Chalcogen-Atom Transfer and Exchange Reactions of NHC-Stabilized Heavier Silaacylium Ions

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Supporting Information

Total: S34 pages

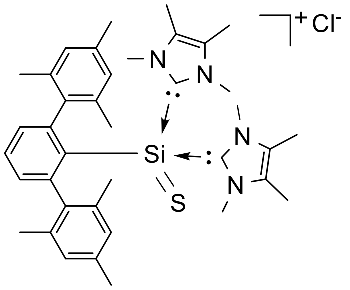
1. Experimental Procedures and NMR Data

General Considerations

All experiments and manipulations were carried out under dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox. All glass junctions were coated with PTFE-based grease Merkel Triboflon III. For compound **2**, the ^{1}H NMR,^{13}C NMR spectra were recorded on Bruker AV-500C spectrometer at ambient temperature, while the ^{1}H, ^{13}C NMR spectra of compounds **3** and **4** were recorded on Bruker 400 MHz spectrometer at 233.2 K for higher resolution. The ^{29}Si NMR spectra of all compounds were measured on Bruker 400 MHz spectrometer. Chemical shifts are referenced to (residual) solvent signals (^{1}H and ^{13}C NMR). Abbreviations: s = singlet, br = broadened, d = doublet, t = triplet, m = multiplet. High resolution mass spectra were recorded on a Thermo Fisher Scientific LTQ Orbitrap XL. UV-VIS spectra were taken on an Agilent Cary 60 spectrophotometer. Melting Points (M_p) were determined in sealed glass capillaries under inert gas by a Büchi M-565. Unless otherwise stated, all reagents were purchased from Sigma-Aldrich or ABCR and used as received. Silyliumylidene **1** was synthesized according to the literature procedure.[S1]

Synthetic procedures

Compound 2



$C_{38}H_{49}ClN_4SSi$
657.43 g/mol

To a solution of **1** (500 mg, 0.80 mmol, 1.00 eq) in acetonitrile (5 mL) was added elemental sulfur (25.6 mg, 0.80 mmol, 1.00 eq) at -78 °C. After 15 min, the reaction mixture was allowed to warm to room temperature and stirred further for 5 h. The color of the solution slowly changed from yellow-orange to light brown. Afterwards, all volatiles were removed under reduced pressure. The residue was washed with dried 15 ml THF and dissolved in 5 ml acetonitrile. This led to a colorless solution of **2**. Slow evaporation at -30 °C afforded white microcrystalline product of **2** in 85% yield with small amount of imidazolium impurity. All attempts to isolate pure compound **2** failed, due to co-crystallization of imidazolium salt along compound **2**.

Alternative procedure

At -78 °C, 1.00 eq of CS_2 was added to a stirred solution of compound **1** (300 mg, 48 mmol, 1.00 eq) through a microliter syringe. The color of the solution immediately turned yellow-orange to dark brown with observable precipitation of carbon monosulfide. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. All volatiles were removed under reduced pressure and the dark brown solid was washed with 40 ml THF and dried, which afforded an off-white solid. Crystallization in 5 ml acetonitrile at -30 °C afforded microcrystalline product of **2** in 56% yield.

M_p: 256 ˚C

^{1} H NMR (500 MHz, 273 K, CD_3CN): δ = 2.03-2.18 {br, 30H; (12H, 4xC-Me, NHC), (12H, 2x$C^{2,6}$- Me, Mes), (6H, 2xC^4 -Me, Mes)} 2.78, 3.97 (br, 12H, 4xN-Me, NHC), 6.63, 6.79 (br, 4H, 2x$C^{3,5}$-H, Mes), 7.08 (d, ^{3} JH−H = 7.61 Hz, 2H, $C^{3,5}$-H, C_6H_3), 7.63 (t, ^{3} JH−H = 7.61 Hz, 1H, C^4 -H, C_6H_3).

^{13}C NMR (125.83 MHz, 298 K, CD_3CN): δ = 8.3, 9.2 (2xs, 2x$C^{4,5}$-Me, NHC), 20.9 (s, C^4-Me, Mes), 21.9, 23.4 (s, $C^{2,6}$-Me, Mes), 34.0, 35.8, 36.7 (s, 4xN-Me, NHC), 128.0-129.4 (br, 2x$C^{4,5}$-Me, NHC), 130.8 (2xC^4 -Mes), 132.4 (s, 2x$C^{3,5}$-H, Mes), 132.8 (s, $C^{3,5}$-H, C_6H_3), 133.9 (s, C^4 -H, C_6H_3), 137.3 (s, Si-C, C_6H_3), 138.7 (2x$C^{2,6}$-Mes), 141.3 (s, 2xC^1 -Mes), 148.6 (s, 2x$C^{2,6}$-C_6H_3), 150.8 (s, 2xSi-C, NHC).

^{29}Si NMR (79.49 MHz, 298 K, CD_3CN): δ = −36.0.

ESI-MS (m/z) = [*m*-TerSi(S)(NHC)$_2$- Cl$^-$] (M)$^+$ 621.34, [*m*-TerSi(S)(NHC) - (NHC) Cl$^-$] 497.24.

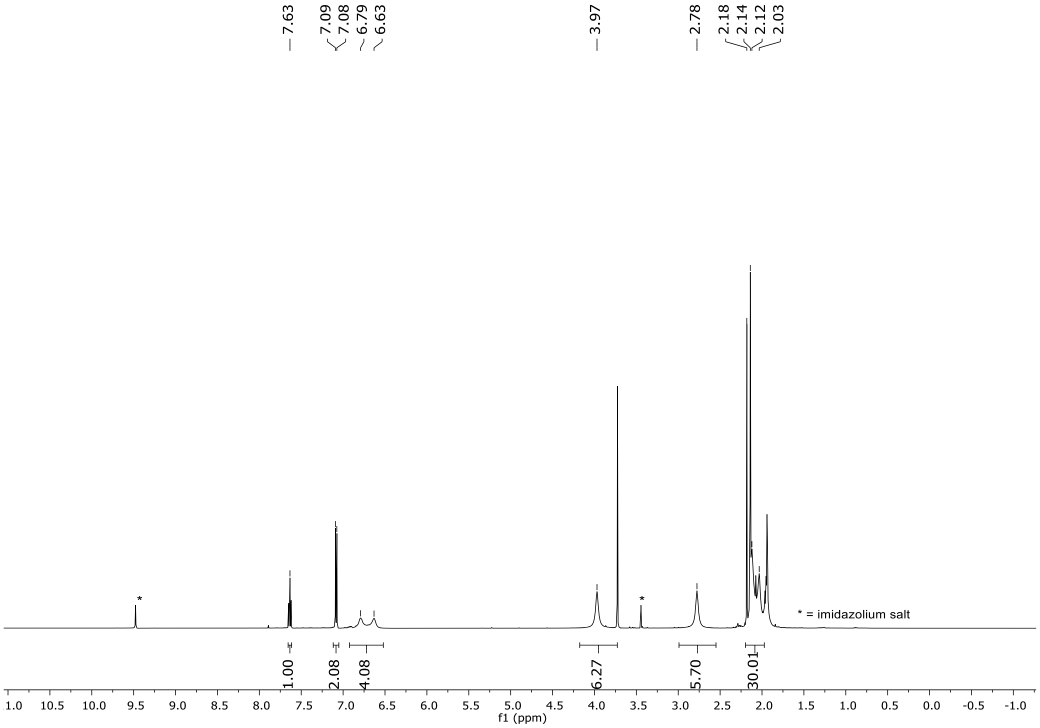


Figure S1. ^{1}H NMR of compound **2** (CD_3CN, 298 K).

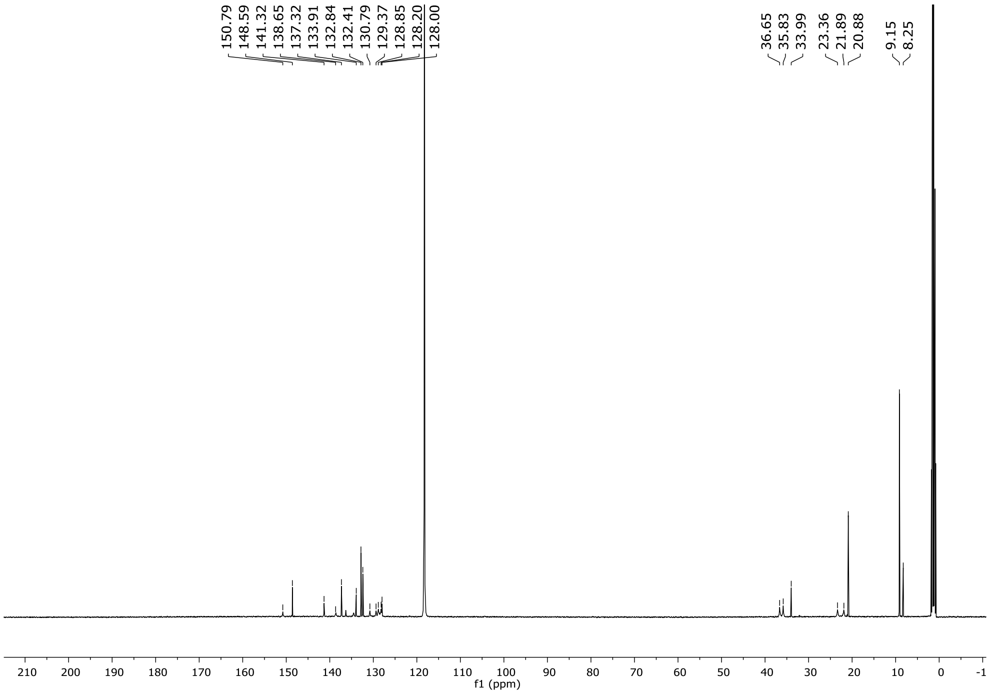


Figure S2. ^{13}C NMR of compound **2** (CD_3CN, 298 K).

