Electronic Supplementary Information

An isolable β-diketiminato chlorosilylene†

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A Synthesis and Characterization

B Crystallographic data

C. Theoretical Calculation

D. References

A Synthesis and Characterization

General Considerations

All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. The NMR spectra were recorded with Bruker spectrometers ARX200 and AV400 referenced to residual solvent signals as internal standards. Abbreviations: *s* = singlet; *d* = doublet; *t* = triplet; *sept* = septet; *m* = multiplet; Elemental analyses and ESI-MS were performed by the analytical labor in the Institute of Chemistry, Technical University of Berlin, Germany. IR spectra were measured from powder samples inside a nitrogen filled glovebox using a Thermofisher Nicolet iS5 IR Spectrometer (ATR-Diamond) and the OMNIC software (Version 9.3.30) for data acquisition. The ligand **LH** was synthesized according to literature.[1]

Single-Crystal X-ray Structure Determination

Crystals were each mounted on a glass capillary in per-fluorinated oil and measured in a cold N_2 flow. The date of **1**, **2**, **3** and **4** were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu- Kα-radiation, λ = 1.5418 Å). The structures were solved by direct method and refined on F^2 with the SHELX-97 [2] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 1588134 (compound **1**), 1588135 (compound **2**), 1588133 (compound **3**), and 1588136 (compound **4**) contain the supplementary crystallographic data for this paper. In the structure of compound **2**, the chlorine atom is disordered over two orientations with refined site occupancies of 0.94 and 0.06. In the structure of compound **4**, the whole molecule is disordered over two orientations with refined site occupancies of 0.82 and 0.18.It is noteworthy that a twin phenomenon cannot be excluded although the refinement model with disorder treatment is satisfied. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Synthesis and Characterization of 1

At -20 °C ^{n}BuLi (13.92 mL, 2.5M in n-hexane) was dropwise added to a suspension of **LH** (13.60 g, 34.81mmol) in toluene (150 mL). The reaction mixture was raised to room temperature and stirred for 2h. To the solution $HSiCl_3$ (3.51 mL) was dropwise added at -20 °C. The reaction mixture was warmed to ambient temperature and was stirred for 3 days. The precipitate was separated away from the solution. Storage of the concentrated solution at -20 °C in a freezer for 1 day afforded 6.20 g (12.66 mmol, 36.4%) of **1** as pure colorless powder. M. p. 171 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D_8] THF, 25ºC): δ = 1.05 (*d*, ^3J(H,H) = 6.9 Hz, 12 H; -CH(CH_3)$_3$), 1.25 (*d*, ^3J(H,H) = 6.9 Hz, 12 H; -CH(CH_3)$_3$), 3.21 (*sept*, ^3J(H,H) = 6.9 Hz, 4 H; -C*H*(CH$_3$)$_3$), 5.58 (*t*, ^3J(H,H) = 6.46 Hz, 1 H; ϒ-C*H*), 6.46 (*t*, ^4J(H,H) = 1.9 Hz 1 H; Si*H*), 7.09 – 7.22 (*m*, 6 H; *Ph*), 7.53 (*dd*, ^3J(H,H) = 6.46 Hz, ^4J(H,H) = 1.9 Hz, 2 H; β-C*H*); ^{13}C{^{1}H} NMR (100.61 MHz, [D_8] THF, 25 ºC): δ = 23.89, 25.60 (CH(*C*H$_3$)$_3$), 30.00 (*C*H(CH$_3$)$_3$), 97.72 (ϒ-*C*), 125.11 (*m*-*Ph*), 128.75 (*p*-*Ph*), 144.95 (*o*-*Ph*), 145.60 (N-*Ph*), 162.97 ppm (β-*C*); ^{29}Si{1H} NMR (79.49 MHz, [D_8]THF, 25ºC): δ = -97.39 ppm (s); IR (cm^{-1}): 2960(s), 2927(w), 2867(w), 2148(w, ν_{SiH}), 1608(s), 1536(vs), 1458(s), 1444(s), 1384(w), 1363(w), 1345(s), 1297(vs), 1259(w), 1194(w), 1182(m), 1145(m), 1102(w), 1077(m), 1059(m), 1002(m), 911(w), 807(w), 788(s), 758(vs), 714(m), 672(vs), 632(w), 603(m), 564(w); HR ESI-MS: *m*/*z*: 391.31063 (calc. 391.31078 [M-$SiCl_2$]$^+$); elemental analysis calcd. (%) for $C_{27}H_{38}N_2SiCl_2$: C 66.24, H 7.82, N 5.72, S 10.35; found: C 65.98, H 7.69, N 5.83. %).

Synthesis and Characterization of 2

To a mixture of **1** (0.99 g, 2.02 mmol) and Et_2O-$LiN(SiMe_3)_2$ (0.49 g, 2.02 mmol) at -70 °C was added toluene (50 mL) under stirring. The mixture was allowed to warm to room temperature and stirred overnight. The precipitate was separated away via centrifugation, and the volatiles were removed under vacuum. From the residue compound **2** was obtained by extraction with diethyl ether. The collected colorless crystals of **2** are amounted to 0.80 g (1.30 mmol, 64%). M.p. 128 °C; ^{1}H NMR (200.13 MHz, [D$_6$] C_6H_6, 25ºC): δ = -0.20 (*s*, 9 H; Si*Me*$_3$), 0.47 (*s*, 9 H; Si*Me*$_3$), 1.21 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.23 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.26 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.27 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.31 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.37 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.41 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.46 (*d*, ^3J(H,H) = 6.8 Hz, 3 H; -CH(C*H*$_3$)$_3$), 3.51 (*sept*, ^3J(H,H) = 6.8 Hz, 1 H; -C*H*(CH$_3$)$_3$), 3.62 (*sept*, ^3J(H,H) = 6.8 Hz, 1 H; -C*H*(CH$_3$)$_3$), 3.84 (*sept*, ^3J(H,H) = 6.8 Hz, 1 H; -C*H*(CH$_3$)$_3$), 3.88 (*sept*, ^3J(H,H) = 6.8 Hz, 1 H; -C*H*(CH$_3$)$_3$), 4.43 (*dd*, ^3J(H,H) = 3.8, 8.9 Hz, 1 H; ϒ-C*H*), 5.04 (*dd*, ^3J(H,H) = 1.9, 3.8 Hz, 1 H; (SiMe$_3$)$_2$N-C*H*), 5.80 (*dddd*, ^3J(H,H) = 1.9, 8.9 Hz, ^4J(H,H) = 0.7 Hz, 1 H; β-C*H*), 6.15 (*t*, ^4J(H,H) = 0.7 Hz, ^1J(Si-H) = 133 Hz, 1 H; Si*H*), 7.03 – 7.20 (*m*, 6 H; *Ph*); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$] C_6H_6, 25 ºC): δ = 1.56, 4.56 (N(Si*Me*$_3$)$_2$, 23.48, 23.72, 24.03, 24.61, 25.22, 25.57, 26.02, 26.33 (CH(*C*H$_3$)$_3$), 27.86, 28.14, 28.40, 28.43 (*C*H(CH$_3$)$_3$), 75.02 ((SiMe$_3$)$_2$N*C*H), 103.16 (ϒ-*C*), 123.73, 123.96, 124.92, 125.33, 127.37, 127.96 (*C*H in *Ph*), 136.14 (β- =*C*H), 138.23, 139.85, 147.05, 148.27, 148.55, 148.55 ppm (*Ph*); ^{29}Si{1H} NMR (79.49 MHz, [D$_6$] C_6H_6, 25ºC): δ = -0.19 (*s*, N(*Si*Me$_3$)$_2$), -2.94 (*s*, N(*Si*Me$_3$)$_2$), -38.2 ppm (*s*, *Si*H); HR ESI-MS: *m*/*z*: 614.35433 (calc. 614.35383 [M+H]$^+$). IR (KBr, cm^{-1}): 2961(s), 2868(m), 2194(s, ν_{SiH}), 1644(s), 1464(s), 1442(s), 1311(s), 1275(s), 1252(vs), 1188(s), 1159(vs), 1104(w), 1055(w), 1043(w), 1014(w), 988(vs), 953(m), 928(s), 902(s), 867(vs), 835(vs), 808(m), 798(vs), 759(s), 734(m); elemental analysis calcd. (%) for $C_{33}H_{56}N_3Si_3Cl$: C 64.50, H 9.18, N 6.84; found: C 64.26, H 9.33, N 6.87.

