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Supporting Information

Dimerization of a marginally stable disilenyl germylene to tricyclic systems: evidence for reversible NHC-coordination

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Contents

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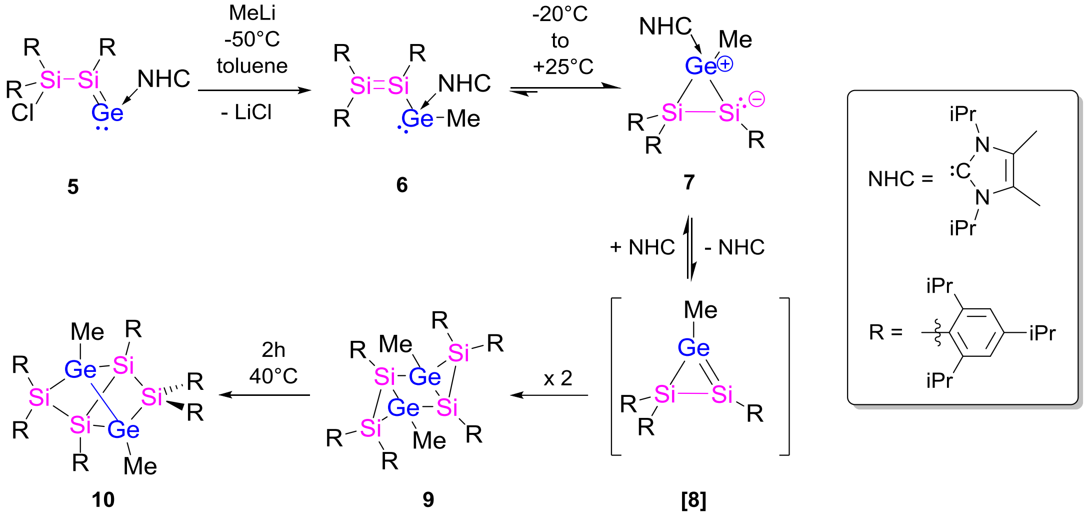
1. Experimental Details

All experiments were carried out under a protective atmosphere of argon applying standard Schlenk or glove-box techniques. Solvents were refluxed over sodium/benzophenone, distilled and stored under argon. [D$_6$]-benzene and [D$_8$]-toluene were dried over potassium, refluxed and distilled under argon. The silagermenylidene **5** is synthesised according to our published procedure.[1] MeLi solutions (1.6 M in diethylether and 3.0 M in diethoxymethane, DEM) were purchased from Sigma Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were referenced to external SiMe$_4$ using the residual signals of the deuterated solvent (^{1}H) or the solvent itself (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced to external SiMe$_4$. Melting points were determined under argon in closed NMR tubes and are uncorrected. CHN analyses were measured on an Elementar Vario Micro Cube.

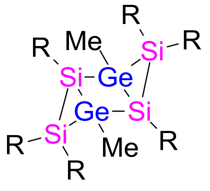


Experiment 1: Synthesis of 2,5-dimethyl-1,3,3,4,6,6-hexakis(2,4,6-triisopropylphenyl)-1,3,4,6-tetrasila-2,5-digermatricyclo[3.1.0.0^{2,4}]hexane **9** and isolation of 4,5-dimethyl-1,2,3,3,6,6-hexakis(2,4,6-triisopropylphenyl)-1,2,3,6-tetrasila-4,5-digermatricyclo[2.2.0.0^{2,5}]hexane **10**

A solution of MeLi (1.6 M in Et$_2$O, 0.76 mL, 1.216 mmol, 1 eq) is added slowly (2 min) to a cold toluene solution (5 mL, −78 °C) of the silagermenylidene **5** (1.16 g, 1.215 mmol). The reaction mixture is allowed to warm to room temperature and the solvent is immediately evaporated. The red solid is dried in high vacuum for one hour and dissolved in *n*-pentane (20 mL). After filtration with a reverse frit, all volatiles were removed again and free NHC is sublimed from the crude product at 5x10^{-6} mbar for 12 h at ambient temperature. The residue is dissolved in toluene and a very concentrated solution is stored at −26 °C. A few pale red crystals of compound **9** and a large amount of colourless crystals of **10** suitable for X-ray diffraction were obtained after three days alongside an unidentified impurity with an SiH bond (Figures S10 to S13).

Due to its instability in solution, we were unable to obtain a pure sample of **9** despite repeated attempts. Conversely, a pure sample of **10** can be obtained by heating the reaction mixture of **9** and **10** to 40 °C for 2 hours. Crystallisation from a saturated toluene solution at room temperature for one day affords colourless crystals of **10**. The total yield (3 crops) of **10** is 0.60 g (63 %).

Selected data of chair-like isomer **9** (extracted from spectra of mixtures with **10** and an unknown CH insertion product)



9

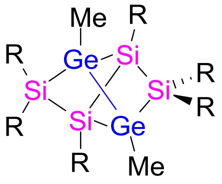
^{1}H NMR (300.13 MHz, [D$_6$]-benzene, 300 K): δ 5.57 (1H, Si*H* of unknown CH insertion product, $^{1}J_{\mathrm{HSi}}$ = 96 Hz) ppm.

^{13}C NMR (75.56 MHz, [D$_6$]-benzene, 300 K): δ 157.35, 157.08, 156.33, 155.89, 155.82, 155.12 155.04, 151.02, 149.98, 149.65, 149.44, 135.37, 133.53, 131.13, 122.69, 121.46, 120.60 (Ar*C*), 121.22 (N*C*(CH$_3$)=*C*(CH$_3$)N of free NHC), 49.84 (*C*H(CH$_3$)$_2$ of free NHC), 36.98, 36.50, 34.97, 34.88, 34.81, 34.73, 34.37, 31.33 (*C*H(CH$_3$)$_2$ of Tip), 29.04, 27.87, 26.62, 26.01, 25.86, 24.84, 24.49, 23.51 (CH(*C*H$_3$)$_2$ of Tip), 24.64 (CH(*C*H$_3$)$_2$ of free NHC), 8.39 (*C*H$_3$ of free NHC), 5.89 (Ge*C*H$_3$) ppm.

^{29}Si NMR (59.62 MHz, [D$_6$]-benzene, 300 K): δ −82.55 (**9**), −96.42 (**9**) and −65.94 (unknown CH insertion product ; SiH, $^{1}J_{\mathrm{SiH}}$ = 96 Hz) ppm.

Note: Due to considerable overlap of the occasionally broad signals of **9** with those of **10** the ^{1}H NMR is beyond interpretation.

Data of doubly edge-capped tetrahedral isomer **10** (obtained from a pure crystalline sample)



10

MP: > 225°C

^{1}H NMR (300.13 MHz, [D$_6$]-benzene, 300 K): δ 7.13 (m, toluene), 7.11 (br, 5H, Tip*H*), 7.06 (br, 4H, Tip*H*), 7.02 (m, toluene), 6.92 (s, 3H, Tip*H*), 4.43 (br, 3H, C*H*(CH$_3$)$_2$ of Tip), 3.87-3.79 (m, 6H, C*H*(CH$_3$)$_2$ of Tip), 3.20 (br, 4H, C*H*(CH$_3$)$_2$ of Tip), 2.90-2.62 (m, 8H, C*H*(CH$_3$)$_2$ of Tip), 2.11 (s, toluene), 1.46-1.30 (m, 42H, CH(C*H*$_3$)$_2$ of Tip), 1.24-1.14 (m, 64H, CH(C*H*$_3$)$_2$ of Tip), 0.35 (br, 12H, CH(C*H*$_3$)$_2$ of Tip and GeC*H*$_3$) ppm.

^{13}C NMR (75.56 MHz, [D$_6$]-benzene, 300 K): δ 156.66 (br), 154.73 (br), 154.25, 149.51, 149.38, 149.27, 139.12 (br), 135.32 (br) (Ar*C*$_{\mathrm{quart}}$), 128.17 (masked by C$_6$D$_6$), 123.95, 123.72, 123.12, 122.83, 121.66 (br) (Ar*C*H), 37.87 (br), 35.71, 35.62, 34.57, 34.48, 30.48 (*C*H(CH$_3$)$_2$ of Tip), 28.70, 25.47, 25.19 (br), 24.95, 24.64, 24.14, 24.10, 23.96 (CH(*C*H$_3$)$_2$ of Tip), 0.35 (Ge*C*H$_3$) ppm.

^{29}Si NMR (59.62 MHz, [D$_6$]-benzene, 300 K): δ 21.97, −37.74 ppm.

Note: Due to the broadness of the signals the ^{29}Si NMR signals cannot be assigned by a ^{29}Si-HMBC correlation.

Element. anal.: Calcd. for $C_{92}H_{144}Ge_2Si_4 \cdot 1.5\ C_7H_8$: C, 74.80; H, 9.55. Found: C, 73.86; H, 9.79.

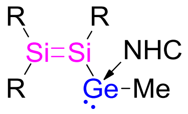
Experiment 2: Low temperature NMR study of the reaction of **5** with MeLi and preparation of a solution of NHC adduct of disilenyl germylene **6**

MeLi (3.0 M in DEM, 106 μL, 0.318 mmol, 1 eq) was added to a cold solution (−78 °C) of **5** (303 mg, 0.317 mmol) in [D_8]-toluene (2 mL) in a Schlenk-flask. One third of the solution was transferred via a pre-cooled glass pipette into a pre-cooled NMR-tube at −78 °C (the remainder was stored at −78°C for use in experiments 3 and 4, see below).

The following distinct ^{29}Si NMR spectra were obtained in the process of warming the sample to ambient temperature:

- at 213 K only starting material **5** with signals at δ= 163.47 and 8.37 ppm is observed (Figure S1a).
- at 253 K two new resonances at δ= 90.07 and 85.40 ppm appeared in the ^{29}Si NMR which correspond to disilenyl germylene **6** (Figure S1c).
- after 30 h at room temperature the signals of **6** had completely disappeared and only resonances of **7** at δ= −64.92 and −66.51 ppm and **9** at δ= −82.55 and −96.42 ppm could be detected (Figure S1d).

Data of disilenyl germylene **6**



6

^{1}H NMR (300.13 MHz, [D_8]-toluene, 253 K, TMS): δ 7.12-6.95 (m, 6H, overlap with toluene-d[8], Tip*H*), 5.70 (m, 2H, C*H*(CH_3)$_2$ of NHC), 4.54 (s, 2H, OC*H*$_2$O, DEM), 4.12-3.91 (m, 5H, C*H*(CH_3)$_2$ of Tip), 3.46 (q, 4H, OC*H*$_2$$CH_3$, DEM), 2.82-2.62 (m, 4H, C*H*(CH_3)$_2$ of Tip), 1.65 (br, 3H, GeC*H*$_3$) 1.51 (s, 6H, C*H*$_3$ of NHC), 1.37-1.13 (m, 44H, CH(C*H*$_3$)$_2$ of Tip and CH(C*H*$_3$)$_2$ of NHC, overlap with DEM: t, 6H, C*H*$_3$), 0.96-0.92 (m, 6H, CH(C*H*$_3$)$_2$ of Tip), 0.84-0.70 (m, 18H, CH(C*H*$_3$)$_2$ of Tip) ppm.

