Activation of CS₂ and CO₂ by Silylium Cations
Carsten Jenne,* Marc C. Nierstenhöfer, and Valentin van Lessen[a]
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S1 Numbering scheme for the [Me₃NB₁₂Cl₁₁]⁻ anion

![Numbering scheme for the [Me₃NB₁₂Cl₁₁]⁻ anion]

Figure S1. Numbering scheme for the [Me₃NB₁₂Cl₁₁]⁻ anion according to IUPAC.

S2 Synthetic details and spectroscopic data

General remarks. IR spectra were measured in the glovebox on a Bruker ALPHA P FT-IR spectrometer equipped with a diamond ATR attachment. NMR spectra were measured on Bruker Avance 400 and Bruker Avance III 600 spectrometers in 5 mm NMR tubes equipped with J. Young Teflon-in-glass valves at 243 K, 253 K, or 300 K. The NMR spectra were referenced on the partly deuterated NMR solvents and chemical shifts are given with respect to Me₄Si (¹H, ¹³C, ²⁹Si) and BF₃·OEt₂ (¹¹B). Two dimensional NMR experiments (HSQC (Heteronuclear Single Quantum Coherence), HMBC (Heteronuclear Multiple Bond Correlation)) were performed to help with the assignment of the resonances.

The single crystal X-ray structure analyses were measured on an Oxford Diffraction Gemini E Ultra diffractometer with an EOS CCD area detector, a four-circle Kappa goniometer and a molybdenum tube (Kα 0.71073 Å). Data reduction, empirical absorption correction and scaling were performed with CrysAlis Pro.¹ The air and moisture sensitive crystals were taken directly from the reaction vessel under a stream of dry nitrogen, transferred into non-fluorinated paraffin oil (Alfa Aesar), selected under a microscope and immediately cooled to 150 Kelvin on the diffractometer. The structures were solved with direct methods using SHELXS and refined with SHELXL using the least squares method against F².² These programs were embedded in the
platform Olex2. All non-hydrogen atoms were refined anisotropically. Graphical representations of the crystal structures were made with Diamond 3.2f.

The density functional theory (DFT) calculations were performed with the program package Gaussian 16. The functional PBE0 and the basic set def2-TZVP used for the quantum chemical calculations were included with the program. The SMD solvation model was used to account for solvation effects. The parameters to describe the solvent o-dichlorobenzene were implemented with Gaussian 16. Note that only reaction energies are discussed and thus errors in absolute energies are averaged out by this procedure. NBO analyses were carried out using NBO 3.1 implemented in the same program package.

Air and moisture sensitive solids were manipulated using standard vacuum and Schlenk techniques or in a glove box with an atmosphere of dry nitrogen (O₂ < 1 ppm; H₂O < 1 ppm). The solid starting materials were weighed and filled into the reactions tubes inside a glove box. All Reactions were performed in H-shaped glass vessels with J. Young Teflon-in-glass valves and an incorporated fine frit. 1,2-Difluorobenzene (Fluorochem), n-pentane (VWR Chemicals, HPLC grade), dichloromethane deut. (Roth), benzene deut. (Sigma-Aldrich), diethylsilane (Sigma-Aldrich), triisobuthylsilane (Sigma-Aldrich), triisopropylsilane (Sigma-Aldrich), ethylidimethylsilane (Sigma-Aldrich), and triethylsilane (Sigma-Aldrich) were dried using CaH₂ (Merck, 90-95 %), condensed onto molecular sieve (4 Å, Roth), and stored under an atmosphere of dry nitrogen. Carbon dioxide (4.5, Messer) was used without further purification. Carbon disulfide (Merck) was dried with molecular sieve (4 Å, Roth) and stored under nitrogen. The starting materials [Ph₃C][Me₃NB₁₂Cl₁₁], [(Et₃Si)₂H][Me₃NB₁₂Cl₁₁], and [(tBu₃Si)₂H][Me₃NB₁₂Cl₁₁] were synthesized by literature procedures. All glass ware was dried at 120 °C over night and reaction vessels were evacuated for 15 minutes before use.

| Isolated cation            | Molecular formula | Molecular weight [g mol⁻¹] |
|----------------------------|-------------------|----------------------------|
| [Et₃SiS(H)Me]⁺             | C₃H₁₉SSi⁺         | 163.38                     |
| [‘Pr₃Si(H)Me]⁺             | C₁₀H₂₅SSi⁺        | 205.46                     |
| [(Me₃Si)₂SMe]⁺             | C₃H₂₀SSi₂⁺        | 193.48                     |
| [(Et₃Si)₂SMe]⁺             | C₁₃H₃₃SSi₂⁺       | 277.64                     |
| [(Bu₃Si)₂SMe]⁺             | C₂₅H₅₇SSi₂⁺       | 445.96                     |
| [(Et₃Si)₃Si]⁺              | C₁₈H₄₄Si₃⁺        | 377.87                     |
| [Et₃SiOC(H)OSiEt₃]⁺         | C₁₃H₂₂O₂Si₂⁺      | 276.56                     |
S2.1 Synthesis of [(Et₃Si)₃S][Me₃NB₁₂Cl₁₁]

\[
2 [(Et₃Si)_2H][Me₃NB₁₂Cl₁₁] + CS₂ + 2 Et₃SiH \xrightarrow{C₆F₂H₄} 2 [(Et₃Si)₃S][Me₃NB₁₂Cl₁₁] + CH₄
\]

[(Et₃Si)₂H][Me₃NB₁₂Cl₁₁] (190 mg, 0.23 mmol, 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS₂ (0.14 mL, 2.30 mmol, 10 eq.) was condensed onto the reaction mixture, which was warmed up to 273 K. Finally, triethylsilane (1.15 mL, 0.52 mmol, 4 eq.) was added dropwise to the reaction mixture under a stream of dry nitrogen. Subsequently, the reaction mixture was stirred for one hour at 273 K and for additional three hours at room temperature. Diffusion of n-pentane into the reaction mixture yielded colorless crystals. The solvent was removed by filtration. Only clean crystals without any attached deposit were picked by hand to give pure [(Et₃Si)₃S][Me₃NB₁₂Cl₁₁] (22 mg, 0.02 mmol, 9%).

\(^1\text{H-NMR}\) (600.14 MHz, CD₂Cl₂, 300 K): \(\delta = 0.82\) (q, \(^3J_{HH} = 7.8\) Hz, 18H, Si-CH₂CH₃), 1.03 (t, \(^3J_{HH} = 7.8\) Hz, 27H, Si-CH₂CH₃), 3.39 (s, 9H, N(CH₃)₃); \(^1^3\text{C-NMR}\) (150.92 MHz, CD₂Cl₂, 300 K): \(\delta = 6.6\) (Si-CH₂CH₃), 7.5 (Si-CH₂CH₃), 57.6 (N(CH₃)₃); \(^2^9\text{Si-NMR}\) (119.24 MHz, CD₂Cl₂, 300 K): \(\delta = 36.9\); \(^1^1\text{B-NMR}\) (192.54 MHz, CD₂Cl₂, 300 K): \(\delta = -15.5\) (s, 1B, B12) - 13.8 (s, 5B, B7-11), -10.9 (s, 5B, B2-6), -9.6 (s, 1B, B1); FT-IR (ATR): \(\tilde{\nu} = 2958\) (w), 2922 (s), 2876 (w), 2853 (w), 1488 (w), 1465 (s), 1412 (vw), 1379 (vw), 1234 (vw), 1124 (vw), 1020 (vs), 951 (s), 820 (w), 750 (s), 683 (w), 675 (w), 611 (w), 578 (s), 544 (vs), 489 (s), 435 (w), 425 (w) cm⁻¹.
Figure S2: \(^1\)H-NMR (600.14 MHz, CD\(_2\)Cl\(_2\), 300 K) spectrum of \([((Et_3Si)_3S][Me_3NB_{12}Cl_{11}])\].

Figure S3: \(^1\)H, \(^{13}\)C-NMR HSQC spectrum (600.13 MHz, 150.91 MHz, CD\(_2\)Cl\(_2\), 300 K) of \([(Et_3Si)_3S][Me_3NB_{12}Cl_{11}])\). ? = unknown impurity.
Figure S4: $^{13}$C-NMR DEPT spectrum (150.92 MHz, CD$_2$Cl$_2$, 300 K) of [(Et$_3$Si)$_3$S][Me$_3$NB$_{12}$Cl$_{11}$]. ? = unknown impurity.

Figure S5: $^{11}$B-NMR spectrum (192.54 MHz, CD$_2$Cl$_2$, 300 K) of [(Et$_3$Si)$_3$S][Me$_3$NB$_{12}$Cl$_{11}$].
**Figure S6:** $^1$H, $^{29}$Si-NMR HMBC spectrum (600.14 MHz, 119.24 MHz, CD$_2$Cl$_2$, 300 K) of [([Et$_3$Si]$_3$S][Me$_3$NB$_{12}$Cl$_{11}$]. $?$ = unknown impurity.

**Figure S7:** FT-IR spectra (diamond ATR, 300 K) of [([Et$_3$Si]$_3$S][Me$_3$NB$_{12}$Cl$_{11}$] (a) and Na[Me$_3$NB$_{12}$Cl$_{11}$] (b).
Table S2: Experimental (FT-IR) and calculated (PBE0/def2-TZVPP) vibrational frequencies of [(Et₃Si)₃S][Me₃NB₁₂Cl₁₁].

| Exp. [cm⁻¹] | Calc. [cm⁻¹] | Vibration | Assignment |
|-------------|---------------|-----------|------------|
| 2958 (w)    | 3132 (s)      | ν         | CH₂, CH₃   |
| 2922 (w)    | 3056 (s)      | ν         | CH₂, CH₃   |
| 2876 (w)    | -             | ν         | CH₂, CH₃   |
| 2853 (w)    | -             | ν         | CH₂, CH₃   |
| 1488 (w)    | 1498 (w)      | δ         | CH₂, CH₃   |
| 1465 (s)    | 1443 (w)      | δ         | CH₂, CH₃   |
| 1412 (vw)   | -             | δ         | CH₂, CH₃   |
| 1379 (vw)   | -             | δ         | CH₂, CH₃   |
| 1234 (vw)   | 1264 (vw)     | δ         | CH₂, CH₃   |
| 1124 (vw)   | 1033 (s)      | δ         | CH₂, CH₃   |
| 1020 (vs)   | -             | ν         | B-Cl       |
| 951 (s)     | -             | ν         | B-Cl       |
| 820 (w)     | -             | -         |            |
| 750 (s)     | 752 (vs)      | ν         | Si-C       |
| 683 (w)     | -             | δ         | CH₂, CH₃   |
| 675 (w)     | 671 (w)       | δ         | CH₂, CH₃   |
| 611 (w)     | -             | -         |            |
| 578 (s)     | 585 (vw)      | δ         | BB-Cl      |
| 544 (s)     | -             | -         |            |
| 489 (w)     | -             | -         |            |
| 435 (w)     | 440 (vs)      | ν         | Si-S       |
| 425 (w)     | -             | ν         | Si-S       |

ν = stretching, δ = deformation

S2.2. Generation of [(Et₃Si)₂CH][Me₃NB₁₂Cl₁₁] and (Et₃Si)₂S at 253 K

[(Et₃Si)₂H][Me₃NB₁₂Cl₁₁] (150 mg, 0.19 mmol, 1 eq.) was dissolved in 1,2-Difluorobenzene (5 ml) in an H-shaped reaction vessel. CS₂ (0.06 mL, 0.09 mmol, 0.5 eq.) was condensed onto the reaction mixture at 77 K, which was warmed up to 253 K and was stirred for one hour. Finally, all volatile compounds were removed in vacuo. The residue was washed twice with n-pentane (3.5 mL). The colorless residue was transferred into an NMR tube and 1,2-difluorobenzene and C₆D₆ (9:1 ratio) were condensed in at 77 K. The NMR sample was allowed to melt only shortly before the measurement and placed in the pre-cooled (253 K) NMR device.

¹H-NMR (600.14 MHz, C₆H₄F₂/C₆D₆, 253 K): δ = 0.50 ([(CH₃CH₂)₃Si]₂S, 0.93 [(CH₃CH₂)₂SiS₂CH]⁺, 0.94 ([(CH₃CH₂)₃Si]₂S, 1.04 [(CH₃CH₂)₃SiS(CH)⁺, 3.36 [(H₂C)₃NB₁₂Cl₁₁]⁺); 11.58 [([(CH₃CH₂)₃SiS]₂CH]⁺); ¹³C-NMR (C₆H₄F₂/C₆D₆, 253 K): δ = 56.7 ([(CH₃)₃NB₁₂Cl₁₁]⁺); ²⁹Si-NMR (C₆H₄F₂/C₆D₆, 253 K): δ = 7.9 ([(CH₃CH₂)₃Si]₂S, 39.0,
49.8, 53.5 $[(\text{CH}_3\text{CH}_2)_2\text{SiS})_2\text{CH}]^+$, 58.2, 77.1; $^{11}$B-NMR ($\text{C}_6\text{H}_4\text{F}_2/\text{C}_6\text{D}_6$, 253 K): $\delta = -15.1$ (s, 1B, B12) -8.9 (s, 1B, B1), -10.2 (s, 5B, B2-6), -13.3 (s, 5B, B7-11), -15.1 (s, 1B, B12).

**Figure S8:** $^1$H-NMR (600.14 MHz, $\text{C}_6\text{H}_4\text{F}_2/\text{C}_6\text{D}_6$, 253 K) spectrum of $[(\text{Et}_3\text{SiSC(H)SiEt}_3)][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ and $(\text{Et}_3\text{Si})_2\text{S}$. 
Figure S9: $^1$H, $^{29}$Si-NMR HMBC spectra (600.13 MHz, 119.25 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 253 K) spectrum of [(Et$_3$SiSC(H)SiEt$_3$)][Me$_3$NB$_{12}$Cl$_{11}$] and (Et$_3$Si)$_2$S.

Figure S10: $^{11}$B-NMR (192.54 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 290 K) spectrum of [(Et$_3$SiSC(H)SiEt$_3$)][Me$_3$NB$_{12}$Cl$_{11}$] and (Et$_3$Si)$_2$S.
Table S3: Comparison of the measured NMR resonances with literature data.

| Solvent | Et$_3$S$_6$ | (Et$_3$S)$_2$S | (Me$_3$Si)$_2$S | [(Et$_3$Si)$_2$CH] | [(Et$_3$Si)$_2$OSi] | [(Et$_3$Si)$_2$S] |
|---------|-------------|---------------|----------------|-------------------|--------------------|----------------|
| C$_6$D$_6$ | C$_6$F$_2$H/C$_6$D$_6$ | CD$_2$Cl$_2$ | C$_6$F$_2$H/C$_6$D$_6$ | C$_6$D$_6$ | CD$_2$Cl$_2$ | CD$_2$Cl$_2$ |
| CH$_2$ | 0.55 | 0.94 | - | 1.04 | 0.44 | 1.03 |
| CH$_3$ | 0.98 | 0.50 | 0.33 | 0.93 | 0.66 | 0.82 |
| CH | - | - | - | 11.58 | 7.03 | - |
| SiH | 3.88 | - | - | - | - | - |
| CH$_2$ | NA | NA | - | - | 3.5 | 6.8 |
| CH$_3$ | NA | 4.1 | - | 4.8 | 7.7 | NA |
| CH | - | - | - | 172.6 | - | - |

$^1$H: [A] = [Me$_3$NB$_2$(Cl)$_{11}$]; [B] = [B(C$_6$F$_5$)$_4$]; [C] = [HCB$_2$(Cl)$_{11}$].

S2.3 Generation of [(Et$_3$Si)$_2$CH][Me$_3$NB$_2$(Cl)$_{11}$], [(Et$_3$Si)$_2$SMe][Me$_3$NB$_2$(Cl)$_{11}$], (Et$_3$Si)$_2$S at 243K

[(Et$_3$Si)$_2$H][Me$_3$NB$_2$(Cl)$_{11}$] (205 mg, 0.25 mmol 1 eq.) was dissolved in 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS$_2$ (0.15 mL, 2.5 mmol 10 eq.) was condensed onto the reaction mixture at 77 K, which then was warmed up to 243 K and stirred for two hours. Finally, all volatile compounds were removed in vacuo. The colorless residue was transferred into an NMR tube and 1,2-difluorobenzene and C$_6$D$_6$ (ratio 9:1) were condensed onto the product at 77 K. The NMR sample was allowed to melt only shortly before the measurement and directly placed in a pre-cooled (243 K) NMR device.

$^1$H-NMR (600.14 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K): $\delta = 0.76 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{CH}]^+$, 0.86 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{CH}]^+$, 0.91 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{SMe}]^+, 1.04 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{CH}]^+$, 2.33 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{SMe}]^+, 3.29 [(\text{H}_3\text{C})_3\text{NB}_2\text{Cl}_{12}]^+; $^{13}$C-NMR (C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K): 11.2 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{SCH}_3]^+ $\delta = 56.5 [(\text{H}_3\text{C})_3\text{NB}_2\text{Cl}_{12}]^+$; $^{29}$Si-NMR (C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K): $\delta = -1.6$, 7.9 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{S}], 13.7, 17.8, 33.3, 46.3 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{SCH}_3]^+$, 53.6 [(\text{CH}_3\text{CH}_2\text{SiS})_2\text{CH}]^+, 68.3, 108.7; $^{11}$B-NMR (C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K): $\delta = -9.1$ (s, 1B, B1), -10.5 (s, 5B, B2-6), -13.6 (s, 5B, B7-11), -15.5 (s, 1B, B12).
**Figure S11**: $^1$H-NMR (600.13 MHz, $C_6H_4F_2/C_6D_6$, 243 K) spectrum of the product containing $[(Et_3SiSC(H)SiEt_3)][Me_3NB_{12}Cl_{11}]$, $[(Et_3Si)_2SMe][Me_3NB_{12}Cl_{11}]$, and $(Et_3Si)_2S$.

