

Electronic Supplementary Information

Unusually Selective Synthesis of Chlorohydroooligosilanes

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1. General Considerations

Due to the sensitivity of starting materials and products all experiments were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system.¹ Neopentasilane $\text{Si}(\text{SiH}_3)_4$, Dodecachloroneopentasilane $\text{Si}(\text{SiCl}_3)_4$, Hexachlorodisilane Si_2Cl_6 and Octachlorotrisilane Si_3Cl_8 were kindly provided by Evonik Creavis GmbH. Nonachloroisotetrasilane $\text{Cl}(\text{Si}(\text{SiCl}_3)_3)$ was synthesized according to published procedures.² Commercially available chemicals were used without further purification unless otherwise noted.

^1H (299.95 MHz) and ^{29}Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer in C_6D_6 or with a D_2O capillary as an internal lock and referenced versus TMS using the internal ^2H -lock signal of the solvent.

2. Synthetic Procedures

2.1. Chlorination of Neopentasilane with HCl/AlCl_3

1.0 g (6.58 mmol) of $\text{Si}(\text{SiH}_3)_4$ were dissolved in 15.0 mL of benzene and a catalytic amount of AlCl_3 was added. The reaction solution was heated to 70°C and subsequently anhydrous gaseous HCl was bubbled through for 15 min. After evaporation of the solvent in vacuo 15 mL of *n*-pentane were added and the precipitated AlCl_3 was filtered off. Subsequent evaporation of the solvent at room temperature in vacuo followed by recondensation of the resulting crude product at 80°C and 0.01 mbar afforded 1.2 g of a mixture of $\text{Si}(\text{SiH}_2\text{Cl})_4$ (85 %) and $(\text{H}_2\text{ClSi})_3\text{SiH}_3$ (15 %) as determined by integration of the ^1H -NMR signals as a colorless liquid.

$\text{Si}(\text{SiH}_2\text{Cl})_4$: ^1H NMR (C_6D_6 , TMS, ppm): 4.87 (s, SiH_2Cl). ^{29}Si NMR (C_6D_6 , TMS, ppm): -125.0 (SiSi_4), -24.5 (SiH_2Cl).

$\text{H}_3\text{SiSi}(\text{SiH}_2\text{Cl})_3$: ^1H NMR (C_6D_6 , TMS, ppm): 4.86 (s, SiH_2Cl , 6H), 3.37 (s, SiH_3 , 3H). ^{29}Si NMR (C_6D_6 , TMS, ppm): -130.7 (SiSi_4), -98.5 (SiH_3), -25.9 (SiH_2Cl)

Figure S1. ^1H -NMR spectrum (Si-H region; 300 MHz, C_6D_6 solution) of product mixture obtained after chlorination of $\text{Si}(\text{SiH}_3)_4$ with HCl/AlCl_3 (volatile fraction obtained after recondensation of crude product at 80°C and 0.01 mbar)

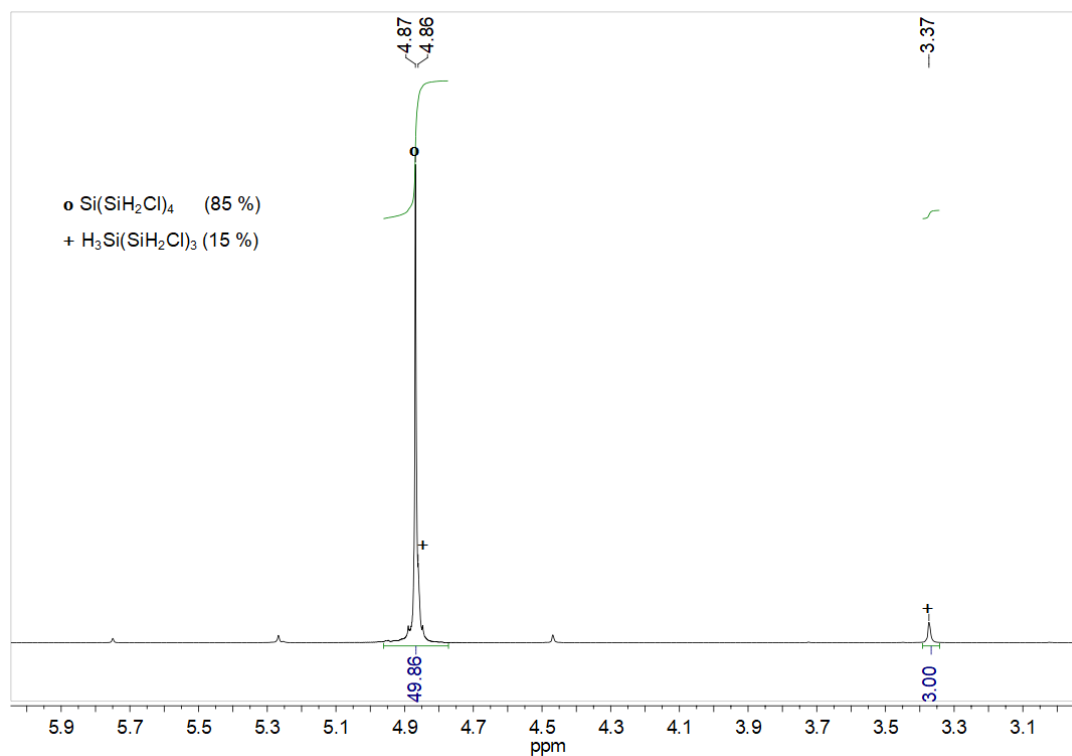
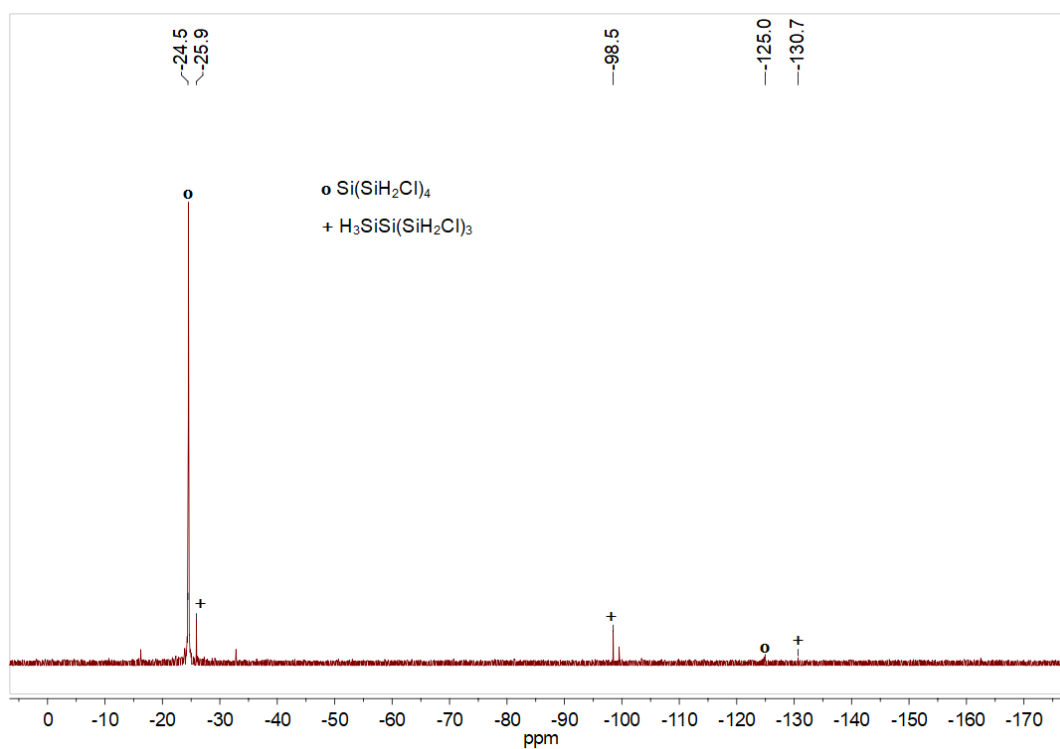


