 / 2 / 419  
Goodness-of-fit on \( F^2 \) 1.077  
Final R indices \([F_o > 4\sigma(F_o)]\) \( R(F), wR(F^2) \) 0.0357, 0.0701  
R indices (all data) \( R(F), wR(F^2) \) 0.0533, 0.0779  
Difference density: max, min 1.060, -0.825 e.Å⁻³  
Deposition number CCDC 2015937
Empirical formula \( \text{C}_{24}\text{H}_{24}\text{Cl}_{8}\text{FGeKO}_{10} \)

Formula weight 886.72

Temperature 100.0 K

Wavelength Mo K\(\alpha\), 0.71073 \(\AA\)

Crystal system Monoclinic

Space group \( P\ c \)

Unit cell dimensions
\( a = 9.7184(7) \ \text{Å} \)
\( b = 15.9776(12) \ \text{Å} \)
\( c = 10.9063(8) \ \text{Å} \)

Volume \( 1623.7(2) \ \text{Å}^3 \)

\( Z \) 2

Density (calculated) 1.814 Mg/m\(^3\)

Absorption coefficient 1.789 mm\(^{-1}\)

\( F(000) \) 888

Theta range for data collection 2.2 to 30.1°

Index ranges 
-13\(\leq h \leq 13\), -22\(\leq k \leq 22\), -15\(\leq l \leq 14\)

Reflections collected 37081

Independent reflections 8998 \([R(\text{int}) = 0.0672]\)

Completeness to theta 25.242° 100.0 %

Max. and min. transmission 0.7460 and 0.4838

Data / restraints / parameters 8998 / 2 / 407

Goodness-of-fit on \( F^2 \) 1.033

Final \( R \) indices \([F_o > 4\sigma(F_o)]\) \( R(F) \), \( wR(F) \) 0.0453, 0.0975

\( R \) indices (all data) \( R(F) \), \( wR(F) \) 0.0734, 0.1118

Difference density: max, min 0.876, -0.951 e.Å\(^{-3}\)

deposition number CCDC 2015936

Figure S30: Molecular structure of \([\text{K@18-crown-6}]\text{[F-Ge(cat^2)Cl_2]}\) as ortep plot.

Figure S31: Molecular structure of \([\text{K@18-crown-6}]\text{[F-Ge(cat^2)Cl_2-OH_2]}\) as ortep plot.
| Property                              | Value                                      |
|--------------------------------------|--------------------------------------------|
| Empirical formula                    | C_{24}H_{26}Cl_{8}FGeK_{11}               |
| Formula weight                       | 904.74                                     |
| Temperature                          | 100.0 K                                    |
| Wavelength                           | Mo Kα, 0.71073 Å                           |
| Crystal system                       | Monoclinic                                 |
| Space group                          | P c                                        |
| Unit cell dimensions                 | a = 9.7518(10) Å, b = 15.8621(15) Å, c = 10.8766(11) Å, β = 104.845(4)° |
| Volume                               | 1626.3(3) Å³                              |
| Z                                    | 2                                          |
| Density (calculated)                 | 1.848 Mg/m³                                |
| Absorption coefficient               | 1.790 mm⁻¹                                 |
| F(000)                               | 908                                        |
| Theta range for data collection      | 2.2 to 30.5°                               |
| Index ranges                         | -13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -15 ≤ l ≤ 15  |
| Reflections collected                | 61517                                      |
| Independent reflections              | 9917 [R(int) = 0.0462]                     |
| Completeness to theta 25.242°        | 99.9%                                      |
| Data / restraints / parameters       | 9917 / 2 / 419                             |
| Goodness-of-fit on F²                | 1.077                                      |
| Final R indices [Fo > 4σ(Fo)]        | R(F), wR(F²) 0.0357, 0.0701               |
| R indices (all data)                 | R(F), wR(F²) 0.0533, 0.0779               |
| Difference density: max, min         | 1.060, -0.825 e.Å⁻³                       |
| deposition number CCDC              | 2015937                                    |
Empirical formula \( \text{C}_{28}\text{H}_{40}\text{Cl}_{10}\text{GeN}_{2}\text{O}_{4} \)

Formula weight 895.71

Temperature 250 K

Wavelength Cu \( \text{K} \alpha \), 1.54184 Å

Crystal system orthorhombic

Space group \( P \text{ca}2_1 \)

Unit cell dimensions
\( a = 14.79859(8) \) Å
\( b = 10.67273(9) \) Å
\( c = 23.43687(11) \) Å

Volume \( 3701.65(4) \) Å\(^3\)

Z 4

Density (calculated) 1.607 Mg·m\(^{-3}\)

Absorption coefficient 8.072 mm\(^{-1}\)