**Figure S12**: $^1$H, $^{29}$Si-NMR HMBC spectrum (600.13 MHz, 119.25 MHz, $C_6H_4F_2/C_6D_6$, 243 K) of the product containing $[(Et_3SiSC(H)SiEt_3)][Me_3NB_{12}Cl_{11}]$, $[MeS(SiEt_3)_2][Me_3NB_{12}Cl_{11}]$, and $[(Et_3Si)_2S]$. 
Figure S13: $^1$H, $^{13}$C-NMR HMBC (600.13 MHz, 150.92 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K) spectrum of the product containing [(Et$_3$SiSC(H)SiEt)$_3$][Me$_3$NB$_{12}$Cl$_{11}$], [(Et$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$], and (Et$_3$Si)$_2$S.
**Figure S14**: $^{13}$C-NMR spectrum (150.92.24 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 243 K) of the product containing [(Et$_3$SiSC(H)SiEt$_3$)[Me$_3$NB$_{12}$Cl$_{11}$], [(Et$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$], and (Et$_3$Si)$_2$S.

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**Figure S15**: $^{13}$B-NMR (192.54 MHz, C$_6$H$_4$F$_2$/C$_6$D$_6$, 290 K) spectrum of the product containing [(Et$_3$SiSC(H)SiEt$_3$)[Me$_3$NB$_{12}$Cl$_{11}$], and (Et$_3$Si)$_2$S.
Table S4: Comparison of the measured NMR resonances with literature data.\textsuperscript{[11]}

|        | \([(\text{Et}_3\text{SiS(H)SiEt}_3)](\text{A})\) | \([(\text{Me}_3\text{Si})_2\text{SMc}])(\text{B})\textsuperscript{[11]} | \([(\text{Et}_3\text{Si})_2\text{SMc}])(\text{A})\) |
|--------|---------------------------------|---------------------------------|---------------------------------|
|        | \(\text{C}_6\text{F}_{12}/\text{C}_6\text{D}_6\) | \(\text{CD}_2\text{Cl}_2\) | \(\text{C}_6\text{F}_{12}/\text{C}_6\text{D}_6\) |
| \(^1\text{H}\) | CH\(_2\) 0.86 | - | 0.91 |
|        | CH\(_3\) 0.76 | 0.68 | 0.91 |
|        | CH 11.49 | - | - |
|        | SCH\(_3\) - | 2.37 | 2.33 |
| \(^{13}\text{C}\) | CH\(_2\) - | - | - |
|        | CH\(_3\) - | -0.2 | - |
|        | SCH\(_3\) - | 10.8 | 11.2 |
| \(^{29}\text{Si}\) | 53.6 | 40.8 | 46.3 |

\(\text{A} = [\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]\); \(\text{B} = [\text{B(C}_6\text{F}_5)_4]\)\textsuperscript{[11]}

S2.4 Synthesis of \([\text{Et}_3\text{SiS(H)Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]\)

\([(\text{Et}_3\text{Si})_2\text{H}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]\) (77 mg, 0.1 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS\(_2\) (0.01 mL, 0.1 mmol 1 eq.) was condensed onto the reaction mixture at 77 K, which subsequently was warmed up to room temperature. Triethylsilane (0.03 mL, 0.19 mmol, 19 eq.) was added and the reaction mixture was stirred for three days at room temperature. Diffusion of \(n\)-pentane into the reaction mixture yielded colorless crystals of \([\text{Et}_3\text{SiS(H)Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]\) suitable for X-ray diffraction analysis, which were selected by hand from the crude product.

\(^{29}\text{Si-NMR}\) (119.25 MHz, CD\(_2\)Cl\(_2\), 300 K) of the crude product: \(\delta = 2.3, 36.8, 38.5, 172.4\).

Figure S16: \(^1\text{H}, ^{29}\text{Si-NMR HMBC spectrum}\) (600.13 MHz, 119.25 MHz, CD\(_2\)Cl\(_2\), 293 K) of \([\text{Et}_3\text{SiS(H)Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]\).
S2.5 Generation of $[\text{Pr}_3\text{Si}(\text{H})\text{Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$, $[\text{Pr}_3\text{SiSC(\text{H})SSiPr}_3][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ and $[\text{Pr}_3\text{Si(\text{C}_6\text{D}_6)}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$.

$[\text{Pr}_3\text{Si}_2\text{H}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]$ (150 mg, 0.17 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS$_2$ (0.01 mL, 0.13 mmol 0.7 eq.) was added by condensation at 77 K and the reaction mixture was warmed up to room temperature. Tri tert butylsilane (0.03 mL, 0.17 mmol, 1 eq.) was added and the reaction mixture was stirred for three days at room temperature. Diffusion of n-pentane into the reaction mixture yielded colorless crystals of $[\text{Pr}_3\text{Si}(\text{H})\text{Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}]-\frac{1}{2} \text{C}_6\text{F}_2\text{H}_4$ suitable for X-ray diffraction analysis, which were selected by hand from the crude product.

$^1\text{H}-\text{NMR}$ (600.14, C$_6$D$_6$, 300 K): $\delta = 0.80 \ [(\text{CH}_3)_2\text{CH}]_2\text{Si}(\text{C}_6\text{D}_6)^+$, 0.85 $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}]_2\text{CH}]^+$, 1.07 $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}]_2\text{CH}]^+$, 1.65 $ [(\text{CH}_3)]_2\text{CH}]_2\text{Si}(\text{C}_6\text{D}_6)^+$, 2.62$[(\text{CH}_3)_3\text{NB}_{12}\text{Cl}_{11}]^+$; 11.96 $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}]_2\text{CH}]^+$; $^{13}\text{C}-\text{NMR}$ (150.92 MHz, C$_6$D$_6$, 300 K): $\delta = 17.5$ $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}(\text{C}_6\text{D}_6)^+$, 17.5 $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}(\text{C}_6\text{D}_6)^+$, 56.2 $ [(\text{CH}_3)_3\text{NB}_{12}\text{Cl}_{11}]^+$; $^{29}\text{Si}-\text{NMR}$ (119.24 MHz, C$_6$D$_6$, 300 K): $\delta = 4.9, 5.0, 13.4, 15.0, 35.0, 44.3, 46.2 [(\text{CH}_3)_2\text{CH}]_2\text{Si}]_2\text{CH}]^+$, 53.7, 56.7, 62.2, 119.1 $ [(\text{CH}_3)_2\text{CH}]_2\text{Si}(\text{C}_6\text{D}_6)^+$, 152.6; $^{11}\text{B}-\text{NMR}$ (192.54 MHz, C$_6$D$_6$, 300 K): $\delta = -9.7$ (s, 1B, B1), -10.5 (s, 5B, B2-6), -13.2 (s, 5B, B7-11), -14.4 (s, 1B, B12).

Figure S17: $^1\text{H}-\text{NMR}$ (600.13 MHz, C$_6$D$_6$, 300 K) spectrum of the product mixture.
**Figure S18**: $^1$H, $^{29}$Si-NMR HMBC (600.13 MHz, 119.25 MHz, C$_6$D$_6$, 300 K) spectrum of the product mixture.

**Figure S19**: $^1$H, $^{13}$C-NMR HMBC (600.13 MHz, 150.92 MHz, C$_6$D$_6$, 300 K) spectrum of the product mixture.
Figure S120: $^{13}$B-NMR (192.54 MHz, C$_6$D$_6$, 300 K) spectrum of the product mixture.

S2.6 Generation of [(Me$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]

[([Me$_2$Et]Si)$_2$H][Me$_3$NB$_{12}$Cl$_{11}$] (220 mg, 0.29 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS$_2$ (0.18 mL, 2.90 mmol 10 eq.) was condensed onto the reaction mixture at 77 K, which was subsequently warmed up to 273 K. Ethyldimethylsilane (0.15 mL, 0.35 mmol, 1.2 eq.) was added dropwise and the reaction mixture was stirred for three days at room temperature. Diffusion of n-pentane into the reaction mixture yielded colorless crystals of [(Me$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$] suitable for X-ray diffraction analysis, which were selected by hand from the crude product.

$^{29}$Si-NMR (119.24 MHz, C$_6$D$_6$, 300 K) of the product mixture: $\delta = 34.0, 42.1, 44.3, 45.5, 45.8, 46.6, 47.8, 49.9, 53.7, 59.3$. 
Figure S21: $^1$H, $^{29}$Si NMR HMBC (600.13 MHz, 119.25 MHz, C$_6$D$_6$, 300 K) spectrum of the product mixture containing [((Me$_2$Et)Si)$_2$H][Me$_3$NB$_{12}$Cl$_{11}$].

S2.7 Generation of [(Et$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]

[((Et$_3$Si)$_2$H)][Me$_3$NB$_{12}$Cl$_{11}$] (350 mg, 0.43 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 mL) in an H-shaped reaction vessel. CS$_2$ (0.02 mL, 0.22 mmol 0.5 eq.) was condensed onto the reaction mixture at 77 K, which subsequently was warmed up to 273 K. Triethylsilane (0.05 mL, 0.43 mmol, 1 eq.) was added dropwise, the reaction mixture was stirred for three days at room temperature, and then the solvent was removed by filtration. Diffusion of n-pentane into the reaction mixture yielded colorless crystals of ([(Et$_3$Si)$_3$S)][Me$_3$NB$_{12}$Cl$_{11}$] and [(Et$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]), which were selected by hand from the crude product.

$^{29}$Si-NMR (119.24 MHz, C$_2$DCl$_2$, 300 K) of the product mixture: $\delta = 9.0$ (Et$_3$Si)$_2$S, 35.7, 36.8/36.9[(Et$_3$Si)$_3$S]$, 63.2.$
Figure S22: $^1$H, $^{29}$Si-NMR HMBC (119.24 MHz, CD$_2$Cl$_2$, 300 K) spectrum of the product mixture.

S2.8 Generation of [(‘Bu$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$] and [(‘Bu$_3$Si)$_2$CH][Me$_3$NB$_{12}$Cl$_{11}$]

[(‘Bu$_3$Si)$_2$H][Me$_3$NB$_{12}$Cl$_{11}$] (176 mg, 0.18 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS$_2$ (0.01 mL, 0.18 mmol 0.5 eq.) was condensed onto the reaction mixture at 77 K, which subsequently was stirred for one hour at 273 K. ‘Buthylsilane (0.03 mL, 0.35 mmol, 1 eq.) was added dropwise and the reaction mixture was stirred for another three days at room temperature. Diffusion of n-pentane yielded colorless crystals of [(‘Bu$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$] suitable for X-ray diffraction analysis, which were selected by hand from the crude product.

$^{29}$Si-NMR (119.24 MHz, C$_2$DCl$_2$, 300 K) of the product mixture: $\delta = -6.9, 0.0, 4.7, 16.5, 44.3, 49.1$ [(‘Bu$_3$Si)$_2$CH]$^+$, 167.9.
Figure S23: $^1$H, $^{29}$Si-NMR HMBC (119.24 MHz, CD$_2$Cl$_2$, 300 K) spectrum of the product mixture

S2.9 Generation of [(Et$_3$Si)$_3$S(SiEt$_2$)][Me$_3$NB$_{12}$Cl$_{11}$]

[(Et$_3$Si)$_2$H][Me$_3$NB$_{12}$Cl$_{11}$] (350 mg, 0.43 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CS$_2$ (0.02 mL, 0.22 mmol 0.5 eq.) was condensed onto the reaction mixture at 77 K, which was warmed up to room temperature. Triethylsilane (0.05 mL, 0.43 mmol, 1 eq.) was added dropwise and the reaction mixture was stirred for three days at room temperature. Diffusion of n-pentane yielded a mixture of colorless crystals of [(Et$_3$Si)$_3$S(SiEt$_2$)][Me$_3$NB$_{12}$Cl$_{11}$] and [(Et$_3$Si)$_3$S][Me$_3$NB$_{12}$Cl$_{11}$], which were selected by hand from the crude product.

$^{29}$Si-NMR (119.24 MHz, C$_2$DCl$_2$, 300 K) of the product mixture: $\delta = -15.0, -10.7, 7.5, 8.5, 31.6, 33.7, 35.6, 36.8, 144.2, 149.9$. 
Figure S24: $^1$H, $^{29}$Si-NMR HMBC (119.24 MHz, CD$_2$Cl$_2$, 300 K) spectrum of the product mixture.

Figure S25: $^1$H-NMR spectrum (600.27 MHz, CD$_2$Cl$_2$, 300 K) of the product mixture.
Figure S26: $^{13}$C-NMR (150.95 MHz, CD$_2$Cl$_2$, 300 K) spectrum of the product mixture

S2.10 Generation of [(Et$_3$SiO)$_2$CH][Me$_3$NB$_{12}$Cl$_{11}$]·(Et$_3$Si)$_2$O

[(Et$_3$Si)$_2$H][Me$_3$NB$_{12}$Cl$_{11}$] (150 mg, 0.19 mmol 1 eq.) was dissolved in dry 1,2-difluorobenzene (5 ml) in an H-shaped reaction vessel. CO$_2$ (7 atm, 56.0 mmol 3.3 eq.) was condensed at 77 K into the reaction mixture, which subsequently was warmed up slowly to room temperature (DANGER OF EXPLOSION!!!) and stirred for three days. All volatiles were removed and 1,2-difluorobenzene (5 ml) was condensed onto the residue. Diffusion of n-pentane yielded colorless crystals of [(Et$_3$SiO)$_2$CH][Me$_3$NB$_{12}$Cl$_{11}$]·(Et$_3$Si)$_2$O suitable for X-ray diffraction analysis, which were selected by hand from the crude product.
## S3 Crystal structures

### S3.1 Crystallographic data

**Table S5**: Crystallographic data, part 1.

| CCDC-Nr. | Formula | Name | Space group | a/µm | b/µm | c/µm | α/° | β/° | γ/° | U/Å³ | Z | μ(Mo-Kα)/mm⁻¹ | No. of data collected | No. of unique data | Rm | R₁, wR₂ (I>2σ(I)) | R₁, wR₂ (all data) |
|----------|---------|------|-------------|------|------|------|------|-----|-----|------|----|-----------------|----------------------|-------------------|----|------------------|-------------------|
| 2034324  | C₁₃H₃₀B₁₂Cl₁₁FNSSi | acvm56 | Pccn | 3032.34(15) | 1582.33(8) | 1423.65(7) | 90 | 90 | 90 | 6830.9(6) | 8 | 1.009 | 19210 | 6696 | 0.0431 | 0.0459, 0.1146 |
| 2034325  | C₁₆H₃₆B₁₂Cl₁₁NSSiF | acvm61 | Pccn | 3245.88(16) | 1608.32(5) | 1438.06(9) | 90 | 90 | 90 | 7507.3(6) | 8 | 0.922 | 27268 | 7365 | 0.0384 | 0.0705, 0.1720 |
| 2034331  | C₁₀H₃₀B₁₂Cl₁₁NSSi₂ | acvm74kl | C2/c | 2702.10(11) | 986.13(5) | 2606.42(15) | 90 | 92.903(4) | 92 | 6936.2(6) | 8 | 1.020 | 30520 | 6794 | 0.0550 | 0.0769, 0.1720 |
| 2034328  | [Et₃Si(H)Me][A] : ½ C₆F₆H₄ | Acvm99.2.2 | P2₁/c | 1246.42(7) | 1613.08(9) | 1990.33(10) | 90 | 90 | 90 | 3916.1(4) | 4 | 0.911 | 21300 | 7700 | 0.0274 | 0.0366, 0.0827 |
| 2034329  | [iPrSiS(H)Me][A] : ½ C₆F₆H₄ | Acvm95.2 | Pca2₁ | 1952.94(5) | 1955.44(5) | 2622.29(5) | 90 | 90 | 90 | 10014.2(3) | 4 | 0.725 | 23639 | 13562 | 0.0827 | 0.0381, 0.0835 |
| 2034331  | [(Me₃Si)₂SMe][A] | [(Et₃Si)₂SMe][A] : ½ C₆F₆H₄ | C₁₆H₃₆B₁₂Cl₁₁NSSi₂ | 2034328 | 150(1) | 149.8(10) | 90 | 90 | 90 | 6936.2(6) | 8 | 1.020 | 27268 | 6794 | 0.0550 | 0.0769, 0.1720 |
| 2034329  | [(Bu₂Si)₂SMe][A] : ½ C₆F₆H₄ | [(Bu₂Si)₂SMe][A] | C₂₈H₆₆B₁₂Cl₁₁NSSi₂ | 2034331 | 150(1) | 150(1) | 90 | 90 | 90 | 10014.2(3) | 8 | 0.725 | 27268 | 6794 | 0.0550 | 0.0769, 0.1720 |

\[ R₁ = \sum |F_o| - |F_c| / \sum |F_o|, \ wR₂ = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^4)])^{1/2}; [A] = [Me₃NB₁₂Cl₁₁]⁻]
Table S6: Crystallographic data, part 2.