Figure S2. bb-decoupled INEPT ^{29}Si -NMR spectrum (60 MHz, C_6D_6 solution) of product mixture obtained after chlorination of $\text{Si}(\text{SiH}_3)_4$ with HCl/AlCl_3 (volatile fraction obtained after recondensation of crude product at 80°C and 0.01 mbar).



2.2. Partial Hydrogenation of Hexachlorodisilane with *i*Bu₂AlH

19.8 mL (110.0 mmol, 3.0 equiv.) of neat *i*Bu₂AlH were slowly added to 10.0 g (37.0 mmol, 1.0 equiv.) of Si₂Cl₆ at 0°C. The resulting mixture was allowed to warm to room temperature and stirred overnight. Subsequently the volatile components were separated by trap to trap distillation at room temperature and 0.01 mbar to give 4.5 g (70 %) of a clear and colorless liquid. NMR analysis of the volatile fraction showed the formation of H₃SiSiCl₃ (**4**, 55 %), H₂ClSiSiCl₃ (39 %) and H₃SiSiH₃ (**7**, 6 %) as the major products along with small amounts of other Cl/H-disilanes and *i*Bu₂AlCl. Relative amounts of the major products were determined by integration of the ¹H-NMR signals.

Si₂H₆: ¹H NMR: (C₆D₆, TMS, ppm): 3.12 (s, SiH₃, 6H) ²⁹Si NMR: (C₆D₆, TMS, ppm): -101.5 (q, ¹J_{SiH} = 192 Hz; SiH₃)

H₃SiSiCl₃: ¹H NMR: (C₆D₆, TMS, ppm): 3.20 (H₃SiSiCl, 3H) ²⁹Si NMR: (C₆D₆, TMS, ppm): -84.9 (q, ¹J_{SiH} = 216 Hz; SiH₃), 12.9 (m, SiCl₃)

H₂ClSiSiCl₃: ¹H NMR (C₆D₆, TMS, ppm): 4.28 (H₂ClSiSiCl₃, 2H) ²⁹Si NMR (C₆D₆, TMS, ppm): -32.3 (t, ¹J_{SiH} = 248 Hz; SiH₂Cl), 3.9(m, SiCl₃)

Figure S3. ¹H-NMR spectrum (Si-H region, 300 MHz, C₆D₆ solution) of product mixture obtained after partial hydrogenation of Si₂Cl₆ (volatile fraction obtained after recondensation of crude product at 25° C and 0.01 mbar)

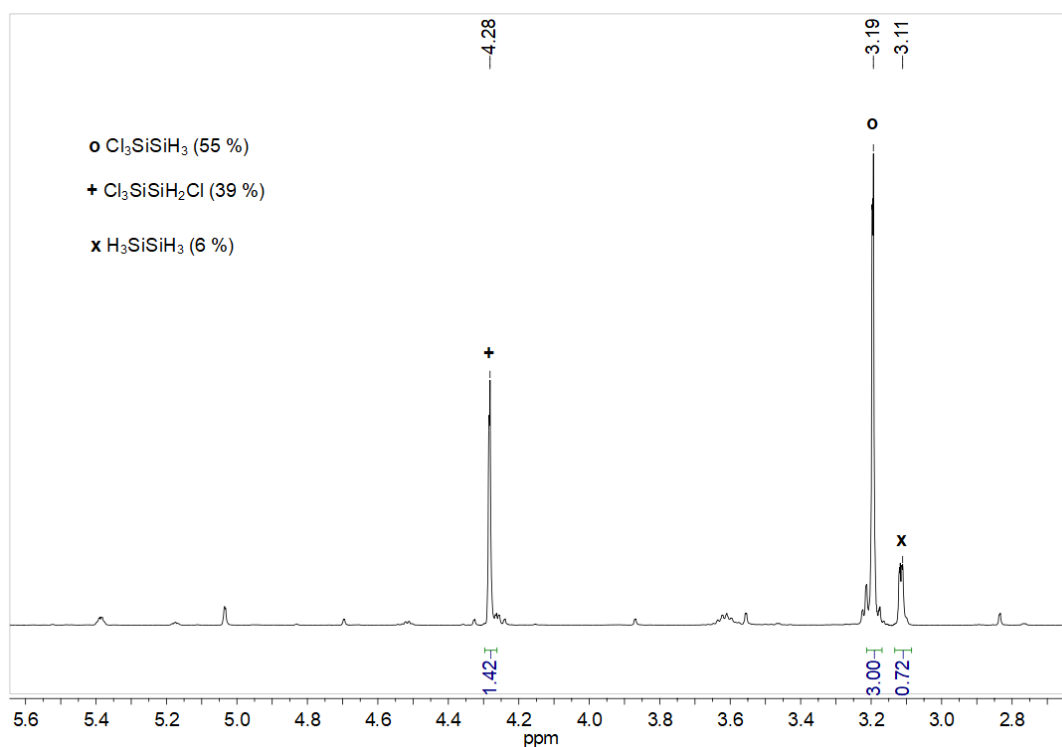
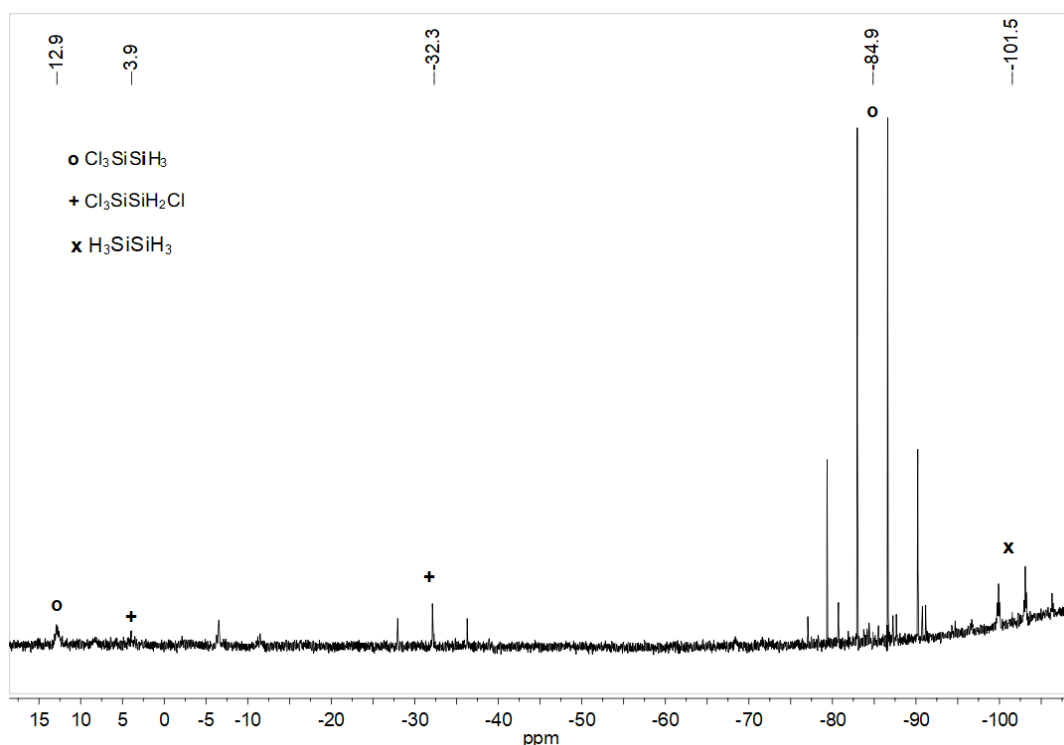