Synthesis and Characterization of 3

To a mixture of **1** (0.64 g, 1.30 mmol) and $K_2Fe(CO)_4$ (0.32 g, 1.30 mmol) at -30 °C was added THF (20 mL) under stirring. The mixture was allowed to warm to room temperature and stirred overnight. A dark brown precipitate was formed. The volatiles were removed under vacuum. From the residue compound **3** was obtained by extraction with diethyl ether (30 mL) as colorless crystals (0.38 g, 0.42 mmol, 65%). M.p. 103 °C (decomposed); ^{1}H NMR (200.13 MHz, [D$_6$] C_6H_6, 25ºC): δ = 0.45 (*d*, ^3J(H,H) = 6.9 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.15 (*d*, ^3J(H,H) = 6.9 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.23 (*d*, ^3J(H,H) = 6.9 Hz, 9 H; -CH(C*H*$_3$)$_3$), 1.27 (*d*, ^3J(H,H) = 6.9 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.29 (*d*, ^3J(H,H) = 6.9 Hz, 3 H; -CH(C*H*$_3$)$_3$), 1.40 (*d*, ^3J(H,H) = 6.9 Hz, 3 H; -CH(C*H*$_3$)$_3$), 3.29 – 3.44 (*m*, 1 H; -C*H*(CH$_3$)$_3$), 3.65 – 3.89 (*m*, 3 H; -C*H*(CH$_3$)$_3$), 4.23 (*d*, ^3J(H,H) = 2.5 Hz, 1 H; β-C*H*), 5.32 (*dd*, ^3J(H,H) = 8.9, 2.5 Hz, 1 H; ϒ-C*H*), 5.74 (*s*, 1 H; Si*H*), 6.33 (*d*, ^3J(H,H) = 8.9 Hz, 1 H; β-(=C*H*)), 6.91 – 7.12 (*m*, 6 H; *Ph*); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$] C_6H_6, 25 ºC): δ = 23.48, 23.89, 24.69, 24.75, 25.38, 25.55, 25.65 (CH(*C*H$_3$)$_3$), 28.12, 28.20, 28.43 (*C*H(CH$_3$)$_3$), 63.66 (β-*C*), 99.00 (ϒ-*C*), 124.01, 124.78, 124.82, 125.78, 127.95, 128.00 (*C*H in *Ph*), 136.30 (β- (=*C*H)), 136.43, 137.22, 147.42, 147.44, 148.59, 149.33 ppm (*Ph*); ^{29}Si{1H} NMR (79.49 MHz, [D$_6$] C_6H_6, 25ºC): δ = -38.29 (*s*); HR ESI-MS: *m*/*z*: 907.50753 (calc. 907.50583 [M+H]$^+$). IR (cm^{-1}): 2963(s), 2926(w), 2867(w), 2238(s, ν_{SiH}), 1977(s), 1934(s), 1646(s), 1450(s), 1383(s), 1363(s), 1330(w), 1252(s), 1209(w), 1183(w), 1155(vs), 1107(m), 1045(m), 963(m), 923(w), 902(w), 868(vs), 830(w), 801(vs), 786(s), 756(s), 750(s), 708(w), 662(w), 592(w), 566(w); elemental analysis calcd. (%) for $C_{54}H_{76}N_4Si_2Cl_2$: C 71.41, H 8.43, N 6.17; found: C 70.99, H 8.33, N 6.27.

Synthesis and Characterization of 4

At -40 °C THF (20 mL) was added to a mixture of **1** (1.52 g, 3.10 mmol) and 1,3-di(tert-butyl)-imidazol-2-ylidene (0.56 g, 3.10 mmol) under stirring. The solution was allowed to warm to room temperature, and the color changed slowly from colorless, via yellow, to orange-red with the formation of small amount of white precipitate. After overnight stirring the precipitate was separated from the solution via filtration and the volatiles were evacuated

under reduced pressure. The residue was extracted with diethyl ether (20 mL), from which compound **4** as orange-red colored crystals was obtained at room temperature with a yield of 0.14 g (0.31 mmol, 10%). M. p. 188 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_6$] C$_6$H$_6$, 25ºC): δ = 1.06 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.16 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.35 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.38 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 3.60 (*sept*, ^{3}J(H,H) = 6.70 Hz, 2 H; -C*H*(CH$_3$)$_3$), 3.81 (*sept*, ^{3}J(H,H) = 6.70 Hz, 2 H; -C*H*(CH$_3$)$_3$), 5.07 (*t*, ^{3}J(H,H) = 6.50 Hz, 1 H; ϒ-C*H*), 7.05 (*d*, ^{3}J(H,H) = 6.50 Hz, 2 H; β-C*H*), 7.10 – 7.19 ppm (*m*, 6 H; *Ph*); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$] C$_6$H$_6$, 25 ºC): δ = 22.62, 24.75, 24.86, 25.27 (CH(*C*H$_3$)$_3$), 27.94, 29.55 (*C*H(CH$_3$)$_3$), 95.84 (ϒ-*C*H), 123.53, 125.28, 128.18 (*C*H in Ph), 141.87, 143.40, 145.70 (N-*Ph*, *o-Ph*), 157.46 ppm (β-*C*); ^{29}Si{1H} NMR (79.49 MHz, [D$_6$]C$_6$H$_6$, 25ºC): δ = -10.73 ppm (s); HR ESI-MS: *m*/*z*: 453.24873 (calc. 453.24674 [M+H]$^{+}$); IR (KBr, cm^{-1}): 2955(m), 2866(w), 1586(m), 1514(m), 1463(m), 1430(m), 1344(m), 1323(w), 1307(w), 1271(s), 1231(vs), 1206(s), 1151(vs), 1059(m), 963(s), 805(m), 782(m), 764(m), 754(s), 641(m); elemental analysis calcd. (%) for $C_{27}H_{37}N_2SiCl$: C 71.57, H 8.23, N 6.18; found: C 71.29, H 8.13, N 6.22.

Synthesis and Characterization of 5

At room temperature toluene (10 mL) was added to a mixture of **4** (0.18 g, 0.40 mmol) and S_8 (0.013 g, 0.050 mmol) under stirring. The reaction mixture turned yellow immediately. One hour later the volatiles were evacuated under reduced pressure and the residue was washed with n-hexane (5 mL). It afforded compound **5** as off-white powder with yield of 0.17 g (0.35 mmol, 88%). M. p. 220 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_6$] C$_6$H$_6$, 25ºC): δ = 1.02 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.09 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.36 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 1.55 (*d*, ^{3}J(H,H) = 6.70 Hz, 6 H; -CH(CH_3)$_3$), 3.58 (*sept*, ^{3}J(H,H) = 6.70 Hz, 2 H; -C*H*(CH$_3$)$_3$), 3.76 (*sept*, ^{3}J(H,H) = 6.70 Hz, 2 H; -C*H*(CH$_3$)$_3$), 4.74 (*t*, ^{3}J(H,H) = 6.52 Hz, 1 H; ϒ-C*H*), 6.92 (*d*, ^{3}J(H,H) = 6.52 Hz, 2 H; β-C*H*), 7.04 – 7.12 ppm (*m*, 6 H; *Ph*); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$] C$_6$H$_6$, 25 ºC): δ = 22.76, 24.65, 24.87, 25.36 (CH(*C*H$_3$)$_3$), 28.47, 29.67 (*C*H(CH$_3$)$_3$), 96.38 (ϒ-*C*H), 124.24, 124.90, 129.11 (*C*H in Ph), 139.43, 144.93, 145.47 (N-*Ph*, *o-Ph*), 162.66 ppm (β-*C*); ^{29}Si{1H} NMR (79.49 MHz, [D$_6$]C$_6$H$_6$, 25ºC): δ = -28.63 ppm (s); HR ESI-MS: *m*/*z*: 391.31103 (calc. 391.31078 [M-SiSCl+H]$^{+}$); IR (KBr, cm^{-1}): 2961(w), 2866(w), 2788(w), 2728(m), 1599(s), 1566(vs), 1521(vs), 1463(m), 1334(m), 1309(vs), 1244(m), 1210(s), 1160(w), 1144(w), 1095(w), 1059(w), 935(w), 816(m), 798(s), 763(s), 701(w), 680(w); elemental analysis calcd. (%) for $C_{27}H_{37}N_2SiSCl$: C 66.84, H 7.69, N 5.77, S 6.61; found: C 66.29, H 7.53, N 5.82, S 6.46.