|                     | [(Et₃Si)₃S][A] | [(Et₃Si)₂S(SiEt₂H)][A] | [Et₃SiOC(H)OSiEt₃][A] · (Et₃Si)₂O |
|---------------------|----------------|-------------------------|-----------------------------------|
| CCDC-Nr.            | 2034326        | 2034327                 | 2034330                           |
| Formula             | C₂₁H₅₆B₁₂Cl₁₁NSSi₃ | C₁₉₅₈H₅₁₁B₁₂Cl₁₁NSSi₃ | C₃₁H₇₈B₂₂Cl₁₂N₂O₃Si₄              |
| Name                | acvm37krist     | acvm101                 | acvmCO2.2                         |
| M                   | 956.65          | 936.77                  | 1674.62                           |
| Temperature / K     | 150(1)          | 152(4)                  | 149.8(4)                          |
| Crystal system      | triclinic       | orthorhombic            | tetragonal                        |
| Space group         | P̅₁             | P₂₁₂₁                 | P₄₁₂₁₂₁                        |
| a/pm                | 976.82(3)       | 1408.64(4)             | 1414.73(3)                       |
| b/pm                | 1385.26(4)      | 1711.38(5)             | 1414.73(3)                       |
| c/pm                | 1700.20(7)      | 18.0545(5)             | 3766.53(10)                      |
| α/°                 | 84.283(3)       | 90                     | 90                               |
| β/°                 | 89.539(3)       | 90                     | 90                               |
| γ/°                 | 84.382(3)       | 90                     | 90                               |
| U/Å³                | 2278.19(13)     | 4352.4(2)              | 7538.6(3)                        |
| Z                   | 2               | 4                      | 4                                |
| μ(Mo-Kα)/mm⁻¹       | 0.816           | 0.852                  | 0.894                            |
| No. of data collected | 18539          | 23048                  | 38814                           |
| No. of unique data  | 9429           | 9945                   | 7395                            |
| R cryst            | 0.0211          | 0.0236                 | 0.0356                           |
| R₁, wR₂ (I>2σ(I))   | 0.0321, 0.0797  | 0.0347, 0.0765        | 0.0399, 0.0892                  |
| R₁, wR₂ (all data) | 0.0400, 0.0842  | 0.0442, 0.0807        | 0.0455, 0.0920                  |

\(^a R₁ = \sum |F_o| - |F_c| / |F_o|, wR₂ = (∑|w(F_o^2-F_c^2)|)^{1/2} / ∑|wF_o^2|^{1/2}; [A] = [Me₃NB₁₂Cl₁₁] \)
S3.2 Treatment of disorder in the crystal structures

Some of the crystal structures suffer from positional disorder in particular of the alkyl chains. The disordered parts were refined over two positions with fixed occupancies. SADI, DFIX, and ISOR restraints within the Shelx software were used.

S3.3 Graphical representations of the crystal structures

Figure S27. Part of the crystal structure of $[\text{Et}_3\text{SiS(H)Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}] \cdot \frac{1}{2} \text{C}_6\text{F}_{2}\text{H}_4$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.

Figure S28. Part of the crystal structure of $[\text{iPr}_3\text{SiS(H)Me}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}] \cdot \frac{1}{2} \text{C}_6\text{F}_{2}\text{H}_4$. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.
**Figure S29.** Part of the crystal structure of [(Me$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.

**Figure S30.** Part of the crystal structure of [(Et$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.
**Figure S31.** Part of the crystal structure of [(tBu$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.

**Figure S32.** Part of the crystal structure of [(Et$_3$Si)$_3$S][Me$_3$NB$_{12}$Cl$_{11}$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii.
Figure S33. Part of the crystal structure of [(Et$_3$Si)$_2$S(SiHEt$_2$)][Me$_3$NB$_{12}$Cl$_{11}$]. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.

Figure S34. Part of the crystal structure of (Et$_3$SiOC(H)OSiEt$_3$)][Me$_3$NB$_{12}$Cl$_{11}$]·(Et$_3$Si)$_2$O. Ellipsoids are drawn at 50% probability and hydrogen atoms are drawn with arbitrary radii. Disordered atoms were omitted for clarity.
## S3.4 Fractional atomic coordinates

Table S7: Fractional atomic coordinates of [(Et₃Si)S(H)Me][Me₃NB₁₂Cl₁₁] · ½ C₆F₂H₄.

| Atom   | x        | y        | z        | U(eq)   |
|--------|----------|----------|----------|---------|
| Cl₁₀   | 3887.5(3)| 5631.5(5)| 9798.7(5)| 31.42(19) |
| Cl₁₇   | 3374.2(2)| 3428.1(5)| 6626.2(5)| 28.23(18) |
| Cl₁₃   | 4160.0(3)| 4395.4(5)| 5133.1(5)| 30.12(19) |
| Cl₁₅   | 4685.5(3)| 6642.9(5)| 8442.7(6)| 31.9(2)   |
| Cl₁₉   | 4875.1(3)| 4479.0(5)| 8978.5(6)| 34.4(2)   |
| Cl₁₆   | 3499.4(3)| 6961.4(5)| 7943.1(7)| 37.0(2)   |
| Cl₁₂   | 3803.8(3)| 3404.4(5)| 8991.8(5)| 33.6(2)   |
| Cl₁₂   | 3154.1(3)| 5534.6(6)| 5954.3(6)| 35.8(2)   |
| Cl₁₄   | 5115.1(2)| 5126.7(6)| 6639.5(6)| 34.0(2)   |
| Cl₁₈   | 4563.9(2)| 3165.5(5)| 7011.6(6)| 29.07(19) |
| Cl₁₁   | 2962.7(2)| 4979.0(5)| 8344.3(6)| 35.7(2)   |
| Si₁    | 6781.7(3)| 5740.9(6)| 7415.2(7)| 37.3(2)   |
| S₁     | 6098.1(3)| 6366.0(5)| 7473.5(6)| 30.3(2)   |
| N₁     | 4253.0(9)| 6640.1(16)| 5955.0(18)| 29.2(6)   |
| B₁₀    | 3711.8(10)| 4272(2)| 7052(2)| 18.5(6)   |
| C₈     | 6976.2(11)| 5588(2)| 8616(3)| 39.2(9)   |
| B₃     | 4101.4(10)| 4794(2)| 6303(2)| 19.3(7)   |
| B₁₁    | 3510.7(10)| 5016(2)| 7886(2)| 22.1(7)   |
| C₉     | 7077.7(13)| 6400(3)| 9168(3)| 48.0(10)  |
| B₁₀    | 3958.6(11)| 5328(2)| 8600(2)| 21.8(7)   |
| C₁₀    | 5855.4(11)| 6065(2)| 8587(2)| 40.0(9)   |
| F₁     | 2732.0(18)| 8203(4)| 7147(4)| 86.1(18)  |
| B₅     | 4353.0(11)| 5850(2)| 7880(2)| 21.0(7)   |
| C₂     | 4506.6(18)| 6351(3)| 5113(3)| 72.4(15)  |
| B₁     | 4147.1(11)| 5883(2)| 6674(2)| 21.6(7)   |
| B₄     | 4554.6(10)| 5120(2)| 7027(2)| 20.6(7)   |
| B₂     | 3618.1(11)| 5334(2)| 6704(2)| 21.9(7)   |
| B₁₂    | 3919.1(11)| 4261(2)| 8214(2)| 20.7(7)   |
| C₅     | 6956.7(15)| 6632(3)| 5727(3)| 42.8(14)  |
| C₁     | 3844.7(16)| 7023(3)| 5559(4)| 80.1(17)  |
| B₉     | 4439.4(10)| 4782(2)| 8209(2)| 21.1(7)   |
| C₃     | 4501(2)| 7331(3)| 6399(3)| 91(2)     |
| C₆     | 6660.1(15)| 4756(3)| 6801(3)| 52.7(11)  |
| B₈     | 4286.2(10)| 4140(2)| 7244(2)| 18.9(7)   |
| B₆     | 3777.2(11)| 6003(2)| 7663(2)| 21.5(7)   |
| C₇     | 6296.5(15)| 4232(3)| 7227(4)| 67.2(14)  |
| Atom | x          | y          | z          | U(eq)    |
|------|------------|------------|------------|----------|
| Cl17A| 6022.0(14) | 4359.5(18) | 9806(3)    | 44.7(9)  |
| Cl12A| 5234.8(14) | 3396(3)    | 8523(4)    | 46.5(8)  |
| Cl9A | 6530.6(16) | 6387(3)    | 6581(4)    | 45.1(9)  |
| Cl10 | 5430.7(12) | 6772.4(17) | 6978(2)    | 42.8(8)  |
| Cl13A| 6325(2)    | 2950(3)    | 8036(3)    | 52.3(10) |
| Cl5A | 5752.6(13) | 5493(4)    | 5157(3)    | 51.1(9)  |
| Cl6A | 4856.1(14) | 4926(3)    | 6741(2)    | 52.6(9)  |
| Cl12 | 6160.1(19) | 6506(2)    | 8912(3)    | 54.9(11) |
| Cl11 | 5122.8(18) | 5573(2)    | 8995(4)    | 53.6(10) |
| Si1  | 6698.0(5)  | 5761.4(9)  | 2420.3(10) | 47.0(4)  |
| Cl8A | 6890(2)    | 4849(4)    | 8304(5)    | 60.3(11) |
| Cl4A | 6673.6(11) | 4261(3)    | 5967(3)    | 58.5(9)  |
| S1A  | 6055.9(10) | 6475.6(14) | 2370.2(15) | 51.8(9)  |
| N1   | 5610.5(15) | 3299(3)    | 6041(3)    | 53.8(12) |
| B2   | 5565.2(15) | 4120(3)    | 7923(4)    | 32.9(11) |
| B5   | 5814.8(16) | 5094(3)    | 6330(3)    | 34.7(11) |
| B4   | 6252.5(17) | 4511(3)    | 6707(4)    | 39.0(12) |
| B10  | 5678.4(17) | 5780(3)    | 7249(3)    | 34.1(11) |
| B1   | 5740.3(16) | 4040(3)    | 6724(4)    | 35.9(11) |
| B6   | 5390.2(16) | 4849(3)    | 7078(4)    | 35.0(11) |
| C16  | 7330.9(18) | 2286(4)    | 4173(5)    | 66.2(16) |
| B7   | 5954.7(17) | 4609(3)    | 8599(3)    | 34.2(11) |
| B9   | 6203.1(17) | 5575(3)    | 7016(4)    | 36.9(12) |
| B3   | 6093.7(16) | 3904(3)    | 7700(4)    | 37.5(12) |
| B12  | 6024.7(18) | 5634(3)    | 8178(3)    | 37.7(12) |

Table S8: Fractional atomic coordinates of [(^3)Pr$_3$SiS(H)Me][Me$_3$NB$_{12}$Cl$_{11}$]·½ C$_6$F$_2$H$_4$. 
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| B11 | 5524.1(17) | 5190(3) | 8222(4) | 36.3(12) |
| B8  | 6377.7(17) | 4841(3) | 7864(4) | 38.8(12) |
| C15 | 7139(2) | 2056(4) | 4945(6) | 73.3(19) |
| C8A | 6931(3) | 6564(5) | 3206(5) | 54(2) |
| C13 | 6214(2) | 4300(4) | 2432(6) | 84(2) |
| C5A | 6870.5(19) | 5682(4) | 1206(4) | 36.4(15) |
| C11A | 6497(2) | 4802(4) | 3032(5) | 46.2(19) |
| C12 | 6878(2) | 4258(4) | 3378(5) | 79(2) |
| C7  | 7243(2) | 5094(4) | 1103(6) | 78(2) |
| C6A | 6958(3) | 6506(5) | 759(5) | 49.1(19) |
| F1  | 7158(3) | 2067(4) | 6599(5) | 204(4) |
| C10A | 6774(4) | 6585(6) | 4189(6) | 68(3) |
| C14 | 7307(3) | 2275(4) | 5771(5) | 90(3) |
| C1B | 5134(6) | 3253(15) | 5940(20) | 108(9) |
| C2B | 5676(9) | 2450(12) | 6467(19) | 95(8) |
| C3B | 5853(9) | 3276(17) | 5153(17) | 110(9) |
| C1A | 5388(7) | 2657(11) | 6496(12) | 111(7) |
| C2A | 5994(5) | 2848(10) | 5682(15) | 114(6) |
| C3A | 5392(6) | 3605(8) | 5201(10) | 99(6) |
| C16B | 4908(8) | 5000(20) | 6730(20) | 131(12) |
| C17B | 6108(9) | 4189(19) | 9714(16) | 114(8) |
| C13B | 6342(9) | 2852(16) | 7840(20) | 116(10) |
| C11 | 6293(11) | 6320(20) | 8920(20) | 103(9) |
| C18B | 6911(9) | 4599(18) | 8080(20) | 79(8) |
| C12 | 5234(9) | 5480(17) | 9070(20) | 89(8) |
| C13 | 5553(8) | 6734(14) | 7070(18) | 113(9) |
| C19B | 6587(8) | 6179(16) | 6418(17) | 59(5) |
| C14B | 6627(8) | 4001(16) | 5816(18) | 111(8) |
| C15B | 5735(8) | 5255(18) | 5156(14) | 84(8) |
| C12B | 5246(9) | 3313(17) | 8370(20) | 102(10) |
| C5B | 7194(13) | 5720(20) | 1460(30) | 107(12) |
| C11B | 6624(9) | 4599(11) | 2580(20) | 76(8) |
| C9  | 7414(3) | 6404(6) | 3206(8) | 120(3) |
| S1B | 6286(4) | 6690(5) | 2249(6) | 80(3) |
| C4  | 5842(2) | 6233(5) | 1264(5) | 80(2) |
| C6B | 7195(13) | 6720(20) | 1050(30) | 100(11) |
| C8B | 7089(9) | 6170(20) | 3289(18) | 77(8) |
| C10B | 6987(14) | 6360(30) | 4150(30) | 106(14) |
Table S9: Fractional atomic coordinates of [(Me₃Si)₂SMe][Me₃NB₁₂Cl₁₁].

| Atom | x       | y       | z       | U(eq)  |
|------|---------|---------|---------|--------|
| Cl₁₁ | 1855.7(5) | 3329.8(13) | 2210.9(6) | 50.5(4) |
| Cl₃  | 777.1(6)  | 8420.1(15) | 690.3(6)  | 62.5(5)  |
| Cl₅  | 2630.0(4) | 5815.9(14) | 1689.6(6) | 49.8(4)  |
| Cl₁₀ | 2017.1(6) | 3503.7(13) | 833.1(6)  | 55.0(4)  |
| Cl₆  | 1770.8(6) | 6651.8(16) | 2720.2(5) | 58.3(4)  |
| Cl₄  | 2032.2(6) | 6981.8(15) | 436.5(6)  | 57.8(4)  |
| Cl₉  | 907.8(7)  | 5107.7(17) | 227.0(6)  | 68.5(5)  |
| Cl₁₂ | 812.4(6)  | 2749.5(15) | 1300.8(8) | 67.9(5)  |
| Cl₁₂ | 652.2(7)  | 8351(2)    | 2075.5(7) | 78.4(6)  |
| Cl₈  | 74.3(5)   | 5801(2)    | 1232.1(8) | 77.1(6)  |
| S₁   | 1106.6(6) | -352(2)    | 3657.3(7) | 66.2(5)  |
| Cl₇  | 657.4(6)  | 4852(2)    | 2465.6(8) | 81.4(6)  |
| Si₂  | 1342.9(7) | -1331(2)   | 4402.3(8) | 68.4(5)  |
| Si₁  | 716.4(7)  | 1648(2)    | 3744.3(8) | 73.1(6)  |
| B₅   | 1971.6(19)| 5962(5)    | 1578(2)   | 31.4(11) |
| N₁   | 1878.1(19)| 8980(4)    | 1610.7(19)| 49.6(12) |
| B₄   | 1687(2)   | 6507(5)    | 973(2)    | 36.6(12) |
| B₃   | 1096(2)   | 7197(6)    | 1095(2)   | 40.3(13) |
| B₁₀  | 1670(2)   | 4752(5)    | 1158(2)   | 36.8(12) |
| B₁   | 1625(2)   | 7536(5)    | 1540(2)   | 35.6(12) |
| B₆   | 1559(2)   | 6358(6)    | 2066(2)   | 36.7(12) |
| B₁₁  | 1593(2)   | 4673(5)    | 1826(2)   | 36.4(12) |
| B₂   | 1023(2)   | 7136(7)    | 1766(2)   | 43.7(14) |
| B₉   | 1139(2)   | 5520(6)    | 861(2)    | 43.6(14) |
| B₇   | 1013(2)   | 5389(7)    | 1946(2)   | 43.7(14) |
| B₁₂  | 1083(2)   | 4387(6)    | 1384(3)   | 44.1(14) |
| B₈   | 731(2)    | 5889(7)    | 1352(3)   | 48.5(16) |
| C₄   | 327(3)    | 1612(10)   | 4295(3)   | 93(3)    |
| C₁₁  | 612(3)    | -1476(10)  | 3434(3)   | 92(3)    |
| C₇   | 790(3)    | -1651(8)   | 4765(3)   | 80(2)    |
| C₁   | 1914(4)   | 9456(8)    | 2143(3)   | 90(3)    |
| C₃   | 2413(3)   | 8990(8)    | 1470(5)   | 113(4)   |
| C₈   | 1782(3)   | -135(9)    | 4715(3)   | 89(3)    |
| C₂   | 1625(4)   | 10017(7)   | 1292(4)   | 106(4)   |
| C₉   | 1661(4)   | -2895(10)  | 4181(4)   | 115(4)   |
| C₅   | 371(4)    | 1782(10)   | 3131(3)   | 96(3)    |
| C₆   | 1243(4)   | 2921(12)   | 3809(5)   | 141(5)   |
Table S10: Fractional atomic coordinates of \([\text{Et}_3\text{Si})_2\text{SMe}][\text{Me}_3\text{NB}_{12}\text{Cl}_{11}].