Figure S4. H-coupled ^{29}Si -NMR spectrum (60 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of Si_2Cl_6 (volatile fraction obtained after recondensation of crude product at 25°C and 0.01 mbar)



2.3. Partial Hydrogenation of Octachlorotrisilane with $i\text{Bu}_2\text{AlH}$

24.5 mL (135.0 mmol, 5 equiv.) of neat $i\text{Bu}_2\text{AlH}$ were slowly added to 10.0 g (27.0 mmol, 1.0 equiv.) of Si_3Cl_8 at 0°C . The resulting mixture was allowed to warm to room temperature and stirred overnight. Subsequently the volatile components were separated by trap to trap distillation at room temperature and 0.01 mbar to give 2.4 g of a clear and colorless liquid. NMR analysis of the volatile fraction showed the formation of a 2 : 1 mixture of $\text{H}_3\text{SiSiH}_2\text{SiCl}_3$ (**5**) and Si_3H_8 as the major products along with small amounts of other Cl/H-silanes and $i\text{Bu}_2\text{AlCl}$. Relative amounts of the major products were determined by integration of the ^1H -NMR signals. Addition of further 12 mL (67.5 mmol, 2.5 equiv.) of $i\text{Bu}_2\text{AlH}$ to the higher boiling residue obtained after trap to trap distillation afforded additional 0.6 g of Si_3H_8 which means a more or less quantitative conversion of the starting material to chlorohydrotrisilanes.

$\text{H}_3\text{SiSiH}_2\text{SiH}_3$:⁵ ^1H NMR (C_6D_6 , TMS, ppm): 3.45 (m, $\text{SiH}_2(\text{SiH}_3)_2$, 2H), 3.63 (t, SiH_3 , 6H); ^{29}Si NMR (C_6D_6 , TMS, ppm): -99.8 (q, $^1\text{J}_{\text{Si-H}} = 199$ Hz, SiH_3), -115.3 (t, $^1\text{J}_{\text{Si-H}} = 193$ Hz, $\text{SiH}_2(\text{SiH}_3)_2$)

$\text{H}_3\text{SiSiH}_2\text{SiCl}_3$:⁶ ^1H NMR (C_6D_6 , TMS, ppm): 3.74 (t, SiH_3 , 3H), 3.93 (q, SiH_2 , 2H); ^{29}Si NMR (C_6D_6 , TMS, ppm): -99.8 (q, $^1\text{J}_{\text{Si-H}} = 207.6$ Hz, t, $^2\text{J}_{\text{Si-H}} = 3.4$ Hz, SiH_3), -91.1 (t, $^1\text{J}_{\text{Si-H}} = 206$ Hz, q, $^2\text{J}_{\text{Si-H}} = 5.2$ Hz, SiH_2), 15.2 (m, SiCl_3)

Figure S5. ^1H -NMR spectrum (Si-H region, 300 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of Si_3Cl_8 (volatile fraction obtained after recondensation of crude product at 25°C and 0.01 mbar)