B. Crystallographic data

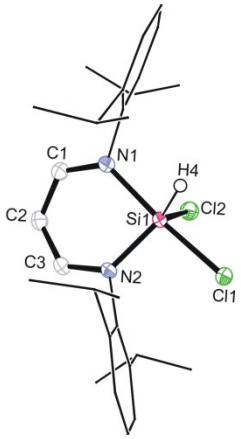

Figure S 1. Molecular structure of compound **1**. Thermal ellipsoids are drawn at 50% probability level. H atoms (except that in Si1) are omitted for clarity.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C27 H38 Cl2 N2 Si
Formula weight	489.58
Temperature	150(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 16.9139(4) Å a= 90°.
	b = 6.73970(10) Å b= 95.840(2)°.
	c = 24.2997(6) Å g = 90°.
Volume	2755.66(10) Å3
Z	4
Density (calculated)	1.180 Mg/m3
Absorption coefficient	2.649 mm-1
F(000)	1048
Crystal size	0.45 x 0.05 x 0.04 mm3
Theta range for data collection	2.63 to 67.49°.
Index ranges	-19<=h<=20, -7<=k<=8, -29<=l<=20
Reflections collected	9614
Independent reflections	4943 [R(int) = 0.0354]
Completeness to theta = 67.49°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.32561
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4943 / 0 / 301
Goodness-of-fit on F2 1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0954
R indices (all data)	R1 = 0.0495, wR2 = 0.1044
Largest diff. peak and hole	0.315 and -0.282 e.Å-3

Table S2. Selected interatomic distances [Å] and angles [°] for compound **1**.

Cl(1)-Si(1)	2.1916(7)
Si(1)-N(2)	1.7985(16)
Si(1)-N(1)	1.9565(16)
Si(1)-Cl(2)	2.0909(7)
N(1)-C(1)	1.314(3)

N(2)-C(3)	1.354(2)
C(3)-C(2)	1.370(3)
C(1)-C(2)	1.382(3)

N(2)-Si(1)-N(1)	90.94(7)
N(2)-Si(1)-Cl(2)	110.49(6)
N(1)-Si(1)-Cl(2)	91.85(5)
N(2)-Si(1)-Cl(1)	93.37(5)
N(1)-Si(1)-Cl(1)	170.93(6)
Cl(2)-Si(1)-Cl(1)	94.10(3)
C(1)-N(1)-Si(1)	126.42(13)
C(3)-N(2)-Si(1)	124.68(13)
N(2)-C(3)-C(2)	127.30(18)
N(1)-C(1)-C(2)	122.51(18)
C(3)-C(2)-C(1)	121.51(19)

Symmetry transformations used to generate equivalent atoms:

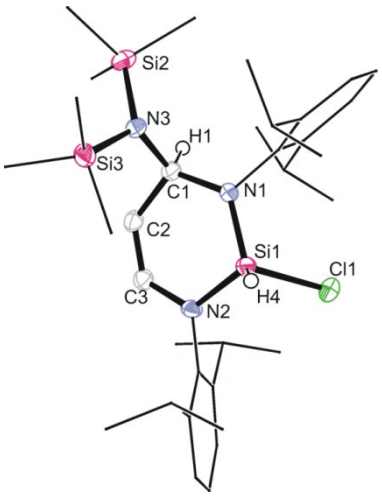

Figure S2. Molecular structure of compound **2**. The chlorine atom is disordered over two orientations with refined site occupancies of 0.94 and 0.06, only the major one is depicted. Thermal ellipsoids are drawn at 50% probability level. H atoms (except those in C1 and Si1) are omitted for clarity.

Table S3. Crystal data and structure refinement for **2**.

Empirical formula	C33 H56 Cl N3 Si3	
Formula weight	614.53	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pca21	
Unit cell dimensions	a = 11.2116(2) Å	α= 90°.
	b = 17.7148(3) Å	β= 90°.
	c = 18.6404(3) Å	γ = 90°.
Volume	3702.19(11) $Å^3$	
Z	4	
Density (calculated)	1.103 Mg/m^3	
Absorption coefficient	2.017 mm^{-1}	
F(000)	1336	
Crystal size	0.45 x 0.23 x 0.19 mm^3	
Theta range for data collection	2.49 to 67.50°.	
Index ranges	-13<=h<=9, -21<=k<=20, -22<=l<=22	
Reflections collected	24032	
Independent reflections	6353 [R(int) = 0.0266]	
Completeness to theta = 67.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.05117	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6353 / 1 / 384	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0750	
R indices (all data)	R1 = 0.0291, wR2 = 0.0758	
Absolute structure parameter	-0.023(10)	
Largest diff. peak and hole	0.244 and -0.174 $e.Å^{-3}$	

Table S4. Selected interatomic distances [Å] and angles [°] for compound **2**.

Cl(1)-Si(1)	2.0496(6)
Si(1)-N(1)	1.7014(13)
Si(1)-N(2)	1.7185(14)
N(1)-C(1)	1.4812(19)
C(1)-N(3)	1.4939(19)

C(1)-C(2)	1.503(2)
Si(2)-N(3)	1.7569(14)
N(2)-C(3)	1.402(2)
C(2)-C(3)	1.336(2)
Si(3)-N(3)	1.7563(14)

N(1)-Si(1)-N(2)	106.63(7)
N(1)-Si(1)-Cl(1)	112.38(5)
N(2)-Si(1)-Cl(1)	110.08(5)
C(1)-N(1)-Si(1)	125.69(11)
N(1)-C(1)-N(3)	114.86(12)
N(1)-C(1)-C(2)	112.13(13)
N(3)-C(1)-C(2)	112.37(13)
C(3)-N(2)-Si(1)	119.06(11)
C(3)-C(2)-C(1)	128.88(15)
C(1)-N(3)-Si(3)	120.21(11)
C(1)-N(3)-Si(2)	111.16(10)
Si(3)-N(3)-Si(2)	122.71(7)
C(2)-C(3)-N(2)	126.21(16)

Symmetry transformations used to generate equivalent atoms:

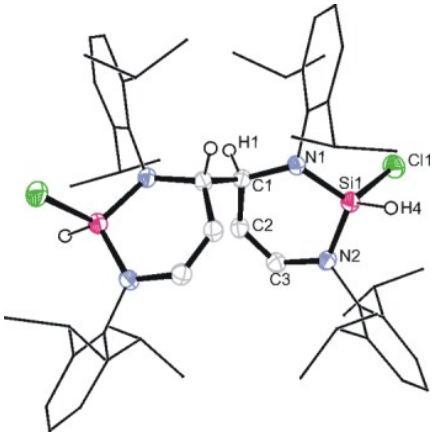

Figure S3 Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability level. H atoms (except those in C1 and Si1) are omitted for clarity.