| Atom | x     | y     | z     | U(eq)  |
|------|-------|-------|-------|--------|
| Cl2  | 5516.8(5) | 6651.9(4) | 2625.8(3) | 21.22(13) |
| Cl8  | 2948.2(5) | 7222.0(4) | 1543.7(3) | 25.33(14) |
| Cl6  | 5076.3(5) | 6325.5(4) | 4382.9(3) | 23.10(14) |
| Cl7  | 3756.5(5) | 7955.0(4) | 3342.9(3) | 26.02(14) |
| Cl5  | 3020.1(5) | 4568.0(4) | 4315.0(3) | 27.69(15) |
| Cl4  | 2131.9(5) | 3884.3(4) | 2509.1(3) | 27.82(15) |
| S1   | 2487.0(5) | 2337.8(4) | 5046.3(3) | 21.31(14) |
| Cl3  | 3814.7(5) | 5100.2(4) | 1477.2(3) | 25.42(15) |
| Cl10 | 531.2(5)  | 5242.6(5) | 3238.4(3) | 30.74(16) |
| Cl9  | 984.9(5)  | 5577.3(4) | 1487.7(3) | 29.72(16) |
| Cl12 | 914.3(5)  | 7348.1(4) | 2623.8(3) | 32.18(16) |
| Cl11 | 2276.6(5) | 6718.3(5) | 4389.4(3) | 31.06(16) |
| Si1  | 2661.3(6) | 1204.2(5) | 4427.5(4) | 25.42(17) |
| Si2  | 740.4(6)  | 2691.5(5) | 5044.1(4) | 29.52(18) |
| N1   | 5071.6(16) | 4511.3(12) | 3239.1(10) | 18.5(4) |
| C1   | 5984(2)   | 4701.8(18) | 2880.4(14) | 30.2(6) |
| B2   | 4266(2)   | 6225.6(16) | 2792.8(12) | 14.4(5) |
| C10  | 3091(2)   | 2025.7(18) | 5922.1(13) | 31.9(6) |
| B6   | 4052(2)   | 6066.8(17) | 3642.7(13) | 16.5(5) |
| B1   | 4103(2)   | 5178.5(17) | 3097.6(13) | 16.2(5) |
| C8   | 2037(2)   | 290.8(17)  | 4766.8(15) | 33.6(7) |
| B3   | 3435(2)   | 5494.9(17) | 2240.8(13) | 17.1(6) |
| C4   | 4175(2)   | 1107.5(19) | 4578.6(16) | 35.3(7) |
| C2   | 4660(2)   | 3665.2(17) | 2997.9(17) | 38.1(7) |
| B5   | 3073(2)   | 5243.6(18) | 3610.5(13) | 18.3(6) |
| B10  | 1812(2)   | 5590.3(18) | 3084.0(14) | 20.2(6) |
| C3   | 5605(2)   | 4424(2)    | 3988.6(13) | 38.2(7) |
| B8   | 3000(2)   | 6553.5(17) | 2264.3(13) | 17.0(6) |
| B9   | 2035(2)   | 5747.2(18) | 2235.9(13) | 18.9(6) |
| C13  | 928(2)    | 3410(2)    | 5786.9(15) | 37.0(7) |
| C5   | 4782(3)   | 1857(2)    | 4381.8(17) | 42.4(8) |
| B4   | 2675(2)   | 4899.3(17) | 2739.9(13) | 17.6(6) |
| B7   | 3380(2)   | 6899.9(17) | 3130.4(13) | 17.2(6) |
| C15  | -92(3)    | 1788(2)    | 5163.7(16) | 39.2(7) |
| C6   | 1992(3)   | 1516(2)    | 3542.4(13) | 39.0(7) |
| C11  | 295(3)    | 3193(2)    | 4180.9(15) | 39.7(7) |
| B11  | 2650(2)   | 6304.5(19) | 3637.6(13) | 19.7(6) |
| B12  | 2000(2)   | 6610.7(18) | 2787.2(14) | 20.2(6) |
| C12  | -714(3)   | 3713(2)    | 4137.9(17) | 46.2(8) |
| Atom  | x    | y    | z    | U(eq)   |
|-------|------|------|------|---------|
| Si3   | 6871.5(6) | 1039.7(7) | 6505.0(5) | 14.5(3) |
| Cl19  | 4199.0(6) | 4847.6(7) | 5516.4(5) | 23.0(3) |
| Cl9   | 5567.5(6) | 11057.2(8) | 2759.3(5) | 27.7(3) |
| Si1   | 4375.7(6) | 4120.9(7) | 3788.2(5) | 14.7(3) |
| S1    | 4643.4(6) | 5095.5(6) | 3357.9(5) | 15.6(3) |
| Cl5   | 4525.7(6) | 11609.5(7) | 3784.4(6) | 29.2(3) |
| Cl24  | 4537.1(5) | 4829.9(7) | 6922.0(5) | 24.2(3) |
| Cl18  | 1961.0(6) | 3408.0(7) | 6567.9(5) | 22.4(3) |
| Si4   | 6805.6(6) | -965.8(7) | 6416.3(5) | 14.6(3) |
| Cl14  | 3933.1(6) | 10214.1(7) | 2887.5(5) | 25.1(3) |
| S2    | 7110.2(5) | 1.0(6) | 6845.8(5) | 14.6(3) |
| Cl21  | 3175.5(6) | 5832.1(7) | 7533.2(5) | 25.7(3) |
| Cl6   | 5122.9(7) | 10761.2(9) | 4975.3(5) | 32.9(4) |
| Cl14  | 2622.6(6) | 3960.9(7) | 5308.5(5) | 21.5(3) |
| Cl10  | 6283.3(7) | 11374.4(8) | 4034.7(6) | 34.4(4) |
| Cl15  | 2731.0(6) | 5901.0(7) | 5304.4(5) | 26.8(3) |
| Cl12  | 6890.2(6) | 9921.8(9) | 3269.5(5) | 32.3(4) |
| Si2   | 4434.4(7) | 6097.6(7) | 3759.3(6) | 17.4(3) |
| Cl20  | 3905.1(6) | 6371.5(7) | 6297.8(6) | 27.0(3) |
| Cl16  | 2150.3(6) | 6529.3(7) | 6568.3(5) | 24.9(3) |
| Cl22  | 3082.6(6) | 3969.3(7) | 7528.5(5) | 23.3(3) |
| Cl18  | 5418.5(7) | 9231.9(8) | 2582.6(5) | 29.4(3) |
| Cl17  | 1568.1(6) | 4987.8(7) | 7319.9(5) | 21.4(3) |
| Cl23  | 3730.7(6) | 3362.5(7) | 6277.9(5) | 22.5(3) |
| Cl3   | 4273.5(7) | 8529.7(7) | 3465.6(6) | 30.4(3) |
| Cl11  | 6542.0(6) | 9713.0(9) | 4667.4(5) | 37.2(4) |
| Cl7   | 6038.3(7) | 8379.5(8) | 3749.8(6) | 37.3(4) |
| Cl12  | 4928.2(7) | 8829.8(8) | 4781.2(5) | 31.8(3) |
| C19   | 5579(2)  | 5102(3)  | 3331(2)  | 22.2(12) |
| N2    | 1292.3(18) | 5015(2)  | 5954.0(17) | 17.1(10) |
| C52   | 7474(2)  | -1112(3) | 5912(2)  | 19.7(11) |
| C56   | 8048(2)  | -33(3)  | 6860(2)  | 19.6(12) |
| B20   | 3387(2)  | 5624(3)  | 6360(2)  | 14.2(12) |

Table S11: Fractional atomic coordinates of [(t-Bu$_3$Si)$_2$SMe][Me$_3$NB$_{12}$Cl$_{11}$].
|   | 3650.2(18) | 10029(2) | 4254.2(17) | 19.9(10) |
|---|------------|----------|------------|----------|
| B5 | 4854(3)    | 10757(3) | 3797(2)    | 15.5(12) |
| C24| 5049(2)    | 3989(3)  | 4281(2)    | 20.2(12) |
| B17| 2233(2)    | 4954(3)  | 6844(2)    | 14.4(12) |
| B24| 3692(3)    | 4876(3)  | 6656(2)    | 14.3(12) |
| B16| 2487(3)    | 5692(3)  | 6475(2)    | 13.6(12) |
| B10| 5751(3)    | 10650(3) | 3899(2)    | 19.9(14) |
| C49| 5300(2)    | -947(3)  | 6417(2)    | 25.3(13) |
| C29| 4945(2)    | 3432(3)  | 2867(2)    | 22.3(12) |
| C32| 5931(2)    | 1011(3)  | 6359(2)    | 22.1(12) |
| C2 | 3625(3)    | 10024(3) | 4826(2)    | 33.5(16) |
| B4 | 4589(2)    | 10103(3) | 3358(2)    | 15.3(12) |
| B7 | 5632(3)    | 9196(3)  | 3767(2)    | 21.6(14) |
| C36| 7479(3)    | 1106(3)  | 5954(2)    | 24.1(12) |
| B9 | 5406(3)    | 10500(3) | 3286(2)    | 15.2(12) |
| B15| 2784(3)    | 5388(3)  | 5872(2)    | 14.2(12) |
| B14| 2731(3)    | 4471(3)  | 5869(2)    | 12.9(12) |
| C48| 5958(2)    | -777(3)  | 6116(2)    | 21.0(12) |
| C28| 4347(2)    | 3494(3)  | 3250(2)    | 20.3(12) |
| B19| 3533(2)    | 4881(3)  | 5986(2)    | 15.5(12) |
| B11| 5879(3)    | 9846(3)  | 4194(2)    | 20.9(14) |
| B8 | 5336(3)    | 9610(3)  | 3202(2)    | 16.3(12) |
| C53| 7532(2)    | -1859(3) | 5727(2)    | 20.1(11) |
| C20| 3519(2)    | 4307(3)  | 4077(2)    | 21.9(12) |
| C47| 7133(3)    | -2036(3) | 7820(2)    | 32.4(14) |
| C30| 4731(3)    | 3003(4)  | 2414(2)    | 39.5(16) |
| C12| 3131(2)    | 6824(3)  | 3810(2)    | 27.2(13) |
| C43| 8252(2)    | 1956(3)  | 7026(2)    | 26.9(13) |
| C33| 5499(2)    | 1647(3)  | 6451(2)    | 20.4(12) |
| C13| 2354(2)    | 6729(3)  | 3839(2)    | 34.9(15) |
| B22| 2991(2)    | 4457(3)  | 6957(2)    | 15.1(12) |
| C18| 5327(3)    | 7180(3)  | 2506(2)    | 33.8(14) |
| B1 | 4418(2)    | 10000(3) | 4030(2)    | 14.9(12) |
| C25| 5121(2)    | 3251(3)  | 4476(2)    | 20.8(12) |
| C1 | 3265(2)    | 10644(3) | 4088(2)    | 28.6(14) |
| C54| 6867(3)    | -2125(3) | 5504(2)    | 30.6(13) |
| C37| 7556(3)    | 1811(3)  | 5702(2)    | 23.0(12) |
| C46| 8026(2)    | -1864(3) | 7148(2)    | 27.4(13) |
| C16| 4821(3)    | 6679(3)  | 2751.9(19) | 23.2(12) |
| B12| 6046(3)    | 9948(3)  | 3538(2)    | 19.3(14) |
| C3 | 3237(2)    | 9423(3)  | 4082(2)    | 29.2(14) |
| C34| 5717(3)    | 2258(3)  | 6132(2)    | 31.7(14) |
|   |     |     |     |     |
|---|-----|-----|-----|-----|
| C31 | 5587(3) | 3119(3) | 3110(2) | 28.7(14) |
| C55 | 8105(3) | -1914(3) | 5327(2) | 34.7(14) |
| C26 | 5727(3) | 3179(4) | 4826(3) | 43.8(18) |
| C45 | 7352(2) | -1594(3) | 7362.6(19) | 18.3(11) |
| C50 | 5147(3) | -1707(3) | 6408(2) | 35.5(16) |
| C11 | 3472(2) | 6124(3) | 3768(2) | 24.9(12) |
| C23 | 2694(3) | 3396(3) | 3805(3) | 42.7(17) |
| B18 | 2395(3) | 4200(3) | 6476(2) | 15.5(12) |
| C8  | 5165(3) | 6741(3) | 4591(2) | 24.6(12) |
| C27 | 4478(3) | 2981(3) | 4737(2) | 34.1(15) |
| C44 | 6775(2) | -1577(3) | 6964.2(19) | 17.5(11) |
| B13 | 2062(3) | 4969(3) | 6170(2) | 14.3(12) |
| C40 | 7010(2) | 1604(3) | 7067(2) | 20.1(11) |
| C51 | 4687(2) | -549(3) | 6204(3) | 34.6(15) |
| C15 | 4903(2) | 6707(3) | 3337.1(19) | 21.2(11) |
| C35 | 4737(2) | 1500(3) | 6349(2) | 24.8(12) |
| C9  | 5933(3) | 6720(4) | 4493(2) | 42.8(17) |
| C17 | 4099(3) | 6837(3) | 2579(2) | 35.1(14) |
| C21 | 2878(2) | 4138(3) | 3760(2) | 32.3(15) |
| C42 | 7604(3) | 2081(3) | 7835(2) | 34.6(15) |
| C41 | 7685(2) | 1653(3) | 7358(2) | 21.8(12) |
| C38 | 8302(3) | 1955(4) | 5554(2) | 35.4(15) |
| C4  | 944(2) | 5657(3) | 6122(2) | 25.0(13) |
| C22 | 2267(3) | 4582(4) | 3935(3) | 44.7(18) |
| B3  | 4735(3) | 9285(3) | 3648(2) | 19.1(13) |
| B23 | 3300(2) | 4157(3) | 6356(2) | 14.9(12) |
| C14 | 3375(3) | 7237(3) | 4276(2) | 35.9(15) |
| B2  | 5065(3) | 9440(3) | 4275(2) | 20.2(13) |
| B21 | 3035(2) | 5359(3) | 6959(2) | 15.7(13) |
| C39 | 7101(3) | 1858(4) | 5229(2) | 43.8(18) |
| C5  | 860(2) | 4429(3) | 6131(2) | 27.0(14) |
| C6  | 1264(3) | 5008(3) | 5379(2) | 32.6(15) |
| C10 | 5031(3) | 6886(4) | 5150(2) | 45.2(18) |
| B6  | 5146(3) | 10344(3) | 4365(2) | 21.2(14) |
| C7  | 4815(3) | 6074(3) | 4409(2) | 29.2(14) |
Table S12: Fractional atomic coordinates of [(Et$_3$Si)$_3$S][Me$_3$NB$_{12}$Cl$_{11}$].