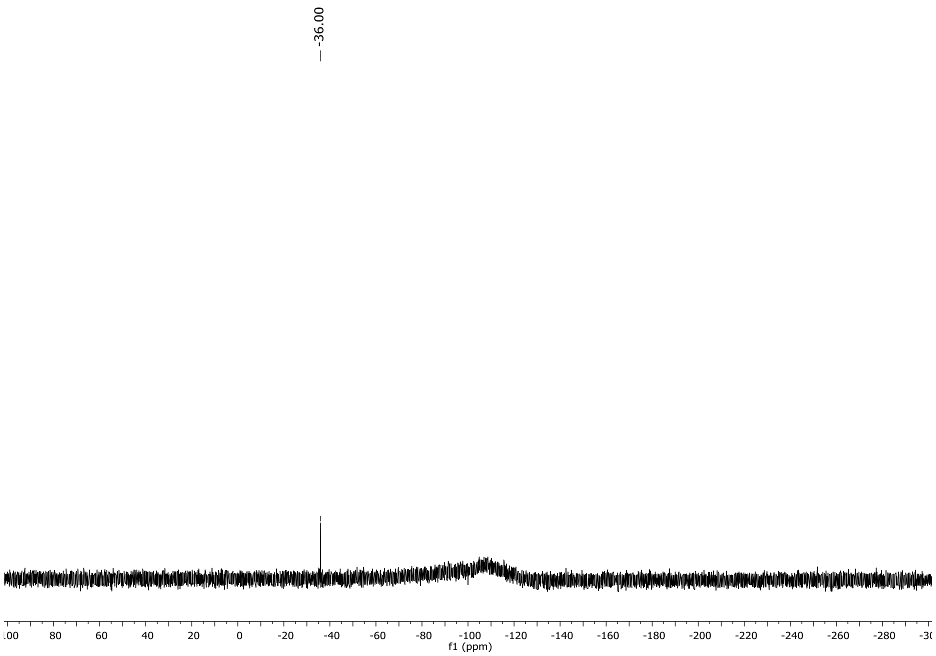


Figure S3. ^{29}Si NMR of compound **2** (CD_3CN, 298 K).

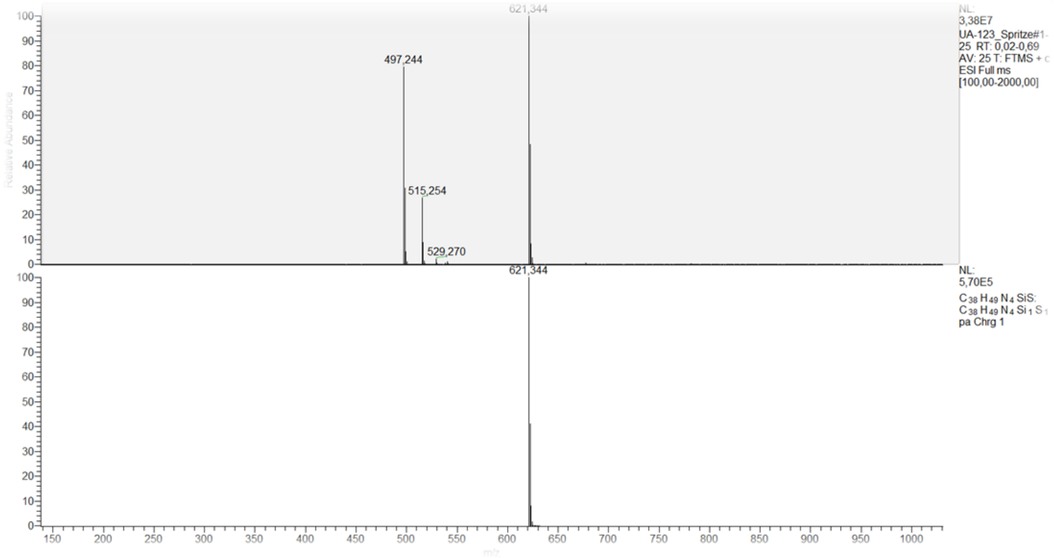


Figure S4. Mass Spectrometric data of **2** (experimental (top), theoretical (bottom)).

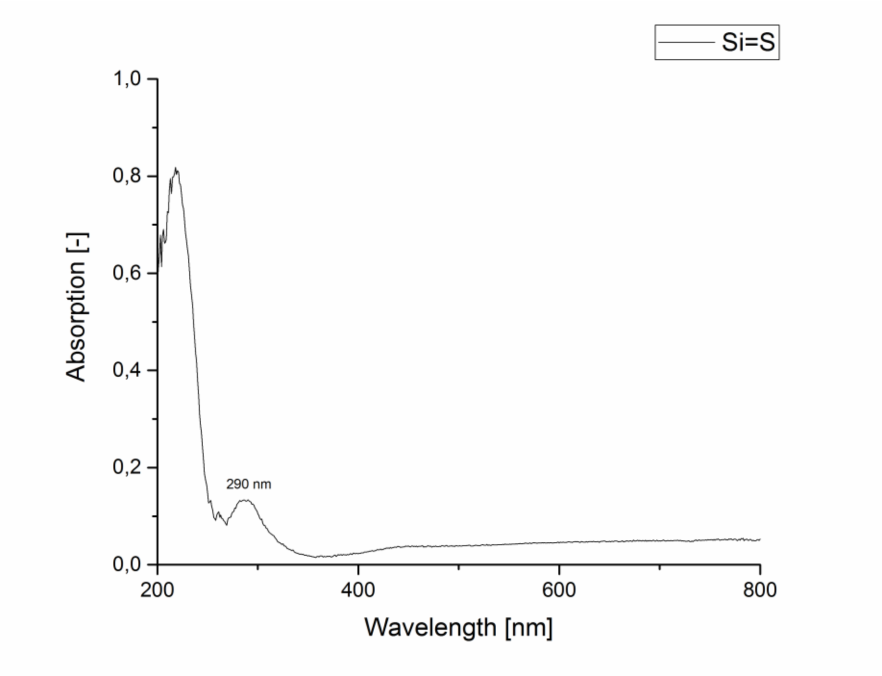


Figure S5. UV-Vis spectra of compound **2** (λ_{max} = 290 nm, 9.0 × 10^{-5} M solution in CH_3CN).

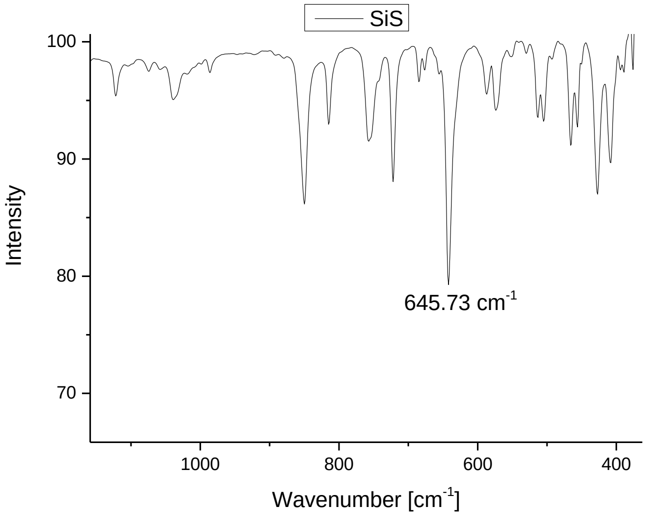
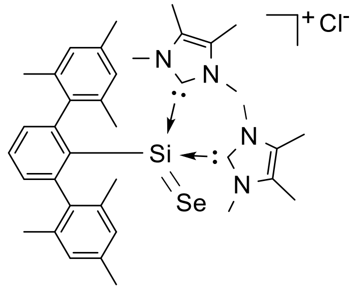


Figure S6. IR spectra of compound **2**.

Compound 3



$C_{38}H_{49}ClN_4SeSi$

704.33 g/mol

A solution of compound **1** (500 mg, 0.80 mmol, 1.00 eq) in acetonitrile (5 mL) was slowly added to a suspension of elemental selenium (63.1 mg, 0.80 mmol, 1.00 eq) in acetonitrile (2 ml) at -78 °C. The resulting mixture was gradually allowed to warm to room temperature and stirred for 8 h. The color of the solution slowly changed from yellow-orange to light yellow. All volatiles were removed *in vacuo*. The residue was washed with dry 15 ml THF and dissolved in 5 ml acetonitrile. Slow evaporation of this solution at -30 °C afforded white crystals of compound **3** (490 mg, 0.69 mmol, 87%), suitable for single crystal X-Ray analysis.

M_p: 242 ˚C

^{1}H NMR (400.13 MHz, 233.2 K, CD_3CN): δ = 1.84, 1.93 (s, 6H, 4xC-Me, NHC), 1.97 (br, 6H, 4xC-Me, NHC), 2.02, 2.10, 2.13, 2.17, 2.21, 2.28 (18H, 2x$C^{2,6}$- Me, 2xC^4 -Me, Mes), 2.48, 2.96, 3.60, 4.26 (s, 12H, 4xN-Me, NHC), 6.56, 6.66, 6.72, 6.90 (s, 4H, 2x$C^{3,5}$-H, Mes), 7.02, 7.14 (d, $^3J_{H-H}$ = 7.50 Hz, 2H, $C^{3,5}$-H, C_6H_3), 7.65 (t, $^3J_{H-H}$ = 7.50 Hz, 1H, C^4 -H, C_6H_3).

^{13}C NMR (100.62 MHz, 233.2 K, CD_3CN): δ = 8.7, 8.8 (s, 2x$C^{4,5}$-Me, NHC), 20.3, 20.5 (s, 2xC^4-Me, Mes), 21.2, 22.0, 22.6, 23.4 (s, 2x$C^{2,6}$-Me, Mes), 34.9, 35.8, 35.9, 37.8 (s, 4xN-Me, NHC), 127.3, 127.7, 128.1, 128.4 (s, 2x$C^{3,5}$-H, Mes), 131.8, 132.8 (s, $C^{3,5}$-H, C_6H_3), 132.1 (s, C^4 -H, C_6H_3), 129.3 (2xC^4 -Mes), 137.1, 137.7 (s, 2x$C^{4,5}$-Me, NHC), 138.4, 138.9 (s, 2x$C^{2,6}$-Mes), 142.2, 144.9 (s, 2xC^1 -Mes), 146.3, 147.5 (s, 2x$C^{2,6}$-C_6H_3), 153.3 (s, 2xSi-C, NHC).

^{29}Si NMR (79.49 MHz, 298 K, CD_3CN): δ = −41.5.

^{77}Se NMR (57.19 MHz, 298 K, CD_3CN): δ = −423.8.

