Supporting Information

Potassium-Catalyzed Hydrosilylation of Activated Olefins: Evidence for Silyl Migration Mechanism

Valeri Leich, Thomas P. Spaniol, and Jun Okuda*,†

†Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1,
52056 Aachen, Germany

Corresponding Author
E-mail jun.okuda@ac.rwth-aachen.de

Table of Contents:

General Experimental Remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glove box techniques. THF-d_8 and benzene were distilled under argon from sodium/benzophenone ketyl prior to use. THF and pentane were purified using a MB SPS-800 solvent purification system. 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), Ph_3SiCl, $LiAlD_4$, $HSiPh_3$, H_2SiPh_2, H_3SiPh, 1,1-diphenylethylene, 1,3-cyclohexadiene, triphenylethylene, 1-phenylcyclohexene, 4-phenyl-1-butene and trans,trans-1,4-diphenyl-1,3-butadiene were purchased from Sigma Aldrich and purified by vacuum sublimation or distillation prior to use.

Elemental analyses were performed on an *elementar vario EL* machine. CI-MS spectra were recorded on a *Varian MAT 212S* or *Finnigan SSQ 7000* machine. Metal content was determined by atom absorption spectroscopy on a *Shimadzu AA-6200* (λ = 460.7 nm, air/acetylene flame) machine. ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were recorded on a *Bruker Avance II 400* or a *Bruker Avance III HD 400* spectrometer at 25 °C in J. Young type NMR tubes. ^2H NMR spectra were recorded on an *Agilent VNMRS 400* spectrometer. Chemical shifts for ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. The resonances in ^1H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC).

$[K(18\text{-crown-}6)SiPh_3]$[S1] was prepared according to a published procedure. Triphenylsilane-d_1[S2] and (2,2'-diphenylethyl)triphenylsilane[S3] are literature known compounds, however missing data was completed.

Synthetic Procedures

Synthesis of [K(18-crown-6)Ph$_2$CCH$_2$SiPh$_3$] (2)

A solution of [K(18-crown-6)SiPh$_3$] (**1**) (480 mg, 0.85 mmol) in THF (4 mL) was added to 1,1’-DPE (153 mg, 0.85 mmol) in THF (4 mL) and stirred for 5 min at 25 °C. The reaction mixture turned red immediately, was layered with pentane, and red crystals grew within 12 h at –30 °C. The supernatant was decanted off and the red powder washed with pentane (3×3 mL). After drying *in vacuo*, [K(18-crown-6)Ph$_2$CCH$_2$SiPh$_3$] (**2**) (584 mg, 0.79 mmol, 93 %) was isolated as red powder. Single crystals of **2** suitable for X-ray diffraction were grown from a concentrated benzene solution at 25 °C over a period of 24 h.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 2.70 (s, 2H, CH$_2$), 3.47 (s, 24H, 18-crown-6), 5.49 (tt, 2H, $^3J_{H,H} = 6.85$ Hz, $^4J_{H,H} = 0.98$ Hz, *para*-Ph$_{DPE}$), 6.32 (dd, 4H, $^3J_{H,H} = 8.56$ Hz, $^3J_{H,H} = 6.85$ Hz, *meta*-Ph$_{DPE}$), 6.82 (dd, 4H, $^3J_{H,H} = 8.56$ Hz, $^4J_{H,H} = 0.98$ Hz, *ortho*-Ph$_{DPE}$), 7.11-7.21 (m, 9H, *para/meta*-Ph$_{Si}$), 7.53-7.57 (m, 6H, *ortho*-Ph$_{Si}$) ppm.

^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 21.16 (Ph$_2$C*C*H$_2$SiPh$_3$), 71.08 (18-K-6), 76.49 (Ph$_2$*C*CH$_2$SiPh$_3$), 107.03 (*para*-Ph$_{DPE}$), 118.37 (*ortho*-Ph$_{DPE}$), 127.63 (*meta*-Ph$_{Si}$), 127.89 (*meta*-Ph$_{DPE}$), 128.60 (*para*-Ph$_{Si}$), 137.30 (*ortho*-Ph$_{Si}$), 140.05 (*ipso*-Ph$_{Si}$), 146.61 (*ipso*-Ph$_{DPE}$) ppm.

^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz): δ –17.35 (Ph$_2$CCH$_2$*Si*Ph$_3$) ppm.

Anal. Calcd for $C_{44}H_{51}KO_6Si$ (743.06 g·mol^{-1}): C, 71.12; H, 6.92; K, 5.26. Found: C, 68.31; H, 6.88; K, 5.25%.

^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] (2)

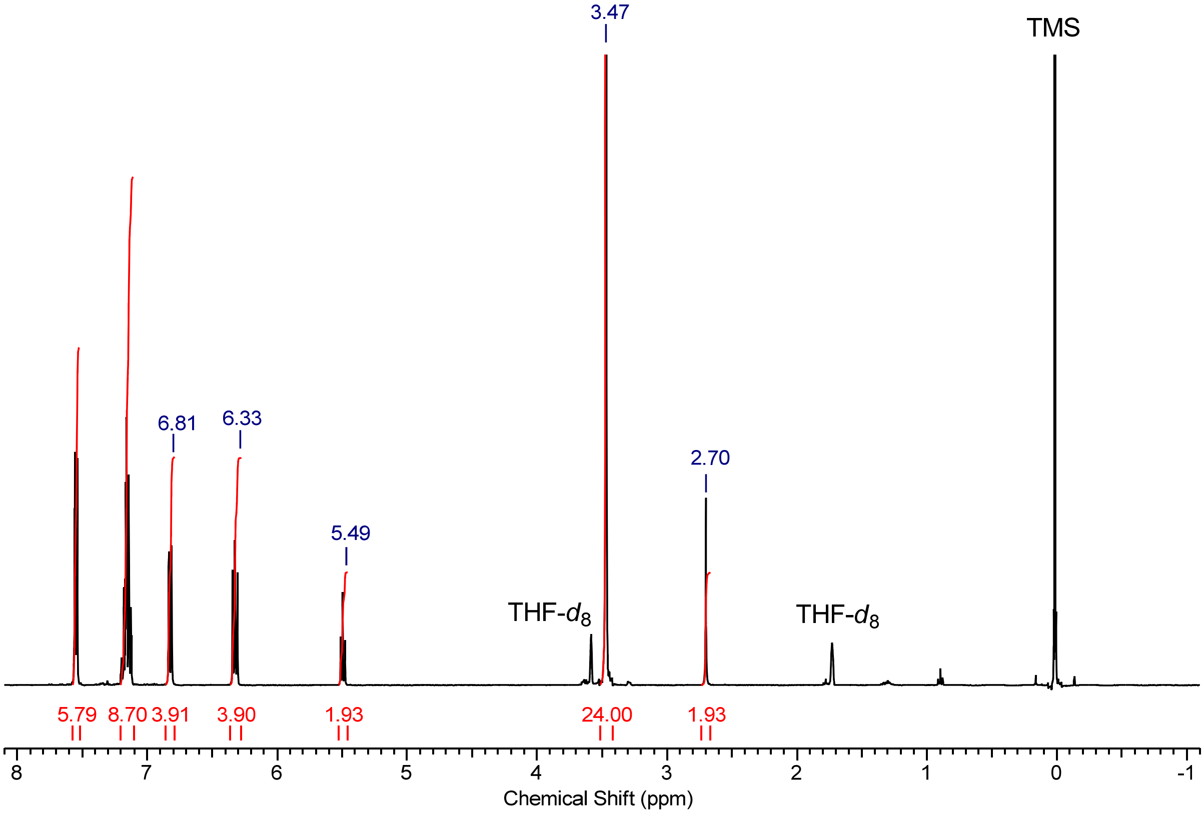

Figure S1. ^{1}H NMR spectrum of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] in THF-d_8 at 25 °C.