\( F_{000} \) 1824

\( \theta \) range for data collection 3.8 to 71.0 °

Reflections collected 131980

Independent reflections [\( R_{int} \)] 7030 [0.0508]

Observed reflections [\( I > 2\sigma(I) \)] 6448

Index ranges -18<=h<=18, -12<=k<=12, -28<=l<=28

Completeness to \( \theta = 67.684 \) ° 100.0 %

Transmission factors: max, min 1.000, 0.810

Data / restraints / parameters 7030 / 1 / 414

Goodness-of-fit on \( F^2 \) 1.069

Final \( R \) indices [\( F_o > 4\sigma(F_o) \)] \( R(F) \), \( wR(F) \) 0.0382, 0.0931

Final \( R \) indices (all data) \( R(F) \), \( wR(F) \) 0.0429, 0.0958

Absolute structure parameter 0.006(12)

Difference density: max, min 1.571, -0.402 e·Å\(^{-3}\)

deposition number CCDC 2015938

*Figure S32: Molecular structure of [Et\(_4\)N\(_2\)][Cl\(_2\)-Ge(cat\(_2\))\(_2\)] as ortep plot.*
Empirical formula  \( \text{C}_{20}\text{H}_{24}\text{Cl}_{8}\text{GeO}_{8}\text{S}_{4} \)
Formula weight 876.82
Temperature 120.0 K
Wavelength Mo \( K\alpha \), 0.71073
Crystal system monoclinic
Spacegroup \( P2_1/n \)
Unit cell dimensions
\[
\begin{align*}
a &= 7.5023(6) \text{ Å} \\
b &= 20.5447(17) \text{ Å} \\
c &= 10.6732(9) \text{ Å} \\
\beta &= 106.287(3) ^\circ
\end{align*}
\]
Volume 1579.1(2) \( \text{Å}^3 \)
\( Z \) 2
Density (calculated) 1.844 Mg \cdot m\(^{-3}\)
Absorption coefficient 1.955 mm\(^{-1}\)
\( F_{000} \) 880.0
\( \theta \) range for data collection 4.4 to 57.4 \(^\circ\)
Reflections collected 78673
Independent reflections \([R_{int}]\) 4076 [0.0465]
Index ranges \(-10\leq h\leq 10, -27\leq k\leq 27, -14\leq l\leq 14\)
Data/restraints/parameters 4076/0/191
Goodness-of-fit on \( F^2 \) 1.077
Final \( R \) indices \([F_o > 4\sigma(F_o)]\) \( R(F), wR(F^2) 0.0184, 0.0459 \)
Final \( R \) indices (all data) \( R(F), wR(F^2) 0.0197, 0.0470 \)
Difference density: max, min 0.49, -0.34 e \( \text{Å}^3 \)

deposition number CCDC 2015939

Figure S33: Molecular structure of Ge\(\text{cat}^{2+}\)-(dmsd-d\(6\))\(_2\) as ortep plot.
Table S3: Crystallographic data and structure refinement.

| Property                                         | Value                      |
|--------------------------------------------------|----------------------------|
| Empirical formula                                | C_{24}H_{30}Cl_{8}GeO_{6}P_{2} |
| Formula weight                                   | 832.68                     |
| Temperature /K                                    | 100.0                      |
| Wavelength                                       | MoKα, 0.71073              |
| Crystal system                                    | triclinic                  |
| Spacegroup                                       | P-1                        |
| Unit cell dimensions                              |                            |
| a = 7.6264(3) Å                                  | α = 91.462(2) °            |
| b = 10.5345(4) Å                                 | β = 94.674(2) °            |
| c = 20.0303(9) Å                                 | γ = 100.513(2) °           |
| Volume                                           | 1575.63(11) Å³             |
| Z                                                | 2                          |
| Density (calculated)                             | 1.692 Mg·m⁻³               |
| Absorption coefficient                           | 1.789 mm⁻¹                 |
| F₀₀₀                                             | 781.0                      |
| θ range for data collection                      | 4.4 to 65.4 °              |
| Reflections collected                            | 69585                      |
| Independent reflections [Rint]                   | 11520 [0.0397]             |
| Index ranges [hkl]                               | -11>=h>=11, -15>=k>=15, -30>=l>=30 |
| Data/restraints/parameters                       | 11520/0.376                |
| Goodness-of-fit on F²                             | 1.05                       |
| Final R indices [F₀ > 4σ(F₀)]                    | R(F), wR(F²) 0.0236, 0.0612 |
| Final R indices (all data)                       | R(F), wR(F²) 0.0316, 0.0627 |
| Difference density: max, min                     | 0.54, -0.34 e·Å⁻³          |

Figure S34: Molecular structure of Ge(catCl)₂-(OPEt)₂ as ortep plot.