ESI-MS (m/z) = [*m*-TerSi(Se)(NHC)$_2$- Cl^-] $(M)^+$ 669.21, [*m*-TerSi(S)(NHC) - (NHC) Cl^-] 545.19

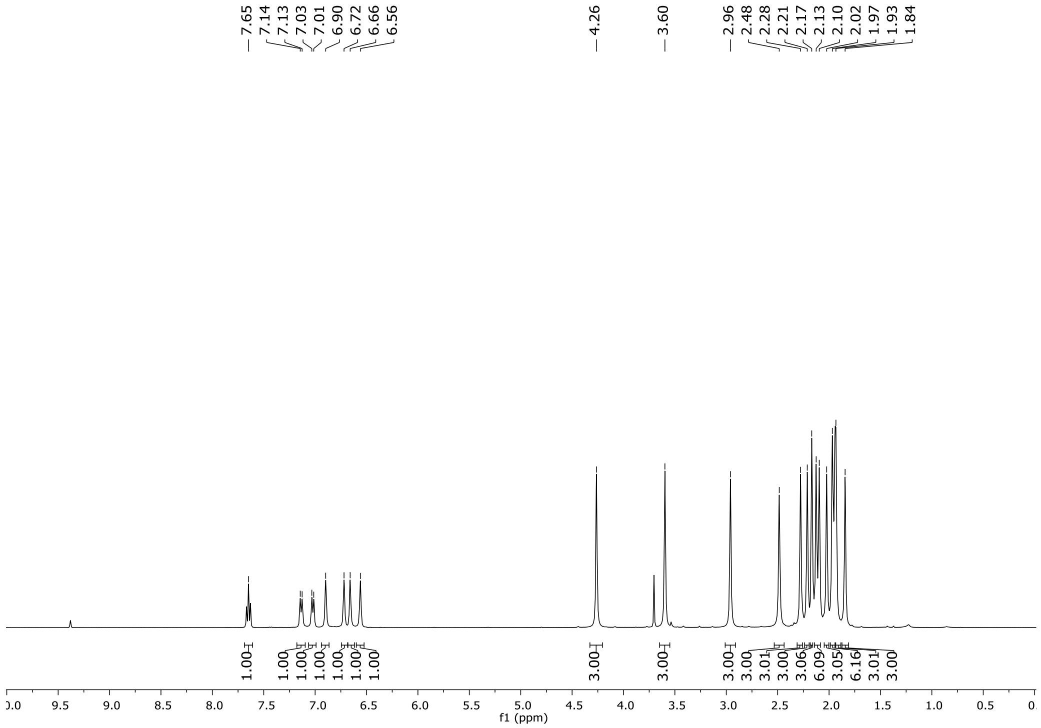


Figure S7. ^{1}H NMR of compound **3** (CD_3CN, 233.2 K).

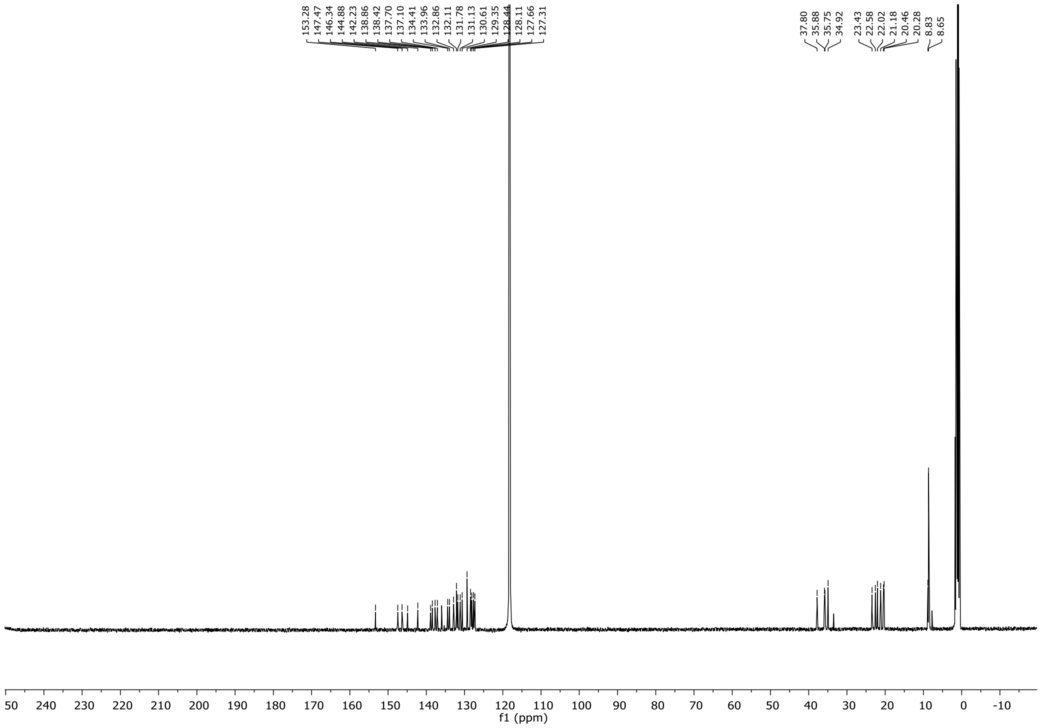


Figure S8. ^{13}C NMR of compound **3** (CD_3CN, 233.2 K).

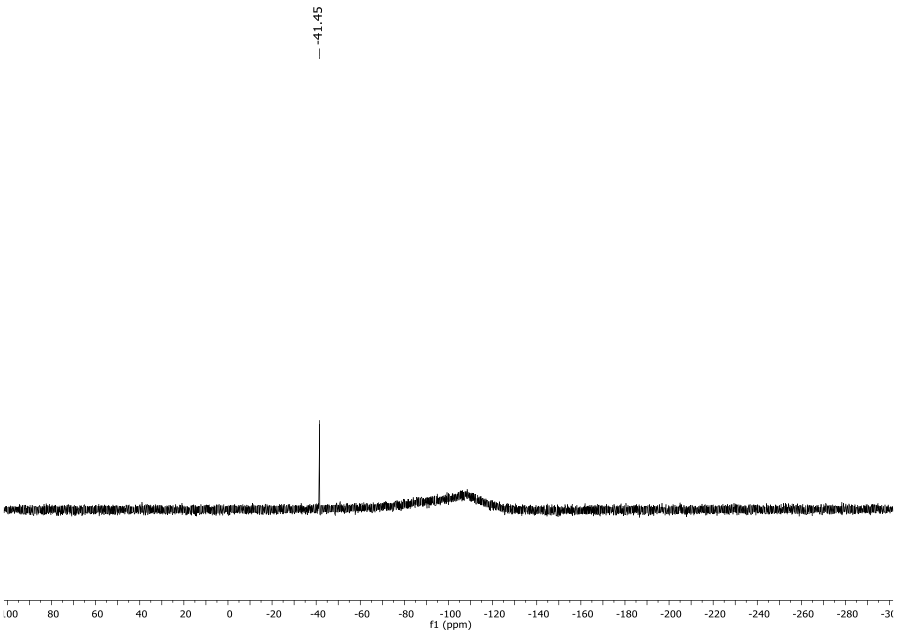


Figure S9. ^{29}Si NMR of compound **3** (CD_3CN, 298 K).

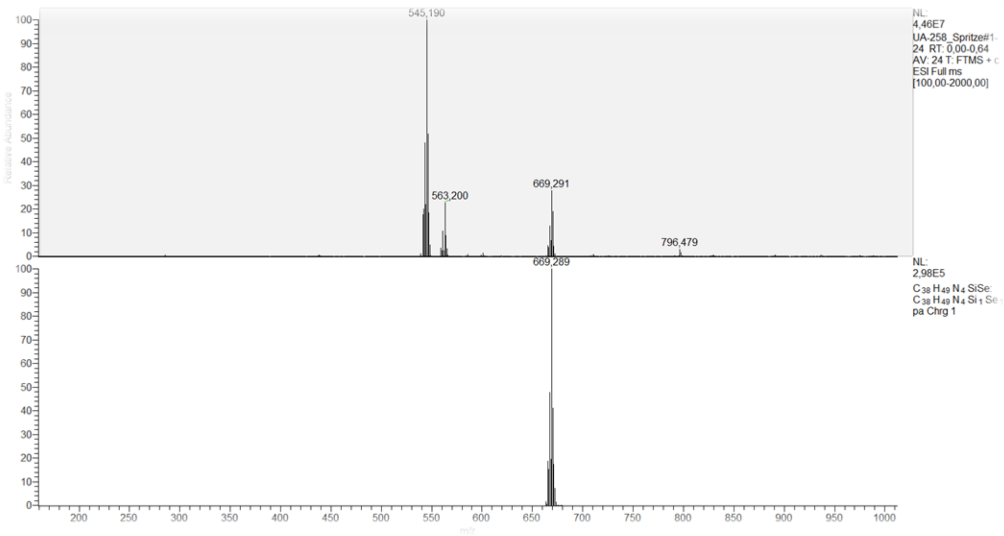


Figure S10. Mass Spectrometric data of compound **3** (experimental (top), theoretical (bottom)).

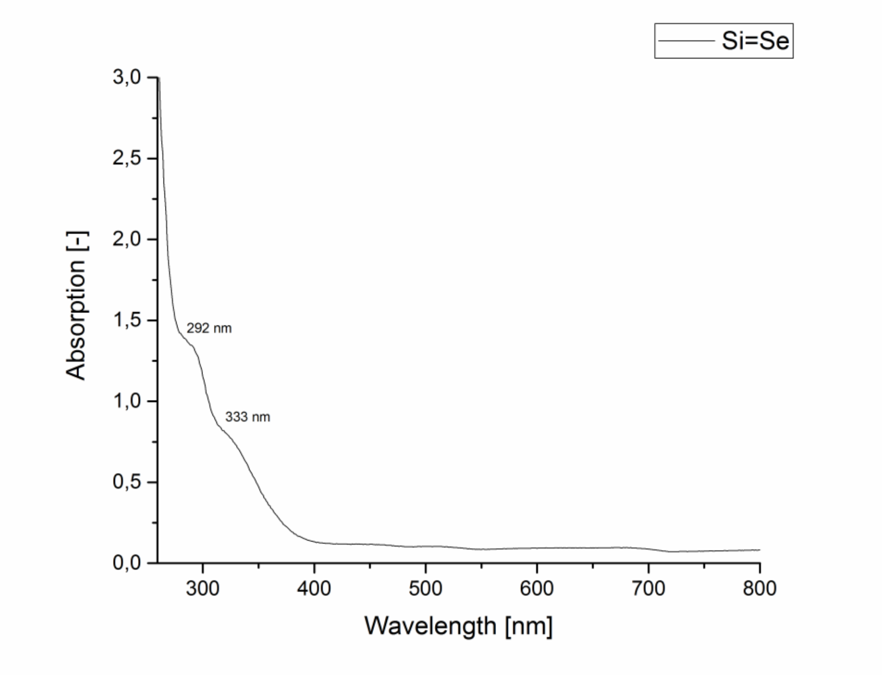


Figure S11. UV-Vis spectra of compound **3** (λ = 292, 333 nm, 1.1 × 10^{-4} M solution in CH_3CN).