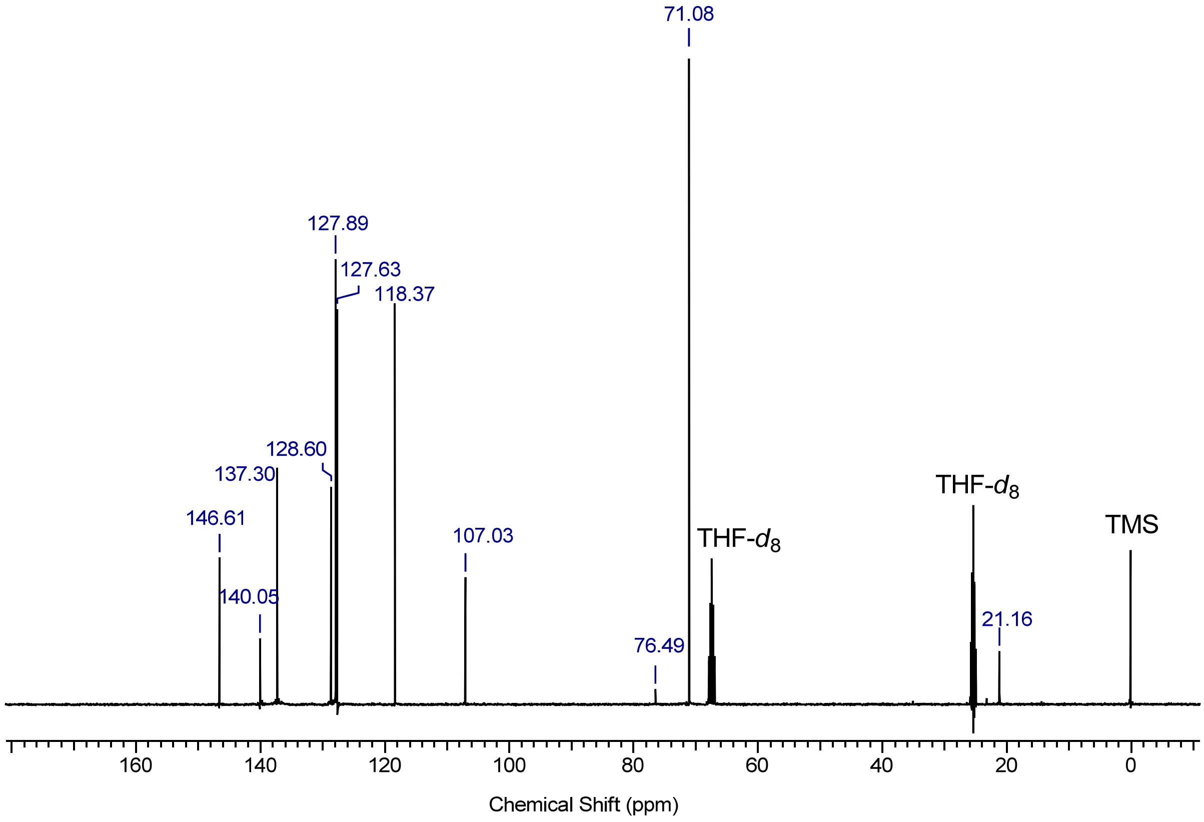

Figure S2. ^{13}C{^{1}H} NMR spectrum of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] in THF-d_8 at 25 °C.

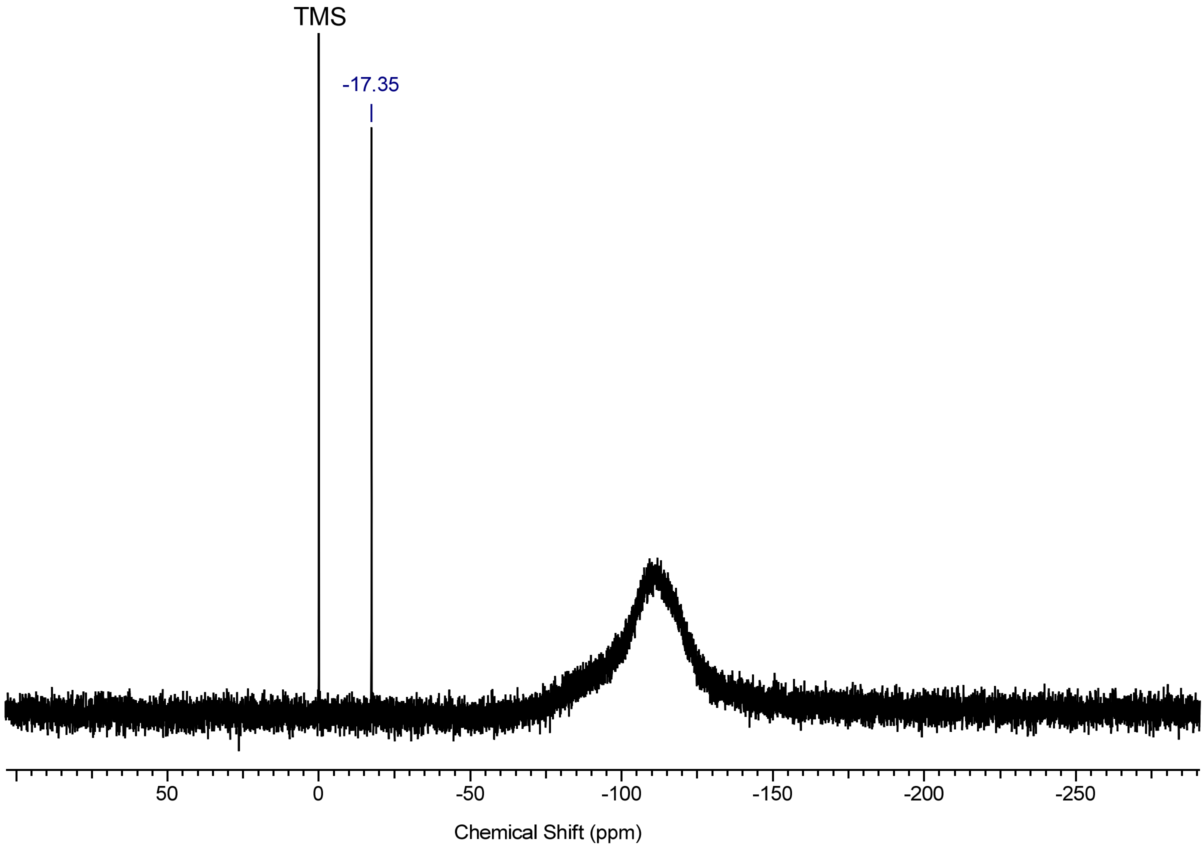

Figure S3. ^{29}Si{^{1}H} NMR spectrum of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] in THF-d_8 at 25 °C.

Synthesis of triphenylsilane-d_1[S2]

A solution of Ph_3SiCl (2.95 g, 10 mmol) in THF (10 mL) was added to a suspension of $LiAlD_4$ (0.42 g, 10 mmol) in THF (30 mL) at –30 °C. Die reaction mixture was stirred at –30 °C for 2 h and warmed to 25 °C over a period of 24 h. The solvent was removed under reduced pressure, the product extracted with pentane and the resulting suspension filtered over a celite column. Pentane was removed under reduced pressure and $DSiPh_3$ (1.64 g, 6.3 mmol, 63%) was isolated as colorless powder after vacuum sublimation (T = 100 °C, $p = 1\times10^{-3}$ mbar).

^{1}H NMR (THF-d_8, 400.1 MHz): δ 7.27-7.52 (m, 9H, *para/meta-* Ph_{Si}), 7.56-7.67 (m, 6H, *ortho-* Ph_{Si}) ppm.

^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 128.91 (*meta*-Ph_{Si}), 130.67 (*para-* Ph_{Si}), 134.30 (*ipso-* Ph_{Si}), 136.61 (*ortho-* Ph_{Si}) ppm.

^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz): δ –18.19 (t, $^{1}J_{D,Si}$ = 30.32 Hz, $Ph_3\mathit{Si}D$) ppm.

^{2}H NMR (THF-d_8, 61.1 MHz): δ 5.63 (d, 1D, $^{1}J_{D,Si}$ = 16.15 Hz, $Ph_3Si\mathit{D}$) ppm.

CI MS (100 eV) *m/z*: 261 (M^+, 100%), 182 (83), 77 (7).

^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra of triphenylsilane-d_1

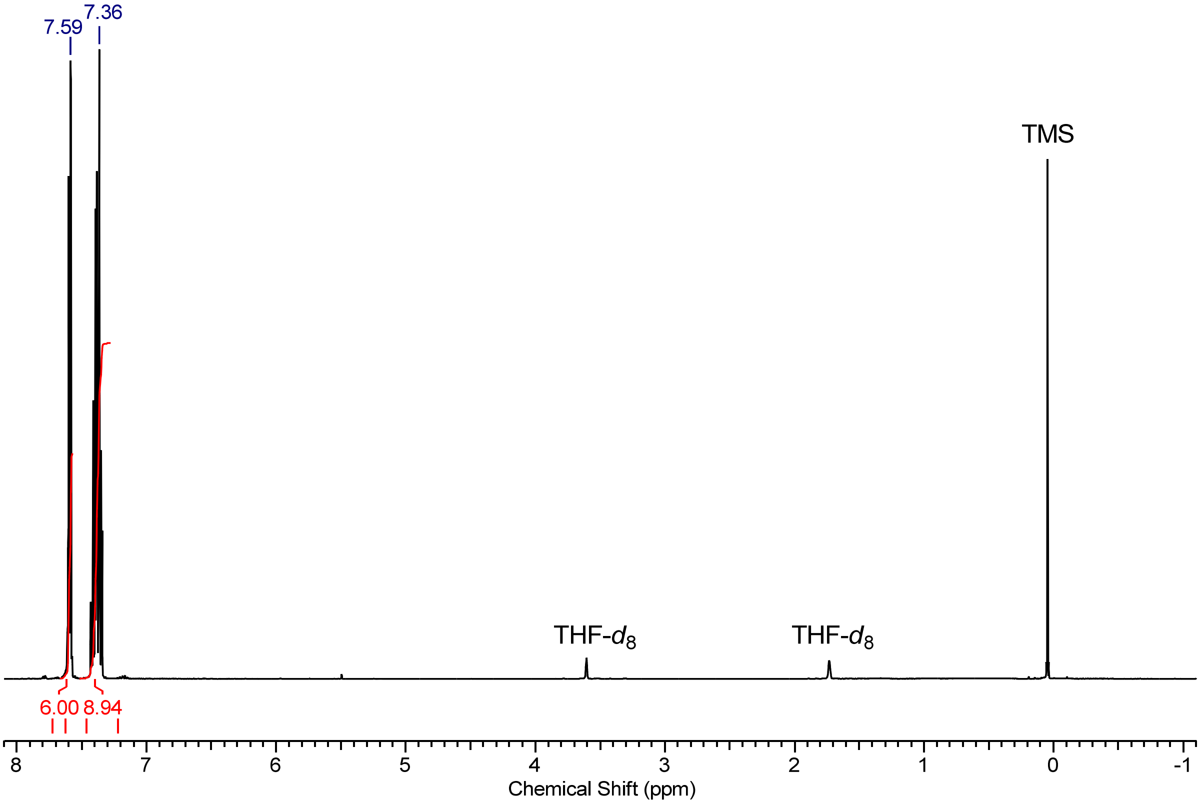

Figure S4. ^{1}H NMR spectrum of triphenylsilane-d_1 in THF-d_8 at 25 °C.