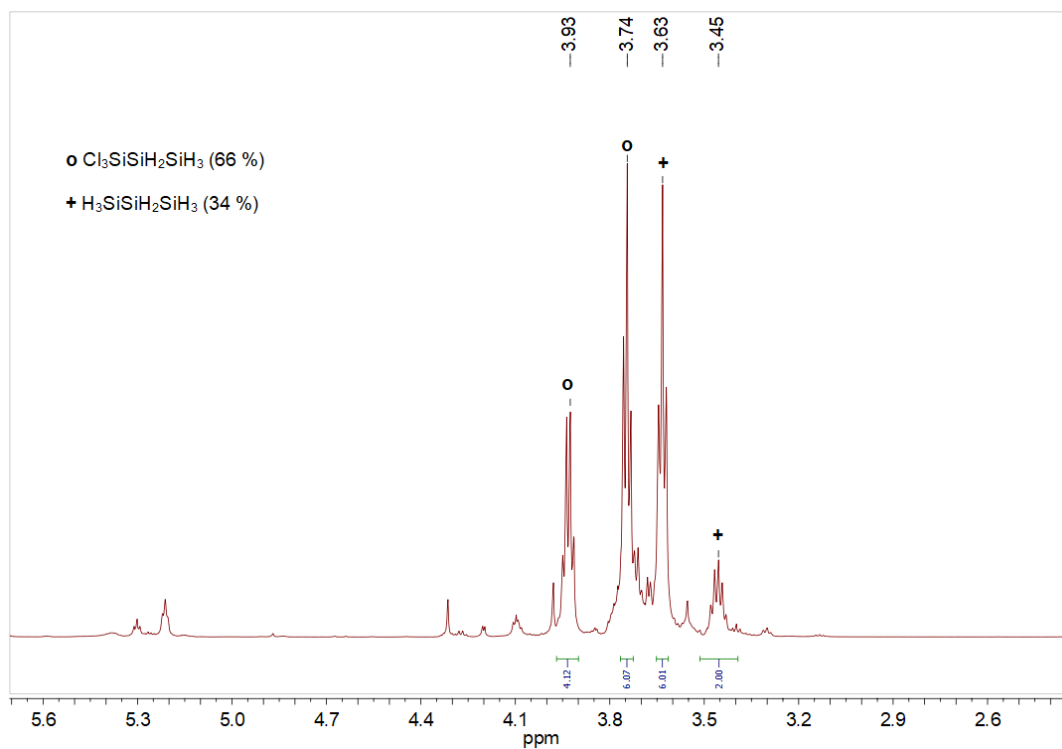
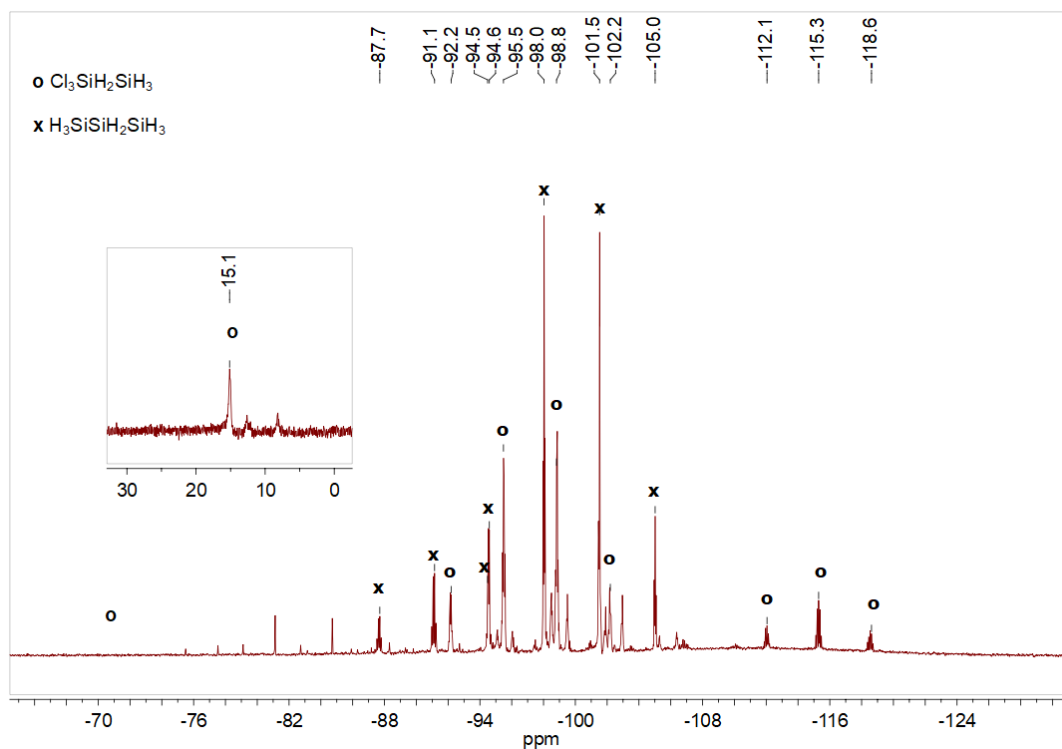


Figure S6. H-coupled ^{29}Si -NMR spectrum (60 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of Si_3Cl_8 (volatile fraction obtained after recondensation of crude product at 25°C and 0.01 mbar)



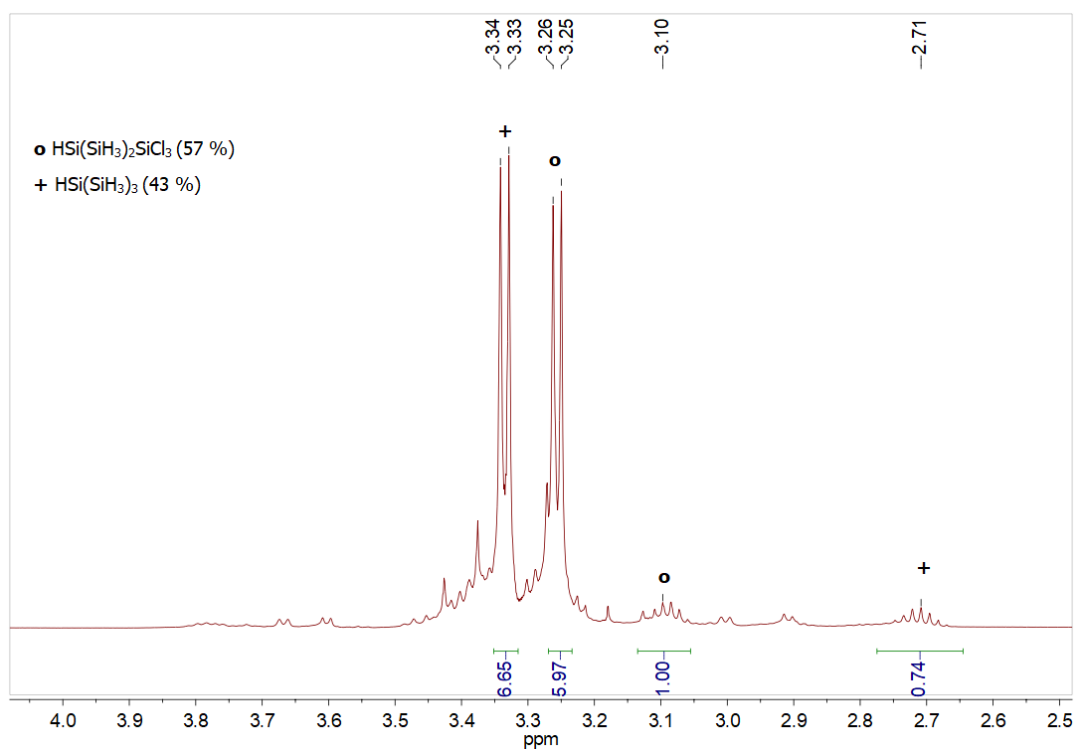
2.3 Hydrogenation of Nonachloroisotetrasilane

42.0 mL (222.0 mmol, 6.0 equiv.) of neat $i\text{Bu}_2\text{AlH}$ were slowly added to 16.0 g (37.0 mmol, 1.0 equiv.) of $\text{HSi}(\text{SiCl}_3)_3$ at 0°C . The resulting clear mixture was allowed to warm to room temperature and stirred overnight. Subsequently the volatile components were separated by trap to trap distillation at 50°C and 0.01 mbar to give 3.2 g of a clear and colorless liquid. NMR analysis of the volatile fraction showed the formation of an approximately 3 : 2 mixture of $\text{HSi}(\text{SiH}_3)_2\text{SiCl}_3$ (**6**) and $\text{HSi}(\text{SiH}_3)_3$ as the major products along with small amounts of other Cl/H-silanes and $i\text{Bu}_2\text{AlCl}$. Relative amounts of the major products were determined by integration of the ^1H -NMR signals.