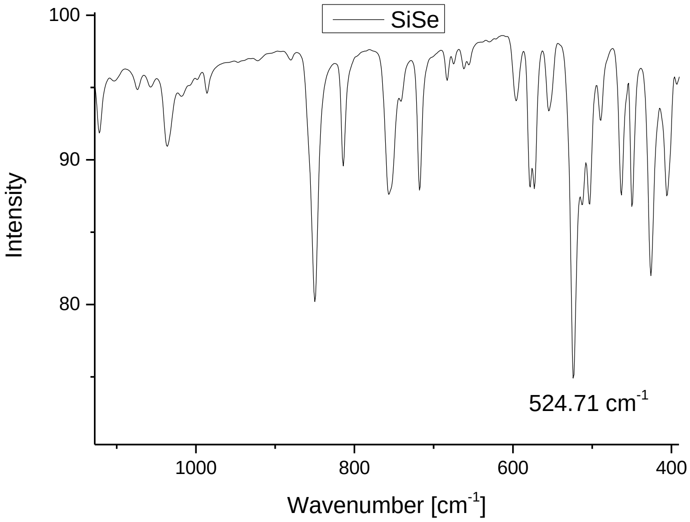
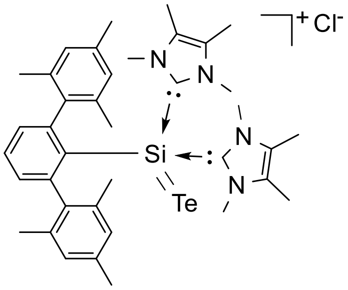


Figure S12. IR spectra of compound **3**.

Compound 4



$C_{38}H_{49}ClN_4TeSi$

752.97 g/mol

At -78 °C, an acetonitrile solution (5 ml) of compound **1** (500 mg, 0.80 mmol, 1.00 eq) was slowly added to a suspension of tellurium (102 mg, 0.80 mmol, 1.00 eq) in acetonitrile (2 ml). The resulting mixture was gradually allowed to warm to room temperature and stirred further for 15 h. The color of the solution slowly changed from yellow-orange to dark yellow. Then, the solution was filtered to remove the unreacted tellurium. At reduced pressure, evaporation of all volatiles from the filtrate afforded compound **4** as yellow solid. Crystallization of compound **4** in 5 ml acetonitrile at -30 °C gave yellow crystals, suitable for single crystal X-Ray analysis (535 mg, 0.71 mmol, 89%).

M_p: 235˚C

^{1}H NMR (400.13 MHz, 233.2 K, CD_3CN): δ= 1.80, 1.87 (s, 6H, 4xC-Me, NHC), 1.95-1.96 (br, 6H, 4xC-Me, NHC), 2.04-2.07, 2.13-2.15 (12H, 2xC^{2,6}- Me, Mes), 2.21 (s, 6H, 2xC^4 -Me, Mes), 2.55, 2.88, 3.50, 4.10 (s, 12H, 4xN-Me, NHC), 6.58, 6.65, 6.71, 6.87 (s, 4H, 2xC^{3,5}-H, Mes), 7.02, 7.11 (d, ^{3} JH−H = 7.50 Hz, 2H, C^{3,5}-H, C_6H_3), 7.64 (t, ^{3} JH−H = 7.50 Hz, 1H, C^4 -H, C_6H_3).

^{13}C NMR (100.63 MHz, 233.2 K, CD_3CN): δ= 8.5, 8.6, 8.7, 8.8 (s, 2xC^{4,5}-Me, NHC), 20.3, 20.5 (s, 2xC^4-Me, Mes), 22.0, 22.3, 22.5, 22.9 (s, 2xC^{2,6}-Me, Mes), 34.66, 35.4, 38.4, 40.9 (s, 4xN-Me, NHC), 128.1, 128.3, 128.6, 128.8 (s, 2xC^{3,5}-H, Mes), 129.6, 129.9 (s, C^{3,5}-H, C_6H_3), 131.6 (s, C^4 -H, C_6H_3), 131.6, 132.2, (2xC^4 -Mes), 135.6, 136.5, 136.9, 137.7, (s, 2xC^{4,5}-Me, NHC), 138.0, 139.1 (s, 2xC^{2,6}-Mes), 142.2, 143.4 (s, 2xC^1 -Mes), 148.5 (s, 2xC^{2,6}-C_6H_3), 154.1 (s, 2xSi-C, NHC).

^{29}Si NMR (79.49 MHz, 298 K, CD_3CN): δ = −72.2.

^{125}Te NMR (94.61 MHz, 298 K, CD_3CN): δ = 1035.6.

ESI-MS (m/z) = [*m*-TerSi(Te)(NHC)$_2$- Cl$^-$] (M)$^+$ 719.28.

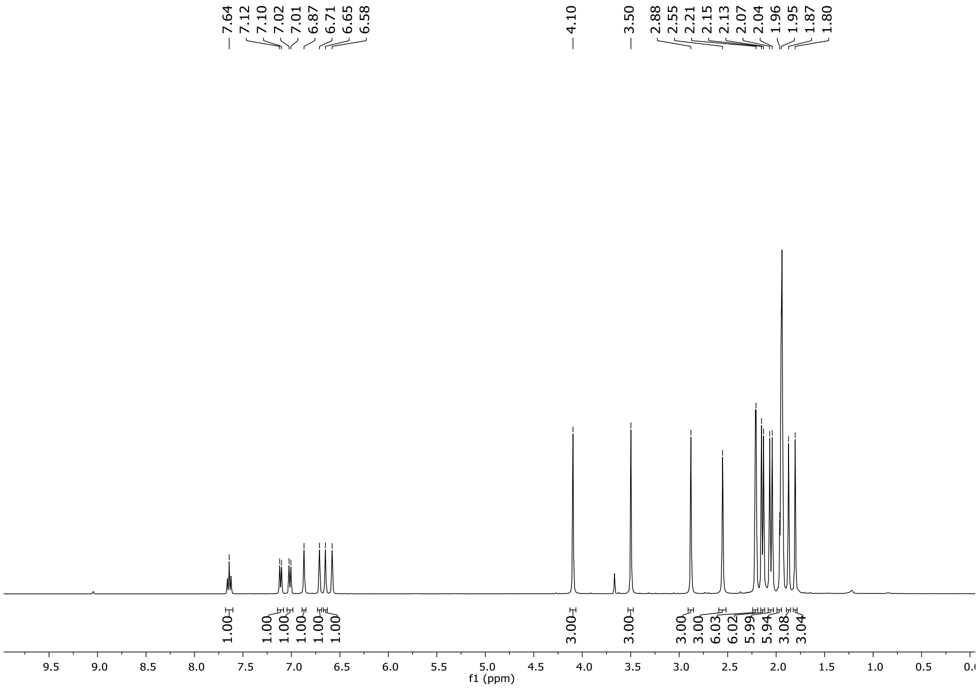


Figure S13. ^{1}H NMR of compound **4** (CD_3CN, 233.2 K).

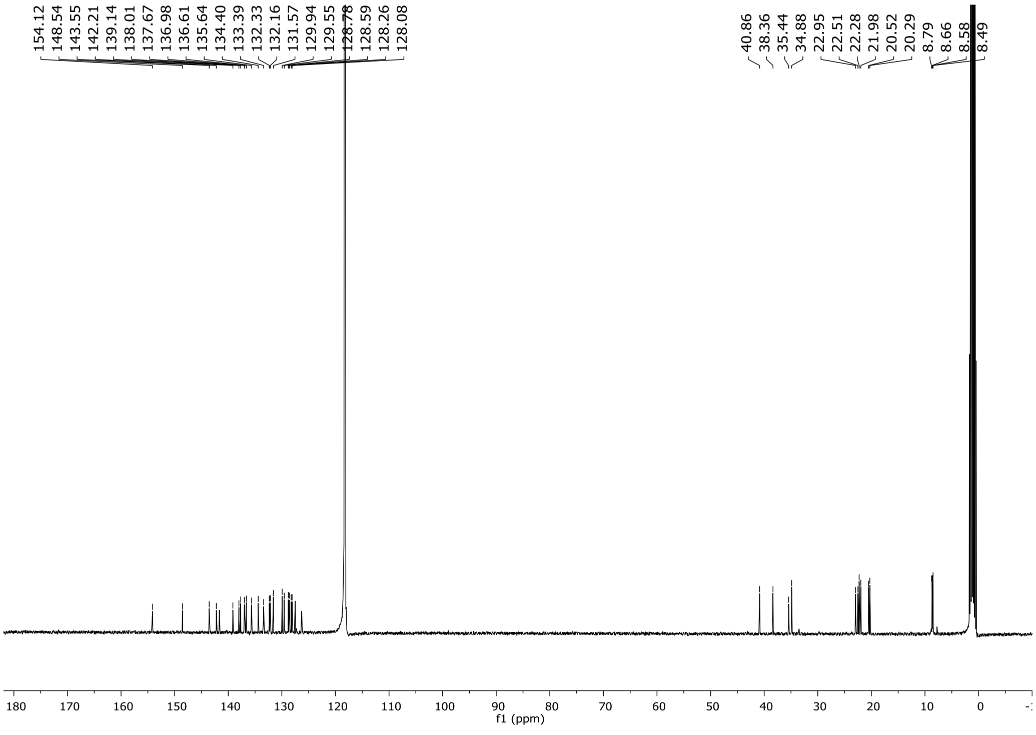


Figure S14. ^{13}C NMR of compound **4** (CD_3CN, 233.2 K).

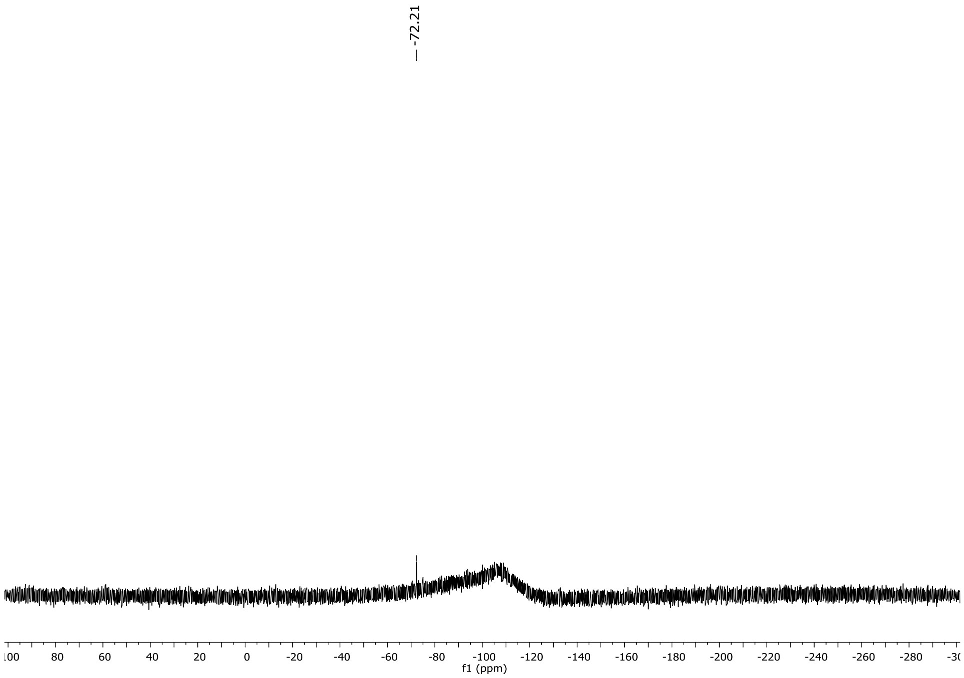


Figure S15. ^{29}Si NMR of compound **4** (CD_3CN, 298 K).