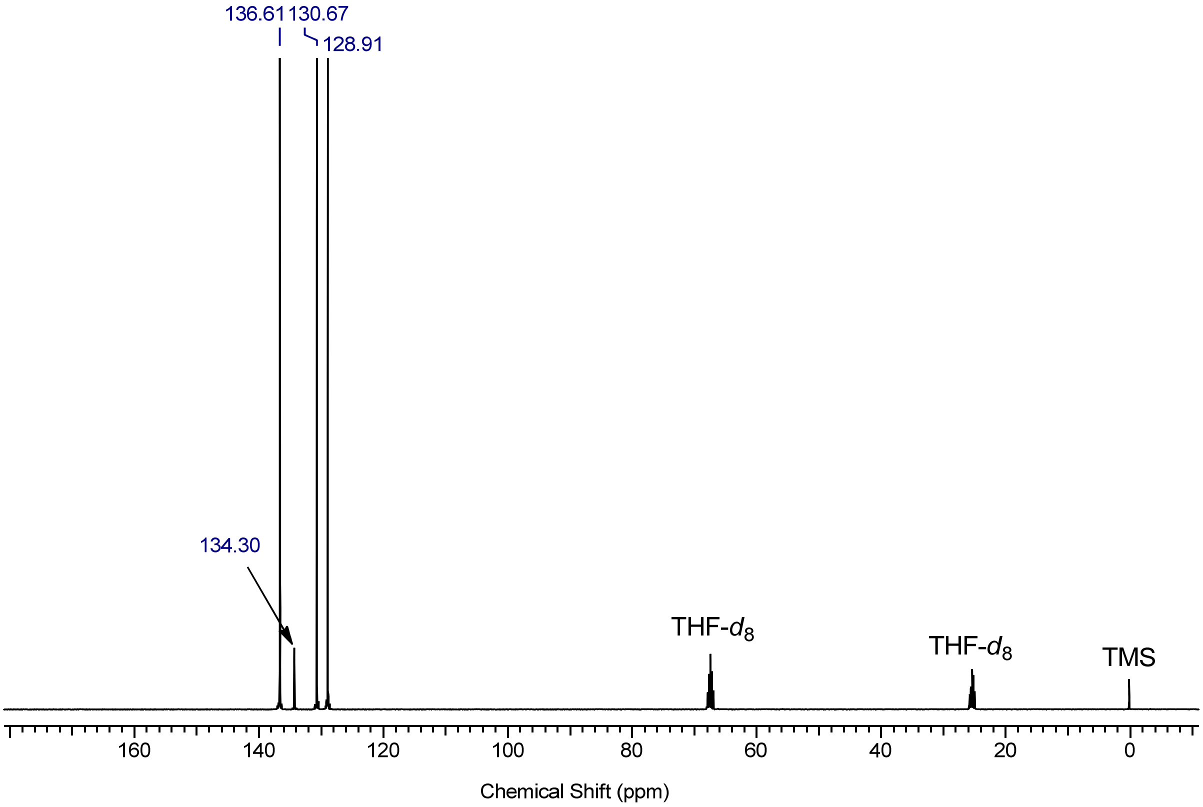

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of triphenylsilane-d_1 in THF-d_8 at 25 °C.

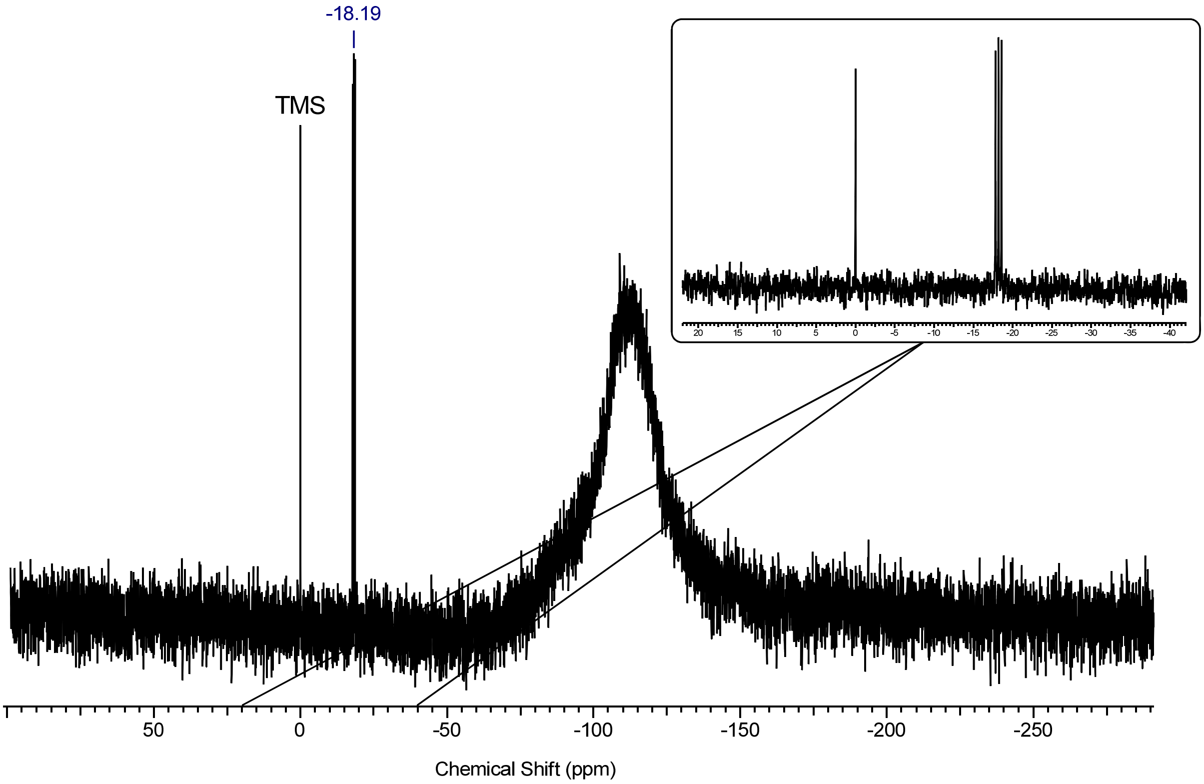

Figure S6. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR spectrum of triphenylsilane-d_1 in THF-d_8 at 25 °C.

Synthesis of (2,2’-diphenylethyl)triphenylsilane (3)[S3]

A solution of 1,1’-DPE (180 mg. 1.00 mmol) and [K(18-crown-6)$\mathrm{SiPh_3}$] (14 mg, 25 µmol) in THF (2 mL) was added to a solution of $\mathrm{Ph_3SiH}$ (286 mg, 1.10 mmol) in THF (6 mL) and stirred at 60 °C over a period of 24 h. The reaction mixture was quenched with water and extracted with $\mathrm{Et_2O}$ (3 × 20 mL). The organic phases were dried over $\mathrm{Na_2SO_4}$ and the solvent was removed under reduced pressure. After crystallization from EtOH/$\mathrm{Et_2O}$ and drying *in vacuo*, (2,2’-diphenylethyl)triphenylsilane (**3**) (350 mg, 0.79 mmol, 79%) was isolated as colorless crystals. Mp 107.2 °C (lit.:[S3] 106-108 °C).

^{1}H NMR (THF-d_8, 400.1 MHz): δ 2.33 (d, 2H, $\mathrm{Ph_2CHC}H_2\mathrm{SiPh_3}$, $^3J_{\mathrm{H,H}}$ = 7.28 Hz), 4.24 (t, 1H, $\mathrm{Ph_2C}H\mathrm{CH_2SiPh_3}$, $^3J_{\mathrm{H,H}}$ = 7.28 Hz), 6.97-7.03 (m, 2H, *para*-$\mathrm{Ph_{DPE}}$), 7.04-7.10 (m, 4H, *meta*-$\mathrm{Ph_{DPE}}$), 7.12-7.17 (m, 4H, *ortho*-$\mathrm{Ph_{DPE}}$), 7.19-7.26 (m, 6H, *meta*-$\mathrm{Ph_{Si}}$), 7.27-7.33 (m, 3H, *para*-$\mathrm{Ph_{Si}}$), 7.33-7.37 (m, 6H, *ortho*-$\mathrm{Ph_{Si}}$) ppm.

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (THF-d_8, 100.6 MHz): δ 22.18 ($\mathrm{Ph_2CH}C\mathrm{H_2SiPh_3}$), 48.14 ($\mathrm{Ph_2}C\mathrm{HCH_2SiPh_3}$), 126.60 (*para*-$\mathrm{Ph_{DPE}}$), 128.45 (*meta*-$\mathrm{Ph_{Si}}$), 128.60 (*ortho*-$\mathrm{Ph_{DPE}}$), 128.96 (*meta*-$\mathrm{Ph_{DPE}}$), 129.95 (*para*-$\mathrm{Ph_{Si}}$), 136.02 (*ipso*-$\mathrm{Ph_{Si}}$), 136.60 (*ortho*-$\mathrm{Ph_{Si}}$), 147.94 (*ipso*-$\mathrm{Ph_{DPE}}$) ppm.