$\text{HSi}(\text{SiH}_3)_3$: ^1H NMR (C_6D_6 , TMS, ppm): 3.34 (d, SiH_3 , 9H), 2.71 (m, SiH , 1H). ^{29}Si NMR (C_6D_6 , TMS, ppm): -94.7 (q, $^1\text{J}_{\text{Si-H}} = 200$ Hz, SiH_3), -137.0 (d, $^1\text{J}_{\text{Si-H}} = 184$ Hz, SiH)

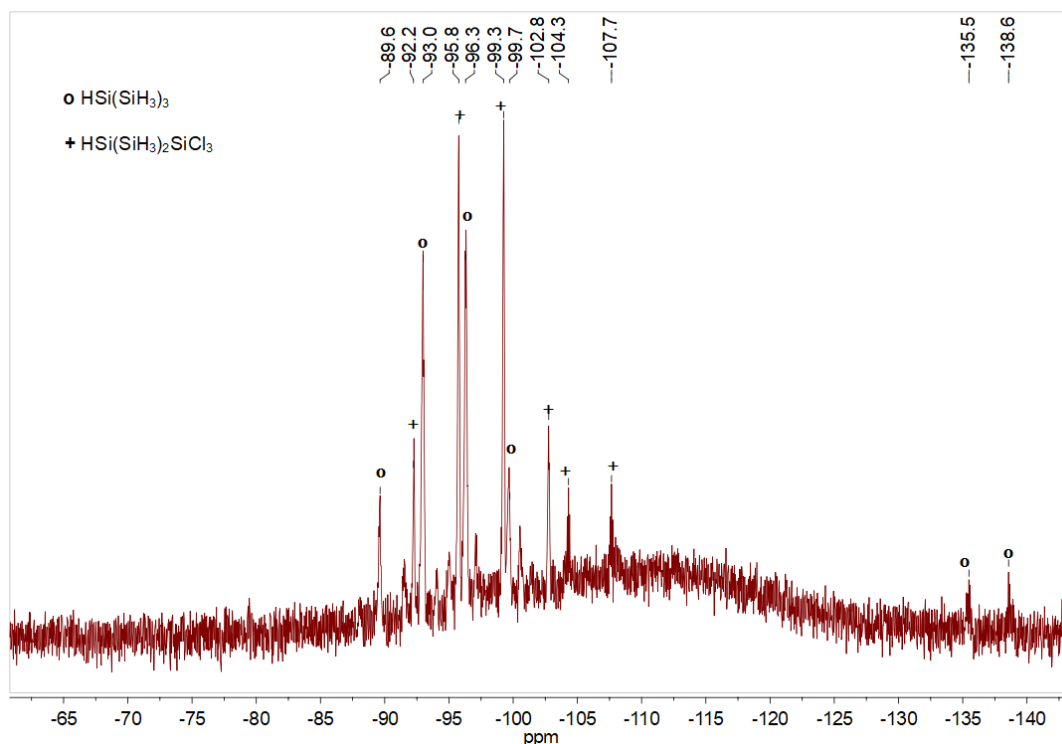
$\text{HSi}(\text{SiH}_3)_2\text{SiCl}_3$: ^1H NMR (C_6D_6 , TMS, ppm): 3.26 (d, SiH_3 , 6H), 3.10 (m, SiH , 1H). ^{29}Si NMR (C_6D_6 , TMS, ppm): -106.1 (d, $^1\text{J}_{\text{Si-H}} = \text{Hz}$, $^2\text{J}_{\text{Si-H}} = 5.5$ Hz SiH), -97.6 (q, $^1\text{J}_{\text{Si-H}} = 209$ Hz, d, $^2\text{J}_{\text{Si-H}} = 2.2$ Hz, SiH_3)¹

Figure S7. ^1H -NMR spectrum (SiH region, 300 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of $\text{ClSi}(\text{SiCl}_3)_3$ (volatile fraction obtained after recondensation of crude product at 50°C and 0.01 mbar)



¹ SiCl_3 resonance not visible for apparative reasons

Figure S8. H-coupled ^{29}Si -NMR spectrum (60 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of $\text{ClSi}(\text{SiCl}_3)_3$ (volatile fraction obtained after recondensation of crude product at 50°C and 0.01 mbar)



2.4 Hydrogenation of Dodecachloroneopentasilane (DCNPS)

204.0 mL (1145 mmol, 9.0 equiv.) of *i*Bu₂AlH were slowly added to 72.0 g (127.0 mmol, 1.0 equiv.) of $\text{Si}(\text{SiCl}_3)_4$ at 0°C . The resulting clear mixture was allowed to warm to room temperature and stirred overnight. Subsequently 3.6 g of $\text{Si}(\text{SiH}_3)_4$ containing about 10 % of $\text{Cl}_3\text{SiSi}(\text{SiH}_3)_3$ (**7**) were separated by trap-to-trap distillation at 50°C and 0.01 mbar. Further trap-to-trap distillation of the resulting higher boiling residue at 80°C and 0.01 mbar gave additional 11.7 g of a 1 : 2 mixture of $\text{Si}(\text{SiH}_3)_4$ ⁵ and $\text{Cl}_3\text{SiSi}(\text{SiH}_3)_3$ (**7**) (fraction 2). 5.6 g (yield 20 %) of **7** contaminated with $\text{Si}(\text{SiH}_3)_4$ and traces of *i*BuAlCl, finally could be isolated from fraction 2 by fractional distillation over a 10 cm Vigreux column at 0.05 mbar mbar.

$\text{Si}(\text{SiH}_3)_4$ ⁵ ^1H NMR (C_6D_6 , TMS, ppm): 3.43 (s, SiH_3 , 6H) ^{29}Si NMR (C_6D_6 , TMS, ppm): -166.0 (*Si*Si₄), -89.8 (*Si*H₃).

$\text{Cl}_3\text{SiSi}(\text{SiH}_3)_3$ ⁷ ^1H NMR (C_6D_6 , TMS, ppm): 3.37 (s, SiH_3 , 9H). ^{29}Si NMR (C_6D_6 , TMS, ppm): -128.1 (*Si*(SiH_3)₃), -93.3 (*Si*H₃), 20.2 (*Si*Cl₃)

Figure S9. ^1H -NMR spectrum (SiH region, 300 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of $\text{Si}(\text{SiCl}_3)_4$ (volatile fraction obtained after recondensation of crude product at 50°C and 0.01 mbar) (fraction 1)