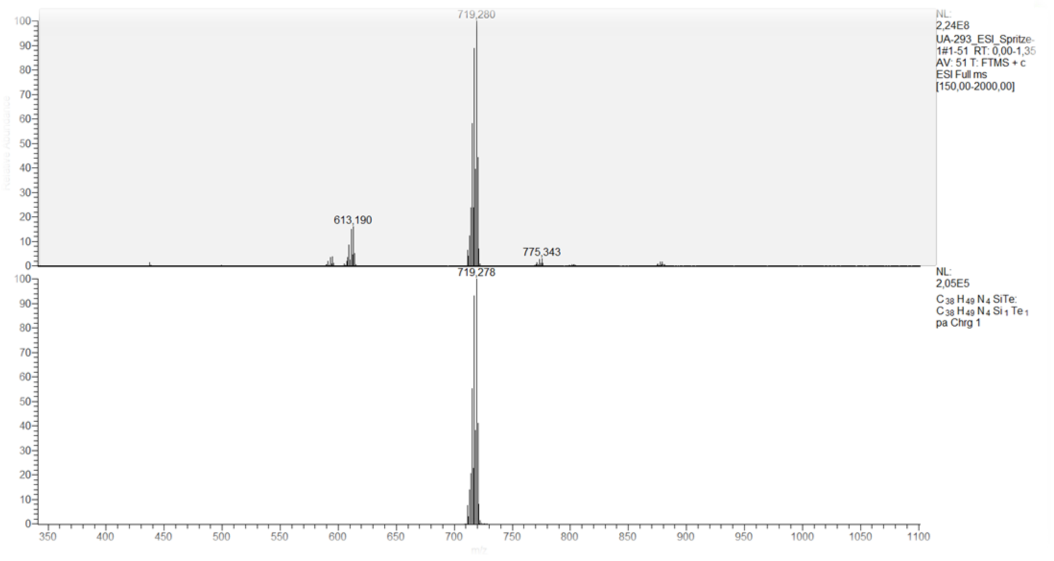


Figure S16. Mass Spectrometric data of compound **4** (experimental (top), theoretical (bottom)).

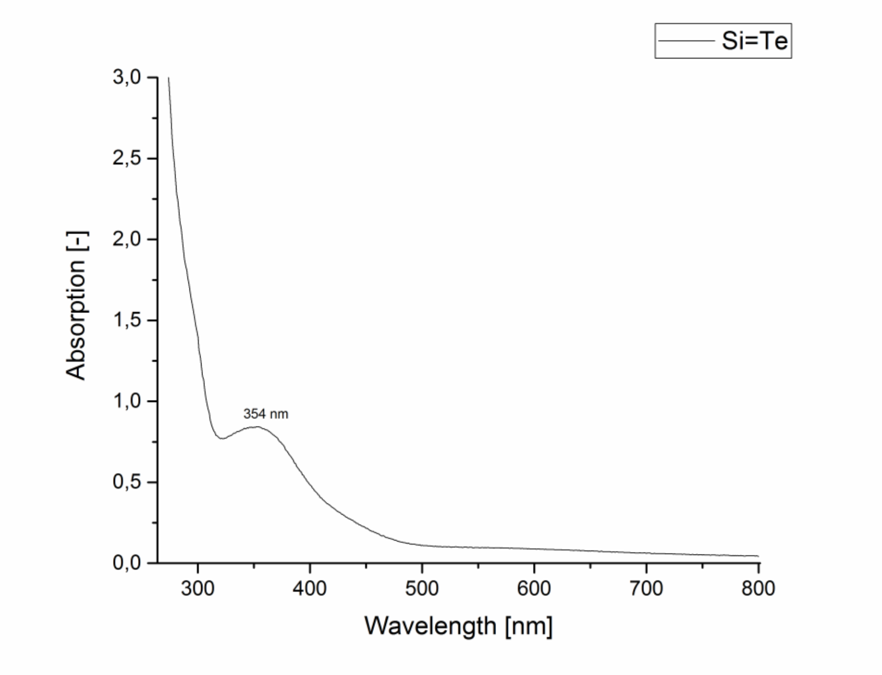


Figure S17. UV-Vis spectra of compound **4** (λ_{max} = 354 nm, 1.8 × 10^{-4} M solution in CH_3CN).

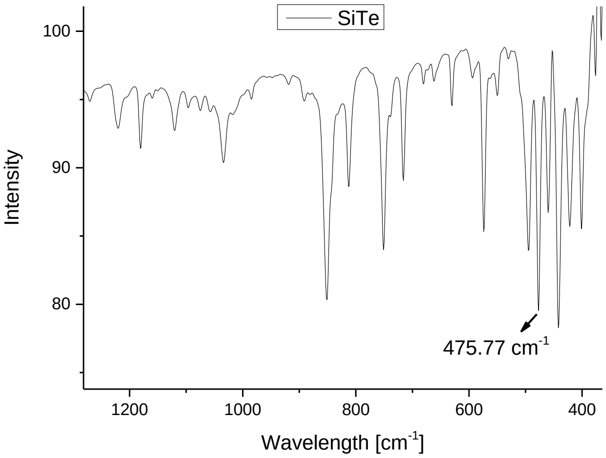
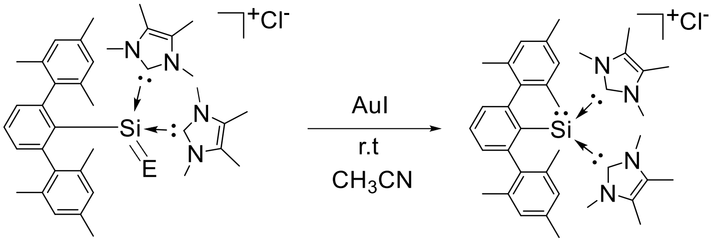


Figure S18. IR spectra of compound **4**.

Reactivity Studies

Regeneration of Silyliumylidene 1



2, E = S
3, E = Se
4, E = Te

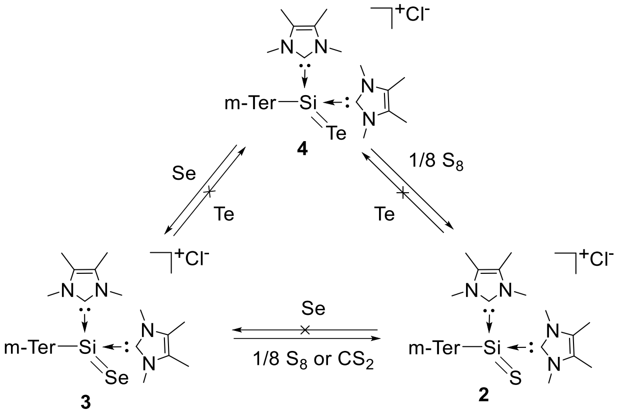
1

A stirred solution of compound **2** (50 mg, 70.9 µmol, 1.00 eq) in CH_3CN (2 ml) was treated with 2.00 equivalent of AuI (45.98 mg, 142 µmol). Immediately the color of the solution changed from colorless to dark orange. The reaction mixture was further stirred for 10 min. Then the dark orange solution was filtered from its mother liquor. Evaporation of all volatiles afforded a mixture of compound (**1** + imidazolium chloride) as yellow-orange solid. Compound **1** was recovered in 38% yield by fractional crystallization (mixture of 5 ml acetonitrile and 1 ml benzene). In similar fashion silyliumylidene **1** was regenerated from compound **3** and **4** in 56% and 47%, respectively.

^{1}H NMR δ (400 MHz, 298 K, CD3CN) = 1.99-2.16 {br, 30H; (12H, 4xC-Me, $NHCMe_4$); (12H, 2xC2,6 -Me, Mes), (6H, 2xC4 -Me, Mes) }, 3.27 (br, s, 12H, 4xN-Me, $NHCMe_4$), 6.66 (s, 4H, 2xC3,5 -H, Mes), 6.92 (d, $^3J_{H\text{-}H}$= 7.5 Hz, 2H, C3,5 -H, C6H3), 7.35 (t, $^3J_{H\text{-}H}$= 7.5 Hz, 1H, C4 -H, C_6H_3).

^{29}Si NMR δ (79.49 MHz, 298 K, CD_3CN) = -68.9.

Chalcogen Scrambling



Compound **4** to **2**: To a mixture of compound **4** (50 mg, 66.4 µmol, 1.00 eq) and elemental sulfur (2.10 mg, 366 µmol, 1.00 eq) was added 5 ml CH_3CN. The color of the solution gradually turned from dark yellow to pale brown. The reaction mixture was stirred further for 8 h. Then the solution was filtered from the mother liquor. Evaporation of the solvent afforded compound **2** in 100% yield, as confirmed by ^{1}H and ^{29}Si NMR spectroscopy.

Compound **4** to **3**: Following the aforementioned methodology no conversion was observed from **4** to **3**. But by changing the reaction conditions, formation of **3** was detected. Stirring the mixture of compound **4** (50 mg, 66.4 µmol, 1.00 eq) and selenium (5.24 mg, 66.4 µmol, 1.00 eq) in CH_3CN (5 ml) for 15 days at 60 °C provided a mixture of compound **3** with some unknown impurities. After filtration of the solvent all volatiles were removed and the solid was washed with THF (3x5 ml). Compound **3** was isolated as a white solid in 45% yield, characterized by ^{1}H and ^{29}Si NMR spectroscopy.

Compound **3** to **2**: Following the same strategy as for conversion **4** to **3**, a mixture of compound **3** (50 mg, 70.9 µmol, 1.00 eq) with sulfur (2.28 mg, 70.9 µmol, 1.00 eq) was stirred at 60 °C in CH_3CN for 22 days, which afforded compound **2** with an yield of 33%, as conformed by ^{1}H and ^{29}Si NMR spectroscopy.