| Atom | $x$       | $y$       | $z$       | U(eq)       |
|------|-----------|-----------|-----------|-------------|
| Cl7  | 5939.3(4) | 3815.4(3) | 864.6(3)  | 29.18(11)   |
| S1   | 5348.6(5) | 2714.4(3) | 6828.0(3) | 25.70(11)   |
| Cl2  | 8693.8(5) | 5101.9(3) | 1445.7(3) | 30.27(11)   |
| Cl12 | 5553.6(4) | 1764.9(4) | 2445.2(3) | 32.67(12)   |
| Cl5  | 11552.4(5)| 1340.2(3) | 2960.0(3) | 33.18(12)   |
| Cl3  | 9123.3(5) | 3292.6(4) | -99.5(3)  | 32.47(11)   |
| Cl6  | 10093.4(5)| 3853.7(4) | 3354.5(3) | 32.48(11)   |
| Cl4  | 10753.7(5)| 930.5(3)  | 858.8(3)  | 33.97(12)   |
| Cl8  | 7207.8(5) | 1304.1(3) | 557.1(3)  | 34.22(12)   |
| Cl9  | 8644.5(5) | 91.3(3)   | 2406.0(3) | 34.80(12)   |
| Si3  | 4012.8(5) | 2242.3(4) | 5891.0(3) | 31.64(13)   |
| Si1  | 7579.2(5) | 2393.7(4) | 6496.9(3) | 29.47(13)   |
| Si2  | 4886.6(6) | 1967.2(4) | 8030.6(3) | 31.64(13)   |
| N1   | 11803.7(14)|3342.3(11)| 1419.4(9) | 24.1(3)     |
| C20  | 4755(2)   | 2770.0(17)| 4949.8(11)| 34.9(5)     |
| C8   | 7806(2)   | 1207.5(14)| 6072.6(12)| 33.4(4)     |
| C18  | 4053(2)   | 888.5(15) | 6021.5(13)| 36.6(5)     |
| C10  | 5686(2)   | 2689.5(14)| 8738.2(12)| 36.8(5)     |
| C15  | 5657(2)   | 184.5(15) | 8926.1(13)| 39.4(5)     |
| C1   | 12532(2)  | 3650.6(17)| 2110.8(13)| 39.3(5)     |
| C2   | 12730.0(19)|2536.9(16)| 1111.0(14)| 40.6(5)     |
| B3   | 8981.6(19)| 2947.0(14)| 944.5(12) | 20.3(4)     |
| B1   | 10330.3(19)|2981.7(14)| 1655.2(12)| 19.9(4)     |
| B4   | 9804.7(19)| 1819.3(14)| 1397.7(12)| 21.1(4)     |
| B5   | 10128(2)  | 1991.4(14)| 2411.6(12)| 21.8(4)     |
| C6   | 7931(2)   | 3435.2(17)| 5769.3(14)| 44.0(6)     |
| B10  | 8492(2)   | 2213.9(15)| 2878.3(12)| 23.3(4)     |
| C14  | 5601(3)   | 670.3(15) | 8089.2(13)| 46.8(6)     |
| Atom | x      | y      | z      | U(eq)  |
|------|--------|--------|--------|--------|
| Cl8  | 3764.4(6) | 5289.1(5) | 2036.2(5) | 28.04(19) |
| Cl12 | 3498.9(6) | 4321.5(5) | 3832.4(5) | 28.54(19) |
| S1   | 120.0(6)  | 3500.6(5) | 3630.3(5) | 23.17(18) |
| Cl2  | 3637.7(7) | 7359.6(6) | 2318.5(5) | 34.6(2) |
| Cl7  | 2160.7(6) | 6108.2(6) | 3406.0(6) | 34.1(2) |
| Cl10 | 5510.4(8) | 4893.1(6) | 4988.5(6) | 37.6(2) |
| Cl9  | 5844.5(7) | 4519.7(6) | 3029.1(6) | 36.0(2) |
| Cl3  | 5917.7(7) | 6295.8(6) | 2036.6(6) | 36.9(2) |
| Cl11 | 3276.0(8) | 5849.8(6) | 5243.3(5) | 35.8(2) |
| Cl6  | 3225.4(8) | 7649.0(6) | 4353.0(6) | 39.9(2) |
| Cl4  | 7044.2(6) | 6097.7(7) | 3876.8(7) | 44.2(3) |
| Cl5  | 5396.5(9) | 6941.3(6) | 5306.4(5) | 41.1(3) |
| Si3  | -404.7(7) | 3627.8(6) | 2472.4(5) | 25.5(2) |
| Si1  | -232.9(8) | 2293.0(6) | 4010.2(7) | 33.9(3) |
| Si2  | -492.6(8) | 4436.9(7) | 4346.5(6) | 33.2(2) |
| N1   | 5635(2)   | 7862.7(17) | 3474.8(18) | 31.4(7) |
| Cl18 | 400.3     | 4345(2)   | 2049(2)   | 31.8(8) |
| Cl11 | 3937(3)   | 5986(2)   | 4419(2)   | 21.8(8) |
| B8   | 4191(3)   | 5713(2)   | 2869(2)   | 19.6(7) |
| B9   | 5194(3)   | 5344(2)   | 3344(2)   | 21.6(8) |
| C16  | -1672(3)  | 3901(3)   | 2472(3)   | 43.8(11) |
| C2   | 5992(3)   | 8003(3)   | 2709(2)   | 42.3(10) |
| B1   | 5146(3)   | 7029(2)   | 3564(2)   | 22.5(8) |
| B6   | 3980(3)   | 6912(2)   | 3977(2)   | 22.9(8) |
| C8   | -1478(3)  | 2086(3)   | 3772(3)   | 48.5(12) |
| B5   | 5007(3)   | 6552(2)   | 4439(2)   | 23.8(8) |
| B3   | 5257(3)   | 6259(2)   | 2879(2)   | 21.9(8) |
| Atom | x        | y        | z        | U(eq)   |
|------|----------|----------|----------|---------|
| Cl11 | 4362.2(9)| 1341.3(8)| 4926.9(3)| 28.4(3) |
| Cl7  | 2240.2(8)| 2338.3(9)| 4536.2(3)| 29.4(3) |
| Cl12 | 4500.3(9)| 2861.0(8)| 4195.5(3)| 30.4(3) |
| Cl6  | 5972.0(8)| 709.6(9) | 4252.1(3)| 31.9(3) |
| Cl8  | 1103.2(9)| 493.1(10)| 3998.2(3)| 36.0(3) |
| Cl12 | 2227.8(9)| -117.9(9)| 4838.4(3)| 35.4(3) |
| Cl13 | 2457.5(9)| 2329.5(9)| 3581.5(3)| 32.8(3) |
| Cl10 | 4574.2(10)| -1105.8(9)| 4640.7(3)| 36.8(3) |
| Cl5  | 4825.4(10)| -1180.5(9)| 3688.3(3)| 39.4(3) |
| Cl4  | 2593.0(10)| -212.2(10)| 3306.9(3)| 38.0(3) |
| Cl9  | 2549.3(11)| -1639.2(9)| 4064.9(4)| 42.0(3) |
| Si1  | 5604.4(11)| 3824.7(13)| 5410.0(4)| 43.1(4) |
| O3   | 8578(2)  | 8578(2)  | 5000     | 33.5(11)|

Table S14: Fractional atomic coordinates of [(Et$_3$SiO)$_2$CH][Me$_3$NB$_{12}$Cl$_{11}$].
| Element | Z  | X    | Y    | Z    |
|---------|----|------|------|------|
| N1      | 7  | 4767(3) | 1307(3) | 3400.1(10) | 27.1(9) |
| Si2     | 14 | 9654(2) | 9148(3) | 4860.3(9) | 46.6(8) |
| Si3     | 14 | 8474(3) | 7459(2) | 4798.2(10) | 49.3(8) |
| C4      | 6  | 3987(4) | 3987(4) | 5000 | 32.7(16) |
| C3      | 6  | 5744(4) | 900(4) | 3386.8(14) | 39.6(13) |
| B3      | 5  | 3039(4) | 1445(4) | 3842.4(13) | 22.7(11) |
| Si2     | 14 | 4181(4) | -236(4) | 3892.6(13) | 25.8(11) |
| B1      | 5  | 4188(4) | 965(4) | 3738.2(13) | 24.3(11) |
| Si3     | 14 | 8474(3) | 7459(2) | 4860.3(9) | 46.6(8) |
| C4      | 6  | 4024(4) | 1702(4) | 4125.5(12) | 20.9(10) |
| C3      | 6  | 4732(4) | 661(4) | 4156.2(13) | 23.6(11) |
| B11     | 5  | 3934(4) | 953(4) | 4505.7(13) | 23.1(10) |
| B9      | 5  | 3056(4) | -488(4) | 4088.1(14) | 28.0(12) |
| B10     | 5  | 4038(4) | -231(4) | 4366.1(13) | 25.1(11) |
| C1      | 6  | 4897(5) | 2351(4) | 3389.5(16) | 47.4(15) |
| B2      | 5  | 4024(4) | 1702(4) | 4125.5(12) | 20.9(10) |
| B6      | 5  | 4732(4) | 661(4) | 4156.2(13) | 23.6(11) |
| B11     | 5  | 3934(4) | 953(4) | 4505.7(13) | 23.1(10) |
| O2      | 8  | 4490(5) | 3512(5) | 5239.0(18) | 30.1(15) |
| B7      | 5  | 2898(4) | 1443(4) | 4315.4(13) | 22.7(10) |
| O1      | 8  | 4759(5) | 4284(5) | 5096.7(19) | 38.9(17) |
| C13     | 6  | 9344(6) | 10182(5) | 4658(2) | 64(2) |
| C8      | 6  | 6399(5) | 5083(5) | 5904(2) | 70(2) |
| C7      | 6  | 5619(5) | 5003(5) | 5642(2) | 67(2) |
| C5      | 6  | 6510(6) | 3690(7) | 5071(3) | 101(3) |
| C6      | 6  | 6717(8) | 2840(8) | 4912(3) | 121(4) |
| C10     | 6  | 5043(10) | 2909(9) | 6045(3) | 50(3) |
| C9      | 6  | 5739(10) | 2812(9) | 5735(4) | 43(3) |
| C12     | 6  | 5741(11) | 2550(10) | 5947(5) | 60(4) |
| C11     | 6  | 5072(11) | 2965(9) | 5687(4) | 55(4) |
| C21     | 6  | 8077(11) | 7819(10) | 4354(4) | 65(4) |
| C20     | 6  | 7559(13) | 6892(13) | 5077(5) | 87(6) |
| C2      | 6  | 4296(4) | 1027(5) | 3061.8(13) | 48.9(16) |
| C19     | 6  | 9710(20) | 6930(30) | 4819(8) | 78(8) |
| C17     | 6  | 10431(13) | 7455(13) | 4587(5) | 63(5) |
| C18     | 6  | 10060(30) | 7130(20) | 4728(7) | 102(17) |
| C16     | 6  | 10157(10) | 8183(11) | 4590(3) | 56(3) |
| C15     | 6  | 8724(11) | 10057(12) | 4278(4) | 68(4) |
| C22     | 6  | 7040(7) | 8032(9) | 4401(4) | 160(7) |
| C14     | 6  | 8610(11) | 10596(10) | 4503(3) | 56(3) |
S4 Density functional calculations

Quantum chemical calculations were performed in order to understand the reaction mechanism for the formation of the \([R_3Si]_3S^+\) cations (R = alkyl). Several reactions were considered based on the experimental findings (compounds identified by their crystal structures). Reactions enthalpy and free Reactions energies in solution (dichlorobenzene) using the SMD solvation model were calculated. The corresponding energies for the reaction with CO₂ can be found in Table S16.

**Table S15:** Calculated reaction enthalpies (1 atm, 0 K) and free reactions energies (1 atm, 298 K) in solution (dichlorobenzene) based on PBE0/def2-TVZPP.

| Step | Reaction | \(\Delta H_{(sol.)}\) [kJ/mol] | \(\Delta G_{(sol.)}\) [kJ/mol] |
|------|----------|-------------------------------|--------------------------------|
| 1    | CS₂ + [SiEt₃]⁺ \(\rightarrow\) [Et₃SiS=Si=C=S]⁺ | -40.8 | 2.1 |
| 1.1[a] | CS₂ + [Et₃SiH-SiEt₃]⁺ \(\rightarrow\) [Et₃SiS=Si=C=S]⁺ + Et₃SiH | 42.9 | 30.6 |
| 2    | [Et₃SiS=Si=C=S]⁺ + Et₃SiH \(\rightarrow\) [Et₃SiSCHSSiEt₃]⁺ | -179.9 | -127.8 |
| 3    | [Et₃SiSCHSSiEt₃]⁺ + Et₃SiH \(\rightarrow\) [Et₃SiSCH₃]⁺ + S(SiEt₃)₂ | -9.1 | -11.7 |
| 4    | S(SiEt₃)₂ + [SiEt₃]⁺ \(\rightarrow\) [(Et₃Si)₃S]⁺ | -130.1 | -68.5 |
| 5.1  | [Et₃SiSCH₃]⁺ + Et₃SiH \(\rightarrow\) [(Et₃Si)₂SCH₃]⁺ | -217.6 | -164.3 |
| 5.2[b] | [Et₃SiSCH₃]⁺ + H₂ \(\rightarrow\) [Et₃SiSHCH₃]⁺ | -166.9 | -131.9 |
| Σ    | CS₂ + 2 [SiEt₃]⁺ + 4 Et₃SiH \(\rightarrow\) 2 [(Et₃Si)₃S]⁺ + CH₄ | -675.2 | -453.5 |

[a] Alternative reaction to step 1

[b] Alternative reaction of [Et₃SiSCH₃]⁺ resulting in the crystallized [Et₃SiSHCH₃]⁺ cation.

**Table S16:** Calculated reaction enthalpies (1 atm, 0 K) and free reactions energies (1 atm, 298 K) in solution based on PBE0/def2-TVZPP (1 atm, 298 K).

| Step | Reaction | \(\Delta H_{(sol.)}\) [kJ/mol] | \(\Delta G_{(sol.)}\) [kJ/mol] |
|------|----------|-------------------------------|--------------------------------|
| 1    | CO₂ + [SiEt₃]⁺ \(\rightarrow\) [Et₃SiO=C=O]⁺ | -25.5 | 10.9 |
| 2    | [Et₃SiO=C=O]⁺ + Et₃SiH \(\rightarrow\) [Et₃SiOCHOSiEt₃]⁺ | -216.3 | -159.6 |
| 3    | [Et₃SiOCHOSiEt₃]⁺ + Et₃SiH \(\rightarrow\) [Et₃SiOCH₂]⁺ + O(SiEt₃)₂ | -26.4 | -24.5 |
| 4    | O(SiEt₃)₂ + [SiEt₃]⁺ \(\rightarrow\) [(Et₃Si)₂O]⁺ | -51.1 | 21.7 |
| 5    | [Et₃SiOCH₂]⁺ + Et₃SiH \(\rightarrow\) [(Et₃Si)₂OCH₃]⁺ | -173.7 | -118.0 |
| 6    | [(Et₃Si)₂OCH₃]⁺ + Et₃SiH \(\rightarrow\) [(Et₃Si)₃O]⁺ + CH₄ | -135.2 | -105.7 |
| Σ    | CO₂ + 2 [SiEt₃]⁺ + 4 Et₃SiH \(\rightarrow\) 2 [(Et₃Si)₃O]⁺ + CH₄ | -628.2 | -375.2 |
Table S17: Calculated energies including ZPE and thermal correction to enthalpy on the PBE0/def2-TZVPP level in the gas phase (1 atm, 298 K).

| Structure                  | Energy [Eh]  | Symmetry |
|----------------------------|--------------|----------|
| Et₃SiH                     | -527.246157  | C₃       |
| [Et₃Si]⁺                    | -526.385148  | C₃       |
| Et₃SiSiEt₃                 | -1053.321841 | D₃       |
| [Et₃SiS=C=S]⁺              | -1360.608878 | C₁       |
| [Et₃SiSCHSSiEt₃]⁺          | -1887.928605 | C₂       |
| [Et₃SiSCH₂]⁺               | -963.09428   | C₁       |
| (Et₃Si)₂S                  | -1451.45509  | C₁       |
| [(Et₃Si)₃S]**a             | -1977.914967 | C₁       |
| [Et₃Si(H)Me]**⁺             | -964.928016  | C₁       |
| [(Et₃Si)₂SMe]**⁺            | -1491.05028  | C₁       |
| CH₄                        | -40.426852   | T₄       |
| CS₂                        | -834.194834  | D₆h      |
| H₂                         | -1.155132    | D₆h      |
| [(Et₃Si)₂H]**⁺⁡             | -1053.678047 | D₃       |
| [(Pr₃Si(H)Me)**⁺⁡           | -1082.665841 | C₁       |
| [(Pr₃Si)₂SMe]**⁺            | -1726.513095 | C₁       |
| 'Pr₃SiH                    | -644.982059  | C₃       |
| 'Pr₃SiSPr₃                 | -1288.785031 | D₃       |
| [(Me₃Si)₂SMe]**⁺⁡           | -1255.585838 | C₁       |
| [(Bu₃Si)₂SMe]**⁺⁡           | -1962.037625 | C₁       |
| [Et₃SiO=C=O]**⁺             | -714.853221  | C₁       |
| [Et₃SiOCCHOEt₃]**⁺²⁡        | -1242.187804 | C₁       |
| [Et₃SiOCH₂]**⁺              | -640.827499  | C₁       |
| (Et₃Si)₂O                  | -1128.605939 | C₂       |
| [(Et₃Si)₂O]**⁺              | -1655.033263 | C₁       |
| [(Et₃Si)₂OMe]**⁺            | -1168.154476 | C₁       |
| CO₂                        | -188.451082  | D₆h      |

*a = Structures were optimized starting from experimental (crystal structure) coordinates.