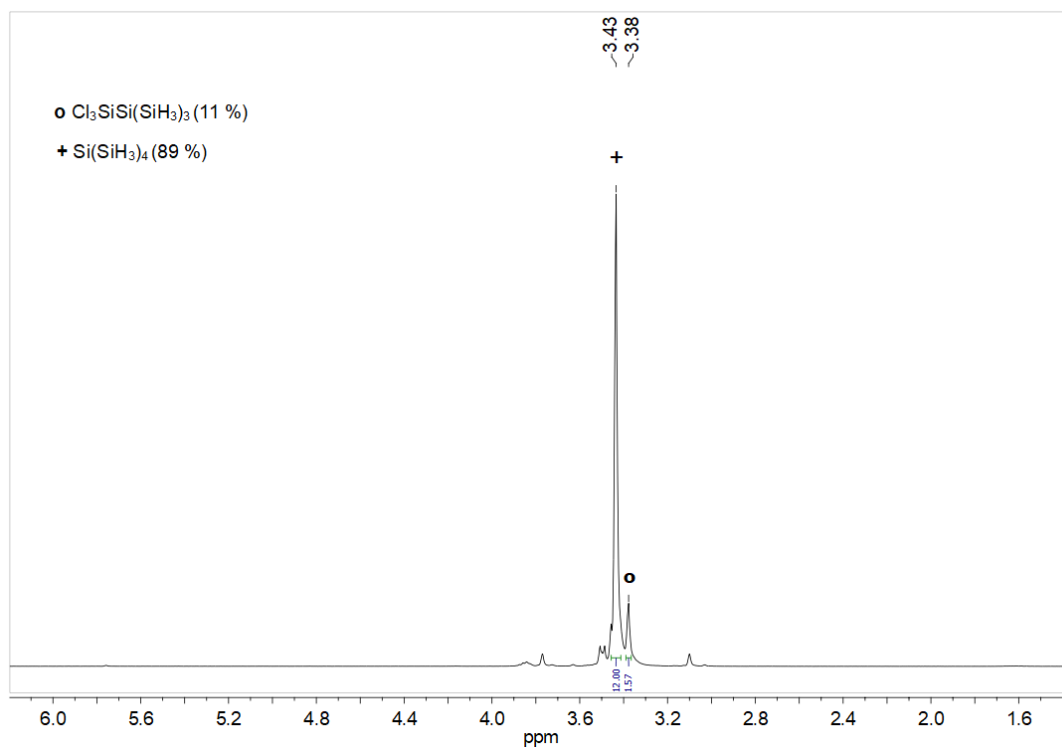


Figure S10. ^1H -NMR spectrum (SiH region, 300 MHz, C_6D_6 solution) of product mixture obtained after partial hydrogenation of $\text{Si}(\text{SiCl}_3)_4$ (volatile fraction obtained after recondensation of crude product at 80°C and 0.01 mbar) (fraction 2)

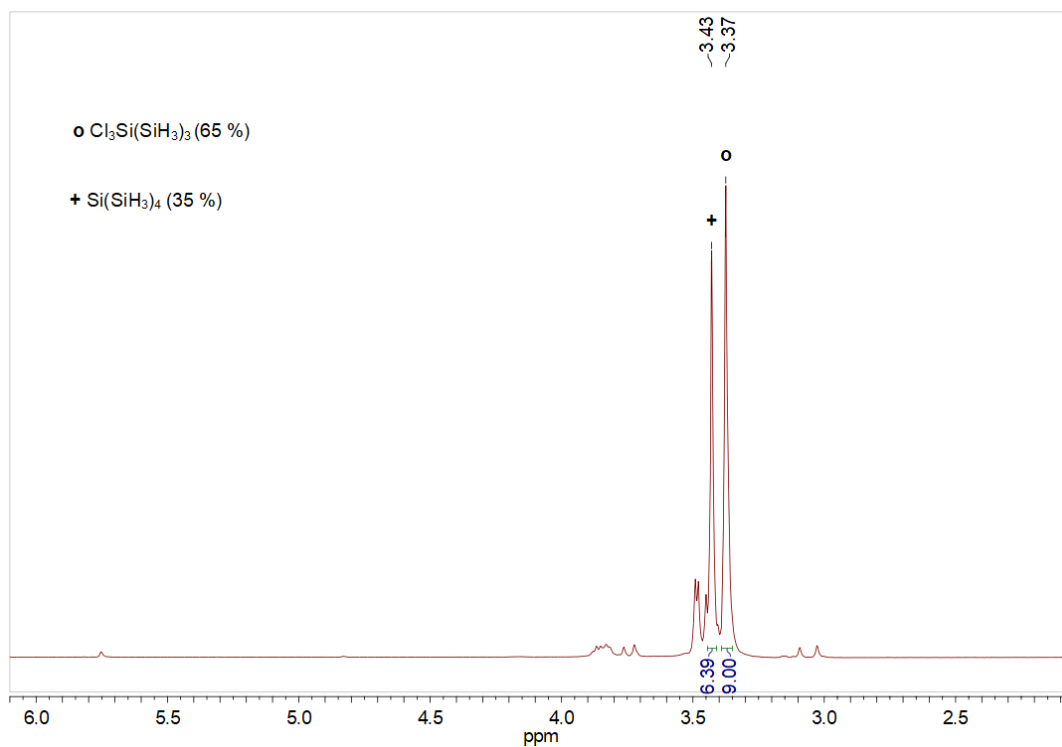
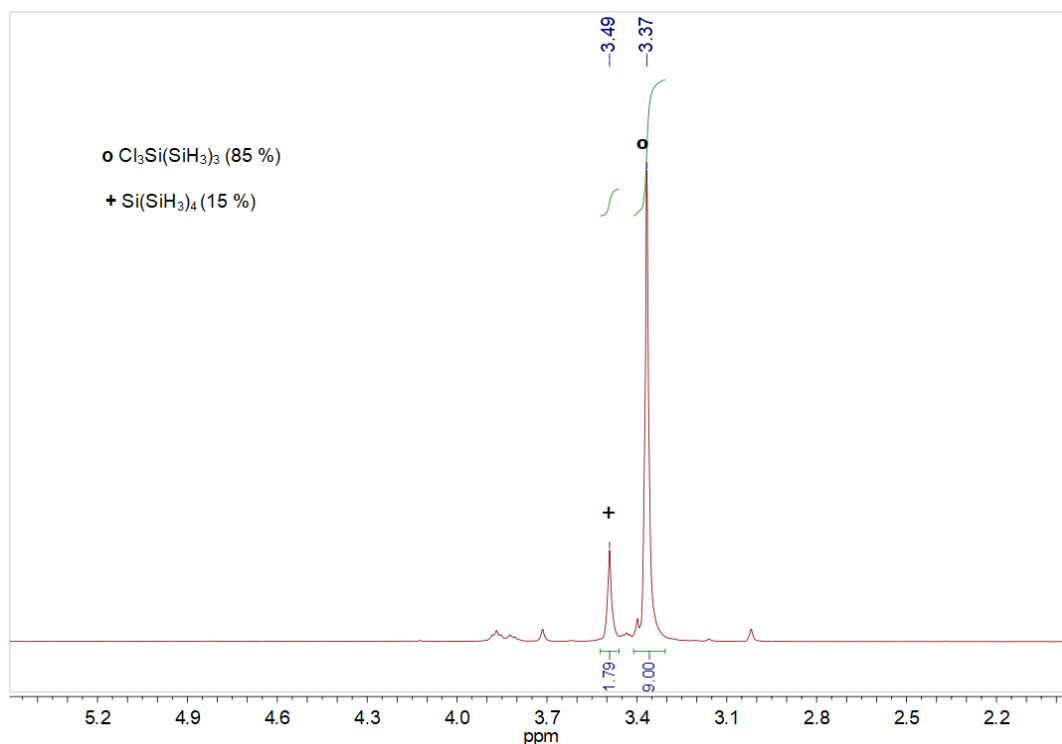