2. X-ray Crystallographic Data

General:

Data for the single crystal structure determination of compound 2 were collected on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Cu IMS microsource (λ = 1.5418 Å). Data for the single crystal structure determination of compounds 3 and 4 were collected on an Agilent SuperNova diffractometer, equipped with a CCD area Atlas detector and a mirror monochromator utilizing CuK_α radiation (λ = 1.5418 Å). The individual crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The crystal structures were solved by direct methods and refined on F^2 using full-matrix least squares with SHELXL-2014. The positions of the H atoms of the carbon atoms were calculated by standard methods.

Compound 2 (CCDC 1547820):

Crystal data

$C_{38}H_{49}N_4SSi\cdot 2.882(C_2H_3N)\cdot Cl$

M_r = 775.74

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

a = 33.9475 (18) Å

b = 16.3237 (9) Å

c = 34.0390 (17) Å

β = 111.394 (2)°

V = 17562.9 (16) $Å^3$

Z = 16

F(000) = 6646

D_x = 1.173 Mg m^{-3}

Melting point: ? K

Cu *K*α radiation, λ = 1.54178 Å

Cell parameters from 9353 reflections

θ = 3.1–68.4°

μ = 1.76 mm^{-1}

T = 100 K

Fragment, clear colourless

0.42 × 0.19 × 0.13 mm

Data collection

Bruker Photon CMOS diffractometer

Radiation source: IMS microsource

Helios optic

15529 independent reflections

13229 reflections with $I > 2\sigma(I)$

R_{int} = 0.047

Detector resolution: 16 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan
SADABS 2016/2, Bruker, 2016

$T_{\min} = 0.638$, $T_{\max} = 0.753$

74606 measured reflections

$\theta_{\max} = 66.6°$, $\theta_{\min} = 2.8°$

$h = -40\quad 37$

$k = -19\quad 19$

$l = -40\quad 40$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.072$

$wR(F^2) = 0.216$

$S = 1.07$

15529 reflections

1106 parameters

199 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.1091P)^2 + 99.5138P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.86$ e Å^{-3}

$\Delta\rho_{\min} = -1.50$ e Å^{-3}

Extinction correction: none

Compound 3 (CCDC 1547819):

Crystal data

$C_{38}H_{49}N_4SeSi{\cdot}3(C_2H_3N){\cdot}Cl$

$M_r = 827.47$

Triclinic, *P*

Hall symbol: -P 1

$a = 15.2505\ (4)$ Å

$b = 16.9089\ (4)$ Å

$c = 17.7605\ (3)$ Å

$F(000) = 1744$

$D_x = 1.274$ Mg m^{-3}

Melting point: ? K

Cu *K*α radiation, λ = 1.54184 Å

Cell parameters from 14403 reflections

θ = 2.6–73.3°

α = 75.462 (2)°

β = 77.484 (2)°

γ = 82.684 (2)°

V = 4314.98 (18) Å^3

Z = 4

μ = 2.31 mm^{-1}

T = 150 K

Rod, colourless

0.18 × 0.15 × 0.08 mm

Data collection

SuperNova, Single source at offset, Atlas diffractometer

Radiation source: sealed X-ray tube, SuperNova (Cu) X-ray Source

mirror

Detector resolution: 10.5435 pixels mm^{-1}

ω scans

Absorption correction: multi-scan
CrysAlis PRO, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

$T_{\min}$ = 0.793, $T_{\max}$ = 1.000

29348 measured reflections

15234 independent reflections

12998 reflections with $I > 2\sigma(I)$

R_{int} = 0.033

$\theta_{\max}$ = 66.6°, $\theta_{\min}$ = 2.6°

h = −18   18

k = −18   20

l = −11   21

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.043

$wR(F^2)$ = 0.126

S = 1.03

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

W = $1/[\Sigma^2(FO^2) + (0.0663P)^2 + 3.769P]$
WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.002

15234 reflections

1007 parameters

0 restraints

$\Delta\rho_{max} = 0.79$ e Å^{-3}

$\Delta\rho_{min} = -0.73$ e Å^{-3}

Extinction correction: none

Compound 4 (CCDC 1547818):

Crystal data

$C_{38}H_{49}N_4SiTe{\cdot}Cl$

$M_r = 752.95$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 18.19020 (15)$ Å

$b = 11.67686 (9)$ Å

$c = 17.23519 (13)$ Å

$\beta = 92.6576 (7)°$

$V = 3656.89 (5)$ Å^3

$Z = 4$

$F(000) = 1552$

$D_x = 1.368$ Mg m^{-3}

Melting point: ? K

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 13055 reflections

$\theta = 3.8–73.5°$

$\mu = 7.64$ mm^{-1}

$T = 150$ K

Rod, yellow

0.37 × 0.07 × 0.03 mm

Data collection

SuperNova, Single source at offset, Atlas diffractometer

Radiation source: sealed X-ray tube, SuperNova (Cu) X-ray Source

mirror

Detector resolution: 10.5435 pixels mm^{-1}

ω scans

Absorption correction: multi-scan
CrysAlis PRO, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01) Empirical absorption correction using spherical

7279 independent reflections

6685 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$

$\theta_{max} = 73.7°$, $\theta_{min} = 2.4°$

$h = -22$ 22

$k = -14$ 8

harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

$T_{min} = 0.337$, $T_{max} = 1.000$

25394 measured reflections

$l = -21$ 21

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.077$

$S = 1.03$

7279 reflections

418 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.0436P)^2 + 1.6767P]$ WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.72$ e Å^{-3}

$\Delta\rho_{min} = -0.99$ e Å^{-3}

Extinction correction: none

3. DFT Calculations

All geometry optimizations were carried out at B97-D/6-31G(d)[Se,Te:cc-pVTZ-PP] level of theory[S2-6]. Harmonic frequency calculations were used to verify the stable minimum energy structures. Further theoretical analyses (Bond Dissociation Energy, Natural Population Analysis, Wiberg Bond Index, Mayer Bond Order, and IR) were conducted at the same level of theory which had been proved to be satisfactory to describe the electronic structure of cationic silicon compounds.[S1] For Bond Dissociation Energy calculations, the most stable spin state was used in all calculations thus for the chalcogen atom the triplet state was used. NMR shifts were calculated using a special basis set instead of 6-31G(d), which was developed for NMR shift calculations, IGLO-III for Si and IGLO-II for other light atoms[S7] and B3LYP functional[S8-10] using the previously optimized geometries. All calculations were executed using Gaussian 09[S11]. The exchange reaction energies were calculated using the previously described level of theory which was used for geometry optimization. For all three chalcogens, E_8 (E = S, Se, Te) ring structures were assumed as reactants for the sake of simplicity. Therefore, the calculated exchange reactions are: $\mathbf{4}^+$ + 1/8 Se_8 -> $\mathbf{3}^+$ + 1/8 Te_8, $\mathbf{4}^+$ + 1/8 S_8 -> $\mathbf{2}^+$ + 1/8 Te_8, and $\mathbf{3}^+$ + 1/8 S_8 -> $\mathbf{2}^+$ + 1/8 Se_8.

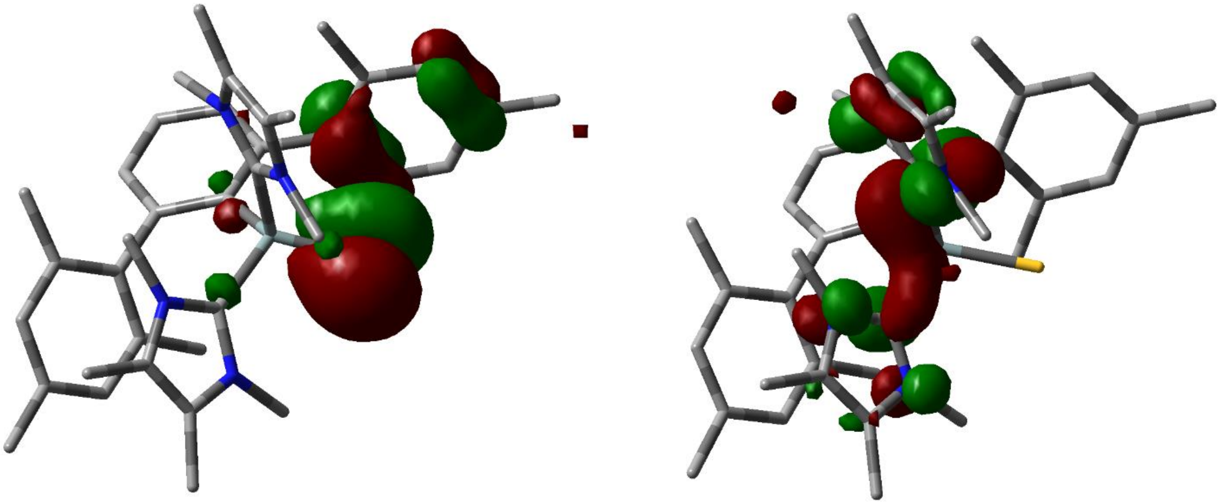


Figure S19. HOMO (left, -6.43 eV) and LUMO (right, -4.17 eV) of $\mathbf{2}^+$. Hydrogens are omitted for clarity.

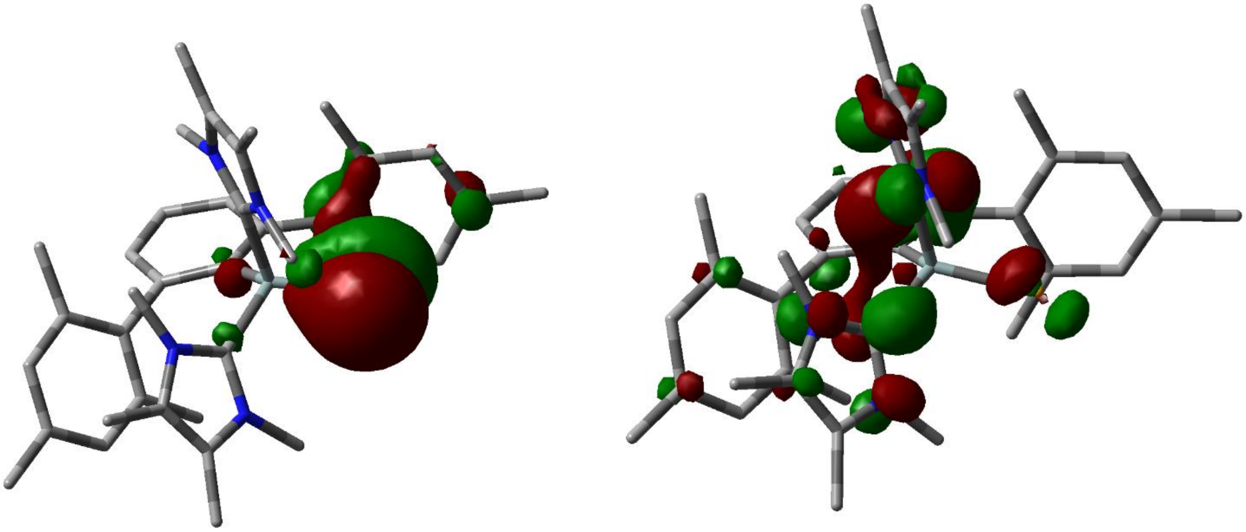


Figure S20. HOMO (left, -6.22 eV) and LUMO (right, -4.10 eV) of **3**$^{+}$. Hydrogens are omitted for clarity.