Table S18: SCF energies on the PBE0/def2-TZVPP level in o-dichlorobenze as solvent. Zero-point correction and thermal correction to Gibbs free energy were taken from the gas phase calculations.

| Structure     | SCF-energy [Eh] | ZPE [Eh] | Thermal correct. [Eh] |
|---------------|-----------------|----------|----------------------|
| Et₃SiH        | -527.4697876    | 0.205325 | 0.168779             |
| Species                                      | E (kcal/mol) | σ       | τ       |
|---------------------------------------------|--------------|---------|---------|
| \([\text{Et}_3\text{Si}]^+\)               | -526.6775706 | 0.195717| 0.157933|
| \([\text{Et}_3\text{SiS}=\text{C}=\text{S}]^+\) | -1360.903964 | 0.205707| 0.161092|
| \([\text{Et}_3\text{SiCHSSiEt}_3]^+\)     | -1888.447601 | 0.416217| 0.355039|
| \([\text{Et}_3\text{SiSCH}_2]^+\)         | -964.030438  | 0.225333| 0.182915|
| \((\text{Et}_3\text{Si})_2\text{S}\)       | -1451.892712 | 0.39846 | 0.342219|
| \([(\text{Et}_3\text{Si})_3\text{S}]^+\)   | -1978.624548 | 0.599133| 0.528328|
| \([\text{Et}_3\text{SiS(H)Me}]^+\)        | -1491.590084 | 0.437474| 0.378971|
| \([(\text{Et}_3\text{Si})_2\text{SMe}]^+\) | -40.47505756 | 0.044738| 0.027425 |
| \(\text{CH}_4\)                             | -834.208243  | 0.007099| -0.015799|
| \(\text{CS}_2\)                             | -1.16795364  | 0.010048| -0.001445|
| \(\text{H}_2\)                              | -715.1568967 | 0.210644| 0.16604 |
| \([\text{Et}_3\text{SiO}=\text{C}=\text{O}]^+\) | -1242.715412 | 0.42231 | 0.362758|
| \([\text{Et}_3\text{SiOCHOSiEt}_3]^+\)     | -641.1546921 | 0.228346| 0.1873  |
| \([\text{Et}_3\text{SiOCH}_2]^+\)          | -1129.041071 | 0.3998  | 0.345472|
| \((\text{Et}_3\text{Si})_2\text{O}\)       | -1655.746632 | 0.604056| 0.539658|
| \([(\text{Et}_3\text{Si})_3\text{O}]^+\)   | -1168.698799 | 0.441845| 0.385462|
| \([(\text{Et}_3\text{Si})_2\text{OMe}]^+\) | -188.4665942 | 0.011902| -0.008778|

\(a = \) Optimized structures using crystal atomic coordinates.

**S4.1. Calculated Structures**

The calculated structures used for the suggested reaction mechanism as well as the structures for different alkyl groups R = Me, 'Pr and 'Bu for comparison with the experimental findings are presented herein.
**Figure S35.** Calculated structures (PBE0/Def2-TZVPP) of Et$_3$SiH ($C_3$) and [Et$_3$Si]$^+$ ($C_{3v}$).

**Figure S36.** Calculated structures (PBE0/Def2-TZVPP) of [Et$_3$SiSCS]$^+$ ($C_1$) and [Et$_3$SiSCHSSiEt$_3$]$^+$ ($C_2$).
Figure S37. Calculated structures (PBE0/Def2-TZVPP) of [Et₃SiSCH₂]⁺ (C₁) and (Et₃Si)₂S (C₁).

Figure S38. Calculated structure (PBE0/Def2-TZVPP) of [(Et₃Si)₃S]⁺ (C₁).
Figure S39. Calculated structures (PBE0/Def2-TZVPP) of \([\text{Et}_3\text{SiSHCH}_3]^+\) \((C_i)\) and \([(\text{Et}_3\text{Si})_2\text{SCH}_3]^+\) \((C_i)\).

Figure S40. Calculated structures (PBE0/Def2-TZVPP) of \([\text{iPr}_3\text{SiSHCH}_3]^+\) \((C_i)\) and \([(\text{Me}_3\text{Si})_2\text{SCH}_3]^+\) \((C_i)\).
**Figure S41.** Calculated structure (PBE0/Def2-TZVPP) of [(tBu3Si)2SCH3]+ (C1).

**Figure S42.** Calculated structure (PBE0/Def2-TZVPP) of [Et3SiOCO]+ (C1).
**Figure S43.** Calculated structure (PBE0/Def2-TZVPP) of [Et$_3$SiOCHOSiEt$_3$]$^+$ ($C_1$).

**Figure S44.** Calculated structures (PBE0/Def2-TZVPP) of [Et$_3$SiOCH$_2$]$^+$ ($C_1$) and (Et$_3$Si)$_2$O ($C_2$).
Figure S45. Calculated structure (PBE0/Def2-TZVPP) of \[\text{[(Et}_3\text{Si)}_2\text{OCH}_3]^+\] \text{(C1).}

Figure S46. Calculated structure (PBE0/Def2-TZVPP) of \[\text{[(Et}_3\text{Si)}_3\text{O}]^+\] \text{(C1).}
### S4.2. Comparison with experimental findings

**Table S19**: Comparison of the bond parameters of the crystallized silylium cations with the calculated structures (PBE0/Def2TZVPP) in gas phase.

| Cation                                    | Parameter | Experimental   | Calculated     |
|-------------------------------------------|-----------|----------------|----------------|
| \([\text{Et}_3\text{SiSHCH}_3]^+\)         | Si–S      | 229.84(12) pm  | 232.8 pm       |
|                                           | S–CH\(_3\) | 181.1(3) pm    | 180.8 pm       |
|                                           | Si–S–CH\(_3\) | 108.35(12)°   | 107.86°        |
|                                           | Si–S      | 224.01(10) pm  | 227.7 pm       |
|                                           | S–CH\(_3\) | 182.2(3) pm    | 181.4 pm       |
| \([\text{Et}_3\text{Si})_2\text{SCH}_3]^+\) | Si–S      | 225.31(7) pm   | 226.7 pm       |
|                                           | S–CH\(_3\) | 111.49(3)°     | 112.63°        |
|                                           | Si–S–CH\(_3\) | 110.88(3)°  | 111.96°        |
|                                           | Si–S–Si   | 108.96(3)°     | 111.19°        |
|                                           | Si–S      | 226.15(19) pm  | 228.2 pm       |
|                                           | S–CH\(_3\) | 105.2(2)°      | 109.75°        |
| \([\text{tBu}_3\text{SiSHCH}_3]^+\)      | Si–S      | 226.15(19) pm  | 228.2 pm       |
|                                           | S–CH\(_3\) | 182.8(4) pm    | 181.2 pm       |
|                                           | Si–S–CH\(_3\) | 104.73(18)°  | 104.68°        |
|                                           | Si–S–Si   | 101.12(19)°    | 100.66°        |
|                                           | Si–S      | 116.96(8)°     | 118.31°        |
| \([\text{Me}_3\text{Si})_2\text{SCH}_3]^+\) | Si–S      | 223.3(3) pm    | 226.9 pm       |
|                                           | S–CH\(_3\) | 103.1(3)°      | 104.83°        |
|                                           | Si–S–CH\(_3\) | 100.9(3)°  | 103.59°        |
S4.3. Optimized coordinates

|          | Si–S–Si | 113.94(10)° | 113.78° |
|----------|---------|-------------|---------|
| Et3SiH \((C_3)\) |         |             |         |
| Si  | 0.0000000000000000 | 0.0000000000000000 | 0.2397710000000000 |
| H   | 0.0000000000000000 | 0.0000000000000000 | 1.7382610000000000 |
| C   | 0.6929120000000000 | 1.6504930000000000 | -0.3463400000000000 |
| H   | 0.0000000000000000 | 2.4384340000000000 | -0.0327180000000000 |
| H   | 0.6759730000000000 | 1.6604880000000000 | 1.4227000000000000 |
| C   | 2.0980910000000000 | 1.9652560000000000 | 0.1611050000000000 |
| H   | 2.4431280000000000 | 2.9437700000000000 | 0.0327180000000000 |
| H   | 2.8256500000000000 | 1.2269370000000000 | 1.4422700000000000 |
| C   | 2.1346500000000000 | 1.9694330000000000 | 1.2531510000000000 |
| C   | -1.7758250000000000 | -0.2251670000000000 | -0.3463400000000000 |
| H   | -2.1117460000000000 | -1.2192170000000000 | -0.0327180000000000 |
| H   | -1.7760110000000000 | -0.2448340000000000 | -1.4422700000000000 |
| C   | -2.7510070000000000 | 0.8343720000000000 | 0.1611050000000000 |
| H   | -2.4753840000000000 | 1.8336160000000000 | -0.1834870000000000 |
| H   | -2.7733460000000000 | 0.8636900000000000 | 1.2531510000000000 |
| H   | -3.7709440000000000 | 0.6439260000000000 | -0.1834870000000000 |
| C   | 1.0829130000000000 | -1.4253260000000000 | -0.3463400000000000 |
| H   | 2.1117460000000000 | -1.2192170000000000 | -0.0327180000000000 |
| H   | 1.1003800000000000 | -1.4156540000000000 | -1.4422700000000000 |
| C   | 0.6529160000000000 | -2.7996280000000000 | 0.1611050000000000 |
| H   | 0.6386960000000000 | -2.8336330000000000 | 1.2531510000000000 |
| H   | 1.3278160000000000 | -3.5876960000000000 | -0.1834870000000000 |
| H   | -0.3502660000000000 | -3.0605530000000000 | -0.1834870000000000 |
| [Et3Si]+ \((C_3)\) |         |             |         |
| Si  | 0.0000000000000000 | 0.0000000000000000 | 0.0000450000000000 |
| C   | 0.0000000000000000 | 1.8341570000000000 | 0.0001250000000000 |
| H   | -0.6162020000000000 | 2.1295380000000000 | 0.8627700000000000 |
| H   | -0.6166910000000000 | 2.1296540000000000 | -0.8621210000000000 |
| C   | 1.3510420000000000 | 2.5458390000000000 | -0.0001550000000000 |
| H   | 1.2032810000000000 | 3.6253740000000000 | -0.0001420000000000 |
| H   | 1.9410130000000000 | 2.2967470000000000 | -0.8826740000000000 |
| H   | 1.9413550000000000 | 2.2967590000000000 | 0.8821380000000000 |
| C   | -1.5884270000000000 | -0.9170790000000000 | 0.0001250000000000 |
| H   | -1.5361330000000000 | -1.5984150000000000 | 0.8627700000000000 |
| H   | -1.5359890000000000 | -1.5988970000000000 | -0.8621210000000000 |
| C   | -2.8802820000000000 | -0.1028830000000000 | -0.0001550000000000 |
| H   | -2.9595480000000000 | 0.5325930000000000 | -0.8826740000000000 |
| H   | -2.9597290000000000 | 0.5328830000000000 | 0.8821380000000000 |
| H   | -3.7413070000000000 | -0.7706150000000000 | -0.0001420000000000 |
| C   | 1.5884270000000000 | -0.9170790000000000 | 0.0001250000000000 |
| H   | 2.1523350000000000 | -0.5311220000000000 | 0.8627700000000000 |
| H   | 2.1526800000000000 | -0.5307570000000000 | -0.8621210000000000 |
| C   | 1.5292410000000000 | -2.4429560000000000 | -0.0001550000000000 |
\[
\text{Et}_3\text{SiSiEt}_3 (D_3)
\]

| Element | X   | Y   | Z   | Comment |
|---------|-----|-----|-----|---------|
| Si      | 0.000000000000 | 0.000000000000 | 1.194263000000 |
| C       | 1.354333000000 | 1.134089000000 | 1.887187000000 |
| H       | 2.319463000000 | 0.819992000000 | 2.963903000000 |
| H       | 1.412354000000 | 0.931574000000 | 1.656607000000 |
| C       | 1.157292000000 | 2.629273000000 | 1.656607000000 |
| H       | 1.967568000000 | 3.216010000000 | 2.096756000000 |
| H       | 0.223687000000 | 2.984718000000 | 2.098650000000 |
| H       | 1.122931000000 | 2.873492000000 | 0.592292000000 |
| C       | 0.304984000000 | -1.739931000000 | 1.887187000000 |
| H       | -0.449597000000 | -2.418709000000 | 1.477256000000 |
| H       | 0.100590000000 | -1.688921000000 | 2.963903000000 |
| C       | 1.698371000000 | -2.316881000000 | 2.096756000000 |
| H       | 2.472998000000 | -1.686078000000 | 2.098650000000 |
| H       | 1.927052000000 | -2.409232000000 | 0.592292000000 |
| H       | 1.801362000000 | -3.311969000000 | 2.096756000000 |
| C       | -1.659316000000 | 0.605842000000 | 1.887187000000 |
| H       | -1.869865000000 | 1.598718000000 | 1.477256000000 |
| H       | -1.512944000000 | 0.757347000000 | 2.963903000000 |
| C       | -2.855663000000 | -0.312392000000 | 1.656607000000 |
| H       | -3.049982000000 | -0.464260000000 | 0.592292000000 |
| H       | -3.768930000000 | 0.095959000000 | 2.096756000000 |
| H       | -2.696685000000 | -1.298640000000 | 2.098650000000 |
| Si      | 0.000000000000 | 0.000000000000 | -1.194263000000 |
| C       | -1.354333000000 | 1.134089000000 | -1.887187000000 |
| H       | -2.319463000000 | 0.819992000000 | -1.477256000000 |
| H       | -1.412354000000 | 0.931574000000 | -2.963903000000 |
| C       | -1.157292000000 | 2.629273000000 | -1.656607000000 |
| H       | -1.967568000000 | 3.216010000000 | -2.096756000000 |
| H       | -0.223687000000 | 2.984718000000 | -2.098650000000 |
| H       | -1.122931000000 | 2.873492000000 | -0.592292000000 |
| C       | -0.304984000000 | -1.739931000000 | -1.887187000000 |
| H       | 0.449597000000 | -2.418709000000 | -1.477256000000 |
| H       | -0.100590000000 | -1.688921000000 | -2.963903000000 |
| C       | -1.698371000000 | -2.316881000000 | -1.656607000000 |
| H       | -2.472998000000 | -1.686078000000 | -2.098650000000 |
| H       | -1.927052000000 | -2.409232000000 | -0.592292000000 |
| H       | -1.801362000000 | -3.311969000000 | -2.096756000000 |
| C       | 1.659316000000 | 0.605842000000 | -1.887187000000 |
| H       | 1.869865000000 | 1.598718000000 | -1.477256000000 |
| H       | 1.512944000000 | 0.757347000000 | -2.963903000000 |
| C       | 2.855663000000 | -0.312392000000 | -1.656607000000 |
| H       | 3.049982000000 | -0.464260000000 | -0.592292000000 |
| H       | 2.696685000000 | -1.298640000000 | -2.098650000000 |
| H       | 3.768930000000 | 0.095959000000 | -2.096756000000 |

\[\text{Et}_3\text{SiS=C=S}^+ (C_1)\]

S54
Si -0.9909890000000 -0.005323000000 0.4454790000000
C -2.4668910000000 0.7974450000000 -0.3513270000000
H -2.1971590000000 1.8148830000000 -1.5038510000000
H -3.1202330000000 0.0386150000000 -1.5038510000000
H -4.0000900000000 0.5737120000000 -1.8619240000000
H -3.4440190000000 -0.9590950000000 -1.2052570000000
C -0.0846500000000 1.0118640000000 1.7069770000000
H 0.8656460000000 0.5248400000000 1.9465220000000
H -0.6889680000000 0.9006370000000 2.6187980000000
C 0.1132260000000 2.4912180000000 1.3840450000000
H 0.8374880000000 3.0016840000000 1.2262540000000
H 0.7176930000000 2.6374550000000 0.4865900000000
H 0.6210890000000 2.9978320000000 2.2050710000000
C 0.0984420000000 2.5466070000000 0.5644070000000
H 0.8888170000000 2.5466070000000 2.3587310000000
H 0.1274890000000 -3.5738080000000 -1.5584110000000
H 0.4989990000000 -2.0720920000000 -1.5047550000000
S 0.4047550000000 0.0049850000000 -1.5047550000000
S 3.2940300000000 0.0078740000000 -0.3625880000000

[Et3SiSCH2SiEt3]+ (C2)