Table S5 Crystal data and structure refinement for **3**

Empirical formula	C54 H76 Cl2 N4 Si2	
Formula weight	908.27	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Tetragonal	
Space group	I41/a	
Unit cell dimensions	a = 20.92430(10) Å	α= 90°.
	b = 20.92430(10) Å	β= 90°.
	c = 23.8905(2) Å	γ = 90°.
Volume	10459.89(11) $Å^3$	
Z	8	
Density (calculated)	1.154 Mg/m^3	
Absorption coefficient	1.837 mm^{-1}	
F(000)	3920	
Crystal size	0.45 x 0.21 x 0.17 mm^3	
Theta range for data collection	2.81 to 67.46°.	
Index ranges	-25<=h<=23, -24<=k<=25, -28<=l<=25	
Reflections collected	35549	
Independent reflections	4706 [R(int) = 0.0502]	
Completeness to theta = 67.46°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.69397	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4706 / 0 / 292	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.1075	
R indices (all data)	R1 = 0.0460, wR2 = 0.1149	
Largest diff. peak and hole	0.446 and -0.223 $e.Å^{-3}$	

Table S6 Selected interatomic distances [Å] and angles [°] for **3**

Cl(1)-Si(1)	2.0703(6)
Si(1)-N(1)	1.7014(13)
Si(1)-N(2)	1.7086(13)
N(1)-C(1)	1.4842(19)
C(1)-C(2)	1.505(2)
C(1)-C(1)#1	1.570(3)

N(2)-C(3)	1.404(2)
C(2)-C(3)	1.333(2)

N(1)-Si(1)-N(2)	106.13(6)
N(1)-Si(1)-Cl(1)	111.76(5)
N(2)-Si(1)-Cl(1)	111.51(5)
C(1)-N(1)-Si(1)	125.25(10)
N(1)-C(1)-C(2)	112.38(12)
N(1)-C(1)-C(1)#1	110.85(15)
C(2)-C(1)-C(1)#1	112.03(10)
C(3)-N(2)-Si(1)	118.61(11)
C(16)-N(2)-Si(1)	121.78(10)
C(3)-C(2)-C(1)	128.32(15)
C(2)-C(3)-N(2)	125.28(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1/2,z

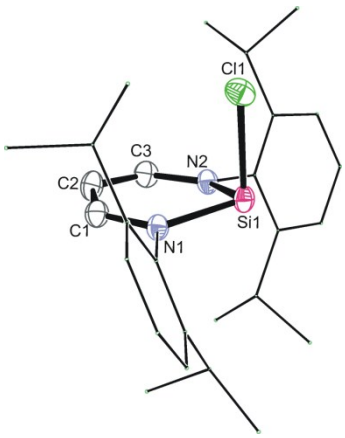

Figure S 4. Molecular structure of compound **4**. The whole molecule is disordered over two orientations with refined site occupancies of 0.82 and 0.18, only the major one is depicted. Notably, a twin structure cannot be excluded although the refinement model is satisfied. Thermal ellipsoids are drawn at 50% probability level. H atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for **4**.

Empirical formula	C27 H37 Cl N2 Si
Formula weight	453.13
Temperature	150(2) K
Wavelength	1.54184 Å

Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 11.8229(3) Å	α= 90°.
	b = 6.68690(10) Å	β= 91.272(2)°.
	c = 16.5376(4) Å	γ = 90°.
Volume	1307.12(5) $Å^3$	
Z	2	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	1.837 mm^{-1}	
F(000)	488	
Crystal size	0.14 x 0.14 x 0.05 mm^3	
Theta range for data collection	2.67 to 67.50°.	
Index ranges	-14<=h<=14, -7<=k<=7, -14<=l<=19	
Reflections collected	8272	
Independent reflections	4140 [R(int) = 0.0257]	
Completeness to theta = 67.50°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.73861	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4140 / 100 / 429	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0904	
R indices (all data)	R1 = 0.0389, wR2 = 0.0915	
Absolute structure parameter	0.472(16)	
Largest diff. peak and hole	0.248 and -0.270 $e.Å^{-3}$	

Table S8. Selected interatomic distances [Å] and angles [°] for compound **4**.

Cl(1)-Si(1)	2.1954(9)
Si(1)-N(2)	1.860(3)
Si(1)-N(1)	1.865(2)
N(1)-C(1)	1.341(6)
C(1)-C(2)	1.370(7)
N(2)-C(3)	1.312(4)
C(2)-C(3)	1.391(4)
N(2)-Si(1)-N(1)	91.57(10)
N(2)-Si(1)-Cl(1)	98.46(8)
N(1)-Si(1)-Cl(1)	96.22(7)

C(1)-N(1)-Si(1)	126.6(3)
N(1)-C(1)-C(2)	124.3(3)
C(3)-N(2)-Si(1)	127.95(19)
C(1)-C(2)-C(3)	122.3(3)
N(2)-C(3)-C(2)	124.0(3)

Symmetry transformations used to generate equivalent atoms:

C. Computational Details

All quantum chemical calculation were performed using the Gaussian 09, Revision D.01 [3] and NBO 6.0 [4] software packages.
Optimization were performed at M05-2X [5]/def2-TZVP [6] level of theory.
Analytical frequencies were computed to verify the optimized geometries as minima.
Si NMR chemical shift were calculated at the HCTH407[7]/6-311+G(3d,p)[8]// M05-2X/def2-TZVP level.

Cartesian coordinates and energies of the optimized geometry of **1** at M05-2X/def2-TZVP level of theory.
Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-2371.622561 E_h
Sum of electronic and zero-point Energies	-2371.019222 E_h
Sum of electronic and thermal Energies	-2370.984226 E_h
Sum of electronic and thermal Enthalpies	-2370.983282 E_h
Sum of electronic and thermal Free Energies	-2371.085056 E_h
Number of imaginary frequencies	0

Cl	1.44847	-0.27586	-2.38583
Si	-0.00465	-0.35461	-0.75453
N	-1.44439	-0.21246	0.60705
Cl	-0.41261	-2.39545	-1.00620
N	1.23688	-0.14974	0.55312
C	1.05602	-0.56331	1.81864
H	1.96873	-0.63035	2.39653
C	-1.34705	-0.57364	1.84848
H	-2.25338	-0.59360	2.44552
C	-4.17333	1.98173	-0.57767
H	-4.35070	3.03185	-0.75524
C	2.62696	0.15298	0.26427
C	-2.73682	0.20456	0.13956
C	-0.11824	-0.86474	2.45203
H	-0.08732	-1.17999	3.47949
C	2.99361	1.48137	0.03511
C	-1.90239	2.61139	0.27477
H	-0.96889	2.10133	0.49886
C	-2.93983	1.57163	-0.09197
C	3.55859	-0.88576	0.26110
C	-3.75507	-0.73341	-0.06712
C	-4.97561	-0.27071	-0.55093
H	-5.77475	-0.97722	-0.71871
C	-3.61323	-2.20801	0.24658
H	-2.58776	-2.40392	0.54247
C	3.17735	-2.34511	0.40464
H	2.09944	-2.42029	0.52185

C	4.33861	1.76000	-0.16082
H	4.65289	2.77459	-0.34469
C	5.28773	0.75145	-0.13454
H	6.32983	0.98757	-0.28839
C	-5.18426	1.06810	-0.81773
H	-6.13768	1.40241	-1.19813
C	4.89658	-0.55669	0.06813
H	5.63621	-1.34357	0.05964
C	1.95552	2.58245	0.00603
H	1.05902	2.17836	-0.46511
C	3.83588	-2.98084	1.63035
H	4.92033	-2.97772	1.53164
H	3.51154	-4.01501	1.73314
H	3.58387	-2.44907	2.54667
C	-3.90469	-3.07418	-0.97918
H	-4.94860	-2.99163	-1.27811
H	-3.70404	-4.11937	-0.74894
H	-3.28020	-2.78104	-1.81884
C	-4.53102	-2.60296	1.40630
H	-4.32314	-2.01594	2.29967
H	-4.39680	-3.65640	1.64680
H	-5.57601	-2.44673	1.14258
C	-2.34356	3.34165	1.54618
H	-3.28751	3.85842	1.37771
H	-1.59822	4.07805	1.84259
H	-2.48525	2.64226	2.36879
C	2.38204	3.78608	-0.82874
H	3.18883	4.33747	-0.34795
H	1.54242	4.46931	-0.93836
H	2.70886	3.48013	-1.82020
C	3.53985	-3.12423	-0.86162
H	3.07201	-2.67558	-1.73394
H	3.19671	-4.15386	-0.77123
H	4.61842	-3.13855	-1.01316
C	-1.63578	3.60428	-0.85349
H	-1.31970	3.09381	-1.76099
H	-0.85110	4.29751	-0.55418
H	-2.52243	4.19279	-1.08219
C	1.59871	3.02759	1.42605
H	1.20468	2.20494	2.02012
H	0.85070	3.81935	1.39736
H	2.48689	3.41414	1.92459
H	-0.78921	0.66772	-1.45734