^{13}C NMR (75.56 MHz, [D_8]-toluene, 253 K, TMS): δ 174.88 (N*C*N), 155.03, 154.39, 153.77, 153.50, 149.24, 148.91, 148.21, 138.92, 138.82, 137.98, 125.94, 122.26, 121.77, 121.40, 121.30, 121.06 (Aryl*C* of Tip and N*C*(CH_3)=*C*(CH_3)N of NHC), 94.94 (O*C*H$_2$O, DEM), 62.91 (O*C*H$_2$$CH_3$, DEM), 52.09 (*C*H($CH_3$)$_2$ of NHC), 37.42, 37.02, 36.65, 34.92, 34.66, 34.47, 28.26, 26.13, 25.02, 24.55, 24.43, 24.34, 24.26, 24.19, 24.11, 21.54, 21.19, 20.06 (*C*H(*C*H$_3$)$_2$ of Tip and *C*H(CH_3)$_2$ of NHC), 15.43 (OCH$_2$*C*H$_3$, DEM), 9.91 (NC(*C*H$_3$)=C(*C*H$_3$)N of NHC), 4.07 (Ge*C*H$_3$) ppm.

^{29}Si NMR (59.62 MHz, [D_8]-toluene, 253 K, TMS): δ 90.11, 85.29 ppm.

Experiment 3: Heating of a mixture of **6**, **7** and **9** to 323K in the absence of additional NHC

The following distinct ^{29}Si NMR spectra were obtained in the process of warming the sample from 300 K to 323 K:

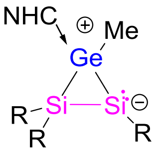
- warming of the sample to 300 K showed after 50 min three sets of signals in the ^{29}Si NMR: δ= 90.07 and 85.40 ppm (**6**), δ= −64.92 and −66.51 ppm (**7**) and δ = −82.55 and −96.42 ppm (**9**) (Figure S2c).
- the temperature is increased to 323 K and two sets of signals were observed at δ = −64.92 and −66.51 ppm (**7**) and δ = −82.55 and −96.42 ppm (**9**) (Figure S2d).
- after 2 hours at 323 K only resonances at δ= −64.92 and −66.51 ppm (**7**) and δ = 21.97, –37.74 ppm (**10**) were observed (Figure S2e).

Experiment 4: NMR study of **6** with 3.8 equivalents of additional NHC and synthesis of intermediate **7** (NHC adduct of germadisilacyclopropene **[8]**)

A cold solution of **6** (−48 °C) is added via syringe in a NMR tube containing NHC (3.8 eq) at room temperature:

- a ^{29}Si NMR of the mixture of **6** and the free NHC was recorded at 300 K and only the signals of **6** were observed even after 50 min at ambient temperature (Figure S2a).
- the temperature was raised to 323 K and a nearly full conversion of **6** was reached after 1 hour at this temperature. The ^{29}Si NMR indicated that the mixture predominantly contained **7** (Figure S2b, extracted data summarized below).
- a ^{1}H NMR clearly shows that neither of compounds **9** and **10** are formed, even if the mixture is heated for 5 hours to 323 K (FigureS3b). Without additional NHC, **6** rearranges after 1h at 323 K to **7** and **9** (see ^{29}Si NMR, figure S2d).

<u>Data of NHC adduct **7** of germadisilacyclopropene</u>



7

^{1}H NMR (300.13 MHz, [D$_8$]-toluene, 323 K, TMS): δ 5.66 (sept, C*H*(CH$_3$)$_2$ of NHC), 1.75 (s, CH(C*H*$_3$)$_2$ of NHC) ppm.

^{13}C NMR (75.56 MHz, [D$_8$]-toluene, 323 K, TMS): δ 175.90 (N*C*N), 156.65, 154.71, 154.45, 154.19, 149.41, 149.27, 149.15, 148.79, 147.72, 140.44, 135.53, 126.36, 123.82, 123.60, 122.75, 122.32, 122.00 (Aryl*C* of Tip and N*C*(CH$_3$)=*C*(CH$_3$)N of NHC), 53.24 (*C*H(CH$_3$)$_2$ of NHC), 36.54, 35.61, 35.52, 34.59, 34.36, 28.57, 25.49, 25.34, 25.16, 24.97, 24.83, 24.05, 23.92 (*C*H(*C*H$_3$)$_2$ of Tip and *C*H(*C*H$_3$)$_2$ of NHC), 10.66 (NC(*C*H$_3$)=C(*C*H$_3$)N of NHC), 1.68 (Ge*C*H$_3$) ppm.

Note: The ^{1}H and ^{13}C NMR spectra of a relatively pure sample of **7** are dominated by the excess NHC used for the stabilization of this species. Therefore, only characteristic resonances of compound **7** are given due to significant overlaps with the dominating NHC and DEM signals.

^{29}Si NMR (59.62 MHz, [D$_8$]-toluene, 323 K, TMS): δ −64.73, −66.49 ppm.

2. Plots of NMR spectra

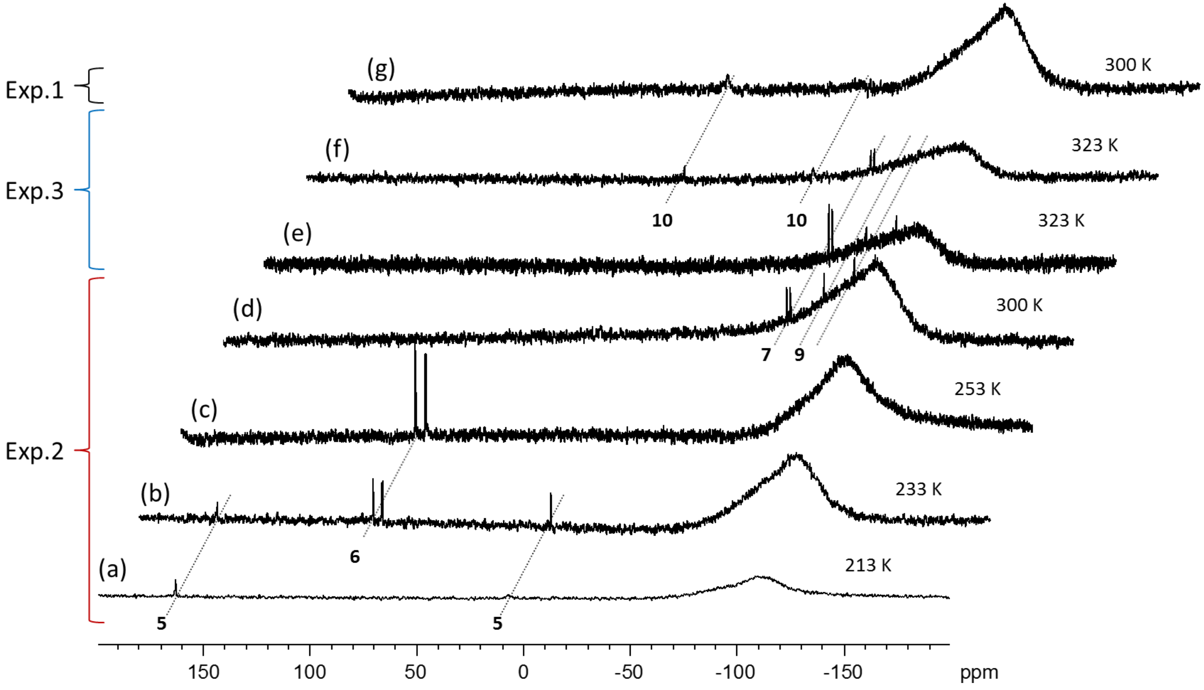


Figure S1. Stacked plot of ^{29}Si NMR spectra of different VT-NMR experiments with identical starting conditions. Experiment 2: (a) starting material **5** at 213 K, (b) **5** and disilenyl germylene **6** at 233 K, (c) **6** at 253 K, (d) mixture of **7** and **9** after 30 h at 300 K. Experiment 3: (e) mixture of **7** and **9** after 1 h at 323 K, (f) mixture of **7** and doubly bridged tetrahedron **10** after 2 h at 323 K. Experiment 1: (g) **10** at 300 K (crystalline sample).

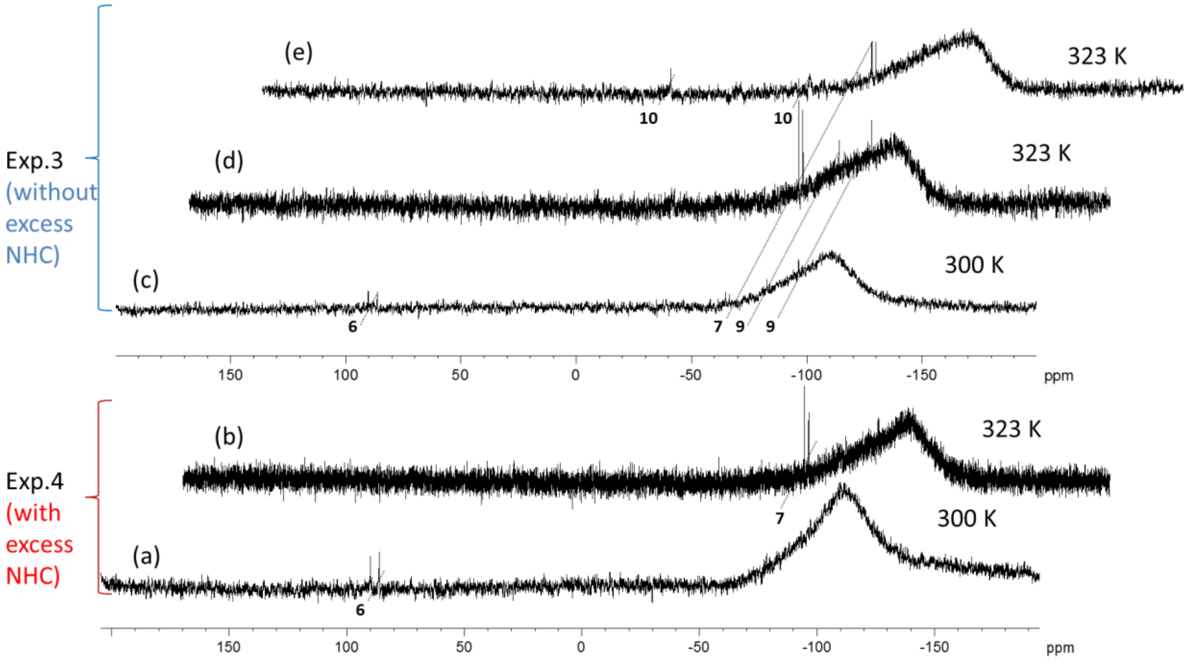


Figure S2. Stacked plots of ^{29}Si NMR spectra of NMR experiments with or without added NHC. Experiment 4 with 3.8 eq of NHC: (a) after 50 min at 300 K **6** is still the major component, (b) after 1 h at 323 K clean conversion to **7** has occurred. Experiment 3 without added NHC: (c) after 50 min at 300 K a mixture of **6**, three-membered ring **7** and chair form of $Si_4Ge_2R_6$ **9** is obtained, (d) after 1 h at 323 K a mixture of **7** and **9** is observed, (e) after 2 h at 323 K a mixture of **7** and $Si_4Ge_2R_6$ doubly bridged tetrahedron **10** is observed.