$^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (THF-d_8, 79.5 MHz): δ –11.25 ($\mathrm{Ph_2CHCH_2}Si\mathrm{Ph_3}$) ppm.

Anal. Calcd for $C_{32}H_{28}Si$ (440.65 g·mol^{-1}): C, 87.22; H, 6.40. Found: C, 86.93; H, 6.35%. CI MS (100 eV) *m/z*: 363 (M^+–C_6H_5, 100%), 259 (30); molecular peak could not be detected.

^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra of (2,2'-diphenylethyl)triphenylsilane (3)

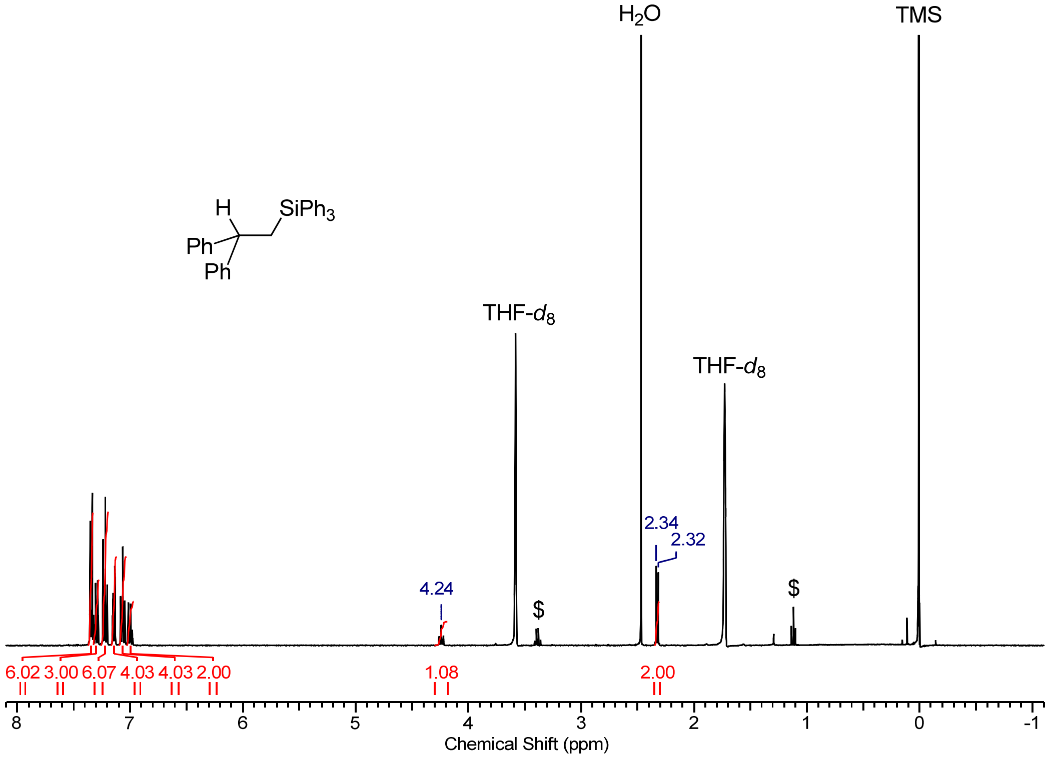

Figure S7. ^{1}H NMR spectrum of (2,2'-diphenylethyl)triphenylsilane in THF-d_8 at 25 °C. $ denotes traces of Et_2O. Residual H_2O from THF-d_8.

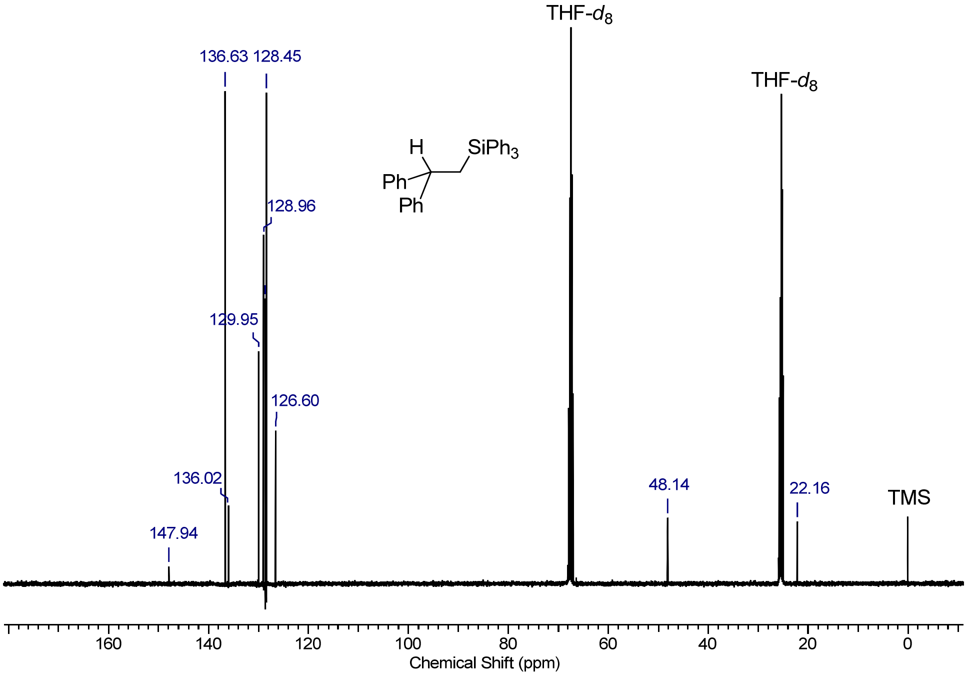

Figure S8. ^{13}C{^{1}H} NMR spectrum of (2,2'-diphenylethyl)triphenylsilane in THF-d_8 at 25 °C.

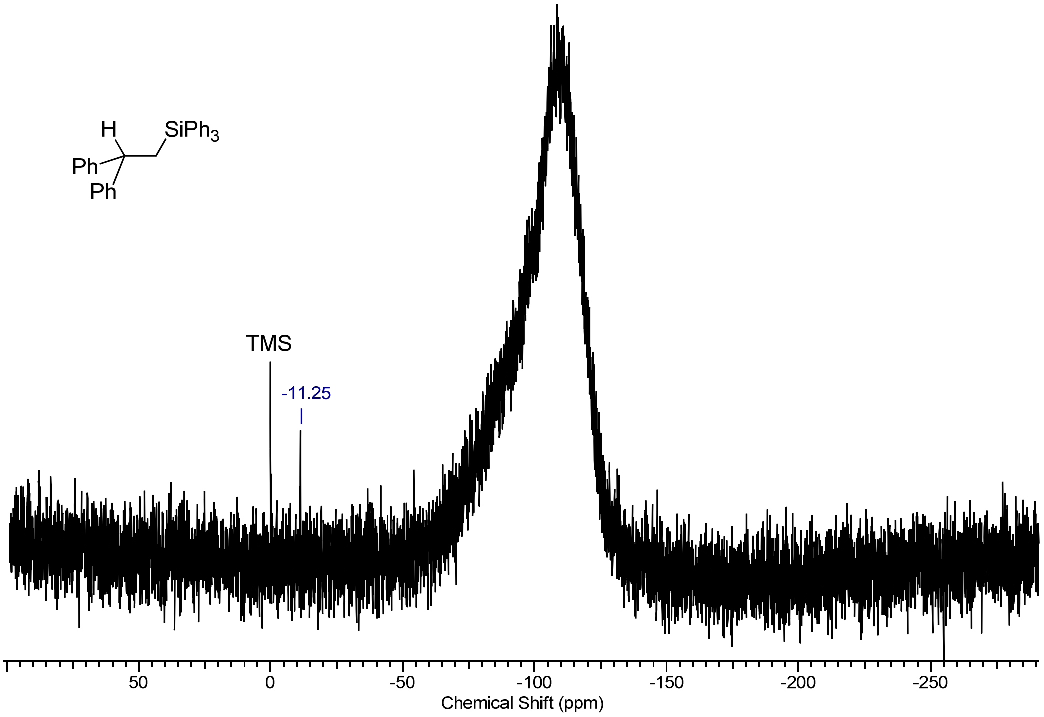

Figure S9. $^{29}Si\{^1H\}$ NMR spectrum of (2,2'-diphenylethyl)triphenylsilane in THF-d_8 at 25 °C.

Synthesis of (2,2'-diphenylethyl)triphenylsilane-d_1 (3-d_1)

A solution of 1,1'-DPE (180 mg. 1.00 mmol) and [K(18-crown-6)$SiPh_3$] (14 mg, 25 µmol) in THF (2 mL) was added to a solution of Ph_3SiD (287 mg, 1.10 mmol) in THF (6 mL) and stirred at 60 °C over a period of 5 d. The reaction mixture was quenched with water and extracted with Et_2O (3 × 20 mL). The organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. After crystallization from EtOH/Et_2O and drying *in vacuo*, (2,2'-diphenylethyl)triphenylsilane-d_1 (**3-d_1**) (324 mg, 0.73 mmol, 73 %) was isolated as colorless crystals.