Cartesian coordinates and energies of the optimized geometry of **2** at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-2784.824989 E_h
Sum of electronic and zero-point Energies	-2783.988735 E_h
Sum of electronic and thermal Energies	-2783.939813 E_h
Sum of electronic and thermal Enthalpies	-2783.938869 E_h
Sum of electronic and thermal Free Energies	-2784.067646 E_h
Number of imaginary frequencies	0

Cl	2.60057	1.49545	1.59413
Si	1.40824	-0.08750	1.00106
N	-0.11221	0.46920	0.45639
C	-0.84094	-0.05153	-0.70878
H	-1.14647	0.84241	-1.25698

Si	-3.50274	-0.01827	-1.11666
N	2.11239	-0.91134	-0.34706
C	0.04990	-0.81600	-1.64910
H	-0.41658	-1.09748	-2.58094
Si	-2.07276	-2.46636	0.06293
N	-2.09362	-0.76816	-0.38411
C	1.33539	-1.13242	-1.48246
H	1.86327	-1.64692	-2.27460
C	-0.48765	2.88544	0.29299
C	-1.04190	4.04688	0.81368
H	-0.92153	4.97677	0.27753
C	-1.73354	4.03812	2.01196
H	-2.14963	4.95344	2.40542
C	-1.88195	2.85277	2.70419
H	-2.41251	2.84964	3.64439
C	-1.36326	1.65981	2.20948
C	-1.53830	0.39353	3.01738
H	-1.26275	-0.43961	2.37684
C	-0.61557	0.41273	4.23883
H	0.42229	0.57333	3.95363
H	-0.68552	-0.52757	4.78464
H	-0.90390	1.22054	4.91144
C	-2.98593	0.18173	3.45693
H	-3.08206	-0.77791	3.96345
H	-3.65782	0.19103	2.60087
H	-3.30873	0.95261	4.15431
C	0.27511	2.97731	-1.01515
H	0.69578	1.99791	-1.23511
C	-0.64181	3.38152	-2.17436
H	-1.48866	2.70843	-2.28600
H	-0.08214	3.38522	-3.10876
H	-1.03577	4.38448	-2.01395
C	1.43316	3.97288	-0.92517
H	1.06390	4.98260	-0.75338
H	1.98478	3.97774	-1.86467
H	2.11562	3.71484	-0.12052
C	3.51947	-1.18993	-0.44891
C	4.34409	-0.29918	-1.14914
C	5.69093	-0.61683	-1.28902
H	6.33762	0.05056	-1.83813
C	6.21689	-1.76439	-0.72872
H	7.26657	-1.99031	-0.84178
C	5.39606	-2.62089	-0.01753
H	5.81488	-3.51288	0.42077
C	4.04019	-2.35630	0.13054
C	3.14874	-3.35845	0.83106
H	2.30991	-2.82132	1.26195
C	3.84232	-4.10236	1.96941
H	3.10391	-4.67368	2.52907
H	4.33499	-3.41290	2.65224
H	4.58345	-4.80804	1.59749
C	2.59872	-4.35621	-0.19176
H	2.03025	-3.85234	-0.97151
H	1.94660	-5.08061	0.29435
H	3.42205	-4.89227	-0.66359
C	3.82701	0.98262	-1.76805
H	2.82718	1.16618	-1.38243
C	3.73640	0.85769	-3.29069
H	4.72388	0.67461	-3.71394
H	3.34790	1.78067	-3.72013

H	3.08351	0.03995	-3.58668
C	4.69937	2.18134	-1.39287
H	4.80478	2.26445	-0.31382
H	4.24990	3.09802	-1.76880
H	5.69228	2.09937	-1.83126
C	-3.46920	-2.90455	1.24032
H	-3.63225	-2.12360	1.97941
H	-3.17225	-3.80987	1.77160
H	-4.41017	-3.10998	0.73981
C	-2.21256	-3.58462	-1.44132
H	-3.08073	-3.33359	-2.04999
H	-2.31571	-4.62290	-1.12457
H	-1.32513	-3.50737	-2.06733
C	-0.50159	-2.92595	0.96627
H	0.38815	-2.69424	0.39034
H	-0.51920	-4.00628	1.11915
H	-0.43278	-2.45458	1.94464
C	-3.25296	0.09656	-2.97928
H	-2.36763	0.66645	-3.25786
H	-4.11446	0.57871	-3.44137
H	-3.15592	-0.90160	-3.40679
C	-5.06262	-1.01827	-0.84567
H	-5.00326	-2.03258	-1.23358
H	-5.85574	-0.50239	-1.38900
H	-5.35071	-1.05996	0.20205
C	-3.83810	1.69225	-0.43666
H	-4.06329	1.64641	0.62767
H	-4.70634	2.10612	-0.95161
H	-3.00995	2.38510	-0.56090
C	-0.66165	1.67999	0.99824
H	1.40087	-0.92736	2.20760

Cartesian coordinates and energies of the optimized geometry of **4** at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1910.764140 E_h
Sum of electronic and zero-point Energies	-1910.171843 E_h
Sum of electronic and thermal Energies	-1910.138620 E_h
Sum of electronic and thermal Enthalpies	-1910.137676 E_h
Sum of electronic and thermal Free Energies	-1910.235681 E_h
Number of imaginary frequencies	0

Cl	-0.02861	-2.37478	-1.10866
Si	0.00945	-0.18913	-0.82622
N	-1.34089	-0.14294	0.49149
C	-1.21863	-0.59470	1.72257
H	-2.13569	-0.67515	2.29694
C	2.66715	0.14344	0.07103
N	1.34334	-0.20632	0.50881
C	-0.02145	-0.91920	2.34064
H	-0.03704	-1.27202	3.35601
C	1.19725	-0.63451	1.74226
H	2.10397	-0.72925	2.33114
C	-2.66806	0.18026	0.03906
C	-2.97073	1.52019	-0.25356
C	-4.25502	1.81837	-0.68504
H	-4.51574	2.83698	-0.92224
C	-5.21586	0.82833	-0.81373
H	-6.21024	1.08292	-1.14811
C	-4.89777	-0.48051	-0.52005

H	-5.64818	-1.24926	-0.62929
C	-3.61930	-0.83670	-0.09703
C	-3.33159	-2.29823	0.17959
H	-2.28237	-2.40950	0.43546
C	-3.57294	-3.15074	-1.06729
H	-4.62617	-3.15152	-1.34516
H	-3.27418	-4.17937	-0.87186
H	-2.98982	-2.78020	-1.90624
C	-4.17378	-2.81451	1.34809
H	-3.99984	-2.23887	2.25596
H	-3.93199	-3.85680	1.54966
H	-5.23616	-2.75407	1.11607
C	-1.94681	2.61787	-0.04728
H	-0.98876	2.24534	-0.40836
C	-1.80475	2.95418	1.43988
H	-1.04863	3.72684	1.57918
H	-1.51428	2.08546	2.02590
H	-2.75172	3.32855	1.82797
C	-2.25393	3.88821	-0.83321
H	-2.40998	3.67624	-1.88895
H	-1.42004	4.58084	-0.74231
H	-3.13719	4.39250	-0.44363
C	2.96356	1.49614	-0.13339
C	4.23520	1.82831	-0.58238
H	4.48440	2.86679	-0.74319
C	5.18769	0.85268	-0.81371
H	6.17154	1.12852	-1.16197
C	4.87828	-0.47590	-0.59214
H	5.62737	-1.23336	-0.76905
C	3.61639	-0.86146	-0.15173
C	3.33550	-2.33290	0.06934
H	2.29217	-2.45171	0.34544
C	3.54959	-3.13731	-1.21333
H	4.59535	-3.12058	-1.51782
H	2.94354	-2.74044	-2.02360
H	3.26209	-4.17450	-1.04900
C	4.20285	-2.88932	1.20048
H	3.96611	-3.93819	1.37141
H	4.04689	-2.34446	2.13035
H	5.25996	-2.81874	0.94756
C	1.97435	2.60244	0.16477
H	1.04598	2.14966	0.50612
C	2.48916	3.49666	1.29469
H	3.40932	3.99973	1.00150
H	2.69336	2.91643	2.19271
H	1.74973	4.25954	1.53475
C	1.66642	3.42931	-1.08277
H	0.94644	4.21088	-0.84423
H	1.25360	2.80142	-1.86963
H	2.56653	3.91081	-1.46183