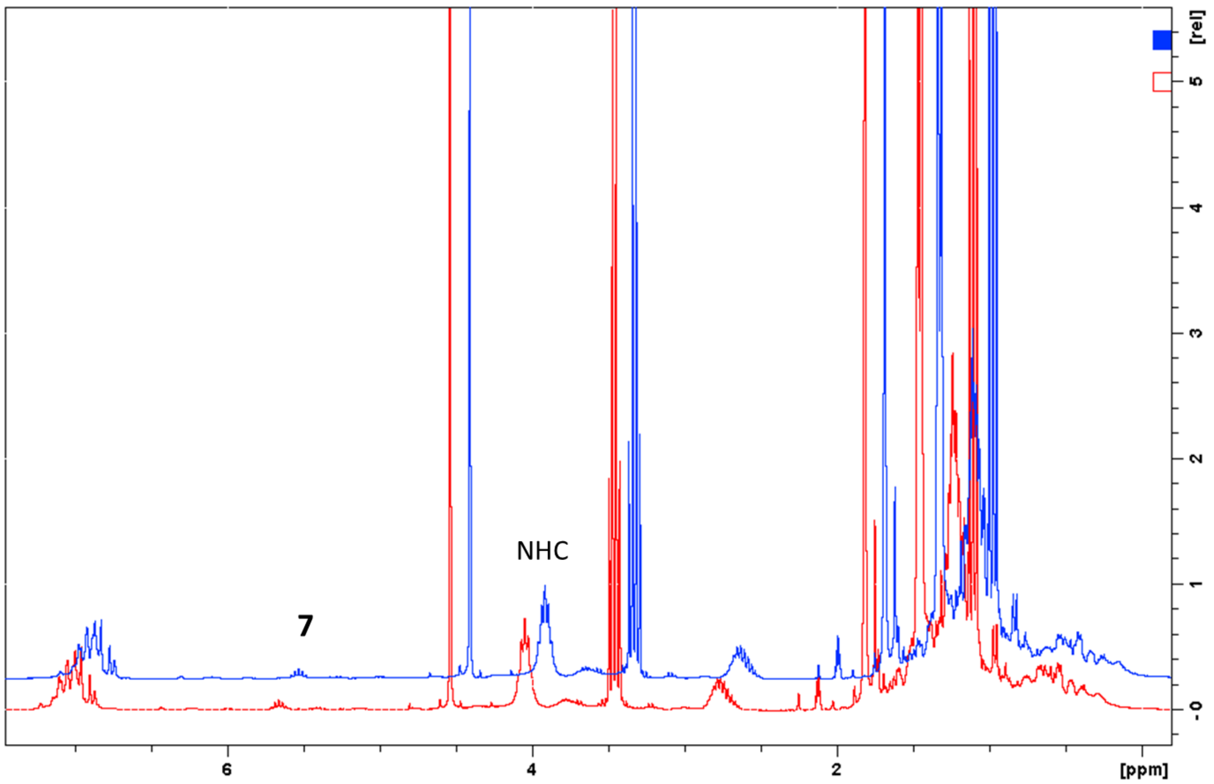


Figure S3. ^{1}H NMR of **7** with 3.8 eq of NHC; red: after 1 h at 323 K, blue: after 5 h at 323 K; **7**: C*H* of isopropyl groups of coordinated NHC; NHC: C*H* of isopropyl groups of free NHC.

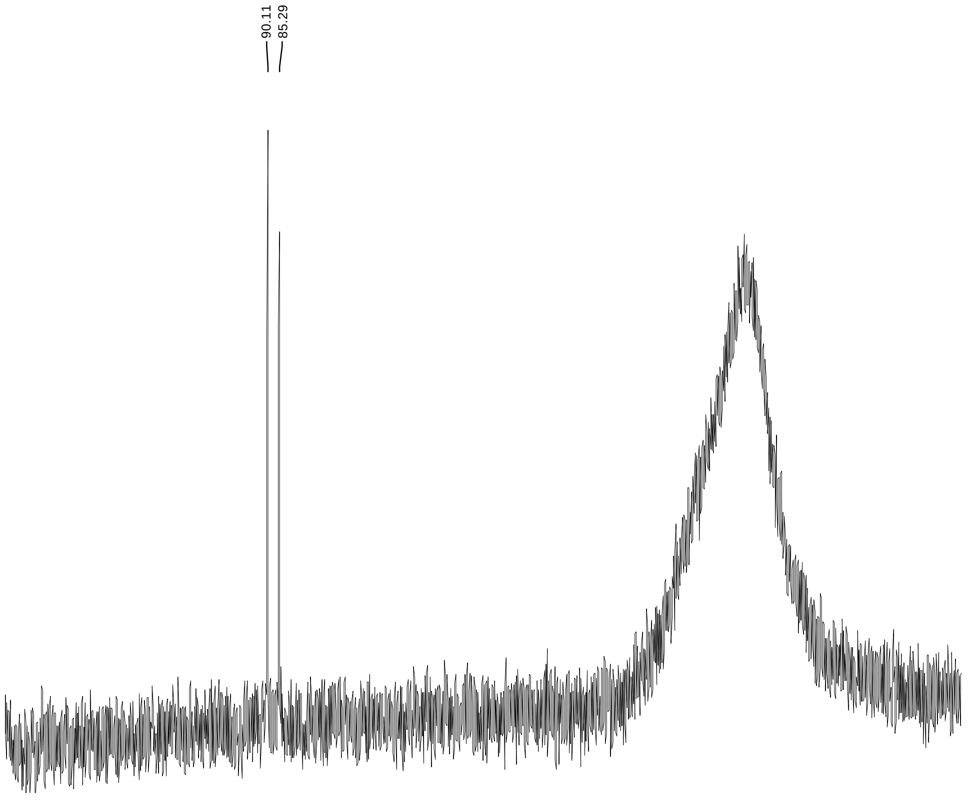


Figure S4. ^{29}Si NMR of the low temperature NMR study: intermediate **6** in [D$_8$]-toluene at 253 K.

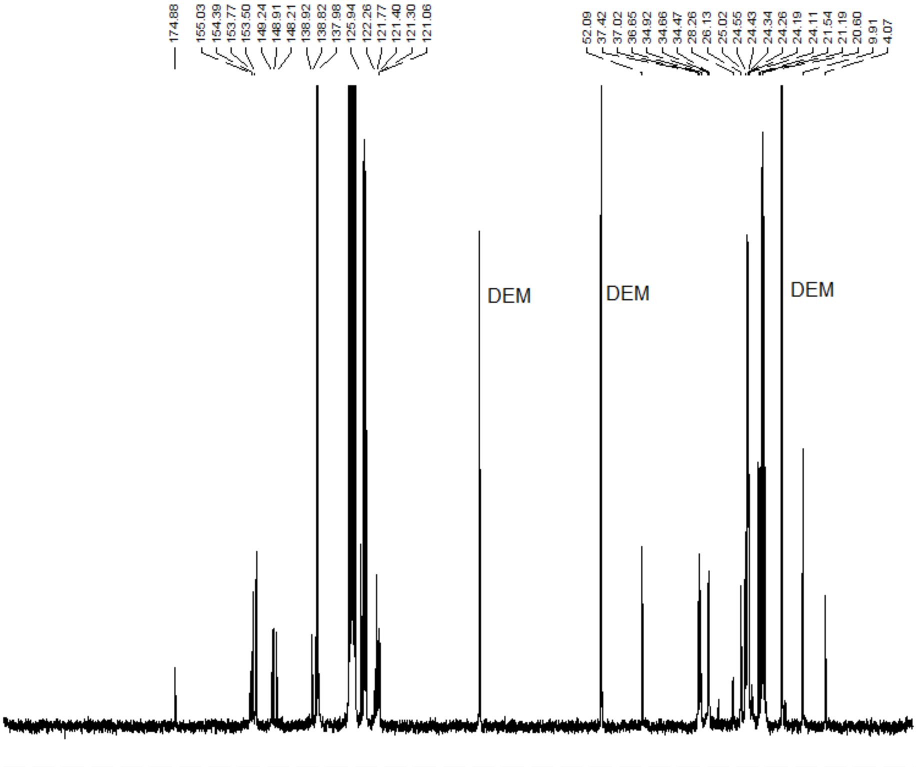


Figure S5. ^{13}C NMR of the low temperature NMR study: intermediate **6** in [D$_8$]-toluene at 253 K (DEM: diethoxymethane).

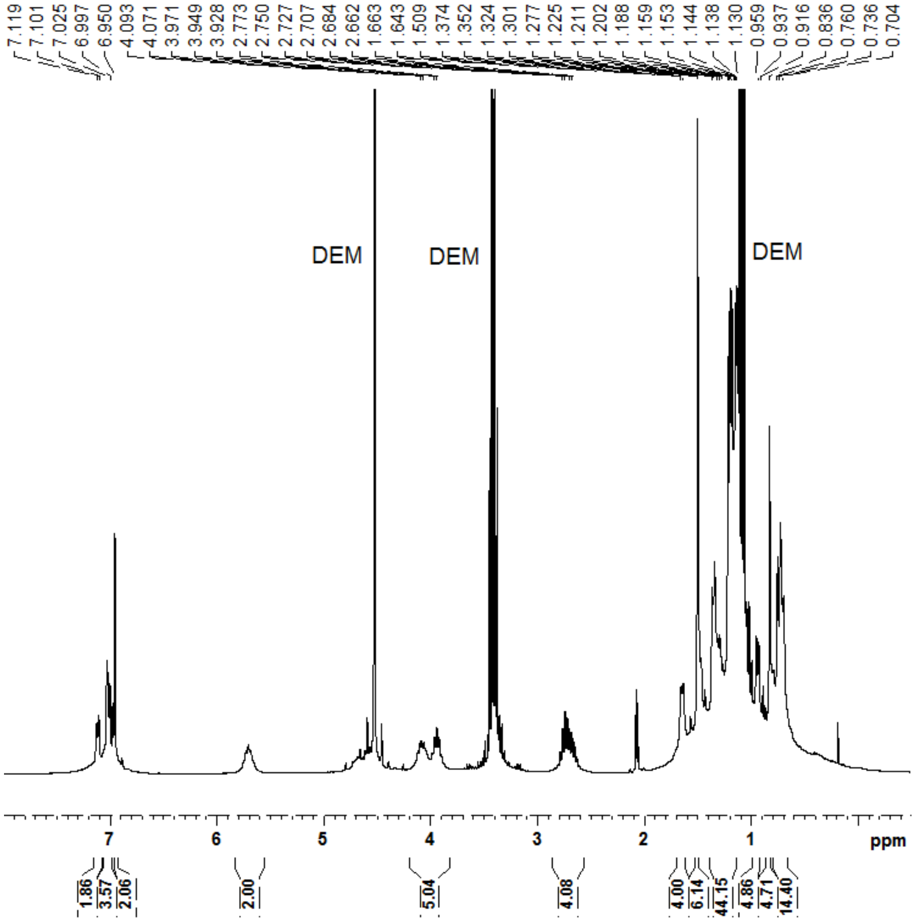


Figure S6. ^{1}H NMR of the low temperature NMR study: proposed intermediate **6** in [D$_8$]-toluene at 253 K (DEM: diethoxymethane).