^1H NMR (THF-d_8, 400.1 MHz): δ 2.32 (s, 2H, $Ph_2CDCH_2SiPh_3$), 6.97-7.03 (m, 2H, *para*-Ph_{DPE}), 7.03-7.10 (m, 4H, *meta*-Ph_{DPE}), 7.12-7.17 (m, 4H, *ortho*-Ph_{DPE}), 7.19-7.26 (m, 6H, *meta*-Ph_{Si}), 7.27-7.33 (m, 3H, *para*-Ph_{Si}), 7.33-7.38 (m, 6H, *ortho*-Ph_{Si}) ppm.

$^{13}C\{^1H$ NMR (THF-d_8, 100.6 MHz): δ 22.18 ($Ph_2CDCH_2SiPh_3$), 126.73 (*para*-Ph_{DPE}), 128.57 (*meta*-Ph_{Si}), 128.70 (*ortho*-Ph_{DPE}), 129.10 (*meta*-Ph_{DPE}), 130.08 (*para*-Ph_{Si}), 136.15 (*ipso*-Ph_{Si}), 136.76 (*ortho*-Ph_{Si}), 148.03 (*ipso*-Ph_{DPE}) ppm.

$^{29}Si\{^1H\}$ NMR (THF-d_8, 79.5 MHz): δ –11.18 ($Ph_2CDCH_2SiPh_3$) ppm.

^2H NMR (THF-d_8, 61.1 MHz): δ 4.24 (s, 1D) ppm.

Anal. Calcd for $C_{32}H_{27}DSi$ (441.66 g·mol^{-1}): C, 87.02; H, 6.62. Found: C, 86.61; H, 6.82%.

CI MS (100 eV) *m/z*: 364 (M^+–C_6H_5, 100%), 259 (16); molecular peak could not be detected.

The resonance for the $Ph_2\mathit{C}DCH_2SiPh_3$ carbon atom of (2,2'-diphenylethyl)triphenylsilane-d_1 expected at around δ 48 ppm in the $^{13}C\{^1H\}$ NMR spectrum was not observed, probably due to low intensity as result of C,D coupling.

^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra of (2,2'-diphenylethyl)triphenylsilane-d_1 (3-d_1)

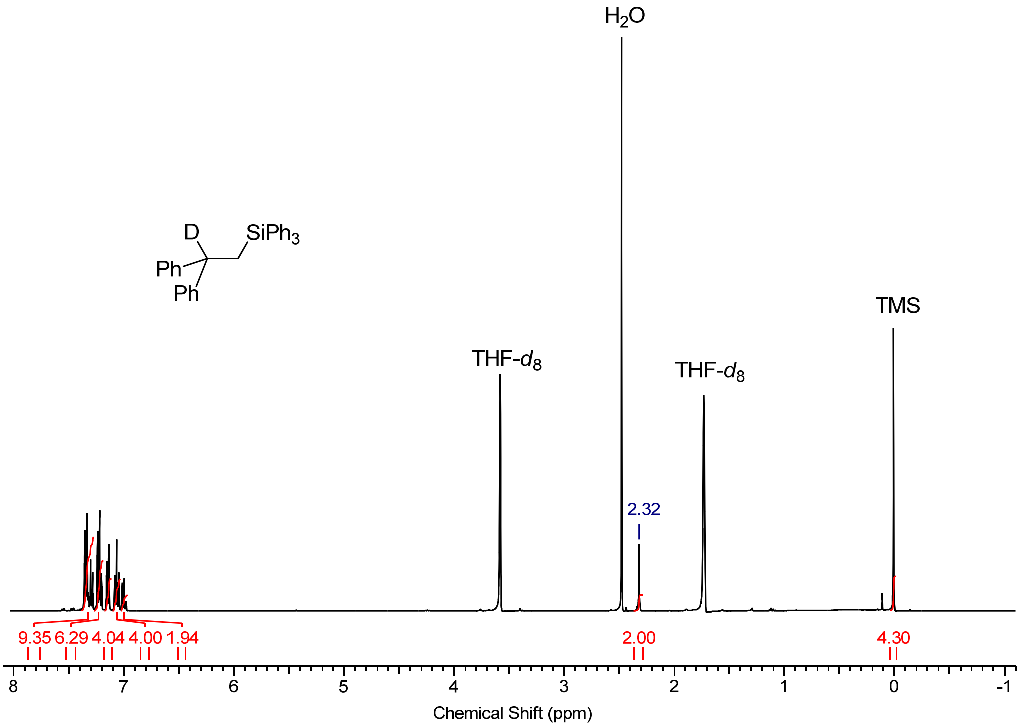

Figure S10. ^{1}H NMR spectrum of (2,2'-diphenylethyl)triphenylsilane-d_1 in THF-d_8 at 25 °C. Residual H_2O from THF-d_8.

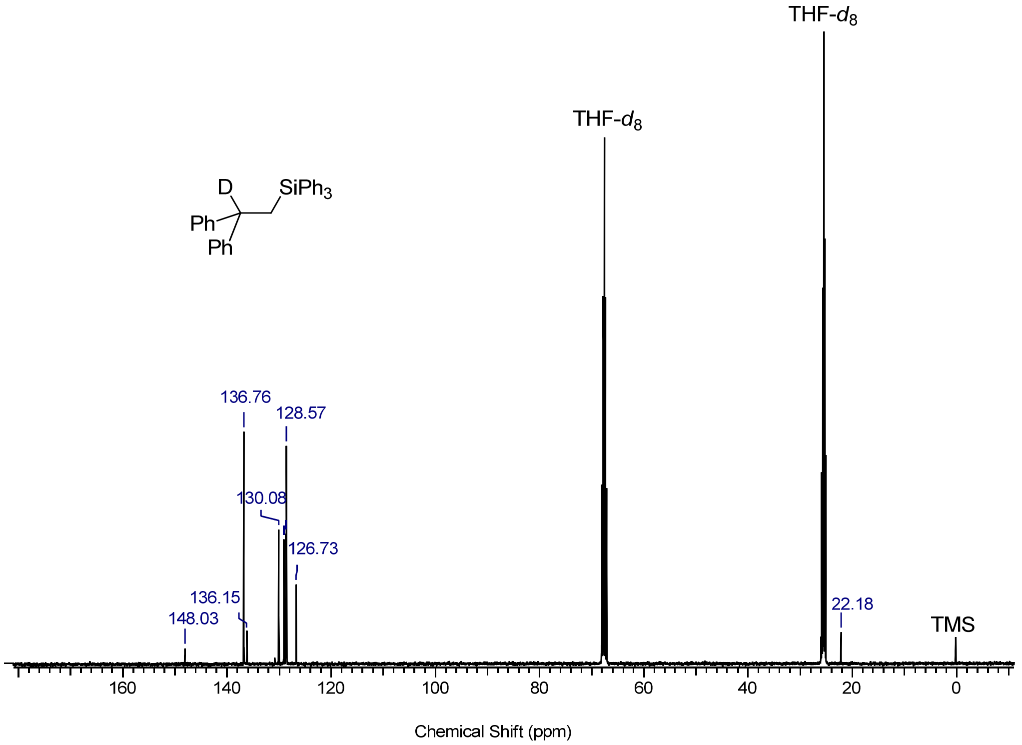

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of (2,2’-diphenylethyl)triphenylsilane-d_1 in THF-d_8 at 25 °C.

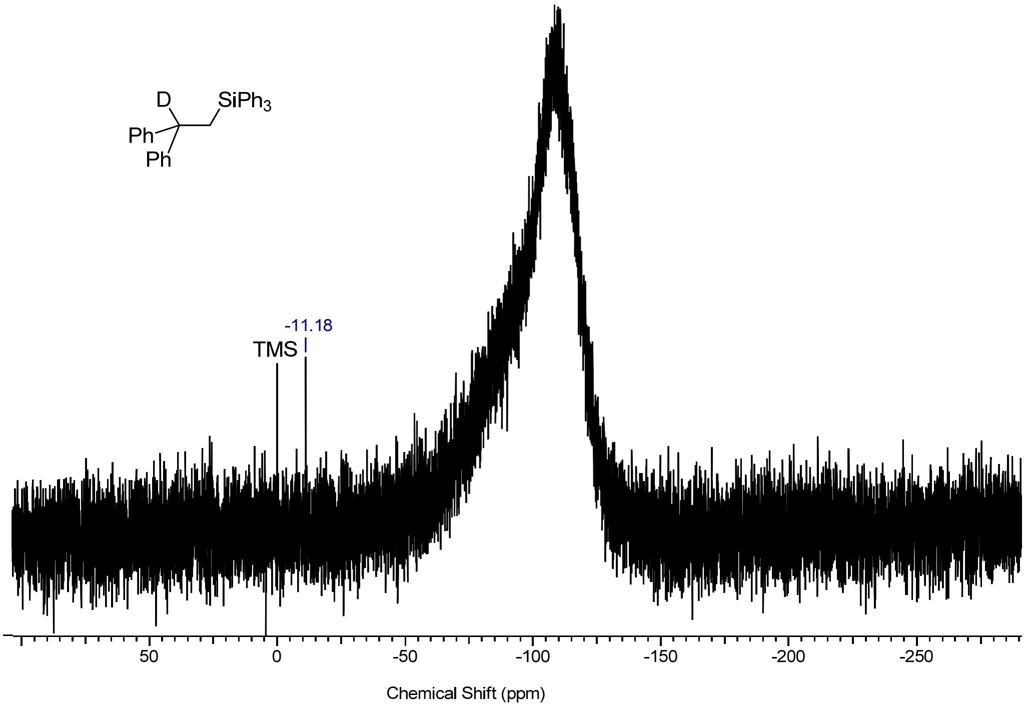

Figure S12. $^{29}Si\{^{1}H\}$ NMR spectrum of (2,2’-diphenylethyl)triphenylsilane-d_1 in THF-d_8 at 25 °C.