Si 0.0000000000000 3.0311000000000 -0.2232650000000
C -0.5645090000000 4.5225730000000 0.7447590000000
H -1.5617650000000 4.3227040000000 1.1404560000000
H -0.6990690000000 5.3237410000000 0.0071650000000
C 0.3719160000000 4.9878030000000 1.8593230000000
C -0.0307490000000 5.8697530000000 2.3587310000000
H 1.3584140000000 5.2530790000000 1.4761930000000
H 0.5107970000000 4.2214620000000 2.6254720000000
C -1.2045580000000 2.4771250000000 -1.5417700000000
H -0.8667610000000 1.5336620000000 -1.9838070000000
H -1.0926030000000 3.2123530000000 -2.3494230000000
C -2.6679780000000 2.3855200000000 -1.1164160000000
H -3.0446360000000 3.3457220000000 -0.7640120000000
H -2.8146330000000 1.6631660000000 -0.3095180000000
H -3.2986840000000 2.0756810000000 -1.9511050000000
C 1.7659760000000 3.1471100000000 -0.8221000000000
H 2.4018810000000 3.4104200000000 0.0282280000000
H 1.7880250000000 4.0225720000000 -1.4840020000000
C 2.3257350000000 1.9287980000000 -1.5500000000000
H 2.3759570000000 1.0550320000000 -0.8953390000000
H 3.3412380000000 2.1173010000000 -1.9011160000000
H 1.7270770000000 1.6638790000000 -2.4241390000000
C 0.0000000000000 0.0000000000000 0.6036530000000
H 0.0000000000000 0.0000000000000 -0.4826960000000
\[
\text{[Et}_3\text{SiSCH}_2]^+ (\text{C}_1)
\]

\begin{tabular}{lcccc}
\hline
Element & x & y & z & \\
\hline
Si & -0.31226700000 & -0.03012000000 & -0.452263000000 & \\
C & -1.79214900000 & -1.13116500000 & -0.195742000000 & \\
H & -1.45000100000 & -2.09823300000 & 0.190149000000 & \\
H & -2.16776600000 & -1.34242300000 & -1.205733000000 & \\
C & -2.91190300000 & -0.55569000000 & 0.670938000000 & \\
H & -3.74303800000 & -1.25819900000 & 0.737001000000 & \\
H & -3.30486100000 & 0.37579400000 & 0.261510000000 & \\
H & -2.58313400000 & -0.35565000000 & 1.693587000000 & \\
C & 1.06586400000 & -0.76077300000 & -1.471109000000 & \\
H & 1.94829200000 & -0.11353400000 & -1.431211000000 & \\
H & 0.70730900000 & -0.65344700000 & -2.504453000000 & \\
C & 1.42553300000 & -2.22014000000 & -1.197089000000 & \\
H & 0.56636000000 & -2.87781500000 & -1.332936000000 & \\
H & 1.79427600000 & -2.37566800000 & -0.180548000000 & \\
H & 2.20550700000 & -2.55930400000 & -1.879186000000 & \\
C & -0.70415300000 & 1.75807000000 & -0.809988000000 & \\
H & -1.38294600000 & 2.13666400000 & -0.039641000000 & \\
H & -1.30624600000 & 1.72770600000 & -1.728366000000 & \\
C & 0.49107500000 & 2.68948100000 & -0.993247000000 & \\
H & 1.09629400000 & 2.76470000000 & -0.086602000000 & \\
H & 0.15655100000 & 3.69883200000 & -1.234715000000 & \\
H & 1.14303500000 & 2.36202900000 & -1.804473000000 & \\
S & 0.47073300000 & 0.10696600000 & 1.728333000000 & \\
C & 2.07546000000 & 0.07753000000 & 1.651300000000 & \\
H & 2.62299500000 & -0.01931300000 & 0.719146000000 & \\
\hline
\end{tabular}
| Atoms | x     | y     | z     |
|-------|-------|-------|-------|
| Si    | 1.862 | 0.082 | 0.027 |
| C     | 3.086 | 0.507 | 1.394 |
| H     | 2.782 | 1.460 | 1.839 |
| C     | 4.050 | 0.695 | 0.905 |
| C     | 3.248 | -0.548 | 2.485 |
| H     | 3.973 | -0.236 | 3.240 |
| H     | 3.594 | -1.500 | 2.075 |
| H     | 2.301 | -0.737 | 2.995 |
| C     | 1.899 | 1.425 | -0.287 |
| H     | 1.910 | 1.161 | -2.079 |
| H     | 2.890 | 1.368 | -1.756 |
| C     | 1.637 | 2.841 | -0.784 |
| H     | 2.398 | 3.155 | -0.090 |
| C     | 1.640 | 2.911 | -0.279 |
| H     | 0.671 | 2.908 | -0.302 |
| C     | 1.636 | 3.567 | -1.600 |
| H     | 2.378 | 3.155 | -2.489 |
| H     | 2.302 | 0.714 | 3.006 |
| Si    | -1.862 | -0.082 | 0.027 |
| C     | -0.086 | -0.518 | 1.390 |
| H     | 2.782 | -1.474 | 1.827 |
| C     | -0.405 | -0.702 | 0.900 |
| C     | -3.248 | 0.528 | 2.489 |
| H     | -3.974 | 0.210 | 3.241 |
| H     | -3.595 | 1.483 | 2.087 |
| H     | -2.302 | 0.714 | 3.006 |
| C     | -1.898 | -1.415 | -1.298 |
| H     | -1.190 | 1.144 | -2.085 |
| H     | -2.889 | 1.355 | -1.766 |
| C     | -1.636 | -2.834 | -0.806 |
| H     | -2.397 | -3.154 | -0.090 |
| H     | -0.670 | -2.906 | -0.302 |
| H     | -1.639 | -3.554 | -1.629 |
| C     | -2.378 | 1.573 | -0.715 |
| H     | -2.093 | 2.363 | -0.012 |
| H     | -3.475 | 1.557 | -0.705 |
| C     | -1.887 | 1.908 | -2.119 |
| H     | -0.800 | 1.994 | -2.159 |
| H     | -2.181 | 1.145 | -2.842 |
| H     | -2.297 | 2.859 | -2.467 |
| S     | -0.000 | -0.004 | 1.119 |

[(EtsSi)S]⁺ (C₁)

| Atoms | x     | y     | z     |
|-------|-------|-------|-------|
| S     | 0.014 | 0.088 | -0.519 |

S57
\[ \text{[Et}_3\text{SiS(H)Me]}^+ (C_1) \]

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Si      | 0.425533000000 | 0.002698000000 | -0.472960000000 |
| S       | -0.647319000000 | 1.656253000000 | -1.564873000000 |
| C       | -1.631628000000 | 1.577074000000 | -1.682898000000 |
| H       | -0.199760000000 | 0.983426000000 | -2.557883000000 |
| C       | -0.802058000000 | 2.524002000000 | -1.168923000000 |
| H       | -1.421697000000 | 3.058824000000 | -1.889255000000 |
| H       | -2.912592000000 | 0.184934000000 | -2.249190000000 |
| C       | 2.900489000000 | -0.002412000000 | 1.022517000000 |
| H       | 2.402936000000 | -0.139982000000 | 1.985421000000 |
| H       | 3.157577000000 | -0.991717000000 | 0.642142000000 |
| C       | 3.835333000000 | 0.523330000000 | 1.218041000000 |
| C       | 0.528799000000 | -1.793668000000 | -0.945380000000 |
| H       | 1.170332000000 | -2.306532000000 | -0.222580000000 |
| H       | 1.095952000000 | -1.797510000000 | -1.885860000000 |
| C       | -0.786655000000 | -2.548527000000 | -1.129027000000 |
| H       | -1.452517000000 | -2.052826000000 | -1.837426000000 |
| H       | -0.602562000000 | -3.554057000000 | -1.508062000000 |
| H       | -1.323123000000 | -2.665322000000 | -0.184281000000 |
| C       | 2.040951000000 | 0.782046000000 | 0.031406000000 |
| H       | 1.848621000000 | 1.796194000000 | 0.396484000000 |
| H       | 2.588718000000 | 0.922316000000 | -0.910078000000 |
| H       | -0.440056000000 | 1.204375000000 | 1.934759000000 |

\[ \text{[Et}_2\text{SiSMe}]}^+ (C_1) \]

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Si      | -1.960878000000 | 0.301469000000 | -0.123502000000 |
| S       | 0.127528000000 | -1.033098000000 | -0.382766000000 |
| Si      | 1.839005000000 | -0.028591000000 | 0.170640000000 |
| C       | -0.311629000000 | -2.298703000000 | 0.904002000000 |
H  -0.221994000000  -1.867762000000  1.897865000000
H   0.462568000000  -3.044736000000  0.739686000000
H  -1.287547000000  -2.762165000000  0.782404000000
C   -2.317768000000  0.399160000000  1.708493000000
H  -2.409014000000  -0.616488000000  2.117736000000
H  -1.468299000000  0.857156000000  2.218676000000
C  -3.727445000000  -1.956595000000 -0.649152000000
H  -2.943760000000  -2.702760000000 -0.795534000000
C  -3.280406000000  -0.572847000000  1.113208000000
H  -4.133123000000  0.739686000000  2.158045000000
H  -3.654774000000  1.527359000000  1.374339000000
C   3.855539000000  2.209640000000  0.547299000000
C  -3.601041000000  1.181765000000  1.996601000000
H  -4.473860000000  0.721462000000  1.529871000000
H   2.235098000000  0.370653000000  2.227226000000
H  -1.036671000000  0.254934000000  2.467800000000
H   1.510400000000  0.908867000000  1.767545000000
H  -1.335429000000  1.271514000000  2.756480000000
C   1.568719000000  0.908867000000  1.767545000000
H   0.900024000000  1.753186000000  1.573152000000
H  -1.036671000000  0.254934000000  2.466555000000
H  -3.537723000000  2.211050000000  1.638906000000
H  -3.792361000000  1.223884000000  3.069573000000
H  -4.013603000000  1.967281000000  0.404678000000
H  -4.592268000000  -2.295481000000  1.220775000000
H  -1.057290000000  2.961721000000  2.749745000000
H  -2.269137000000  1.699876000000  2.900271000000
H   3.839003000000  2.076735000000  2.293720000000
H   4.389312000000  0.721551000000  2.227226000000
H   2.645041000000  1.926897000000  3.353577000000
H   3.537621000000  0.580879000000  2.661249000000
H   3.531989000000  -1.819588000000  1.712510000000
H   3.892422000000  -3.173810000000  0.651934000000

CH₄ (Tₐ)

C  0.000000000000  0.000000000000  0.000000000000
H  0.628669000000  0.628669000000  0.628669000000
H  -0.628669000000  -0.628669000000  0.628669000000
H  0.628669000000  -0.628669000000  0.628669000000

S60
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | -0.628669000000 | 0.628669000000 | -0.628669000000 |

**CS$_2$ ($D_{ch}$)**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 0.000000000000 | 0.000000000000 | 0.000000000000 |
| S    | 0.000000000000 | 0.000000000000 | 1.548469000000 |
| S    | 0.000000000000 | 0.000000000000 | -1.548469000000 |

**H$_2$ ($D_{ch}$)**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | 0.000000000000 | 0.000000000000 | 0.372581000000 |
| H    | 0.000000000000 | 0.000000000000 | -0.372581000000 |

**[(Et$_3$Si)$_2$H]$^+$ ($D_3$)**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Si   | 0.000000000000 | 0.000000000000 | 1.641523000000 |
| C    | 1.427439000000 | 1.125116000000 | 2.036460000000 |
| H    | 2.322548000000 | 0.749969000000 | 1.531292000000 |
| H    | 1.619296000000 | 0.965859000000 | 3.106563000000 |
| C    | 1.221655000000 | 2.612056000000 | 1.757828000000 |
| H    | 2.098916000000 | 3.185811000000 | 2.058437000000 |
| H    | 0.367872000000 | 3.013350000000 | 2.305811000000 |
| H    | 1.054418000000 | 2.809049000000 | 0.696911000000 |
| C    | 0.260660000000 | -1.798756000000 | 2.036460000000 |
| H    | -0.511782000000 | -2.386370000000 | 0.696911000000 |
| H    | 0.026810000000 | -1.885281000000 | 2.305811000000 |
| C    | 1.651280000000 | -2.364012000000 | 1.757828000000 |
| H    | 2.425702000000 | -1.825261000000 | 2.058437000000 |
| H    | 1.905499000000 | -2.317677000000 | 0.696911000000 |
| H    | 1.709535000000 | -3.410620000000 | 2.058437000000 |
| C    | -1.688099000000 | 0.673640000000 | 2.036460000000 |
| H    | -1.810766000000 | 1.636401000000 | 1.531292000000 |
| H    | -1.646106000000 | 0.919422000000 | 3.106563000000 |
| C    | -2.872934000000 | -0.248044000000 | 1.757828000000 |
| H    | -2.959917000000 | -0.491372000000 | 0.696911000000 |
| H    | -3.808451000000 | 0.224809000000 | 2.305811000000 |
| H    | -2.793574000000 | -1.188088000000 | 2.305811000000 |
| H    | 0.000000000000 | 0.000000000000 | 0.000000000000 |

**Si**

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -1.427439000000 | 1.125116000000 | -2.036460000000 |
| H    | -2.322548000000 | 0.749969000000 | -1.531292000000 |
| H    | -1.619296000000 | 0.965859000000 | -3.106563000000 |
| C    | -1.221655000000 | 2.612056000000 | -1.757828000000 |
| H    | -2.098916000000 | 3.185811000000 | -2.058437000000 |
| H    | -0.367872000000 | 3.013350000000 | -2.305811000000 |
| H    | -1.054418000000 | 2.809049000000 | -0.696911000000 |
| C    | -0.260660000000 | -1.798756000000 | -2.036460000000 |
| H    | 0.511782000000 | -2.386370000000 | -1.531292000000 |
| H    | -0.026810000000 | -1.885281000000 | -3.106563000000 |
| C    | -1.651280000000 | -2.364012000000 | -1.757828000000 |
| H    | -2.425702000000 | -1.825261000000 | -2.305811000000 |
| H    | -1.905499000000 | -2.317677000000 | -0.696911000000 |
| H    | -1.709535000000 | -3.410620000000 | -2.058437000000 |
| C    | 1.688099000000 | 0.673640000000 | -2.036460000000 |
\[ [\text{PrSiS(H)Me}]^{\text{rd}} (C_1) \]

\[
\begin{array}{cccc}
\text{Si} & -0.157740000000 & 0.002229000000 & -0.022872000000 \\
C & -1.315638000000 & -1.007267000000 & -1.106306000000 \\
H & -0.768928000000 & -1.937892000000 & -1.306935000000 \\
C & -1.600876000000 & -0.324313000000 & -2.444505000000 \\
H & 2.369610000000 & -1.947807000000 & 0.532102000000 \\
H & 2.793574000000 & -0.696911000000 & -2.305811000000 \\
C & 2.872934000000 & -0.248044000000 & -1.757828000000 \\
H & 2.959917000000 & -0.491372000000 & -0.696911000000 \\
H & 2.793574000000 & -1.188088000000 & -2.305811000000 \\
H & 3.808451000000 & 0.224809000000 & -2.058437000000 \\
\end{array}
\]

\[ [(\text{PrSi})_2\text{SMe}]^{\text{C}_1} \]

\[
\begin{array}{cccc}
\text{Si} & 2.140212000000 & 0.035486000000 & -0.014322000000 \\
S & 0.000678000000 & -0.357798000000 & -0.822679000000 \\
Si & -2.077667000000 & 0.059528000000 & 0.084289000000 \\
C & 0.006999000000 & 0.564155000000 & -2.383070000000 \\
\end{array}
\]
|   |   |   |   |
|---|---|---|---|
| H | -2.5964950000000 | 1.2681480000000 | -2.9852810000000 |
| H | -4.3350820000000 | 1.1335030000000 | -2.8381960000000 |
| H | -3.4354260000000 | 2.1236650000000 | -1.6976090000000 |
| C | -1.6872600000000 | -2.6922480000000 | 0.9805190000000 |
| H | -2.0844640000000 | -3.1112820000000 | 0.0545820000000 |
| H | -0.6043600000000 | -2.6271480000000 | 0.8720880000000 |
| H | -1.8934340000000 | -3.4130270000000 | 1.7758040000000 |
| C | 1.0944190000000 | 2.8897110000000 | -0.1455640000000 |
| H | 2.0883030000000 | 3.8219280000000 | -0.6430290000000 |
| H | 0.7319620000000 | 2.7606420000000 | -0.2687260000000 |
| H | 2.0033990000000 | 3.0270310000000 | 0.9205850000000 |
| H | -4.0541680000000 | -1.3585170000000 | -2.9030390000000 |

\[ \text{Pr}_3\text{SiH} (C_3) \]

|   |   |   |   |
|---|---|---|---|
| Si | 0.0000000000000 | 0.0000000000000 | 0.7021880000000 |
| H | 0.0000000000000 | 0.0000000000000 | 2.2013700000000 |
| C | 1.2997600000000 | 1.2953810000000 | -0.2116760000000 |
| H | 2.1790480000000 | 1.0146500000000 | 0.8069050000000 |
| C | 0.8672050000000 | 2.6882640000000 | 0.6686700000000 |
| C | 1.7248360000000 | 1.3062190000000 | -1.2549140000000 |
| H | 2.1404600000000 | 0.3475470000000 | -0.1570429000000 |
| H | 0.8904090000000 | 1.5367990000000 | -0.9213700000000 |
| H | 2.4932240000000 | 2.0670550000000 | -1.4273850000000 |
| H | 0.0000000000000 | 3.0425120000000 | 0.1045540000000 |
| H | 1.6698580000000 | 3.4168340000000 | 0.5162460000000 |
| H | 0.6002790000000 | 2.7078970000000 | 1.7282180000000 |
| C | 0.4719530000000 | -1.7733160000000 | 0.2116760000000 |
| H | -0.2108110000000 | -2.3944360000000 | 0.8069050000000 |
| C | 1.8945020000000 | -2.0951540000000 | 0.6686700000000 |
| C | 0.2688010000000 | -2.1468610000000 | -1.2549140000000 |
| H | -0.7692450000000 | -2.0274660000000 | -1.5704290000000 |
| H | 0.8857020000000 | -1.5395160000000 | -1.9213700000000 |
| H | 0.5435100000000 | -3.1927230000000 | -1.4273850000000 |
| H | 2.6348930000000 | -1.5212560000000 | 0.1045540000000 |
| H | 2.1241360000000 | -3.1545560000000 | 0.5162460000000 |
| H | 2.0449680000000 | -1.8738060000000 | 1.7282180000000 |
| C | -1.7717130000000 | 0.4779350000000 | 0.2116760000000 |
| H | -1.9682370000000 | 1.3797850000000 | 0.8069050000000 |
| C | -2.7617080000000 | -0.5931100000000 | 0.6686700000000 |
| C | -1.9936370000000 | 0.8406420000000 | -1.2549140000000 |
| H | -1.3712150000000 | 1.6799190000000 | -1.5704290000000 |
| H | -1.7761110000000 | 0.0027170000000 | -1.9213700000000 |
| H | -3.0367340000000 | 1.1256680000000 | -1.4273850000000 |
| H | -2.6348930000000 | -1.5212560000000 | 0.1045540000000 |
| H | -3.7939940000000 | -0.2622770000000 | 0.5162460000000 |
| H | -2.6452470000000 | -0.8340910000000 | 1.7282180000000 |

\[ \text{Pr}_3\text{SiSiPr}_3 (D_3) \]

|   |   |   |   |
|---|---|---|---|
| Si | 0.0000000000000 | 0.0000000000000 | 1.2130180000000 |
| Si | 0.0000000000000 | 0.0000000000000 | -1.2130180000000 |
| C | -1.6876770000000 | 0.6922720000000 | -1.8192560000000 |