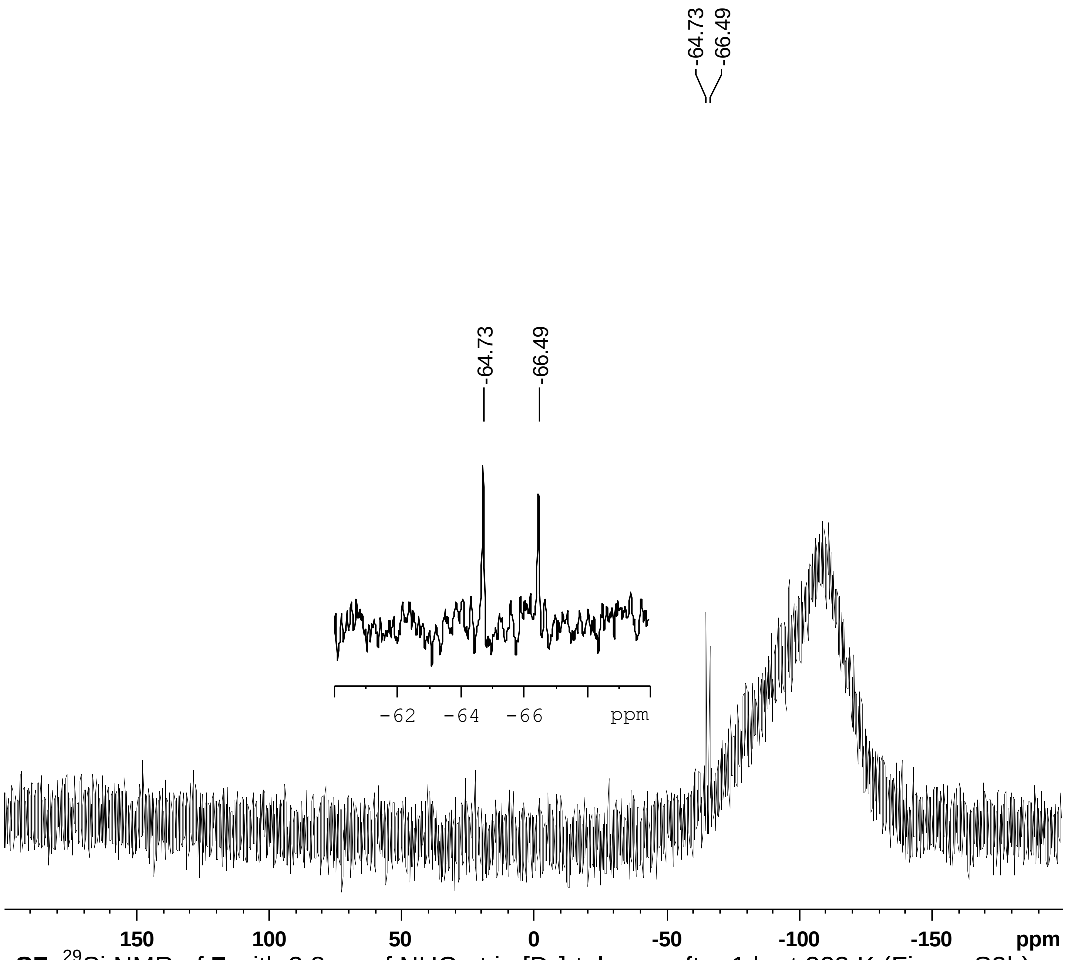


Figure S7. ^{29}Si NMR of **7** with 3.8 eq of NHC at in [D$_8$]-toluene after 1 h at 323 K (Figure S2b)

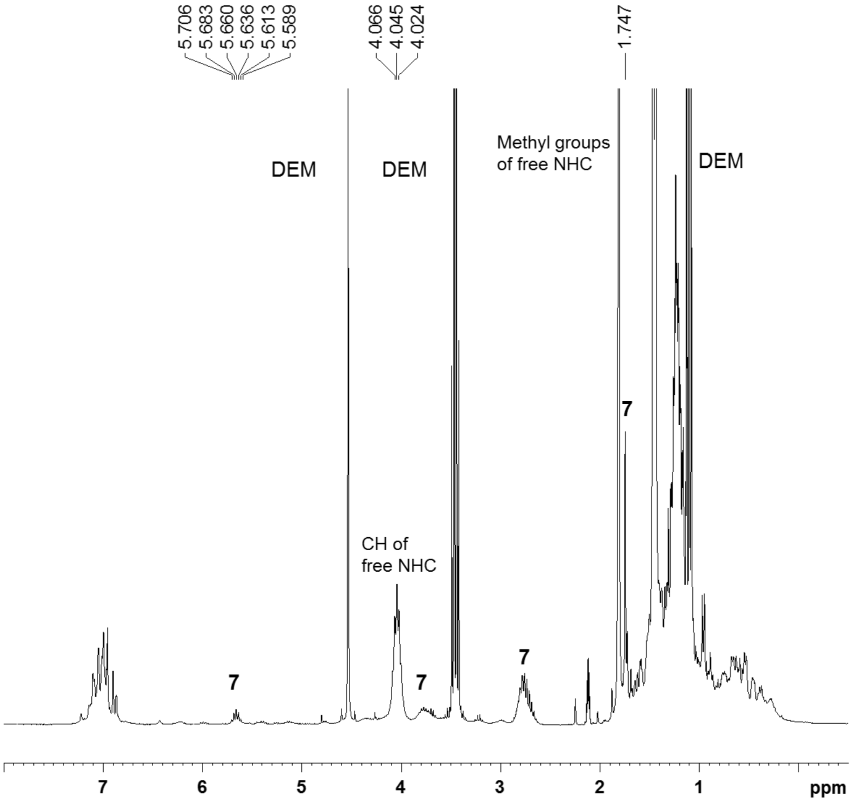


Figure S8. ^{1}H NMR of **7** with 3.8 eq of NHC at in [D$_8$]-toluene after 1 h at 323 K; DEM: diethoxymethane. Selected characteristic signals of **7** are indicated.

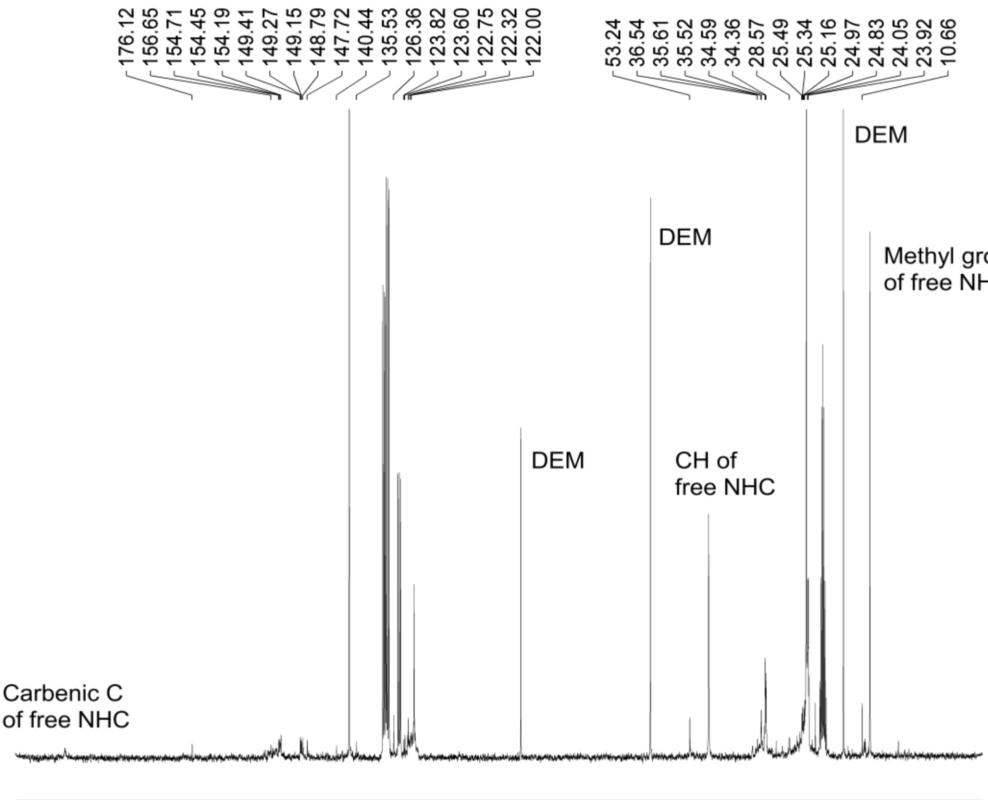


Figure S9. ^{13}C NMR of **7** with 3.8 eq of NHC at in [D$_8$]-toluene after 1 h at 323 K; DEM: diethoxymethane.

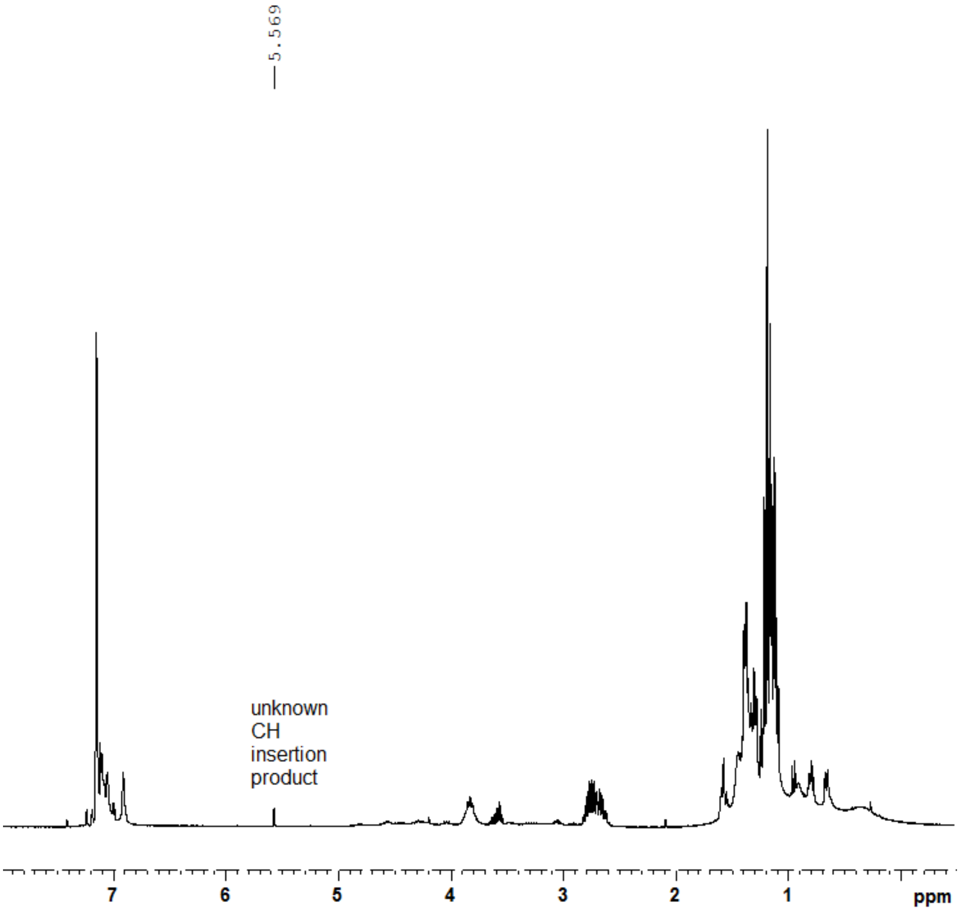


Figure S10. ^{1}H NMR of mixture of **9**, **10** and an unknown CH insertion product in [D$_6$]-benzene at 300 K.