Cartesian coordinates and energies of the optimized geometry of [**4**-H]$^+$ at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1911.180827 E_h
Sum of electronic and zero-point Energies	-1910.578329 E_h
Sum of electronic and thermal Energies	-1910.544894 E_h
Sum of electronic and thermal Enthalpies	-1910.543950 E_h
Sum of electronic and thermal Free Energies	-1910.643821 E_h
Number of imaginary frequencies	0

Cl	0.00032	-1.79391	-1.61234
Si	-0.00009	-0.11332	-0.48015
N	-1.34259	-0.10460	0.64761
C	-1.20887	-0.33175	1.94761
H	-2.13445	-0.36765	2.50842
N	1.34248	-0.10413	0.64754
C	0.00001	-0.48904	2.60344
H	0.00008	-0.66994	3.66305
C	1.20881	-0.33143	1.94753
H	2.13442	-0.36720	2.50831
C	-2.66682	0.10749	0.08768
C	-3.48647	-1.00080	-0.14771
C	-4.74079	-0.75430	-0.69295
H	-5.40638	-1.58230	-0.88152
C	-5.14892	0.53135	-0.99829
H	-6.12658	0.69731	-1.42423
C	-4.31274	1.60583	-0.75493
H	-4.64934	2.60512	-0.98403
C	-3.05148	1.42044	-0.20280
C	-2.19647	2.62697	0.12420
H	-1.20938	2.28859	0.43719
C	-2.01131	3.54717	-1.08191
H	-1.60001	3.01179	-1.93564
H	-1.33720	4.36182	-0.82533
H	-2.95718	3.98938	-1.38675
C	-2.80459	3.39419	1.30139
H	-3.79208	3.76900	1.03854
H	-2.17721	4.24399	1.56322
H	-2.91057	2.75714	2.17795
C	-3.08982	-2.42034	0.19912
H	-2.02800	-2.44078	0.43673
C	-3.86326	-2.90304	1.42983
H	-3.69136	-2.26540	2.29562
H	-3.56672	-3.91832	1.68508
H	-4.93272	-2.90248	1.22654
C	-3.31502	-3.37726	-0.97240
H	-4.37610	-3.51381	-1.16949
H	-2.89867	-4.35363	-0.73323
H	-2.84412	-3.01145	-1.88143
C	2.66675	0.10770	0.08763
C	3.48651	-1.00069	-0.14695
C	4.74094	-0.75444	-0.69205
H	5.40662	-1.58252	-0.87999
C	5.14905	0.53104	-0.99812
H	6.12680	0.69679	-1.42396
C	4.31275	1.60561	-0.75563
H	4.64931	2.60477	-0.98532
C	3.05140	1.42049	-0.20360
C	2.19629	2.62719	0.12250
H	1.20921	2.28897	0.43568
C	2.01119	3.54652	-1.08428
H	2.95707	3.98854	-1.38935
H	1.33702	4.36132	-0.82836
H	1.60001	3.01050	-1.93767
C	2.80429	3.39527	1.29920
H	2.91017	2.75885	2.17623
H	2.17685	4.24524	1.56035
H	3.79180	3.76992	1.03620

C	3.08984	-2.42010	0.20035
H	2.02797	-2.44051	0.43777
C	3.86310	-2.90239	1.43134
H	4.93260	-2.90179	1.22824
H	3.56661	-3.91764	1.68681
H	3.69100	-2.26454	2.29692
C	3.31529	-3.37740	-0.97082
H	2.84447	-3.01194	-1.88003
H	2.89900	-4.35372	-0.73136
H	4.37641	-3.51390	-1.16774
H	-0.00046	1.04891	-1.36389

Cartesian coordinates and energies of the optimized geometry of [**4**-H_2] at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1911.953579 E_h
Sum of electronic and zero-point Energies	-1911.343116 E_h
Sum of electronic and thermal Energies	-1911.309466 E_h
Sum of electronic and thermal Enthalpies	-1911.308522 E_h
Sum of electronic and thermal Free Energies	-1911.407731 E_h
Number of imaginary frequencies	0

Cl	1.11682	-1.19154	-1.93333
Si	-0.34358	-0.56786	-0.41003
N	-1.76373	0.01298	0.87192
N	0.90885	-0.25579	0.88093
C	0.67039	-0.41723	2.18968
H	1.56316	-0.46609	2.80025
C	-1.72728	-0.16442	2.15269
H	-2.64356	-0.01916	2.71839
C	-4.33755	2.12082	-0.72462
H	-4.48352	3.15062	-1.01362
C	2.31533	-0.09592	0.57370
C	-2.99781	0.40544	0.26720
C	-0.53979	-0.48056	2.83049
H	-0.55405	-0.61894	3.89657
C	2.77134	1.15607	0.15267
C	-2.08899	2.77477	0.20185
H	-1.17324	2.24508	0.45358
C	-3.15102	1.74421	-0.11241
C	3.17967	-1.17943	0.74328
C	-3.99360	-0.54719	0.03222
C	-5.16605	-0.12243	-0.58626
H	-5.95204	-0.83878	-0.77540
C	-3.85143	-2.00110	0.43138
H	-2.86502	-2.14406	0.86456
C	2.69982	-2.57156	1.10140
H	1.61186	-2.57328	1.10080
C	4.13459	1.31715	-0.05559
H	4.51607	2.27081	-0.38330
C	5.01608	0.26897	0.14758
H	6.07340	0.41467	-0.01487
C	-5.33992	1.19527	-0.96327
H	-6.25656	1.50347	-1.44298
C	4.53835	-0.96691	0.53665
H	5.22711	-1.78849	0.66589
C	1.81023	2.30862	-0.05219
H	0.88686	1.90017	-0.46090
C	3.18594	-2.99133	2.49086

H	4.27464	-3.01283	2.51925
H	2.82245	-3.98964	2.72924
H	2.84688	-2.30886	3.26793
C	-3.95823	-2.92301	-0.78371
H	-4.94459	-2.85282	-1.23980
H	-3.80042	-3.95704	-0.48131
H	-3.21506	-2.66527	-1.53488
C	-4.89180	-2.38174	1.48645
H	-4.81793	-1.74270	2.36489
H	-4.75105	-3.41567	1.79734
H	-5.89993	-2.28430	1.08632
C	-2.50531	3.59328	1.42619
H	-3.43169	4.13018	1.22397
H	-1.73451	4.32022	1.67867
H	-2.67051	2.95070	2.28984
C	2.31562	3.34316	-1.05342
H	3.15092	3.91319	-0.64913
H	1.51884	4.04942	-1.27899
H	2.63103	2.87204	-1.98185
C	3.15486	-3.59613	0.05982
H	2.85029	-3.29048	-0.93694
H	2.71233	-4.56639	0.28126
H	4.23735	-3.71359	0.07546
C	-1.78558	3.68913	-0.98194
H	-1.50372	3.11168	-1.86026
H	-0.96384	4.35723	-0.72759
H	-2.64274	4.30943	-1.23826
C	1.48807	2.98643	1.28222
H	1.04303	2.29081	1.99113
H	0.79243	3.81147	1.12985
H	2.40143	3.38586	1.72219
H	-0.82790	0.52216	-1.27237
H	-0.95533	-1.91169	-0.36904

Cartesian coordinates and energies of the optimized geometry of **A** at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1444.913086 E_h
Sum of electronic and zero-point Energies	-1444.553206 E_h
Sum of electronic and thermal Energies	-1444.531918 E_h
Sum of electronic and thermal Enthalpies	-1444.530974 E_h
Sum of electronic and thermal Free Energies	-1444.604327 E_h
Number of imaginary frequencies	0