Hydrosilylation of alkenes

Hydrosilylation experiments were performed as follows: A solution of catalyst (2.5 μmol) in THF-d_8 (0.6 mL) in a Young's NMR tube was treated with 1,1'-DPE (0.10 mmol). Immediately the reaction mixture turned deep red. Silane (0.11 mmol) was added and the reaction mixture was heated for the indicated period of time. The conversions of the substrates were determined by ^{1}H NMR spectroscopy. A typical workup was carried out as follows: the reaction mixture was quenched with water, extracted with Et_2O, dried over Na_2SO_4, filtered and the ether was removed under reduced pressure.

Characterization of (1,2,2'-triphenylethyl)diphenylsilane

The catalytic hydrosilylation reaction was performed as stated before. Triphenylethylene (25.6 mg, 0.10 mmol) and Ph_2SiH_2 (20 mg,0 0.11 mmol) were used as starting materials and the product was isolated without further purification and characterized *via* ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectroscopy, CI-MS, and elemental analysis.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 3.91 (d, 1H, $^3J_{H,H}$ = 13.05 Hz, $Ph_2CHC\mathit{H}PhSiHPh_2$), 4.60 (d, 1H, $^3J_{H,H}$ = 13.05 Hz, $Ph_2C\mathit{H}CHPhSiHPh_2$), 4.63 (s, 1H, $^1J_{Si,H}$ = 100.14 Hz, Si*H*), 6.81-7.00 (m, 8H, $Ph_{DPE/Si}$), 7.35-7.15 (m, 15H, $Ph_{DPE/Si}$), 7.42-7.47 (m, 2H, $Ph_{DPE/Si}$) ppm.
^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 40.52 ($Ph_2CH\mathit{C}HPhSiHPh_2$), 54.54 ($Ph_2\mathit{C}HCHPhSiHPh_2$, 125.54 ($Ph_{DPE/Si}$), 126.18 ($Ph_{DPE/Si}$), 127.27 ($Ph_{DPE/Si}$), 128.27 ($Ph_{DPE/Si}$), 128.32 ($Ph_{DPE/Si}$), 128.38 ($Ph_{DPE/Si}$), 128.62 ($Ph_{DPE/Si}$), 128.95 ($Ph_{DPE/Si}$), 129.18 ($Ph_{DPE/Si}$), 129.61 ($Ph_{DPE/Si}$), 130.04 ($Ph_{DPE/Si}$), 130.28 ($Ph_{DPE/Si}$), 130.61 ($Ph_{DPE/Si}$), 130.82 ($Ph_{DPE/Si}$), 133.82 (*ipso*-$Ph_{DPE/Si}$), 134.68 (*ipso*-$Ph_{DPE/Si}$), 136.45 ($Ph_{DPE/Si}$), 137.17 ($Ph_{DPE/Si}$), 141.66 (*ipso*-$Ph_{DPE/Si}$), 145.42 (*ipso*-$Ph_{DPE/Si}$), 145.58 (*ipso*-$Ph_{DPE/Si}$) ppm.
^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz): δ –12.92 ($Ph_2CHCHPh\mathit{Si}HPh_2$) ppm.

Anal. Calcd for $C_{32}H_{28}Si$ (440.66 g·mol^{-1}): C, 87.22; H, 6.40. Found: C, 84.72; H, 6.45%.
CI MS (100 eV) *m/z*: 285 ($M^+–2·C_6H_5–H$, 8%), 257 (100), 256 (70), 181 (22), 179 (25), 167 (16); molecular peak could not be detected.

^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra of (1,2,2'-triphenylethyl)diphenylsilane

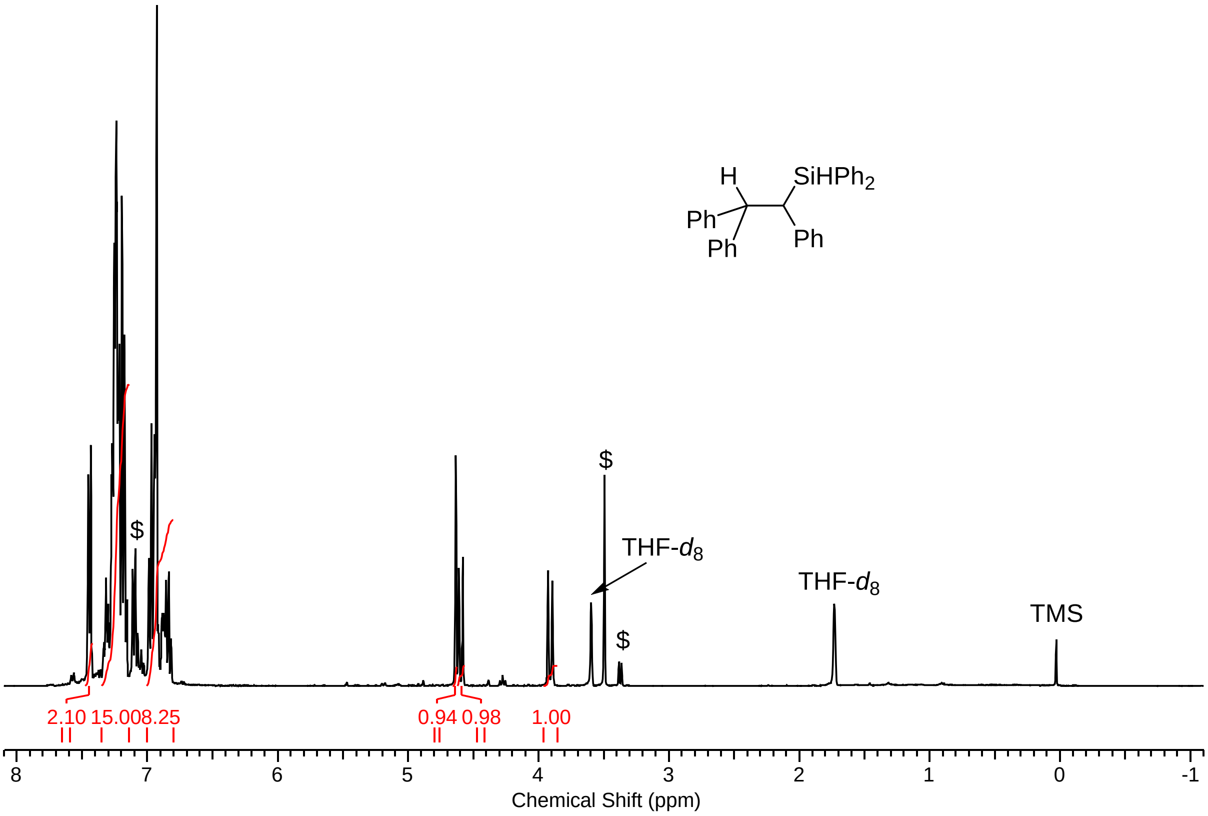

Figure S13. ^{1}H NMR spectrum of (1,2,2'-triphenylethyl)diphenylsilane in THF-d_8 at 25 °C. $ denotes an impurity.

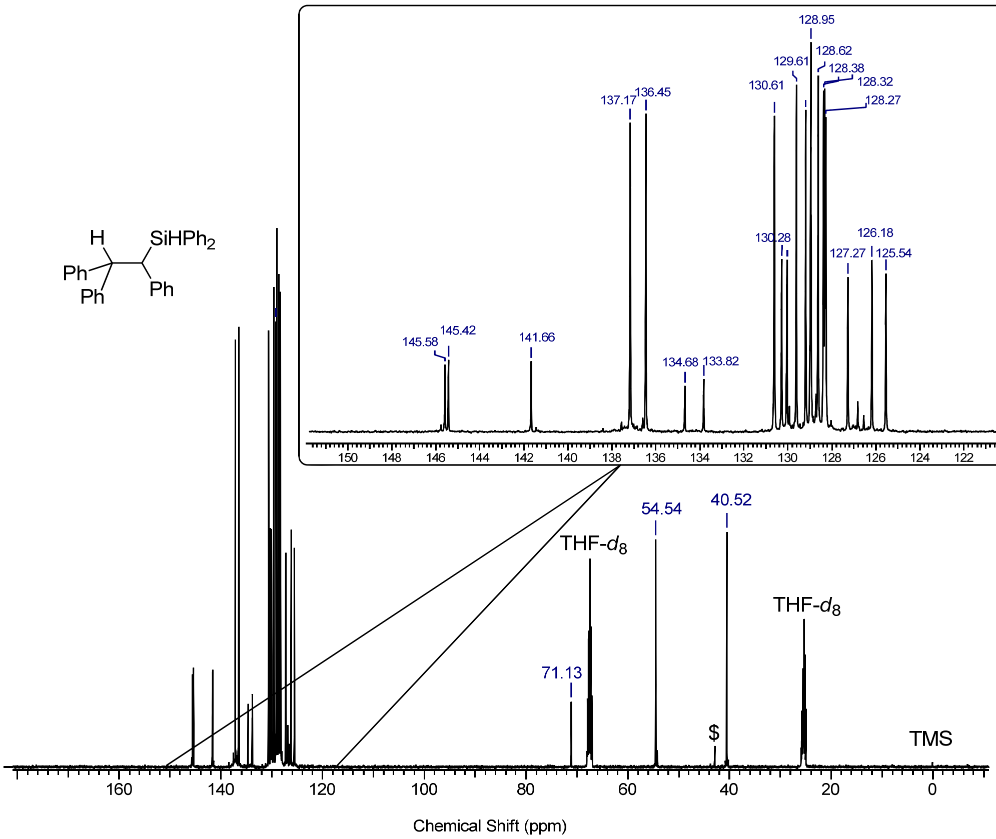

Figure S14. $^{13}C\{^1H\}$ NMR spectrum of (1,2,2'-triphenylethyl)diphenylsilane in THF-d_8 at 25 °C. $ denotes an impurity.