Figure S11. ^1H -NMR spectrum (SiH region, 300 MHz, C_6D_6 solution) of **7** obtained by distillation of fraction 2 over a 10 cm Vigreux column at 0.05 mbar



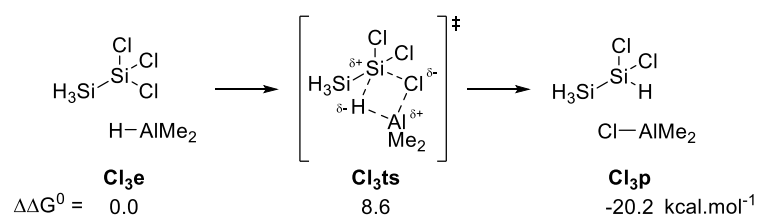
3. Calculations

3.1. Computational Methods

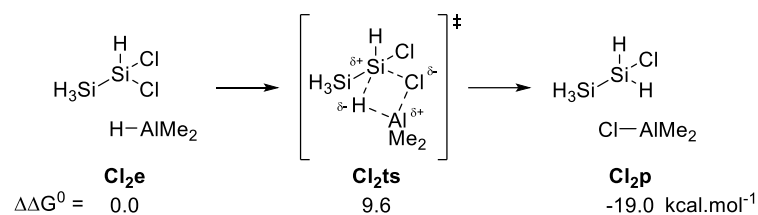
All computational studies were conducted using the Gaussian09 software package.⁸ Geometry optimizations of all structures (local minima (LMs) and transition states (TSs)) were performed with M06-2X-D3 as hybrid meta exchange-correlation functional⁹ with empirical dispersion¹⁰ together with the aug-cc-pVTZ basis set of Dunning *et al.* for all atoms.¹¹ Solvent effects were considered by using the self-consistent reaction field (SCRF) method and Solvation Model based on Density (SMD)¹² for pentane with a dielectric constant $\epsilon = 1.84$.¹³ The connectivity of TS structures was confirmed by intrinsic reaction coordinate (IRC) analyses at the same computational level.¹⁴ All stationary points (LMs and TSs) were characterized by harmonic frequency calculations, yielding none or one imaginary frequency, respectively. Single-point energy calculations were carried out on the same level of theory (SMD(*n*-pentane) M06-2X-D3/aug-cc-pVTZ). The relative Gibbs free energies ($\Delta\Delta G^0$) at 298.15 K and 1 atm are reported in $\text{kcal}\cdot\text{mol}^{-1}$. All computed structures were visualized using the Gabedit software package.¹⁵

3.2. Computed Reaction Profiles

1. Reduction Step



2. Reduction Step



3. Reduction Step

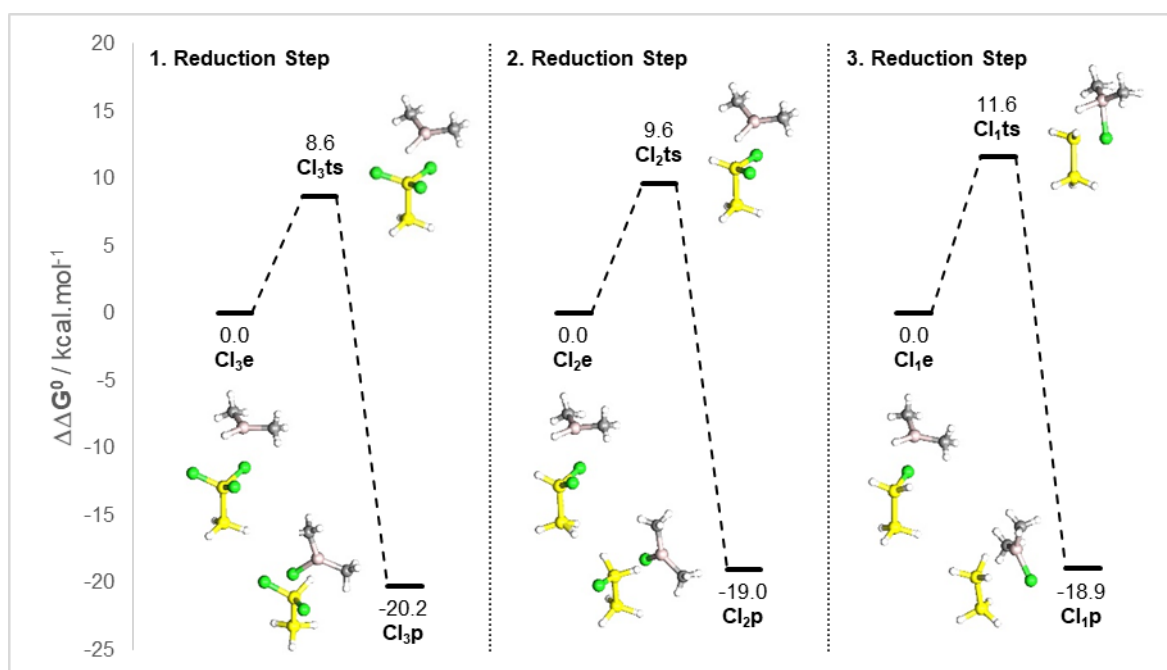
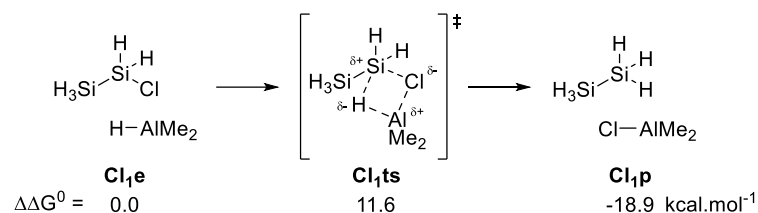
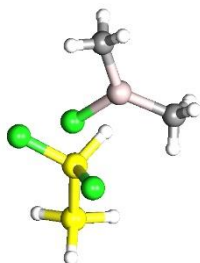


Figure S12. Computed reaction profiles for the three reduction steps of $\text{H}_3\text{SiSiCl}_3$ with HAlMe_2 at the SMD(pentane) M06-2X-D3/aug-cc-pVTZ level of theory. Relative free energies $\Delta\Delta G^0$ are in relation to the starting point of each partial reduction.