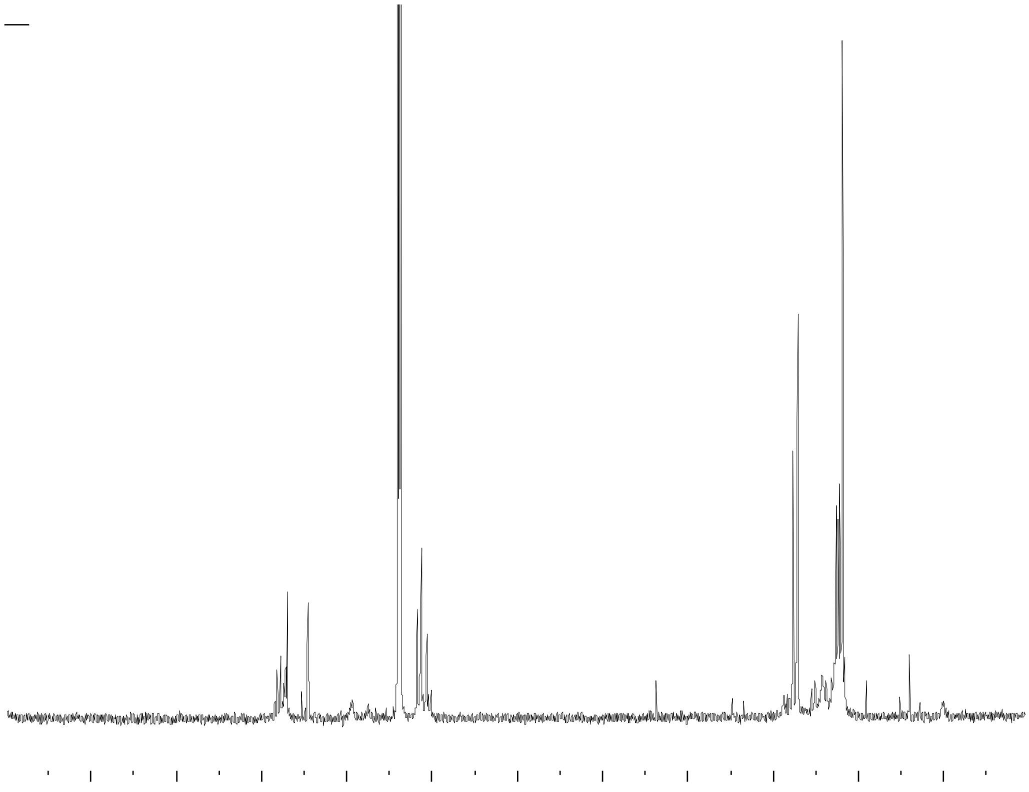


Figure S11. ^{13}C NMR of mixture of **9**, **10** and an unknown CH insertion product in [D$_6$]-benzene at 300 K.

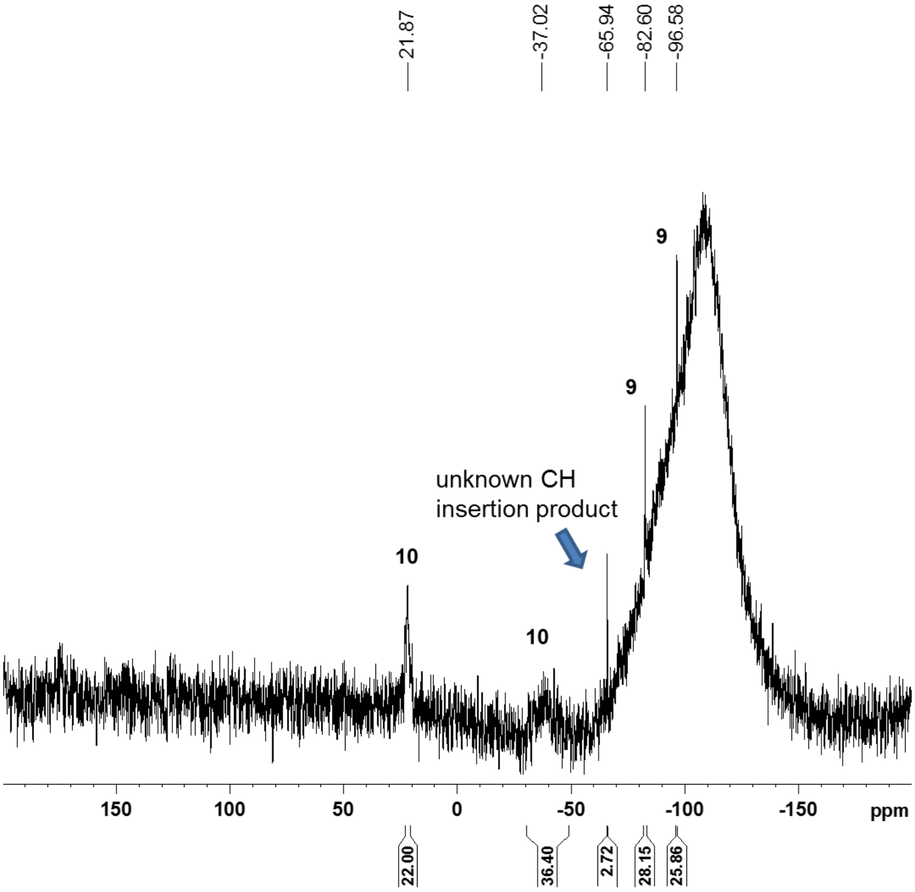


Figure S12. ^{29}Si NMR of mixture of **9**, **10** and an unknown CH insertion product in [D$_6$]-benzene at 300 K (Experiment 1).

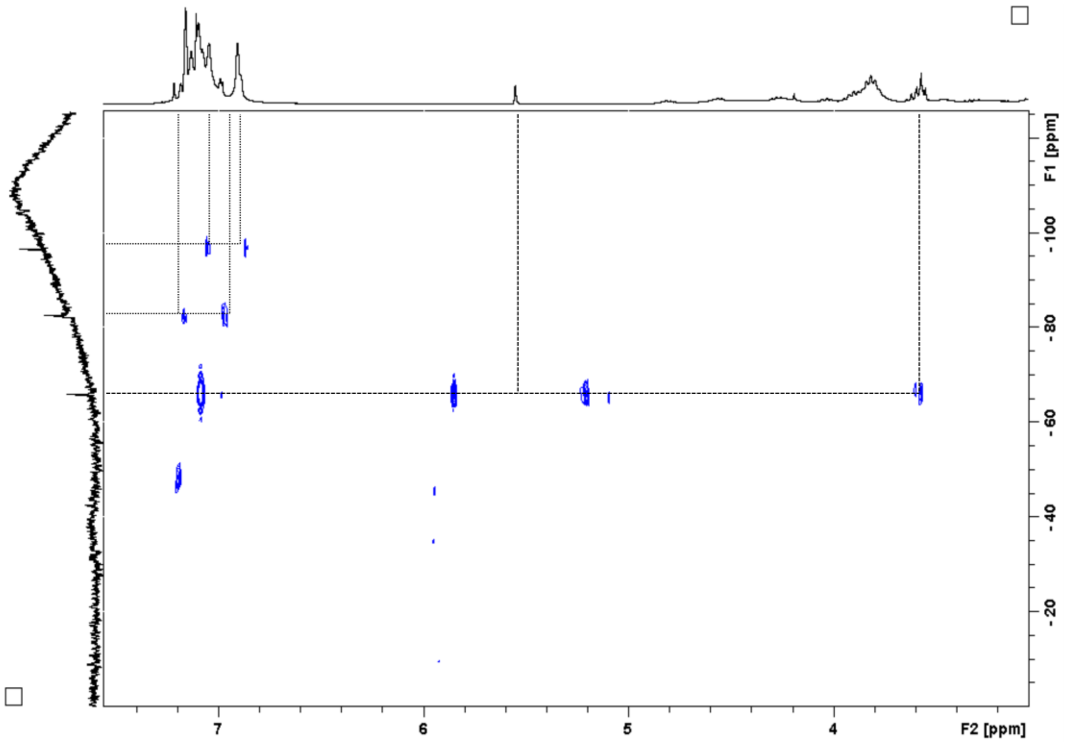


Figure S13. ^{29}Si^{1}H-HMBC correlation of mixture of **9**, **10** and an unknown CH insertion product in [D$_6$]-benzene at 300 K.

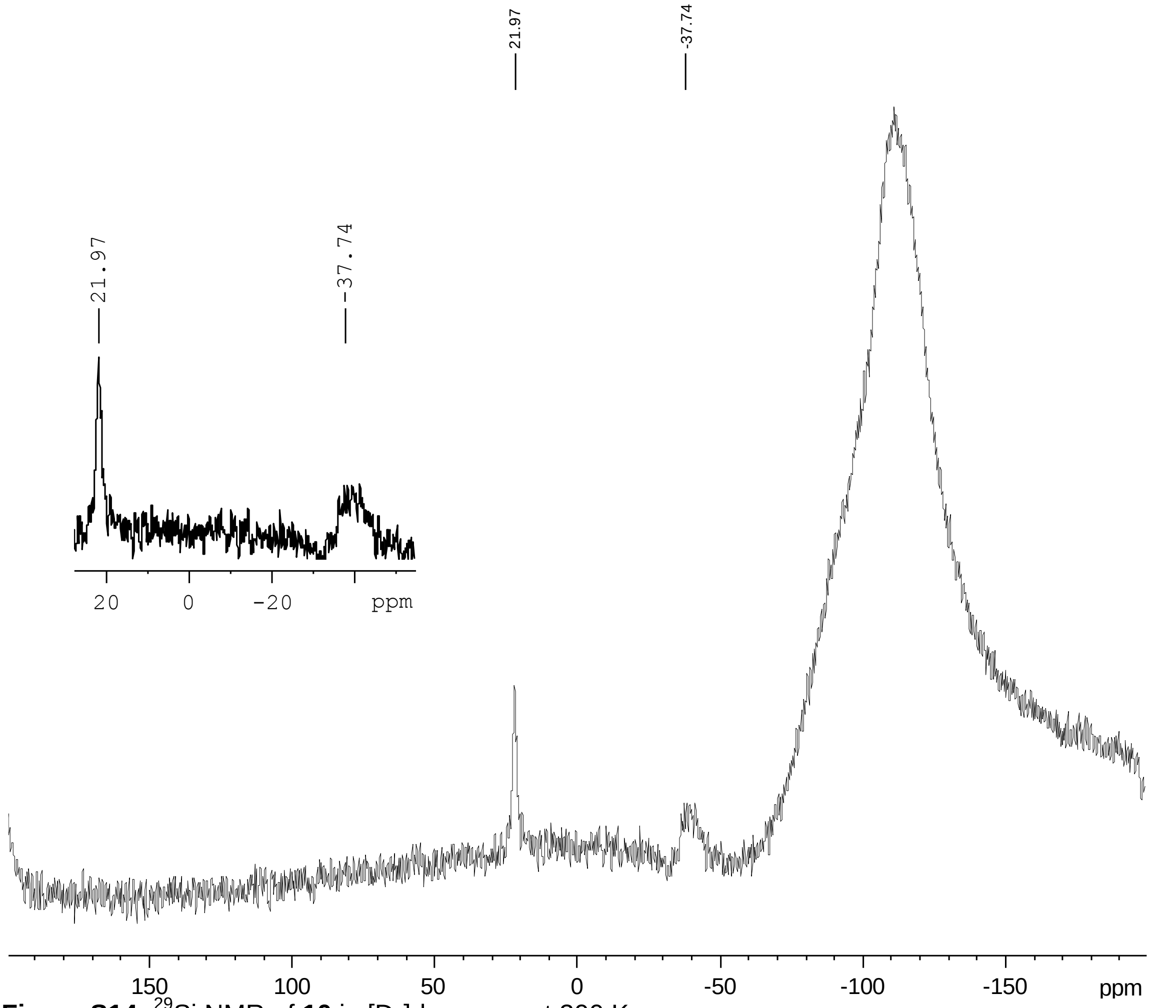


Figure S14: ^{29}Si NMR of **10** in [D$_6$]-benzene at 300 K.