Figure S35: Molecular structure of Ge(catCl)₂-(P(O)OBu)₂ as ortep plot.

Empirical formula  
C_{30}H_{30}Cl_{8}GeO_{12}P_{2}
| Property                        | Value                  |
|--------------------------------|------------------------|
| Formula weight                 | 1096.92                |
| Temperature                    | 120.0 K                |
| Wavelength                     | MoKα 0.71073           |
| Crystal system                 | monoclinic             |
| Spacegroup                     | P2₁/n                  |
| Unit cell dimensions           |                        |
| a                              | 8.5302(5) Å            |
| b                              | 16.9619(10) Å          |
| c                              | 16.5336(9) Å           |
| β                              | 91.236 °               |
| Volume                         | 2391.7(2) Å³           |
| Z                              | 2                      |
| Density (calculated)           | 1.523 Mg·m⁻³           |
| Absorption coefficient         | 1.209 mm⁻¹             |
| F₀₀₀                           | 1128.0                 |
| θ range for data collection    | 4.8 to 61.0 °          |
| Reflections collected          | 40225                  |
| Independent reflections [R(int)] | 7104 [0.0360]         |
| Index ranges                   | h: -12 >= h >= 12, -22 >= k >= 24, -23 >= l >= 22 |
| Data/restraints/parameters     | 7104/0/271             |
| Goodness-of-fit on F²          | 1.056                  |
| Final R indices [F > 4σ(F)]    | R(F) 0.0286, wR(F) 0.0626 |
| Final R indices (all data)     | R(F), wR(F) 0.0367, 0.0660 |
| Difference density: max, min   | 0.60, -0.45 e Å⁻³      |
| deposition number CCDC         | 2015941                |
6. NMR Spectra

Figure S37: $^{13}$C NMR (D$_2$O) of 1-(H$_2$O)$_4$. 

Figure S36: $^1$
Figure S38: $^1$H NMR (CD$_2$Cl$_2$) of 1-(P(O)OBu)$_2$.

Figure S39: $^{13}$C NMR (CD$_2$Cl$_2$) of 1-(P(O)OBu)$_2$. 
Figure S40: $^{31}$P NMR (CD$_2$Cl$_2$) of 1-($\text{P(O)OBu}_3$)$_2$.

Figure S41: $^{13}$C NMR (DMSO-d$_6$) of 1-(DMSO-d$_6$)$_2$.
Figure S42: $^1$H NMR (DMSO-d$_6$) of [Et$_4$N]$_2$[Cl$_2$-Ge(cat$^\text{III}$)$_2$].

Figure S43: $^{13}$C NMR (DMSO-d$_6$) of [Et$_4$N]$_2$[Cl$_2$-Ge(cat$^\text{III}$)$_2$].
Figure S44: $^1$H NMR (acetone-d$_6$) of 1-(acetone)$_2$.

Figure S45: $^{13}$C NMR (acetone-d$_6$) of 1-(acetone)$_2$. 
Figure S46: $^1$H NMR (CD$_2$Cl$_2$) of [K@18-crown-6][F-Ge(cat$^2$)]$_2$. Contains residual acetonitrile.

Figure S47: $^{19}$F NMR (CD$_2$Cl$_2$) of [K@18-crown-6][F-Ge(cat$^2$)]$_2$. 
Figure S48: $^1$C NMR (CD$_2$Cl$_2$) of [K@18-crown-6][F-Ge(cat)$^2$]. Contains residual acetonitrile.

Figure S49: $^1$H NMR (CD$_2$Cl$_2$) of [Ph$_4$P][Cl-Ge(cat)$^2$]. Contains residual pentane.
Figure S51: $^{31}$P NMR (CD$_2$Cl$_2$) of [Ph$_4$P][Cl-Ge(catCl)$_2$].

Figure S50: $^{13}$C NMR (CD$_2$Cl$_2$) of [Ph$_4$P][Cl-Ge(catCl)$_2$]. Contains residual pentane.
7. IR spectra

**Figure S52**: IR (ATR) spectrum of 1-(H$_2$O)$_n$.

**Figure S53**: IR (ATR) spectrum of 1-(P(O)OBu)$_3$. 
Figure S55: IR (ATR) spectrum of \([\text{Et}_4\text{N}]\)\([\text{Cl}_2\text{Ge(catCl)}_2]\)

Figure S52: IR (ATR) spectrum of donor-free 1. It shows the absence of acetone.
Figure S53: IR (ATR) spectrum of 1-(CH$_3$CN)$_2$.

Figure S54: IR (ATR) spectrum of 1-(acetone)$_2$. 
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