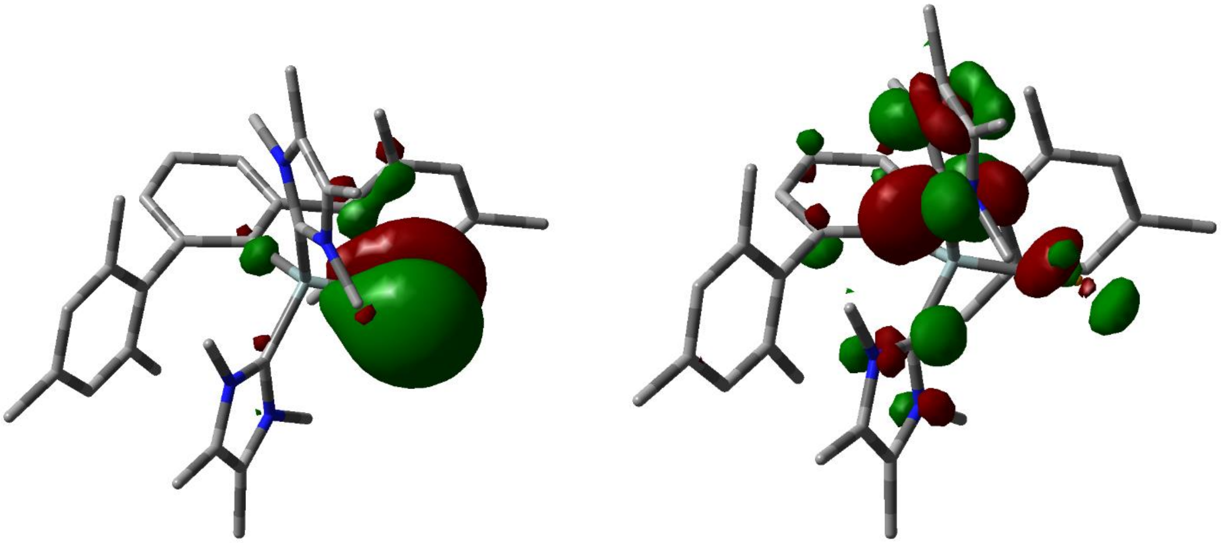


Figure S21. HOMO (left, -5.95 eV) and LUMO (right, -4.15 eV) of **4**$^{+}$. Hydrogens are omitted for clarity.

Table S1. NBO-Analysis of $[L(NHC)_2Si=S]^+$ compound.

NBO	atom	Occupation	polarization	s-character	p-character	d-character
σ-bond	Si	1.96	36.38%	31.40%	67.85%	0.74%
	S		63.62%	24.51%	75.16%	0.33%
σ-bond	Si	1.95	23.12%	19.60%	79.16%	1.24%
	C(NHC)		76.88%	44.33%	55.67%	0.00%
σ-bond	Si	1.95	23.12%	19.60%	79.16%	1.24%
	C(NHC)		76.88%	44.33%	55.67%	0.00%
σ-bond	Si	1.95	27.40%	29.14%	69.88%	0.98%
	C		72.60%	31.79%	68.19%	0.02%
Lone Pair	S	1.96	-	75.41%	24.58%	0.01%
Lone Pair	S	1.77	-	0.02%	99.87%	0.11%
Lone Pair	S	1.74	-	0.03%	99.85%	0.12%

Table S2. NBO-Analysis of $[L(NHC)_2Si=Se]^+$ compound.

NBO	atom	Occupation	polarization	s-character	p-character	d-character
σ-bond	Si	1.94	41.31%	31.15%	68.56%	0.29%
	Se		58.69%	17.60%	81.39%	0.97%
σ-bond	Si	1.95	23.51%	19.87%	78.93%	1.20%
	C(NHC)		76.49%	44.04%	55.96%	0.01%
σ-bond	Si	1.95	23.51%	19.87%	78.93%	1.20%
	C(NHC)		76.49%	44.04%	55.96%	0.01%
σ-bond	Si	1.95	27.42%	29.09%	69.95%	0.96%
	C		72.58%	31.74%	68.24%	0.02%
Lone Pair	Se	1.97	-	82.31%	17.65%	0.03%
Lone Pair	Se	1.76	-	0.01%	99.60%	0.34%
Lone Pair	Se	1.74	-	0.01%	99.57%	0.37%

Table S3. NBO-Analysis of $[L(NHC)_2Si=Te]^+$ compound.

NBO	atom	Occupation	polarization	s-character	p-character	d-character
σ-bond	Si	1.92	49.38%	29.95%	69.83%	0.23%
	Te		50.62%	13.35%	85.65%	0.91%
σ-bond	Si	1.95	23.90%	20.58%	78.25%	1.16%
	C		76.10%	44.11%	55.88%	0.01%
σ-bond	Si	1.95	23.90%	20.58%	78.25%	1.16%
	C		76.10%	44.11%	55.88%	0.01%
σ-bond	Si	1.94	27.68%	28.56%	70.56%	0.88%
	C		72.32%	31.78%	68.20%	0.02%
Lone Pair	Te	1.97	-	86.63%	13.35%	0.02%
Lone Pair	Te	1.77	-	0.00%	99.77%	0.17%
Lone Pair	Te	1.74	-	0.04%	99.71%	0.18%

Table S4. Calculated WBI, MBO, and symmetric valence (Si-S) vibration (in cm^{-1}) of reference compounds for $[L(NHC)_2Si{=}S]^+$.

	WBI	MBO	IR
$H_2Si{=}S$	1.92	2.05	688
$H_3Si\text{-}S^-$	1.29	1.47	573
$H_3Si\text{-}S\text{-}SiH_3$	0.93	0.98	457

Table S5. Calculated WBI, MBO, and symmetric valence (Si-Se) vibration (in cm^{-1}) of reference compounds for $[L(NHC)_2Si{=}Se]^+$.

	WBI	MBO	IR
$H_2Si{=}Se$	1.95	1.96	530
$H_3Si\text{-}Se^-$	1.27	1.29	422
$H_3Si\text{-}Se\text{-}SiH_3$	0.97	0.95	367

Table S6. Calculated WBI, MBO, and symmetric valence (Si-Te) vibration (in cm^{-1}) of reference compounds for $[L(NHC)_2Si{=}Te]^+$.

	WBI	MBO	IR
$H_2Si{=}Te$	1.94	2.01	439
$H_3Si\text{-}Te^-$	1.24	1.22	348
$H_3Si\text{-}Te\text{-}SiH_3$	1.01	0.96	317

Table S7. Cartesian geometry of **2**$^+$ in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
C	-0.018655	-2.093585	3.043031
C	0.319432	-1.537791	1.793176
C	-0.707836	-1.098367	0.894186
C	-2.070431	-1.363404	1.258899
C	-2.365015	-1.906187	2.527681
C	-1.35352	-2.24196	3.432117
C	-3.256159	-1.22569	0.342244
C	-3.509178	-2.287399	-0.566134
C	-4.659304	-2.2452	-1.364206
C	-5.575851	-1.18196	-1.292342
C	-5.331878	-0.167023	-0.357068
C	-4.196149	-0.177916	0.471883
C	-2.550227	-3.452012	-0.703396
C	-6.790435	-1.140705	-2.1967
Si	-0.408597	-0.0034	-0.658543
C	-0.618934	1.875242	-0.042299
N	-0.918513	2.425783	1.173714
C	-0.999082	3.815072	1.09015
C	-0.729449	4.144861	-0.215793
N	-0.499058	2.946187	-0.886763
C	-0.99911	1.751687	2.475877
C	-0.079653	2.900993	-2.298474
C	-0.690837	5.482358	-0.887173
C	-4.02549	0.944201	1.478649
C	-1.348133	4.679065	2.261118
C	1.776879	-1.545221	1.445674
C	2.221621	-2.385714	0.385606
C	3.5812	-2.401096	0.046049
C	4.529659	-1.626416	0.738052
C	4.087702	-0.871807	1.833138
C	2.732156	-0.837366	2.214688
C	5.977967	-1.608573	0.29953
C	1.259177	-3.310651	-0.334223
C	2.355914	-0.037593	3.450622
S	-1.473	-0.282809	-2.354825
C	1.522097	0.155924	-1.080664
N	2.439198	0.996668	-0.511132
C	3.647245	0.968928	-1.202256
C	3.477871	0.083427	-2.236386
N	2.172609	-0.389739	-2.14973
C	2.240354	1.815251	0.685525
C	1.69037	-1.444642	-3.052816

C	4.443033	-0.390037	-3.275757
C	4.851935	1.738715	-0.768244
H	-1.066726	0.674542	2.335049
H	-0.102442	2.003172	3.062054
H	-1.890708	2.10761	3.004013
H	-1.329934	5.735766	1.963934
H	-2.357634	4.450545	2.641793
H	-0.639311	4.54525	3.094925
H	-0.856413	6.275696	-0.146431
H	0.280646	5.665198	-1.374588
H	-1.473803	5.569297	-1.658669
H	-0.426701	1.958011	-2.741904
H	-0.535106	3.748446	-2.82335
H	1.017128	2.97646	-2.356439
H	1.511438	1.330288	1.334598
H	3.190762	1.874821	1.22555
H	1.89713	2.824927	0.414016
H	5.653795	1.628853	-1.509968
H	4.636969	2.813559	-0.654054
H	5.226952	1.360202	0.198197
H	5.405107	0.125514	-3.15643
H	4.621492	-1.474498	-3.187765
H	4.07407	-0.195514	-4.296052
H	0.609331	-1.559902	-2.929175
H	1.909508	-1.147644	-4.086662
H	2.219271	-2.376997	-2.811735
H	-3.577696	0.583328	2.416688
H	-3.378176	1.745504	1.082539
H	-4.998995	1.399643	1.716815
H	-2.239636	-3.849636	0.276179
H	-3.009143	-4.267841	-1.281776
H	-1.640293	-3.128837	-1.234988
H	-7.211897	-2.147659	-2.345899
H	-7.577724	-0.491908	-1.782264
H	-6.523743	-0.747264	-3.19349
H	0.529113	-2.769377	-0.953522
H	1.80609	-4.009554	-0.984948
H	0.669106	-3.89547	0.388305
H	1.310626	0.29912	3.425051
H	2.46875	-0.647605	4.362764
H	3.013489	0.838849	3.566289
H	6.63358	-1.203171	1.085137
H	6.331368	-2.619757	0.042221
H	6.10457	-0.981845	-0.601538