S64
C     2.853658000000  -0.252756000000  1.531120000000
C     1.734120000000  1.146721000000  3.278667000000
H     0.998265000000  1.921228000000  3.496523000000
H     1.557799000000  0.322507000000  3.972481000000
H     2.720749000000  1.560153000000  3.278667000000
H     2.774083000000  -1.181239000000  2.102150000000
H     3.804425000000  0.213560000000  1.809703000000
H     2.922067000000  -0.524978000000  0.476625000000

\[(\text{Me}_3\text{Si})_2\text{SMe}]^{\#a} (C_1)

S     0.000665000000  0.709214000000  -0.721604000000
Si    -1.899911000000  -0.272012000000  0.041443000000
Si     1.902164000000  -1.899911000000  -0.041443000000
C     1.706042000000  -0.696023000000  1.835168000000
H     1.452527000000   0.169094000000  2.450991000000
H     2.720749000000   1.560153000000  3.278667000000
H     2.774083000000  -1.181239000000  2.102150000000
H     3.804425000000   0.213560000000  1.809703000000
H     2.922067000000  -0.524978000000  0.476625000000

\[(\text{tBu}_3\text{Si})_2\text{SMe}]^{\#a} (C_1)

Si     1.991102000000  0.236090000000  -0.157385000000
S     -1.914549000000  -0.201682000000  0.025548000000
Si    -1.088720000000  -2.457821000000  1.007657000000
Si     0.582205000000  -1.808809000000  2.519546000000
C     2.267983000000  -1.385032000000  -1.063722000000

S66
| Atom | X       | Y       | Z       | Coordinates       |
|------|---------|---------|---------|-------------------|
| H    | -3.000416000000 | -1.759171000000 | 1.497310000000 |
| C    | -2.189229000000 | -3.827132000000 | -0.419781000000 |
| H    | -2.885803000000 | -4.666751000000 | -0.401412000000 |
| H    | -2.064794000000 | -3.486893000000 | 0.610575000000 |
| H    | -1.224242000000 | -4.209931000000 | -0.766108000000 |
| C    | -3.326538000000 | 1.488113000000  | 2.697915000000  |
| H    | -4.347724000000 | 1.646643000000  | 2.341053000000  |
| H    | -2.650413000000 | 2.045571000000  | 2.046962000000  |
| H    | -3.257537000000 | 1.928290000000  | 3.693993000000  |
| C    | 1.662019000000  | 3.092915000000  | -0.865732000000 |
| H    | 1.287178000000  | 3.167972000000  | 0.163133000000  |
| C    | 0.797857000000  | 3.993368000000  | -1.740848000000 |
| H    | 1.122529000000  | 3.941110000000  | -2.783647000000 |
| H    | 0.873689000000  | 5.035056000000  | -1.423320000000 |
| H    | -0.255220000000 | 3.708631000000  | -1.703481000000 |
| C    | -4.286408000000 | 0.941180000000  | -2.013888000000 |
| H    | -5.315882000000 | 1.241872000000  | -2.214411000000 |
| H    | -4.319701000000 | -0.088631000000 | -1.644690000000 |
| H    | -3.753817000000 | 0.935022000000  | -2.969224000000 |
| C    | -2.866132000000 | -3.273131000000 | -2.758640000000 |
| H    | -1.907529000000 | -3.598874000000 | -3.172043000000 |
| H    | -3.280882000000 | -2.518237000000 | -3.429580000000 |
| H    | -3.539240000000 | -4.132503000000 | -2.764377000000 |
| C    | -1.735171000000 | -1.516437000000 | -1.363972000000 |
| H    | -1.874686000000 | -0.961448000000 | -2.298597000000 |
| H    | -0.701538000000 | -1.877280000000 | -1.400135000000 |

[Et₃SiO=C=O]⁺ (C₁)

| Atom | X       | Y       | Z       | Coordinates       |
|------|---------|---------|---------|-------------------|
| Si   | -0.595639000000 | -0.002519000000 | -0.395526000000 |
| C    | -1.488426000000 | -1.553611000000 | 0.052080000000  |
| H    | -0.769060000000 | -2.379011000000 | 0.059507000000  |
| H    | -2.140619000000 | -1.759512000000 | -0.808787000000 |
| C    | -2.308331000000 | -1.518120000000 | 1.342163000000  |
| H    | -2.810812000000 | -2.472738000000 | 1.497083000000  |
| H    | -3.077716000000 | -0.745748000000 | 1.313157000000  |
| H    | -1.682723000000 | -1.334484000000 | 2.217342000000  |
| C    | 0.558439000000  | -0.061889000000 | -1.839357000000 |
| H    | 1.214126000000  | 0.814893000000  | -1.805118000000 |
| H    | -0.087777000000 | 0.115654000000  | -2.711030000000 |
| C    | 1.355470000000  | -1.351771000000 | -2.034803000000 |
| H    | 0.703941000000  | -2.219095000000 | -2.145313000000 |
| H    | 2.033619000000  | -1.554394000000 | -1.202123000000 |
| H    | 1.969324000000  | -1.287376000000 | -2.933075000000 |
| C    | 1.416738000000  | 1.606415000000  | -0.020479000000 |
| H    | 1.797402000000  | 1.563617000000  | 1.005124000000  |
| H    | -2.315919000000 | 1.615314000000  | -0.652880000000 |
| C    | -0.592050000000 | 2.871544000000  | -0.255540000000 |
| H    | 0.289966000000  | 2.909740000000  | 0.386962000000  |
| H    | -1.186255000000 | 3.757898000000  | -0.033881000000 |
| H    | -0.257440000000 | 2.954796000000  | -1.290282000000 |

S68
| Element | Atomic Position | X-C | Y-C | Z-C |
|---------|-----------------|-----|-----|-----|
| C       | 1.907583000000 | 0.004340000000 | 1.318240000000 |
| O       | 0.748906000000 | 0.001130000000 | 1.108976000000 |
| O       | 3.020846000000 | 0.008152000000 | 1.549374000000 |

$$\text{[Et}_3\text{SiOCHOSiEt}_3]^+ \ (C_1)$$

| Si     | 2.440868000000 | -0.047458000000 | 0.059155000000 |
|--------|-----------------|------------------|-----------------|
| C      | 0.041506000000 | -0.072532000000 | -1.332509000000 |
| O      | 0.748906000000 | 0.001130000000 | 1.108976000000 |
| C      | 3.020846000000 | 0.008152000000 | 1.549374000000 |

S69
### [Et₃SiOCH₃]$^+$ (C₁)

| Element | X | Y | Z |
|---------|---|---|---|
| Si      | -0.154986000000 | -0.018797000000 | -0.323852600000 |
| C       | -1.620132000000 | -1.148822000000 | -0.351690000000 |
| H       | -1.338904000000 | -2.907630000000 | 0.131082000000 |
| H       | -1.775401000000 | -1.407194000000 | 0.187373000000 |
| C       | -2.907956000000 | -0.588251000000 | 0.252893000000 |
| H       | -3.710345000000 | -0.154986000000 | 1.306955000000 |
| H       | -2.277389000000 | -0.154986000000 | 1.306955000000 |
| C       | 1.431256000000  | -0.721801000000 | 0.461457000000 |
| H       | 2.267542000000  | 0.057670000000 | -0.743097000000 |
| H       | 1.338467000000  | -0.632186000000 | -0.743097000000 |
| C       | 1.743385000000  | -2.081820000000 | -0.617023000000 |
| H       | 0.960544000000  | -0.018797000000 | 1.306955000000 |
| H       | 1.849587000000  | -2.318101000000 | 0.461457000000 |
| C       | -0.465244000000 | 1.771328000000 | -1.075960000000 |
| H       | -1.321304000000 | 2.104681000000 | -0.105076000000 |
| H       | -0.812986000000 | 1.793291000000 | -1.740721000000 |
| C       | 0.724888000000  | 2.712006000000 | -0.523248000000 |
| H       | 1.081363000000  | 2.737693000000 | -0.510760000000 |
| H       | 0.447085000000  | 3.734555000000 | -0.780214000000 |
| H       | 1.564960000000  | 2.434597000000 | -1.161638000000 |
| O       | 0.139814000000  | 0.101165000000 | 1.512107000000 |
| C       | 1.186932000000  | 0.093002000000 | 2.143130000000 |
| H       | 2.153087000000  | -0.335910000000 | 1.644090000000 |
| H       | 1.141230000000  | 0.213944000000 | 3.228614000000 |

### (Et₃Si)₂O (C₂)

| Element | X | Y | Z |
|---------|---|---|---|
| Si      | 1.636781000000 | 0.016215000000 | -0.000446000000 |
| C       | 2.244988000000 | 0.045450000000 | 1.776516000000 |
| H       | 1.903540000000 | 0.985479000000 | 2.216004000000 |
| H       | 3.339391000000 | 0.106733000000 | 1.758642000000 |
| C       | 1.803606000000 | -1.127833000000 | 2.653505000000 |
| H       | 2.160231000000 | -1.022343000000 | 3.681025000000 |
| H       | 2.183020000000 | -2.079939000000 | 2.275457000000 |
| H       | 0.714759000000 | -1.206210000000 | 2.693280000000 |
| C       | 2.262331000000 | 1.483655000000 | -0.943391000000 |
| H       | 1.899527000000 | 1.409043000000 | -1.974448000000 |
| H       | 3.354537000000 | 1.404826000000 | -1.011679000000 |
| C       | 1.869922000000 | 2.835913000000 | -0.352795000000 |
| H       | 2.278658000000 | 2.970089000000 | 0.651371000000 |
| H       | 0.784584000000 | 2.935867000000 | -0.276477000000 |
| H       | 2.231469000000 | 3.666926000000 | -0.963345000000 |
| C       | 2.234708000000 | -1.588250000000 | -0.839037000000 |
| H       | 1.909497000000 | -2.443002000000 | -0.235798000000 |

S70
|    |                |                |
|----|----------------|----------------|
| H  | 3.330318000000 | -1.595052000000 | -0.790000000000 |
| C  | 1.775415000000 | -1.768396000000 | -2.284182000000 |
| H  | 0.685613000000 | -1.770385000000 | -2.357215000000 |
| H  | 2.133107000000 | -2.709301000000 | -2.709301000000 |
| H  | 2.141645000000 | -0.963360000000 | -2.925548000000 |
| Si | -1.636702000000 | 0.015840000000 | -0.002514000000 |
| C  | -2.245664000000 | 0.147648000000 | 1.770260000000 |
| H  | -1.904542000000 | -0.743962000000 | 2.308189000000 |
| H  | -3.340071000000 | 0.080835000000 | 1.758630000000 |
| C  | -1.805082000000 | 1.404009000000 | 2.517823000000 |
| H  | -2.162797000000 | 1.408830000000 | 3.550355000000 |
| H  | -2.184067000000 | 2.310282000000 | 2.039874000000 |
| H  | -0.716277000000 | 1.486287000000 | 2.550196000000 |
| C  | -2.262558000000 | -1.575784000000 | -0.780767000000 |
| H  | -1.899603000000 | -1.610873000000 | -1.814041000000 |
| H  | -3.354318000000 | -1.505195000000 | -0.856668000000 |
| C  | -1.868981000000 | -2.857597000000 | -0.500770000000 |
| H  | -2.277325000000 | -2.884480000000 | 0.962804000000 |
| H  | -0.783608000000 | -2.948733000000 | 0.035982000000 |
| H  | -2.230590000000 | -3.748805000000 | -0.568780000000 |
| C  | -2.234126000000 | 1.490052000000 | -1.003300000000 |
| H  | -1.908548000000 | 2.403878000000 | -0.494222000000 |
| H  | -3.329736000000 | 1.502328000000 | -0.955090000000 |
| C  | -1.775125000000 | 1.515679000000 | -2.459527000000 |
| H  | -0.685347000000 | 1.509216000000 | -2.532656000000 |
| H  | -2.142053000000 | 0.647477000000 | -3.011912000000 |
| H  | -2.132352000000 | 2.406452000000 | -2.981898000000 |
| O  | 0.000078000000 | -0.000189000000 | -0.001433000000 |

|    |                |                |
|----|----------------|----------------|
| O  | -0.008280000000 | 0.041457000000 | 0.040230000000 |
| Si | -1.712151000000 | -0.591581000000 | -0.021747000000 |
| Si | 0.298033000000 | 1.793906000000 | -0.332439000000 |
| Si | 1.377345000000 | -1.128511000000 | -0.065502000000 |
| C  | -2.921700000000 | 0.835715000000 | 0.070026000000 |
| H  | -2.870322000000 | 1.306860000000 | 1.053818000000 |
| H  | -2.697920000000 | 1.612440000000 | -0.662095000000 |
| C  | -0.336878000000 | 2.035593000000 | -2.079272000000 |
| H  | 0.411392000000 | 1.627444000000 | -2.766701000000 |
| H  | -1.245279000000 | 1.457992000000 | -2.262396000000 |
| C  | -1.838706000000 | -1.457363000000 | -1.683866000000 |
| H  | -2.237047000000 | -0.726030000000 | -2.395532000000 |
| H  | -0.840094000000 | -1.699982000000 | -2.057316000000 |
| C  | 2.598157000000 | -0.735881000000 | 1.289136000000 |
| H  | 3.332993000000 | -1.546825000000 | 1.201630000000 |
| H  | 3.161942000000 | 0.170557000000 | 1.071419000000 |
| C  | 3.573006000000 | -1.146048000000 | -1.919552000000 |
| H  | 3.896723000000 | -2.116818000000 | -1.541723000000 |
| H  | 4.119159000000 | -0.383348000000 | -1.360833000000 |
| C  | -2.054153000000 | -1.701066000000 | 1.441320000000 |
| H  | -3.090314000000 | -2.011570000000 | 1.249474000000 |

\[ ([\text{Et}_3\text{Si}]\text{O})^+ (\text{C}_1) \]
| Atom | Coordinates | Bond Lengths | Angle (°) |
|------|-------------|--------------|----------|
| C    | -1.482637000000 | -2.625980000000 | 1.390655000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.531618000000 | -3.015526000000 | 1.271817000000 |
| C    | -0.135867000000 | -3.104940000000 | -0.346213000000 |
| C    | -0.584803000000 | 3.509450000000 | -2.411949000000 |
| H    | -1.381697000000 | 3.935909000000 | -1.799819000000 |
| H    | -0.876390000000 | 3.628060000000 | -3.456231000000 |
| H    | 0.307191000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |
| H    | 0.531618000000 | -3.015526000000 | 1.271817000000 |
| H    | -0.135867000000 | -3.104940000000 | -0.346213000000 |
| C    | -0.584803000000 | 3.509450000000 | -2.411949000000 |
| H    | -1.381697000000 | 3.935909000000 | -1.799819000000 |
| H    | -0.876390000000 | 3.628060000000 | -3.456231000000 |
| H    | 0.307191000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |
| H    | 0.531618000000 | -3.015526000000 | 1.271817000000 |
| H    | -0.135867000000 | -3.104940000000 | -0.346213000000 |
| C    | -0.584803000000 | 3.509450000000 | -2.411949000000 |
| H    | -1.381697000000 | 3.935909000000 | -1.799819000000 |
| H    | -0.876390000000 | 3.628060000000 | -3.456231000000 |
| H    | 0.307191000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |
| H    | 0.531618000000 | -3.015526000000 | 1.271817000000 |
| H    | -0.135867000000 | -3.104940000000 | -0.346213000000 |
| C    | -0.584803000000 | 3.509450000000 | -2.411949000000 |
| H    | -1.381697000000 | 3.935909000000 | -1.799819000000 |
| H    | -0.876390000000 | 3.628060000000 | -3.456231000000 |
| H    | 0.307191000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |
| H    | 0.531618000000 | -3.015526000000 | 1.271817000000 |
| H    | -0.135867000000 | -3.104940000000 | -0.346213000000 |
| C    | -0.584803000000 | 3.509450000000 | -2.411949000000 |
| H    | -1.381697000000 | 3.935909000000 | -1.799819000000 |
| H    | -0.876390000000 | 3.628060000000 | -3.456231000000 |
| H    | 0.307191000000 | -2.879216000000 | 0.215148000000 |
| C    | 0.771911000000 | -2.879216000000 | 0.215148000000 |

\[ \text{CO}_2 (D_{\text{eh}}) \]

| Element | Coordinates | Bond Lengths | Angle (°) |
|---------|-------------|--------------|----------|
| C       | 0.000000000000 | 0.000000000000 | 0.000000000000 |
| O       | 0.000000000000 | 0.000000000000 | 1.156797000000 |
| O       | 0.000000000000 | 0.000000000000 | -1.156797000000 |

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S5 Literature

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