C	0.40510	2.45362	0.02812
C	-0.05802	-0.04455	-0.11610
C	0.46604	-2.50971	-0.48738
N	0.72054	1.02676	-0.05530
N	0.70383	-1.06703	-0.47411
Si	2.14742	0.07615	-0.86846
C	1.65818	-3.12165	-1.21685
H	1.70217	-2.76368	-2.24430
H	2.58728	-2.85661	-0.71314
H	1.56656	-4.20582	-1.22613
C	0.43307	-3.02955	0.94969
H	1.34410	-2.74146	1.46989
H	-0.42371	-2.62213	1.48299
H	0.34998	-4.11571	0.94929
C	-0.81958	-2.89292	-1.21705
H	-1.70531	-2.58101	-0.67039

H	-0.84061	-2.44582	-2.20975
H	-0.85291	-3.97616	-1.32530
C	-0.12333	2.96459	-1.31160
H	-1.08096	2.50461	-1.54691
H	-0.26346	4.04405	-1.26971
H	0.58613	2.73373	-2.10478
C	1.72963	3.14094	0.34867
H	2.12744	2.77188	1.29175
H	2.46179	2.94019	-0.43395
H	1.58419	4.21734	0.41464
C	-0.59637	2.75638	1.13971
H	-1.59302	2.39730	0.89867
H	-0.27161	2.30322	2.07477
H	-0.64928	3.83520	1.27826
C	-1.52677	-0.08320	0.10003
C	-2.03343	-0.30842	1.37302
C	-2.39131	0.09769	-0.97212
C	-3.40427	-0.35339	1.57201
H	-1.35386	-0.43607	2.20254
C	-3.76114	0.05684	-0.76895
H	-1.98924	0.25543	-1.96222
C	-4.26803	-0.16979	0.50245
H	-3.79743	-0.52782	2.56185
H	-4.43209	0.19701	-1.60255
H	-5.33527	-0.20323	0.65962
Cl	3.34993	-0.29272	0.89578

Cartesian coordinates and energies of the optimized geometry of [**A**-H]$^+$ at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1445.316215 E_h
Sum of electronic and zero-point Energies	-1444.945865 E_h
Sum of electronic and thermal Energies	-1444.924660 E_h
Sum of electronic and thermal Enthalpies	-1444.923716 E_h
Sum of electronic and thermal Free Energies	-1444.996476 E_h
Number of imaginary frequencies	0

C	0.25042	2.55720	-0.18673
C	-0.12245	-0.00065	-0.12621
C	0.57210	-2.49126	-0.24282
N	0.61335	1.12072	-0.13020
N	0.72886	-1.01799	-0.31696
C	1.87374	-3.05449	-0.80005
H	2.01210	-2.75706	-1.83911
H	2.72797	-2.72085	-0.20883
H	1.84998	-4.14022	-0.75914
C	0.39984	-2.90884	1.21294
H	1.23521	-2.55849	1.81696
H	-0.52843	-2.51622	1.62107
H	0.36303	-3.99448	1.27356
C	-0.60210	-2.96776	-1.08840
H	-1.55457	-2.66188	-0.66605
H	-0.52313	-2.59298	-2.10738
H	-0.58355	-4.05497	-1.12190
C	-0.30837	2.88628	-1.56667
H	-1.23905	2.35284	-1.74502
H	-0.51348	3.95278	-1.62874
H	0.40732	2.63030	-2.34694
C	1.55875	3.30366	0.04337
H	1.96477	3.08225	1.02860

H	2.29840	3.04033	-0.71671
H	1.38680	4.37430	-0.02784
C	-0.75069	2.91549	0.90353
H	-1.72758	2.47976	0.71521
H	-0.39403	2.59004	1.87883
H	-0.86296	3.99741	0.92364
C	-1.58130	-0.08869	0.05939
C	-2.09149	-0.20947	1.34656
C	-2.42645	-0.03767	-1.04287
C	-3.46264	-0.28405	1.52764
H	-1.42542	-0.23497	2.19639
C	-3.79582	-0.10912	-0.84972
H	-2.01902	0.04250	-2.03972
C	-4.31224	-0.23222	0.43231
H	-3.86629	-0.37853	2.52354
H	-4.45855	-0.07222	-1.70015
H	-5.37980	-0.28783	0.57821
Cl	3.46074	0.09898	0.95454
Si	2.05451	0.14730	-0.47619
H	2.63115	0.29376	-1.81252

Cartesian coordinates and energies of the optimized geometry of [**A**-H_2] at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1446.103417 E_h
Sum of electronic and zero-point Energies	-1445.725280 E_h
Sum of electronic and thermal Energies	-1445.703828 E_h
Sum of electronic and thermal Enthalpies	-1445.702883 E_h
Sum of electronic and thermal Free Energies	-1445.776099 E_h
Number of imaginary frequencies	0

C	0.20370	2.54376	-0.14264
C	-0.24288	-0.00288	-0.26076
C	0.28740	-2.46165	-0.34449
N	0.48691	1.12690	-0.44795
N	0.54981	-1.02084	-0.34222
C	1.46254	-3.09897	-1.08515
H	1.48190	-2.76991	-2.12248
H	2.40251	-2.82181	-0.61322
H	1.36422	-4.18279	-1.06308
C	0.26629	-2.97617	1.09504
H	1.18062	-2.68818	1.60770
H	-0.58721	-2.56994	1.63373
H	0.18480	-4.06253	1.09466
C	-1.00621	-2.85504	-1.05666
H	-1.89181	-2.57274	-0.49479
H	-1.05441	-2.39937	-2.04470
H	-1.01511	-3.93726	-1.17902
C	0.78496	3.39009	-1.27591
H	0.29065	3.14304	-2.21407
H	0.62085	4.44516	-1.06271
H	1.85130	3.22194	-1.38782
C	0.88272	2.89708	1.18184
H	0.46572	2.29354	1.98734
H	1.95264	2.70831	1.12884
H	0.72414	3.94894	1.41613
C	-1.28097	2.87659	-0.03742
H	-1.81118	2.63455	-0.95462

H	-1.76665	2.37295	0.79295
H	-1.36080	3.94981	0.12765
C	-1.70659	-0.06145	-0.02785
C	-2.18893	-0.29917	1.25179
C	-2.58935	0.08410	-1.08953
C	-3.55535	-0.38959	1.46853
H	-1.49530	-0.40177	2.07324
C	-3.95267	-0.01562	-0.87197
H	-2.20339	0.26631	-2.08189
C	-4.43704	-0.25183	0.40723
H	-3.93022	-0.56893	2.46458
H	-4.63808	0.08972	-1.69893
H	-5.50028	-0.32773	0.57626
Cl	3.11412	-0.51239	1.02216
Si	2.09814	0.30942	-0.64582
H	2.96089	1.52412	-0.69866
H	2.38416	-0.33103	-1.94868

Cartesian coordinates and energies of the optimized geometry of $LiN(SiMe_3)_2$ at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-880.982509 E_h
Sum of electronic and zero-point Energies	-880.753686 E_h
Sum of electronic and thermal Energies	-880.735655 E_h
Sum of electronic and thermal Enthalpies	-880.734711 E_h
Sum of electronic and thermal Free Energies	-880.799380 E_h
Number of imaginary frequencies	0

Si	-0.96187	0.14903	0.34615
Si	2.08436	-0.04562	-0.01139
C	2.47413	0.99584	-1.53413
H	2.33870	0.41256	-2.44491
H	3.49991	1.36461	-1.51484
H	1.80555	1.85515	-1.58771
C	2.46117	1.02964	1.49105
H	1.85243	1.93488	1.47939
H	3.50784	1.33440	1.50435
H	2.24804	0.49408	2.41569
C	3.29792	-1.48799	-0.00051
H	3.15708	-2.10244	0.88879
H	4.32973	-1.13752	-0.00886
H	3.15771	-2.12001	-0.87902
C	-1.23335	0.55979	2.15967
H	-1.11737	-0.33053	2.77689
H	-2.22845	0.97158	2.32936
H	-0.50214	1.29359	2.49653
C	-1.32843	1.69915	-0.65124
H	-0.60939	2.47991	-0.40127
H	-2.32618	2.08576	-0.44355
H	-1.24563	1.50275	-1.71946
C	-2.33658	-1.12346	-0.10407
H	-2.34889	-1.39080	-1.16718
H	-3.31513	-0.69089	0.09679
H	-2.29794	-2.03759	0.50094
N	0.48991	-0.62845	-0.02149
Li	-0.27638	-2.16925	-0.54207