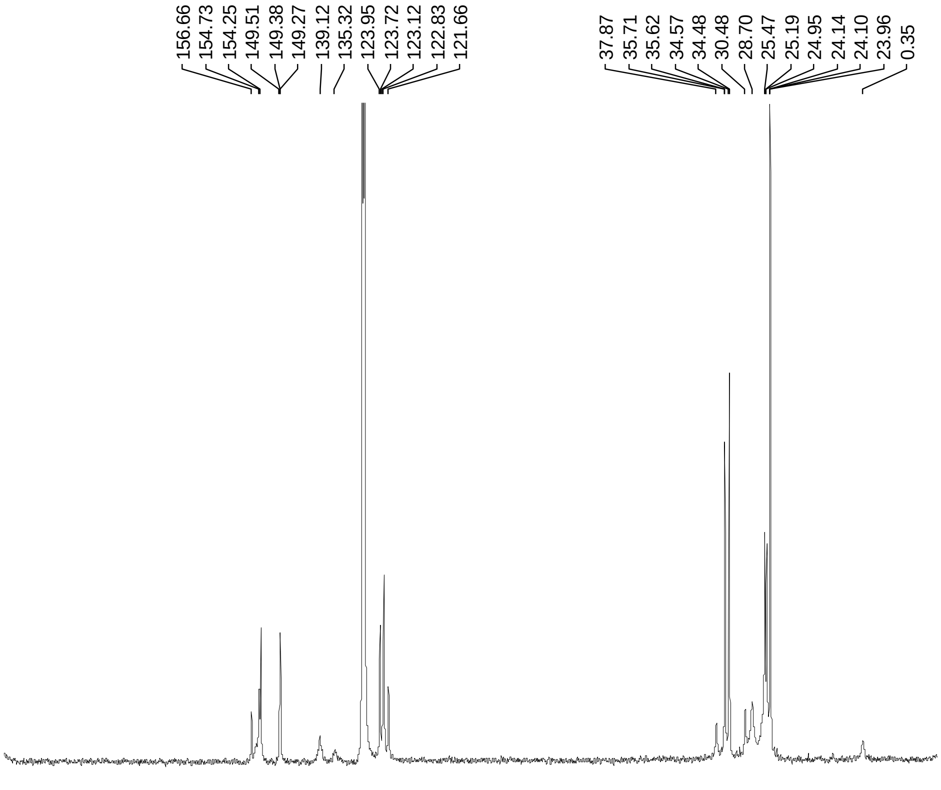


Figure S15: ^{13}C NMR of **10** in [D$_6$]-benzene at 300 K.

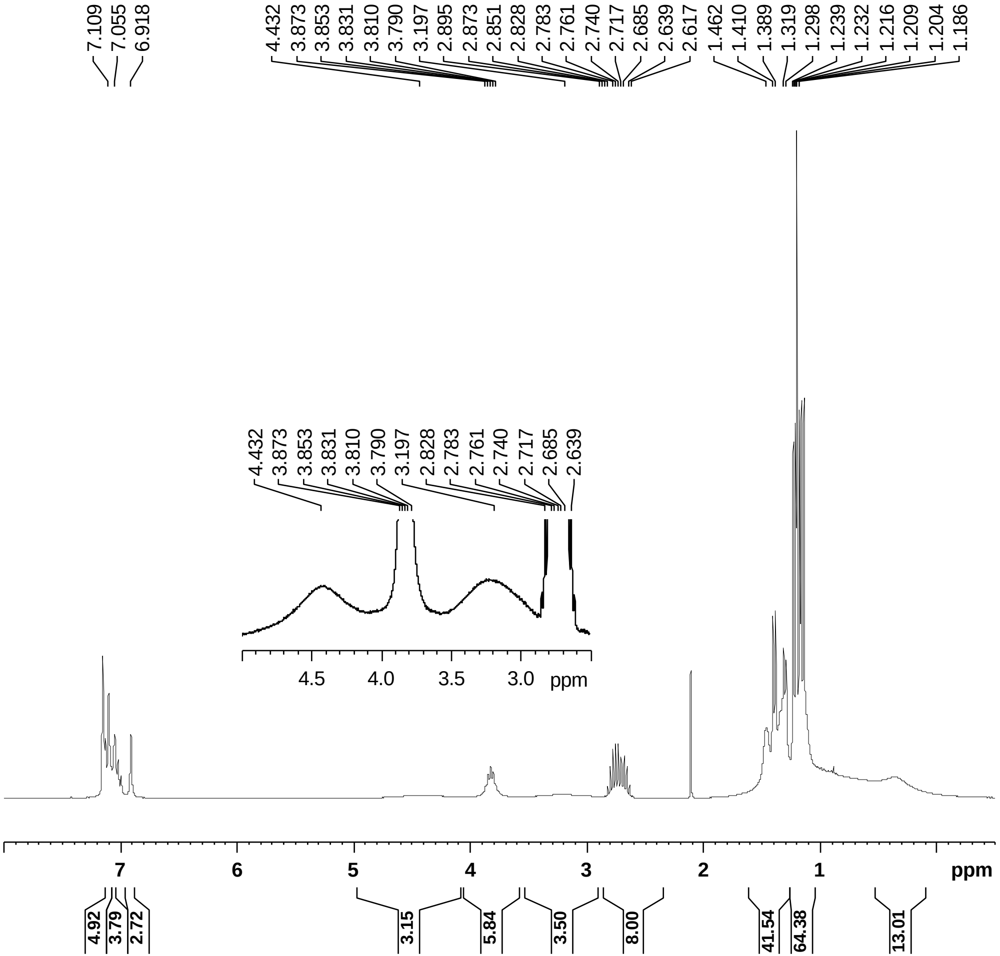


Figure S16: ^{1}H NMR of **10** in [D$_6$]-benzene at 300 K.

3. X-ray data

Table S1: Crystal data and structure refinement for **9**

Identification code	sh3530
Empirical formula	C92 H144 Ge2 Si4, C7 H8
Formula weight	1599.74
Temperature	152(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 16.3223(6) Å α= 71.4780(19)°.
	b = 17.6076(7) Å β= 77.6430(18)°.
	c = 18.3797(8) Å γ = 67.4580(17)°.
Volume	4600.3(3) Å^3
Z	2
Density (calculated)	1.155 Mg/m^3
Absorption coefficient	0.749 mm^{-1}
F(000)	1732
Crystal size	0.303 x 0.248 x 0.210 mm^3
Theta range for data collection	1.297 to 27.210°.
Index ranges	-20<=h<=20, -22<=k<=22, -23<=l<=23
Reflections collected	77965
Independent reflections	20276 [R(int) = 0.0508]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.7011
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20276 / 49 / 1051
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1187
R indices (all data)	R1 = 0.0828, wR2 = 0.1344
Extinction coefficient	n/a
Largest diff. peak and hole	1.332 and -0.616 e.Å^{-3}

Table S2: Crystal data and structure refinement for 10

Identification code	sh3557
Empirical formula	C92H144 Ge2 Si4 x 0.5 C7 H8
Formula weight	1557.70
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 33.8499(14) Å α = 90°.
	b = 26.2285(14) Å β = 97.911(2)°.
	c = 20.2919(8) Å γ = 90°.
Volume	17844.3(14) Å^3
Z	8
Density (calculated)	1.160 Mg/m^3
Absorption coefficient	0.771 mm^{-1}
F(000)	6760
Crystal size	0.389 x 0.230 x 0.046 mm^3
Theta range for data collection	1.215 to 26.502°.
Index ranges	-42<=h<=42, -32<=k<=32, -25<=l<=15
Reflections collected	136792
Independent reflections	18398 [R(int) = 0.0917]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18398 / 110 / 987
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0951
R indices (all data)	R1 = 0.0883, wR2 = 0.1105
Extinction coefficient	n/a
Largest diff. peak and hole	0.873 and -0.653 e.Å^{-3}

4. Computational details

Computational Method:

Gaussian 09 and GaussView 5.0 package programs were used for calculations and visualization.[2,3] The proposed mechanism the formation of **9-Me** using simplified model system with methyl groups instead of Tip substituents (**5a**-**Me**) were calculated at B3LYP/6-31+G(d,p) level of theory (Figure S17). Frequency analyses were performed to determine the character of optimized structures as minima or transition states. The relative Gibbs free energies given in kcal/mol. The chemical reaction channels have been checked by the intrinsic reaction coordinate (IRC) method to verify the energy profiles at the B3LYP/6-31+G(d,p) level of theory for the processes from transition states to intermediates.[4]