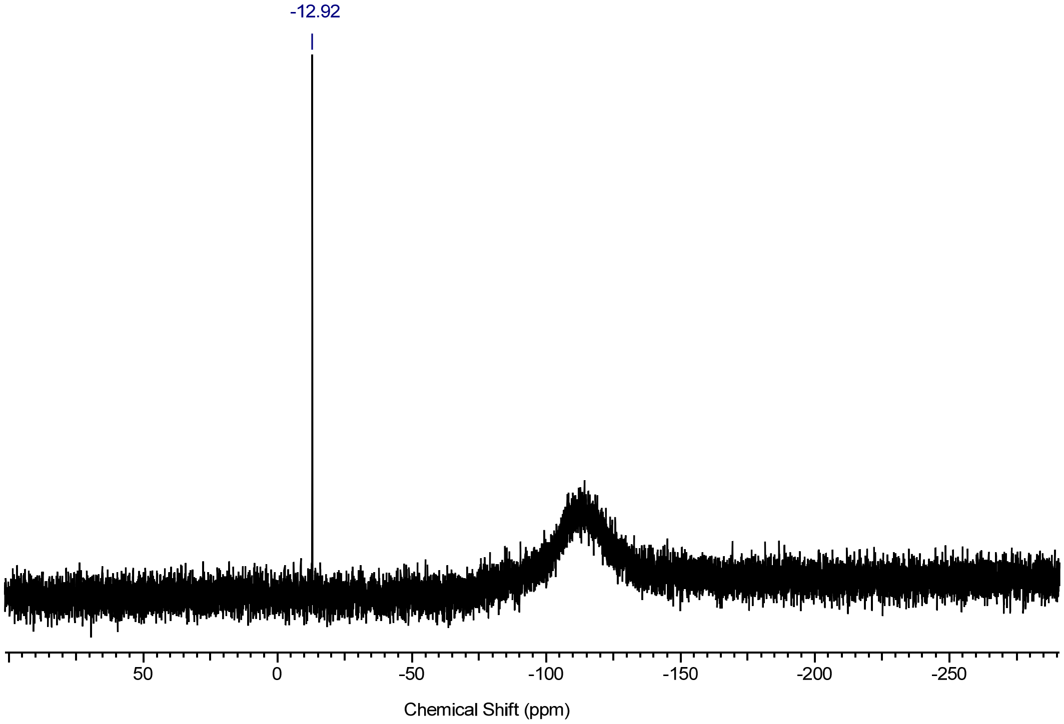

Figure S15. $^{29}Si\{^1H\}$ NMR spectrum of (1,2,2'-triphenylethyl)diphenylsilane in THF-d_8 at 25 °C.

Characterization of (1,2,2’-triphenylethyl)phenylsilane

The catalytic hydrosilylation reaction was performed as stated before. Triphenylethylene (25.6 mg, 0.10 mmol) and $PhSiH_3$ (12 mg,0 0.11 mmol) were used as starting materials and the product was isolated without further purification, and characterized by ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectroscopy, CI-MS and elemental analysis.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 3.68 (ddd, 1H, $^{3}J_{H,H}$ = 13.05 Hz, $^{3}J_{H,SiH}$ = 3.51 Hz, $^{3}J_{H,SiH}$ = 1.76 Hz, $Ph_2CHC\mathit{H}PhSiH_2Ph$), 4.08 (dd, 1H, $^{1}J_{Si,H}$ = 99.63 Hz, $^{2}J_{SiH,SiH}$ = 7.03 Hz, $^{3}J_{SiH,H}$ = 1.76 Hz, Si*H*), 4.19 (dd, 1H, $^{1}J_{Si,H}$ = 98.63 Hz, $^{2}J_{SiH,SiH}$ = 7.03 Hz, $^{3}J_{SiH,H}$ = 3.51 Hz, Si*H*), 4.60 (d, 1H, $^{3}J_{H,H}$ = 13.05 Hz, $Ph_2C\mathit{H}CHPhSiH_2Ph$), 6.85-6.95 (m, 2H, $Ph_{DPE/Si}$), 6.98-7.17 (m, 11H, $Ph_{DPE/Si}$), 7.22-7.31 (m, 5H, $Ph_{DPE/Si}$), 7.44-7.50 (m, 2H, $Ph_{DPE/Si}$) ppm.

$^{13}C\{^{1}H\}$ NMR (THF-d_8, 100.6 MHz): δ 38.87 ($Ph_2CH\mathit{C}HPhSiH_2Ph$), 54.20 ($Ph_2\mathit{C}HCHPhSiH_2Ph$), 125.69 ($Ph_{DPE/Si}$), 126.36 ($Ph_{DPE/Si}$),127.43 ($Ph_{DPE/Si}$), 128.25 ($Ph_{DPE/Si}$), 128.72 ($Ph_{DPE/Si}$), 128.87 ($Ph_{DPE/Si}$), 129.39 ($Ph_{DPE/Si}$), 129.70 ($Ph_{DPE/Si}$), 130.26 ($Ph_{DPE/Si}$), 132.05 (*ipso*-$Ph_{DPE/Si}$), 136.76 ($Ph_{DPE/Si}$), 137.55 ($Ph_{DPE/Si}$), 142.63 (*ipso*- $Ph_{DPE/Si}$), 145.28 (*ipso*-$Ph_{DPE/Si}$), 145.44 (*ipso*- $Ph_{DPE/Si}$) ppm.

$^{29}Si\{^{1}H\}$ NMR (THF-d_8, 79.5 MHz): δ –24.97 ($Ph_2CHCHPh\mathit{Si}H_2Ph$) ppm.

One expected resonance of (1,2,2’-triphenylethyl)phenylsilane could not be detected in the $^{13}C\{^{1}H\}$ NMR spectrum.

Anal. Calcd for $C_{26}H_{24}Si$ (364.56 g·mol^{-1}): C, 85.66; H, 6.64. Found: C, 84.54; H, 6.78%.
CI MS (100 eV) *m/z*: 364 (M^{+}, 40%), 363 (88), 287 (95), 257 (77), 181 (100), 167 (94).

^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra of (1,2,2'-triphenylethyl)phenylsilane

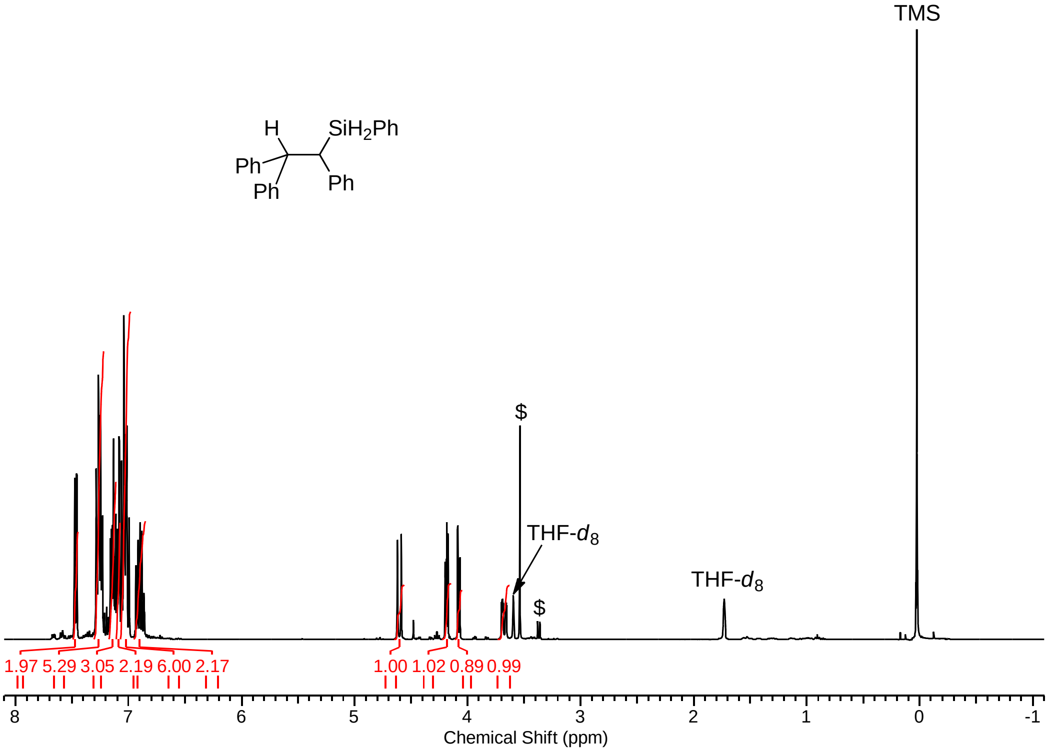

Figure S16. ^{1}H NMR spectrum of (1,2,2'-triphenylethyl)phenylsilane in THF-d_8 at 25 °C. $ denotes an impurity.