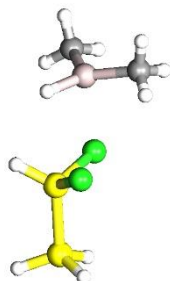
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₃p (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -2284.312206 a.u. (0 imaginary frequencies)

C	2.209970	1.531636	-1.527870	H	0.159361	0.839913	0.524287
Al	0.296449	1.809188	-1.395258	H	2.587997	1.909314	-2.481533
C	-0.669698	3.376663	-0.797402	H	2.758367	2.045571	-0.736408
Cl	-0.889944	0.276805	-2.334035	H	2.462874	0.470516	-1.485330
Si	-0.517744	-0.391207	1.031040	H	-0.860609	4.060076	-1.628524
Si	-0.065831	-2.350719	-0.171663	H	-1.640000	3.104768	-0.378095
H	-1.218227	-2.677842	-1.028096	H	-0.115443	3.933018	-0.039301
H	1.157299	-2.112685	-0.962309	Cl	0.201155	-0.538304	2.961623
H	0.167504	-3.410549	0.831149	Cl	-2.517347	0.077005	1.125048

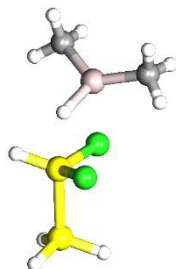
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₂e (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1824.605239 a.u. (0 imaginary frequencies)

C	0.925292	2.545932	1.822324	H	-0.204270	-3.709043	0.678967
Al	0.751241	2.356588	-0.115905	H	-0.707626	2.182813	-0.735683
C	2.212743	2.852064	-1.319724	H	1.925490	2.277768	2.170595
Cl	1.143179	-0.272136	-0.241081	H	0.747436	3.579470	2.133548
Si	-0.837489	-0.930994	-0.563988	H	0.208231	1.924821	2.363030
Cl	-1.951544	-0.324180	1.054017	H	3.188840	2.565244	-0.921453
Si	-0.749411	-3.265271	-0.618633	H	2.107600	2.391983	-2.304576
H	-2.120723	-3.775968	-0.814784	H	2.241255	3.934053	-1.477654
H	0.129546	-3.683972	-1.728989	H	-1.299728	-0.212454	-1.756455

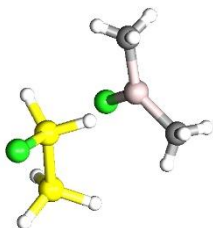
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₂ts (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1824.593654 a.u. (1 imaginary frequency)

C	4.125509	6.108596	-1.872105	H	2.658140	0.315823	-3.012546
Al	3.864374	5.706944	-3.756243	H	2.386986	5.091433	-4.107550
C	4.731579	6.558637	-5.275487	H	5.186261	6.111086	-1.609682
Cl	4.385901	3.340631	-3.970583	H	3.730210	7.093888	-1.613924
Si	2.210573	3.177247	-4.290498	H	3.627807	5.379398	-1.230280
Cl	0.943781	3.506445	-2.667688	H	5.816137	6.587618	-5.145717
Si	2.187217	0.825827	-4.319316	H	4.525980	6.034893	-6.210917
H	0.807608	0.350784	-4.567358	H	4.396749	7.591129	-5.399974
H	3.078182	0.322088	-5.390315	H	1.798322	3.674709	-5.613614

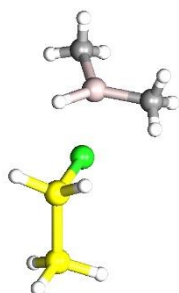
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₂p (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1824.636928 a.u. (0 imaginary frequencies)

C	1.450123	1.533530	1.794327	H	0.026537	-1.957859	1.356584
Al	1.441335	1.438706	-0.142010	H	-0.542441	0.914820	-0.261705
C	1.373433	2.885201	-1.429936	H	2.464173	1.700821	2.166124
Cl	2.071599	-0.465633	-0.953925	H	0.829026	2.349106	2.168945
Si	-1.174676	-0.245987	-0.983074	H	1.095882	0.603193	2.242205
Cl	-3.201262	0.198720	-0.837555	H	2.365643	3.320189	-1.575308
Si	-0.699029	-2.265278	0.107777	H	1.028975	2.539316	-2.406093
H	-1.987310	-2.920276	0.416604	H	0.713233	3.690858	-1.103303
H	0.113678	-3.123307	-0.774061	H	-0.793779	-0.125392	-2.398322

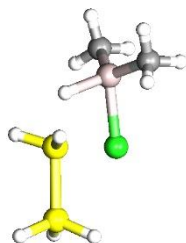
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₂e (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1364.929790 a.u. (0 imaginary frequencies)

C	2.316073	1.885938	-0.374747	H	0.073087	1.851837	1.687530
Al	0.466433	2.212820	0.182526	H	2.395179	1.787139	-1.460273
C	-0.684050	3.437869	-0.819674	H	2.970093	2.713059	-0.084135
Cl	-0.547181	-0.025891	-0.676528	H	2.735570	0.980270	0.069312
Si	-0.339805	-1.132019	1.130753	H	-0.549895	3.332774	-1.899015
Si	-0.704613	-3.362750	0.527752	H	-1.742426	3.282902	-0.600342
H	-2.031013	-3.470839	-0.112638	H	-0.457217	4.479261	-0.573984
H	0.351194	-3.781580	-0.415776	H	1.027296	-0.847885	1.596915
H	-0.658882	-4.201958	1.743903	H	-1.348782	-0.577434	2.046892

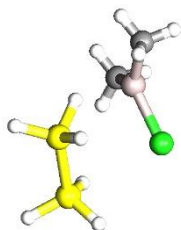
Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₂ts (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1364.914946 a.u. (1 imaginary frequency)

C	6.156770	5.654670	-4.583623	H	3.948374	4.683748	-2.832830
Al	4.247427	5.526061	-4.236812	H	6.350698	5.823706	-5.645884
Cl	3.522631	3.484970	-5.135761	H	6.618883	6.481295	-4.039510
Si	3.552626	2.941247	-2.856753	H	6.682236	4.740769	-4.298865
Si	2.940298	0.739269	-3.456753	H	2.851300	7.109689	-5.656776
H	1.636309	0.719581	-4.158324	H	1.886615	6.518092	-4.307888
C	2.882152	6.863262	-4.592271	H	3.074019	7.794269	-4.054179
H	3.960218	0.128466	-4.340269	H	4.886076	2.813990	-2.227749
H	2.828064	-0.080159	-2.224202	H	2.470954	3.403707	-1.958208

Optimized Cartesian Coordinates and Zero Point Vibrational Energy Corrected Absolute Energy in Hartree of Cl₁p (Calculated with SMD(pentane) M06-2X-D3/aug-cc-pVTZ):



E = -1364.961283 a.u. (0 imaginary frequencies)

C	2.374482	2.182569	-0.185269	H	0.360609	0.525906	1.209437
Al	0.656303	1.385384	-0.607141	H	2.797030	2.673720	-1.065657
Cl	0.769664	-0.451298	-1.734494	H	2.301104	2.935116	0.602143
Si	0.428606	-0.907688	1.673247	H	3.094864	1.426963	0.134182
Si	-1.266422	-2.127028	0.603012	H	-1.259814	2.737296	-1.577788
H	-2.135859	-1.189904	-0.136019	H	-1.891646	1.516628	-0.486037
C	-1.085918	2.240807	-0.619537	H	-1.179311	2.999255	0.160032
H	-0.675267	-3.118266	-0.315312	H	1.797187	-1.365138	1.369106
H	-2.066696	-2.826119	1.633043	H	0.243855	-0.792296	3.135356

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