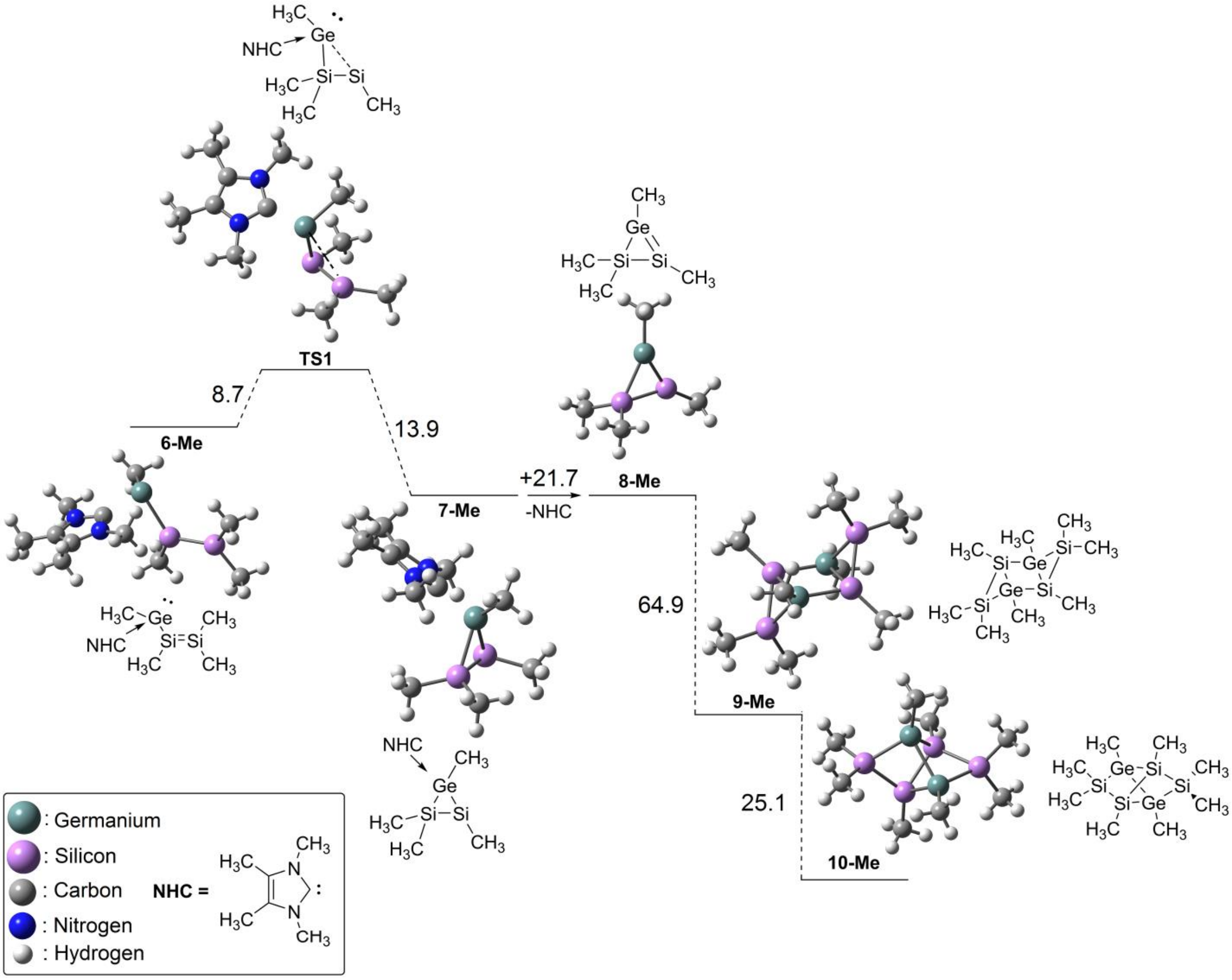


Figure S17. Proposed mechanism and intermediates for the formation of **9-Me** using simplified model system with methyl groups instead of Tip substituents at B3LYP/6-31+G(d,p) level of theory. ΔG energy values at 298 K are given in kcal mol^{-1}

An intrinsic reaction coordinate (IRC) calculation has been carried out to investigate the energy profile between the proposed van der Waals complex of two molecules of **8-Me** (step 1) and the dimer **9-Me** (step 201) at B3LYP/6-31G(d) level of theory. As can be seen from Figure S18, the isomerization from step 1 to **9-Me** (step 201) passes from point 0.0 to point 20.1 with the step size of 0.1. In step 42, the formation of Si-Ge single bonds between two **8-Me** molecules takes place. Then, rearrangement of SiGeSiGe four-membered ring to **9-Me** occurs strongly suggesting that dimerization of the **8-Me** to the **9-Me** proceeds without energy barrier.

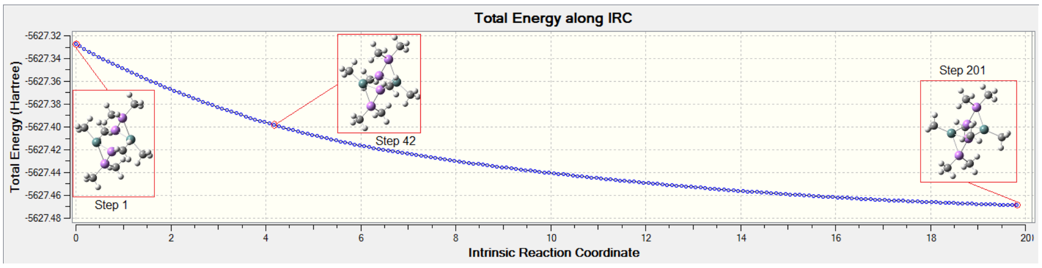


Figure S18. The IRC plot for the formation of **9-Me** at B3LYP/6-31+G(d,p) level of theory.

Table S3. Cartesian coordinates and energy values for the **6-Me**.

Ge,-0.5065990848,1.0092206313,-1.0790815417
Si,1.4074397086,-0.5150371844,-1.1185964953
Si,3.412342328,0.2631872176,-1.3879442254
N,-2.4169076423,-0.6418844761,0.8168568176
N,-0.8414587631,0.4567705971,1.7954698993
C,-1.3230486356,0.1295811154,0.5602128693
C,-2.6025640192,-0.8188227837,2.1903156996
C,-1.6036400773,-0.1239979116,2.8086167792
C,-3.7332494812,-1.610317417,2.7593970284
H,-3.6717450574,-1.6234514549,3.8495152139
H,-3.721765796,-2.6518323693,2.4165012166
H,-4.7075509866,-1.1856623035,2.4887044825
C,-1.2953443743,0.0484817598,4.2594114645
H,-1.9916574119,-0.5377875325,4.8628205468
H,-1.3843301376,1.094154284,4.5775658939
H,-0.2812549205,-0.2884310815,4.5028665743
C,-1.5479080202,0.2655856354,-2.6603763204
H,-2.5780111627,0.6413411461,-2.6665018986
H,-1.0418143395,0.7077209827,-3.5250682202
H,-1.551124449,-0.8199183927,-2.804230132
C,1.2153422806,-2.4070895287,-1.4086778332
H,2.1830478876,-2.8935505073,-1.5715717668
H,0.7401622454,-2.8787605627,-0.540909097
H,0.5852145448,-2.604899747,-2.2832725653
C,4.9831857893,-0.7917948505,-1.5809366041
H,5.5396642993,-0.5009001396,-2.4799344342
H,5.6522021198,-0.6694267939,-0.7208603754
H,4.7332460348,-1.853576636,-1.6686798006
C,3.8179038299,2.1046468657,-1.1703889942
H,4.3565531432,2.4900522945,-2.0443703108
H,2.894051854,2.6809595132,-1.0616736506
H,4.4454201526,2.2822109482,-0.2888258783
C,0.3385012964,1.2877321281,2.0081473419
H,1.2490906385,0.7199528153,1.7924604692
H,0.2966702968,2.1392480578,1.3228714367
H,0.3509122532,1.6407718728,3.039303584
C,-3.2677468273,-1.265920646,-0.1870568936
H,-3.2584128966,-2.3538464497,-0.0690939433
H,-4.2970638767,-0.9059706002,-0.0938340405
H,-2.8873079637,-1.0102670574,-1.1698781224

```
Zero-point correction=                          0.334345 (Hartree/Particle)
 Thermal correction to Energy=                  0.359206
 Thermal correction to Enthalpy=                0.360150
 Thermal correction to Gibbs Free Energy=       0.277969
 Sum of electronic and zero-point Energies=         -3196.851527
 Sum of electronic and thermal Energies=            -3196.826666
 Sum of electronic and thermal Enthalpies=          -3196.825722
 Sum of electronic and thermal Free Energies=       -3196.907903
```

Table S4. Cartesian coordinates and energy values for the **7-Me**.

Ge,5.8961948656,9.7818937202,3.0748212799
Si,5.2150924208,9.8862958857,5.4616240178
Si,6.8757139622,8.3341370567,4.7344747866
N,8.1606014729,11.1111075471,1.6703560107
N,7.0658015325,12.5327908473,2.8775326961
C,7.0975658901,11.224150645,2.5144109605
C,8.0985052077,13.239989418,2.2656372682
C,8.7896328367,12.3421594143,1.498105357
C,8.3156284652,14.7032292703,2.4680708608
H,8.5783689849,14.9384290894,3.5061248735
H,7.4246270182,15.286788156,2.2105514479
H,9.1343725916,15.0510463379,1.8349190809
C,9.9826964394,12.5239526154,0.6190878133
H,10.2597741295,13.5791655395,0.5732257034
H,9.7861844222,12.1870485979,-0.405277465
H,10.8551459999,11.9718249847,0.9887902575
C,6.6236461164,6.4718226102,4.3706577606
H,6.8170327445,5.8802853857,5.2744262194
H,5.5970008618,6.2622081657,4.0527449486
H,7.3015098,6.1164890396,3.5851178399
C,3.5514839864,8.8519969855,5.5004806564
H,3.3989076603,8.4908507267,6.525805979
H,2.7067201064,9.5082046831,5.2584963224
H,3.5053264438,7.9840307015,4.8339014389
C,8.6949095632,8.6069097979,5.2504889537
H,8.9178220831,8.0519397971,6.1711370817
H,9.3959880474,8.2710529663,4.4769966769
H,8.8835145013,9.6669960906,5.4500857893
C,5.1753353721,8.9936910508,1.3937509153
H,4.6210191254,9.7442086259,0.8228927597
H,5.9377296459,8.5417664413,0.7520564372
H,4.4730018453,8.2105934262,1.6923934589
C,8.6027334484,9.8518038698,1.0846930164
H,8.283810214,9.0427604514,1.747958259
H,8.1642356587,9.7017687885,0.0936865843
H,9.690850246,9.8484562015,1.0027448425
C,6.0392138388,13.1306381795,3.7329294724
H,5.1775499458,13.4364365923,3.131422134
H,5.718708485,12.3973468046,4.4797400286
H,6.4592523805,14.001149313,4.237710356

Zero-point correction= 0.334376 (Hartree/Particle)
Thermal correction to Energy= 0.358875
Thermal correction to Enthalpy= 0.359820
Thermal correction to Gibbs Free Energy= 0.280186
Sum of electronic and zero-point Energies= -3196.861945
Sum of electronic and thermal Energies= -3196.837446
Sum of electronic and thermal Enthalpies= -3196.836502
Sum of electronic and thermal Free Energies= -3196.916136

Table S5. Cartesian coordinates and energy values for the **8-Me**.