Cartesian coordinates and energies of the optimized geometry of $HN(SiMe_3)_2$ at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-874.035123 E_h
Sum of electronic and zero-point Energies	-873.795968 E_h
Sum of electronic and thermal Energies	-873.779022 E_h
Sum of electronic and thermal Enthalpies	-873.778078 E_h
Sum of electronic and thermal Free Energies	-873.838962 E_h
Number of imaginary frequencies	0

Si	-1.06283	0.00318	0.33130
Si	2.07002	-0.11254	-0.03844
C	2.42238	0.83065	-1.61925
H	2.30776	0.18044	-2.48572
H	3.43912	1.22330	-1.61963
H	1.73596	1.66827	-1.73479
C	2.30211	1.05066	1.41168
H	1.60896	1.89016	1.36875
H	3.31276	1.45822	1.40714
H	2.14650	0.52940	2.35488
C	3.26004	-1.55179	0.09028
H	3.11661	-2.09224	1.02465
H	4.29127	-1.20294	0.05272
H	3.11597	-2.24993	-0.73414
C	-1.32054	0.23665	2.17277
H	-1.27956	-0.72047	2.69106
H	-2.29111	0.69143	2.37121
H	-0.55302	0.88224	2.59726
C	-1.14026	1.68433	-0.49272
H	-0.35394	2.34666	-0.13210
H	-2.09607	2.16257	-0.28006
H	-1.03600	1.59074	-1.57276
C	-2.41426	-1.10496	-0.33972
H	-2.31505	-1.23100	-1.41694
H	-3.39694	-0.68170	-0.13583
H	-2.37378	-2.08992	0.12519
N	0.45824	-0.75835	-0.01761
H	0.39305	-1.73408	-0.26423

Cartesian coordinates and energies of the optimized geometry of ^{tBu}NHC at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-619.456816 E_h
Sum of electronic and zero-point Energies	-619.101399 E_h
Sum of electronic and thermal Energies	-619.083865 E_h
Sum of electronic and thermal Enthalpies	-619.082921 E_h
Sum of electronic and thermal Free Energies	-619.144815 E_h
Number of imaginary frequencies	0

N	-1.45870	0.02323	-0.09678
N	0.66070	0.24083	-0.05813
C	-2.78146	-0.63689	-0.04445
C	-0.31379	-0.69512	-0.08023
C	2.93370	0.64933	-0.95789
H	2.47703	0.60830	-1.94544

H	3.91943	0.19219	-1.01713
H	3.07075	1.68660	-0.67370
C	-3.35343	-0.49855	1.36543
H	-2.67893	-0.97069	2.07712
H	-4.32299	-0.99143	1.41943
H	-3.48311	0.54197	1.65152
C	2.56529	0.10941	1.47605
H	2.45886	1.15152	1.76599
H	3.61516	-0.16596	1.56626
H	1.98169	-0.50122	2.16228
C	2.08752	-0.13566	0.04574
C	-3.73119	-0.04040	-1.08430
H	-4.08127	0.94989	-0.81600
H	-4.60353	-0.68524	-1.17053
H	-3.24135	0.00674	-2.05549
C	-1.21107	1.39591	-0.05286
C	0.13767	1.53460	-0.02821
C	-2.22789	2.48814	-0.08665
H	-1.75891	3.42573	0.19395
H	-3.04482	2.31477	0.60770
H	-2.65287	2.61672	-1.08067
C	0.91180	2.81062	-0.02943
H	1.34109	3.02448	-1.00680
H	1.71891	2.80574	0.69719
H	0.25148	3.63305	0.22652
C	-2.61803	-2.12048	-0.35830
H	-2.19476	-2.26037	-1.34989
H	-1.95895	-2.60297	0.35422
H	-3.60428	-2.58141	-0.31828
C	2.24331	-1.61913	-0.27193
H	1.66727	-2.23124	0.41230
H	1.89996	-1.83495	-1.28067
H	3.30020	-1.86953	-0.18899

Cartesian coordinates and energies of the optimized geometry of ^{tBu}NHC-HCl at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-1080.321030E_h
Sum of electronic and zero-point Energies	-1079.950094 E_h
Sum of electronic and thermal Energies	-1079.930474 E_h
Sum of electronic and thermal Enthalpies	-1079.929529 E_h
Sum of electronic and thermal Free Energies	-1079.996265 E_h
Number of imaginary frequencies	0

N	-0.88990	0.77261	0.45836
N	1.28087	0.85486	0.32797
C	-2.23519	0.20349	0.76200
C	3.28441	0.16638	-0.91734
H	2.60758	-0.46296	-1.49446
H	4.23780	-0.34543	-0.80349
H	3.47162	1.09786	-1.44162
C	-2.99610	1.16889	1.66555
H	-2.45967	1.31359	2.60161
H	-3.97138	0.74095	1.88892
H	-3.15390	2.13853	1.20403
C	3.47633	1.42161	1.27975
H	3.51848	2.39129	0.79427
H	4.49646	1.06306	1.40129
H	3.03322	1.54524	2.26641
C	2.69181	0.39327	0.47115

C	-2.96505	-0.06924	-0.55072
H	-3.25895	0.84485	-1.05608
H	-3.86996	-0.63171	-0.32931
H	-2.32176	-0.66594	-1.19663
C	-0.57083	1.84571	-0.36210
C	0.78612	1.89620	-0.44498
C	-1.53925	2.72454	-1.07612
H	-1.07638	3.68688	-1.27124
H	-2.43914	2.90404	-0.50111
H	-1.82559	2.28826	-2.03118
C	1.59157	2.83388	-1.27582
H	1.83560	2.38431	-2.23619
H	2.51428	3.13372	-0.79357
H	1.01208	3.73187	-1.46551
C	0.24413	0.18562	0.80756
H	0.31164	-0.70403	1.38934
Cl	0.19904	-1.79540	-1.25426
C	-2.05990	-1.12477	1.49081
H	-1.50488	-1.82704	0.86914
H	-1.57025	-0.99331	2.45542
H	-3.05181	-1.52768	1.67926
C	2.70537	-0.93803	1.21559
H	2.31867	-0.83691	2.22940
H	2.14093	-1.68751	0.66131
H	3.74079	-1.26047	1.29132

Cartesian coordinates and energies of the optimized geometry of :SiH_2 at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-290.604992 E_h
Sum of electronic and zero-point Energies	-290.593157 E_h
Sum of electronic and thermal Energies	-290.590287 E_h
Sum of electronic and thermal Enthalpies	-290.589343 E_h
Sum of electronic and thermal Free Energies	-290.612883 E_h
Number of imaginary frequencies	0

Si	0.00000	0.00000	0.13319
H	0.00000	1.08288	-0.93230
H	0.00000	-1.08288	-0.93230

Cartesian coordinates and energies of the optimized geometry of $[SiH_3]^+$ at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-290.924037 E_h
Sum of electronic and zero-point Energies	-290.901804 E_h
Sum of electronic and thermal Energies	-290.898819 E_h
Sum of electronic and thermal Enthalpies	-290.897875 E_h
Sum of electronic and thermal Free Energies	-290.922127 E_h
Number of imaginary frequencies	0

Si	0.00000	0.00000	0.00019
H	0.00000	1.27059	0.73194
H	0.00000	-1.27059	0.73194
H	0.00000	0.00000	-1.46650

Cartesian coordinates and energies of the optimized geometry of LiCl at M05-2X/def2-TZVP level of theory. Thermochemistry at 298.150 K, 1.00000 Atm.

Electronic energy	-467.804062469 E_h
Sum of electronic and zero-point Energies	-467.802549 E_h
Sum of electronic and thermal Energies	-467.800061 E_h
Sum of electronic and thermal Enthalpies	-467.799117 E_h
Sum of electronic and thermal Free Energies	-467.823236 E_h
Number of imaginary frequencies	0

Li	0.00000000	0.00000000	0.00000000
Cl	0.00000000	0.00000000	2.02306900

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