H	-6.051335	0.650585	-0.254755
H	-4.844969	-3.066167	-2.062147
H	3.915845	-3.054497	-0.764916
H	4.816788	-0.305799	2.421003
H	0.784203	-2.43247	3.700062
H	-1.600628	-2.663762	4.408383
H	-3.411147	-2.092204	2.778302

Table S8. Cartesian geometry of **3**$^{+}$ in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
C	0.132015	-1.385794	3.457049
C	0.423221	-1.067817	2.115526
C	-0.640971	-0.795976	1.19022
C	-1.984813	-1.016102	1.639912
C	-2.232499	-1.319458	2.996522
C	-1.188332	-1.467516	3.913658
C	-3.201176	-1.076359	0.755334
C	-3.472071	-2.293051	0.082195
C	-4.657206	-2.412582	-0.661845
C	-5.585517	-1.364622	-0.755433
C	-5.309939	-0.175727	-0.058253
C	-4.141112	-0.020097	0.701155
C	-2.496493	-3.452467	0.10886
C	-6.85459	-1.508012	-1.571459
Si	-0.40372	0.083281	-0.503782
C	-0.305227	2.023639	-0.117595
N	-0.569482	2.757096	1.007791
C	-0.47464	4.125058	0.74885
C	-0.126967	4.250935	-0.573626
N	-0.03095	2.958167	-1.083405
C	-0.865095	2.277485	2.364937
C	0.374904	2.681348	-2.470069
C	0.104257	5.479661	-1.397193
C	-3.883922	1.296742	1.403745
C	-0.747307	5.164902	1.790033
C	1.872492	-1.178074	1.737928
C	2.27595	-2.265416	0.909475
C	3.630587	-2.422669	0.590249
C	4.620601	-1.561703	1.101661
C	4.215966	-0.539583	1.969715
C	2.861484	-0.345788	2.311849
C	6.077103	-1.764474	0.737822
C	1.272776	-3.298827	0.440289
C	2.518389	0.761158	3.292605
Se	-1.784615	-0.170397	-2.153635

C	1.457716	-0.159235	-1.122303
N	2.560871	0.619657	-0.889646
C	3.645819	0.190945	-1.650077
C	3.206939	-0.885653	-2.379251
N	1.868983	-1.073452	-2.049731
C	2.673986	1.742484	0.044689
C	1.086155	-2.158871	-2.660051
C	3.940239	-1.7799	-3.327212
C	4.997454	0.823519	-1.568776
H	-0.911992	1.189963	2.37496
H	-0.075365	2.631248	3.042474
H	-1.829713	2.688523	2.686032
H	-0.584631	6.166366	1.370311
H	-1.788708	5.111142	2.149309
H	-0.087543	5.048572	2.665999
H	0.020541	6.372712	-0.763731
H	1.105752	5.47938	-1.858168
H	-0.637447	5.569015	-2.208477
H	-0.136189	1.7694	-2.810971
H	0.07215	3.527805	-3.096806
H	1.466997	2.554684	-2.52234
H	1.935189	1.634418	0.838327
H	3.669846	1.713245	0.498057
H	2.525992	2.697223	-0.482072
H	5.677126	0.345618	-2.286604
H	4.962759	1.901624	-1.797055
H	5.425973	0.701833	-0.559808
H	4.966063	-1.414567	-3.469556
H	3.995744	-2.811045	-2.938927
H	3.449705	-1.821411	-4.313207
H	0.075913	-2.167597	-2.244724
H	1.016156	-1.981083	-3.741937
H	1.59948	-3.109822	-2.464804
H	-3.51681	1.143651	2.430925
H	-3.123199	1.883105	0.858857
H	-4.800942	1.903733	1.449761
H	-2.071068	-3.616595	1.111234
H	-2.986789	-4.381414	-0.219796
H	-1.653453	-3.259556	-0.578058
H	-6.919854	-2.503323	-2.036856
H	-7.750961	-1.363677	-0.94429
H	-6.895483	-0.752327	-2.374371
H	0.444369	-2.854178	-0.125349
H	1.758218	-4.063269	-0.184996

H	0.810556	-3.803653	1.304746
H	1.48259	1.10409	3.173179
H	2.62018	0.412488	4.334566
H	3.198941	1.619808	3.172163
H	6.711585	-0.964951	1.150405
H	6.451826	-2.726413	1.126614
H	6.214628	-1.78561	-0.356791
H	-6.02323	0.65221	-0.105351
H	-4.858339	-3.351833	-1.184289
H	3.928661	-3.259411	-0.048079
H	4.971092	0.120388	2.407643
H	0.960458	-1.59538	4.136319
H	-1.397531	-1.700302	4.95966
H	-3.267265	-1.470183	3.310548

Table S9. Cartesian geometry of **4**$^{+}$ in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
C	0.627481	-0.776761	3.661111
C	0.766901	-0.601413	2.268977
C	-0.398955	-0.51637	1.43484
C	-1.672354	-0.765153	2.044755
C	-1.769277	-0.923799	3.442299
C	-0.63359	-0.892649	4.256891
C	-2.948808	-0.99197	1.283445
C	-3.240581	-2.303696	0.837594
C	-4.444606	-2.539	0.150943
C	-5.382498	-1.520524	-0.072076
C	-5.09822	-0.238507	0.431408
C	-3.90205	0.039352	1.105353
C	-2.321502	-3.478708	1.122098
C	-6.664785	-1.785314	-0.834914
Si	-0.320924	0.181186	-0.361805
C	0.056145	2.103117	-0.193256
N	-0.196438	2.970632	0.840401
C	-0.088887	4.296201	0.418404
C	0.250029	4.260597	-0.911253
N	0.342917	2.916969	-1.262063
C	-0.566047	2.668657	2.230505
C	0.532001	2.503158	-2.658529
C	0.477695	5.375535	-1.883454
C	-3.611224	1.452946	1.560463
C	-0.326263	5.456707	1.332409
C	2.195021	-0.6489	1.788761
C	2.704129	-1.889679	1.315578
C	4.063101	-2.000817	0.981009

C	4.96352	-0.938205	1.16866
C	4.458506	0.261315	1.694731
C	3.095533	0.424664	2.005503
C	6.441474	-1.103035	0.871612
C	1.833587	-3.127854	1.257727
C	2.633291	1.75762	2.561917
Te	-2.06295	0.07631	-2.008149
C	1.290987	-0.608343	-1.139184
N	2.526326	-0.116406	-1.459582
C	3.284605	-1.076381	-2.127463
C	2.495782	-2.195075	-2.232563
N	1.282248	-1.884931	-1.626216
C	3.07276	1.198162	-1.119508
C	0.136935	-2.807274	-1.634405
C	2.786305	-3.533048	-2.834953
C	4.694759	-0.832556	-2.558174
H	-0.602456	1.592463	2.383573
H	0.17927	3.116699	2.899873
H	-1.552683	3.102592	2.432994
H	-0.197122	6.39777	0.781656
H	-1.347974	5.441115	1.746813
H	0.377202	5.458526	2.181976
H	0.325525	6.34183	-1.384658
H	1.503182	5.360989	-2.290277
H	-0.220455	5.314699	-2.734288
H	0.856459	1.462319	-2.705503
H	-0.428536	2.575082	-3.189361
H	1.285919	3.16072	-3.113197
H	2.47357	1.642522	-0.325175
H	4.094545	1.065068	-0.751291
H	3.072785	1.847611	-2.006993
H	5.079559	-1.710491	-3.094115
H	4.773467	0.038428	-3.229659
H	5.345764	-0.650418	-1.687234
H	3.790421	-3.531909	-3.279663
H	2.751449	-4.332215	-2.074955
H	2.061143	-3.790244	-3.624074
H	-0.546902	-2.567204	-0.816529
H	-0.412409	-2.697851	-2.580546
H	0.516419	-3.828986	-1.508298
H	-3.220638	1.477729	2.590459
H	-2.854611	1.913645	0.89983
H	-4.517555	2.07539	1.514443
H	-2.563828	-3.94011	2.096061

H	-2.434073	-4.258415	0.352299
H	-1.264681	-3.182448	1.174243
H	-6.796568	-2.859533	-1.03557
H	-7.544085	-1.428335	-0.273117
H	-6.661833	-1.256874	-1.80387
H	0.820505	-2.904813	0.906636
H	2.279999	-3.89454	0.605993
H	1.725835	-3.565764	2.265339
H	1.888184	1.622048	3.358159
H	3.483385	2.32389	2.971447
H	2.164911	2.382097	1.78095
H	6.900213	-0.151294	0.558637
H	6.986096	-1.447004	1.76818
H	6.611474	-1.85099	0.081036
H	-5.817923	0.570284	0.278271
H	-4.656577	-3.548725	-0.211829
H	4.435736	-2.957924	0.605605
H	5.142476	1.096004	1.874729
H	1.530024	-0.841454	4.272898
H	-0.723607	-1.00994	5.338703
H	-2.75545	-1.098597	3.877054

Table S10. Cartesian geometry of S_8 in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
S	-0.957901	-2.24518	0.491358
S	0.911755	-2.264405	-0.491352
S	2.245363	-0.958048	0.490987
S	2.26379	0.912463	-0.491598
S	0.959224	2.244618	0.491698
S	-0.913087	2.263866	-0.491692
S	-2.244556	0.95859	0.491591
S	-2.264588	-0.911905	-0.490992

Table S11. Cartesian geometry of Se_8 in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
Se	-1.034473	-2.50561	0.573179
Se	1.037731	-2.504262	-0.573179
Se	2.506455	-1.034142	0.571591
Se	2.501906	1.039251	-0.572449
Se	1.036071	2.503759	0.572604
Se	-1.039327	2.50241	-0.572603
Se	-2.503256	1.035996	0.572449
Se	-2.505107	-1.037401	-0.571591

Table S12. Cartesian geometry of Te_8 in Angstrom [Å].

Atomtype	X Coordinate	Y Coordinate	Z Coordinate
Te	0.435937	-3.079786	0.69479
Te	2.486138	-1.869391	-0.69457
Te	3.080281	0.436008	0.694446
Te	1.869317	2.486031	-0.694658
Te	-0.435968	3.079778	0.694803
Te	-2.486114	1.86941	-0.694584
Te	-3.080297	-0.436025	0.69444
Te	-1.869295	-2.486025	-0.694666

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