Ge,6.4235781086,9.6348853824,3.2043655318
Si,5.2298385049,9.528178367,5.0326043759
Si,6.9239637895,7.9702379154,4.8406302323
C,6.5920258909,6.1295965985,4.4997181938
H,6.4967335304,5.5718607611,5.4402988285
H,5.6732323503,5.9940234526,3.9226672391
H,7.4223889811,5.68648114,3.9355984286
C,8.5195143286,8.0568997421,5.8707427502
H,8.4117947788,7.4854036988,6.8016756481
H,9.3612096862,7.6258902925,5.3140789752
H,8.7693673691,9.0902629273,6.1262268901
C,6.7617173712,10.5186926815,1.4874017786
H,6.6519086003,9.8009710509,0.6704310025
H,6.0431208217,11.3308315916,1.354522018
H,7.7757033712,10.9263681984,1.4712127649
C,3.8128181301,10.1608553641,6.135959011
H,3.0792390381,9.3662371189,6.3071566577
H,4.2020620302,10.4887398732,7.1054230239
H,3.3087477087,11.0057977835,5.6568864199

Zero-point correction= 0.148872 (Hartree/Particle)
Thermal correction to Energy= 0.162465
Thermal correction to Enthalpy= 0.163409
Thermal correction to Gibbs Free Energy= 0.107277
Sum of electronic and zero-point Energies= -2813.521911
Sum of electronic and thermal Energies= -2813.508318
Sum of electronic and thermal Enthalpies= -2813.507374
Sum of electronic and thermal Free Energies= -2813.563506

Table S6. Cartesian coordinates and energy values for the **9-Me**.

Ge,1.6211681006,0.2898488733,-0.3831745448
Si,0.3063955841,0.0958610424,1.6971451591
Si,1.8994638773,-1.5163226356,1.166794066
C,1.3890645213,-3.2845670533,0.7142921896
H,1.3369129465,-3.9222246453,1.605202639
H,0.4003221628,-3.2672653155,0.2461465971
H,2.0982325155,-3.733537569,0.0093077878
C,3.5430093657,-1.4565474945,2.1189826745

H,3.4786569533,-2.0280544798,3.0520983308
H,4.3489908946,-1.8851631827,1.5124637294
H,3.8229028522,-0.4286705431,2.3712328682
Si,-0.3063873056,-0.0957841158,-1.6970817996
Ge,-1.6211149172,-0.2897678038,0.3832052913
Si,-1.8995949544,1.5163040497,-1.1668260479
C,-1.3892460404,3.2845730734,-0.7143789494
H,-0.400581665,3.267261172,-0.2460674208
H,-1.3369234801,3.922207483,-1.6052928091
H,-2.0985252244,3.7335627608,-0.0095163321
C,-3.5430943918,1.4564625111,-2.119086501
H,-4.3491106722,1.8850518868,-1.5125919278
H,-3.4786800257,2.0280225995,-3.0521655148
H,-3.8229727792,0.4286013215,-2.37140962
C,-0.2849596996,-1.2331367416,-3.2256918436
H,0.1530639128,-2.2005079513,-2.9595846784
H,-1.2989528245,-1.402304038,-3.6024157108
H,0.3136783785,-0.7955298324,-4.0318252481
C,-3.0499984496,-1.5704606658,0.8079189267
H,-2.6173254599,-2.5430512015,1.0562401133
H,-3.630548515,-1.2121082611,1.6620745555
H,-3.7204256692,-1.6864716148,-0.04778193
C,3.0500691463,1.5704249682,-0.8081648325
H,3.6302021605,1.2121975091,-1.6626579229
H,2.617397427,2.5431185736,-1.0560936794
H,3.7208836945,1.6861711954,0.0472652927
C,0.2851354981,1.2328959141,3.2259749808
H,-0.3131389632,0.7949967417,4.0322200804
H,1.299227681,1.4021642139,3.6023939161
H,-0.1531486894,2.2002551141,2.9602538389

Zero-point correction= 0.301397 (Hartree/Particle)
Thermal correction to Energy= 0.328845
Thermal correction to Enthalpy= 0.329789
Thermal correction to Gibbs Free Energy= 0.243887
Sum of electronic and zero-point Energies= -5627.172949
Sum of electronic and thermal Energies= -5627.145501
Sum of electronic and thermal Enthalpies= -5627.144557
Sum of electronic and thermal Free Energies= -5627.230459

Table S7. Cartesian coordinates and energy values for the **10-Me**.

Ge,7.9451774912,8.8232858417,6.8842984089
Ge,7.2643820869,11.2015826787,6.7492810088
Si,6.6443365868,9.0365330986,4.8354331897
Si,8.3413069705,10.6873005448,4.6253113778
Si,5.1320491154,10.5423575469,5.8434501129
Si,9.9639046009,9.3298581025,5.6717453637
C,7.6342766226,7.6020071956,8.388005217
H,7.9141514575,6.5836902762,8.105979579
H,6.5794440048,7.6151302485,8.6736076806
H,8.2398917002,7.9125961123,9.2431873093

C,7.7244397264,12.6230234831,8.0209599714
H,7.4084374896,13.5926852315,7.6276049962
H,8.8037614831,12.6426144099,8.1915159491
H,7.2157539783,12.4426864749,8.9713809928
C,3.8779359025,9.8268041706,7.0836454993
H,3.0440841793,9.3283777149,6.5746325077
H,4.3617361857,9.0963060286,7.7402113477
H,3.4569645332,10.6191866321,7.7144735084
C,4.2398246579,11.790092629,4.7156982871
H,3.3970730728,11.3212696619,4.1929443845
H,3.8457269287,12.6339723528,5.2943992438
H,4.9249988872,12.1896254301,3.9606987331
C,6.3152455056,7.6189308611,3.6035197496
H,5.6595778604,6.8622426833,4.0465333062
H,5.8414098267,7.9929944331,2.6897436685
H,7.2575459679,7.1347496388,3.3267593342
C,8.526590209,11.9113417544,3.1751659264
H,8.9038150927,11.4067363796,2.2793390942
H,7.5564416699,12.3578175335,2.9334482791
H,9.2195136281,12.7188328554,3.4331495169
C,11.3371215326,10.2064334567,6.6560092496
H,11.8294783922,9.5095507236,7.3451878926
H,12.1078152493,10.620914251,5.9948948871
H,10.9200372735,11.0268144496,7.249120776
C,10.7407496095,7.9266611305,4.6459469351
H,11.5195243552,8.3091868569,3.9747731998
H,11.2005593997,7.1713497987,5.2943460427
H,9.982182486,7.4284191484,4.033208183

Zero-point correction= 0.302611 (Hartree/Particle)
Thermal correction to Energy= 0.329053
Thermal correction to Enthalpy= 0.329997
Thermal correction to Gibbs Free Energy= 0.248353
Sum of electronic and zero-point Energies= -5627.216198
Sum of electronic and thermal Energies= -5627.189756
Sum of electronic and thermal Enthalpies= -5627.188812
Sum of electronic and thermal Free Energies= -5627.270455

Table S8. Cartesian coordinates and energy values for the **NHC**.

N,8.3628548283,11.2564945749,1.6314502008
N,7.4211317749,12.550457475,3.030803469
C,7.5951035039,11.2213434393,2.7621139316
C,8.0554174287,13.3893252669,2.1043751759
C,8.6603347753,12.5581676152,1.2055614673
C,8.009594245,14.8804902841,2.1859111762
H,8.4457694755,15.2543406092,3.1207843875
H,6.9828663941,15.2634259553,2.1298825654
H,8.5711793139,15.3262037394,1.3609002771
C,9.4834419094,12.8543725315,-0.0056945158
H,9.5872307132,13.9337097231,-0.1431986115
H,9.0309381982,12.4481817616,-0.9190781593

H,10.493962549,12.4338653765,0.0715939085
C,8.8133753545,10.0504712288,0.9560822829
H,8.427239021,9.2001916865,1.5178415623
H,8.4331890801,10.0071297746,-0.0705988458
H,9.9074400754,9.9980126669,0.9288835858
C,6.6508239157,13.0221900728,4.1699757884
H,5.7982406193,13.629501437,3.8462558049
H,6.2845479776,12.1435408437,4.7005034344
H,7.2717730771,13.6195016176,4.8468122444

Zero-point correction= 0.182237 (Hartree/Particle)
Thermal correction to Energy= 0.192412
Thermal correction to Enthalpy= 0.193356
Thermal correction to Gibbs Free Energy= 0.147620
Sum of electronic and zero-point Energies= -383.283383
Sum of electronic and thermal Energies= -383.273209
Sum of electronic and thermal Enthalpies= -383.272265
Sum of electronic and thermal Free Energies= -383.318001

Table S9. Cartesian coordinates and energy values for the **TS1**.

Ge,4.6447208861,9.7637063656,6.8500689327
Si,5.215949946,7.2165231038,6.5344559248
Si,6.542901525,8.1630950818,5.0059809261
N,2.5553493442,9.2641319309,9.1627360251
N,4.6336275961,9.1609158077,9.7305774781
C,3.8168111585,9.2964582829,8.6441542354
C,2.5815704258,9.0903353348,10.5490506962
C,3.8968507409,9.0206465526,10.9058036899
C,1.3454590647,9.0222986017,11.3833689637
H,1.6091019555,8.8817243133,12.4336272365
H,0.6959947347,8.1877521372,11.092467598
H,0.7513992989,9.9415599475,11.3122343612
C,4.5297421231,8.833579264,12.2452514182
H,3.7601449616,8.7016949067,13.0088243199
H,5.1380126403,9.6978818612,12.5378025021
H,5.1755226796,7.9483191241,12.2695064538
C,3.0662435683,9.9351655965,5.5831711035
H,2.4215477639,10.7753294014,5.8678889765
H,3.5279606296,10.200281304,4.6253753123
H,2.4539721416,9.0432789388,5.4143520369
C,3.7845783055,6.3504235697,5.5253149325
H,3.5417040771,6.8158087941,4.5645600368
H,4.0492246674,5.3027718777,5.3380419763
H,2.8725811161,6.3495982691,6.1345887891
C,6.5453556077,8.1086954945,3.1009523899
H,6.5520074269,9.1274228946,2.6925624147
H,7.4449701057,7.602910156,2.7262433939
H,5.6690831815,7.5849525097,2.7082920913
C,8.0848802586,9.1322563588,5.5299955625
H,8.1966817102,9.1543185667,6.617008963

```
H,8.9861921856,8.6805886882,5.0961517283
H,8.0279183685,10.1680875605,5.1736701275
C,6.0892567933,9.14425446,9.6514588715
H,6.433931903,8.1878311725,9.2462518659
H,6.4142015957,9.9430684178,8.977983507
H,6.5066752459,9.3053727348,10.64545664
C,1.320575141,9.3342681915,8.394585355
H,0.6972074452,8.4600948748,8.604130664
H,0.7599236503,10.2406243829,8.6454467371
H,1.5691991904,9.3496455795,7.3391888431
```

```
Zero-point correction=                           0.333531 (Hartree/Particle)
 Thermal correction to Energy=                   0.357632
 Thermal correction to Enthalpy=                 0.358576
 Thermal correction to Gibbs Free Energy=        0.279328
 Sum of electronic and zero-point Energies=         -3196.839801
 Sum of electronic and thermal Energies=            -3196.815699
 Sum of electronic and thermal Enthalpies=          -3196.814755
 Sum of electronic and thermal Free Energies=       -3196.894004
```

Table S10. Imaginary frequencies and vibrational frequencies (cm^{-1}) of optimized structures at B3LYP/6-31+G(d,p).

	6	**7**	**8**	**9**	**10**	**NHC**	**TS1**
Vibrational Frequencies	21.07	18.70	45.68	32.64	54.56	122.51	-84.97
Imaginary Frequencies	0	0	0	0	0	0	1

5. Literature references

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