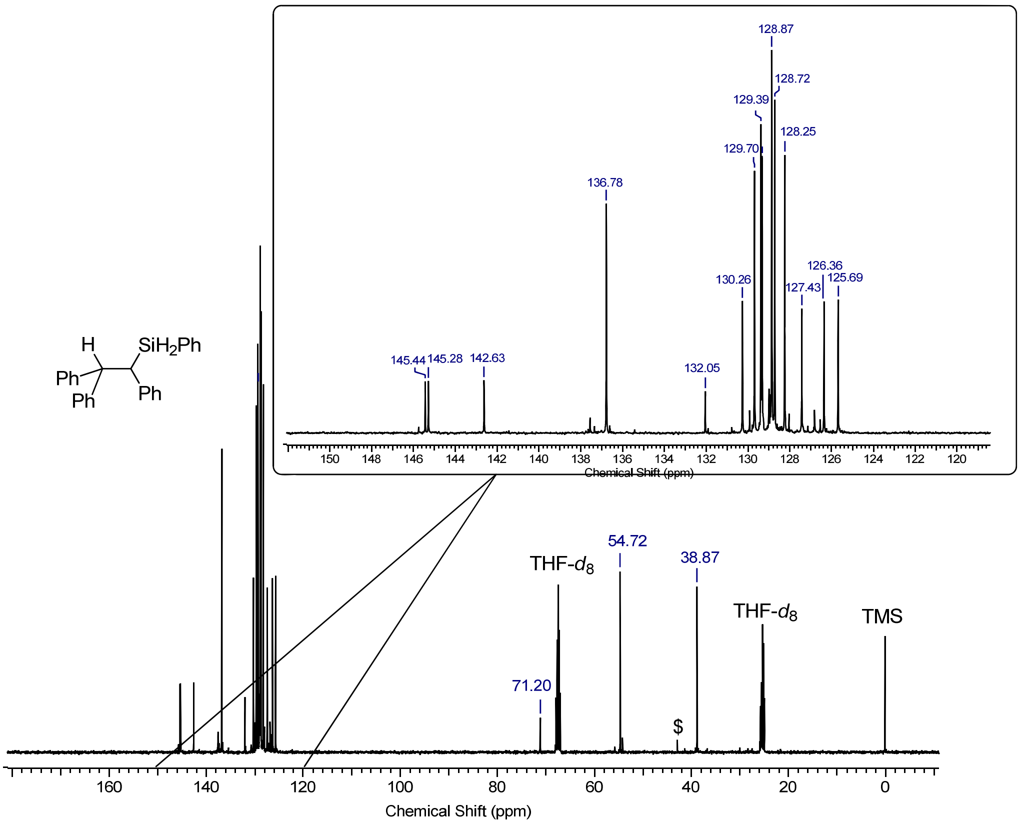

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of (1,2,2'-triphenylethyl)phenylsilane in THF-d_8 at 25 °C. $ denotes an impurity.

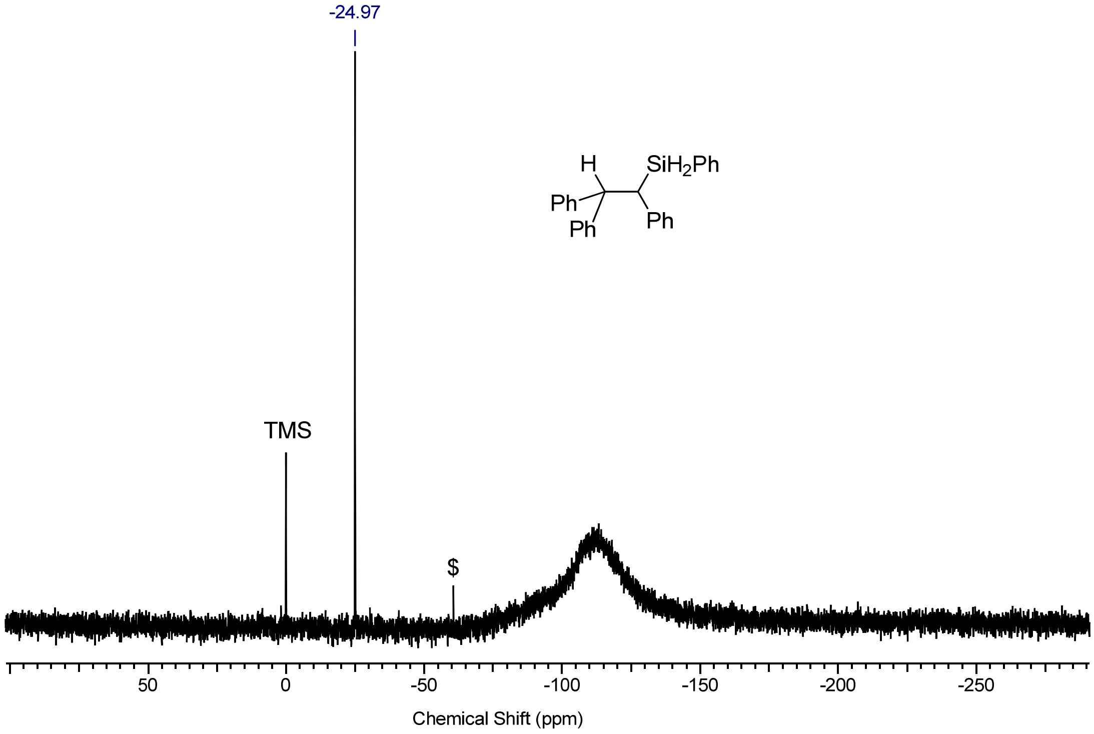

Figure S18. $^{29}Si\{^{1}H\}$ NMR spectrum of (1,2,2'-triphenylethyl)phenylsilane in THF-d_8 at 25 °C. $ denotes an impurity.

in situ ^{1}H NMR Spectra of stoichiometric reactions

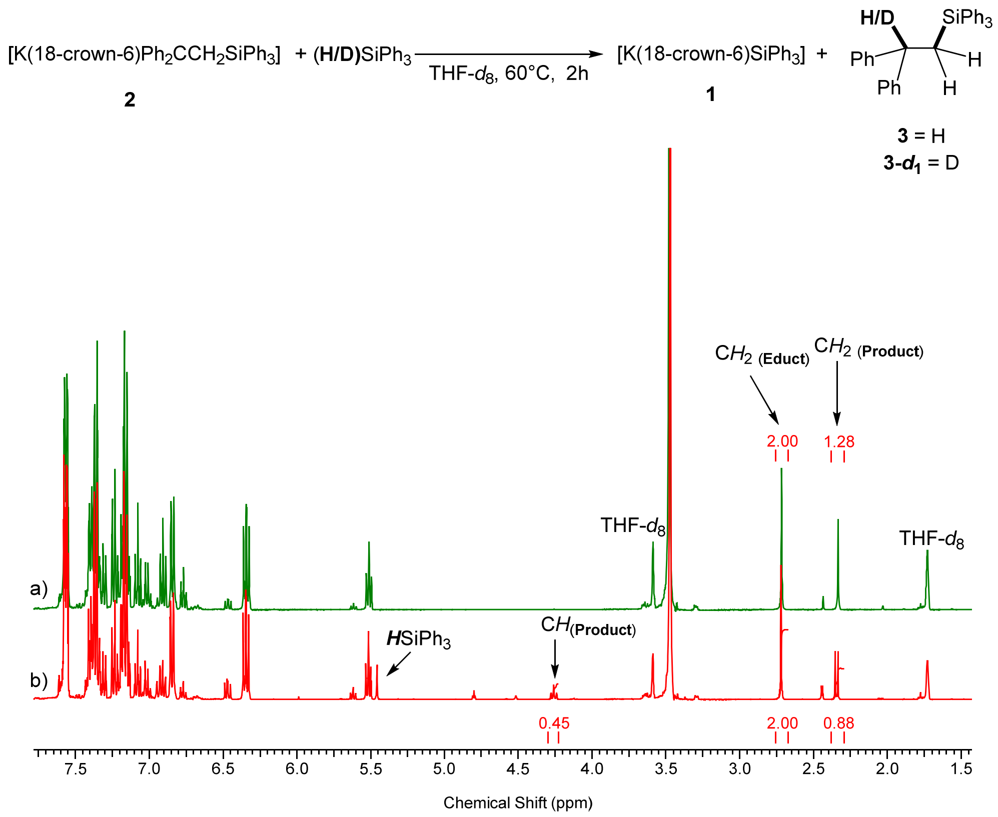

Figure S19. ^{1}H NMR Spectrum of the *in situ* reaction of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] with a) $DSiPh_3$ or b) $HSiPh_3$ in THF-d_8 at 25 °C.

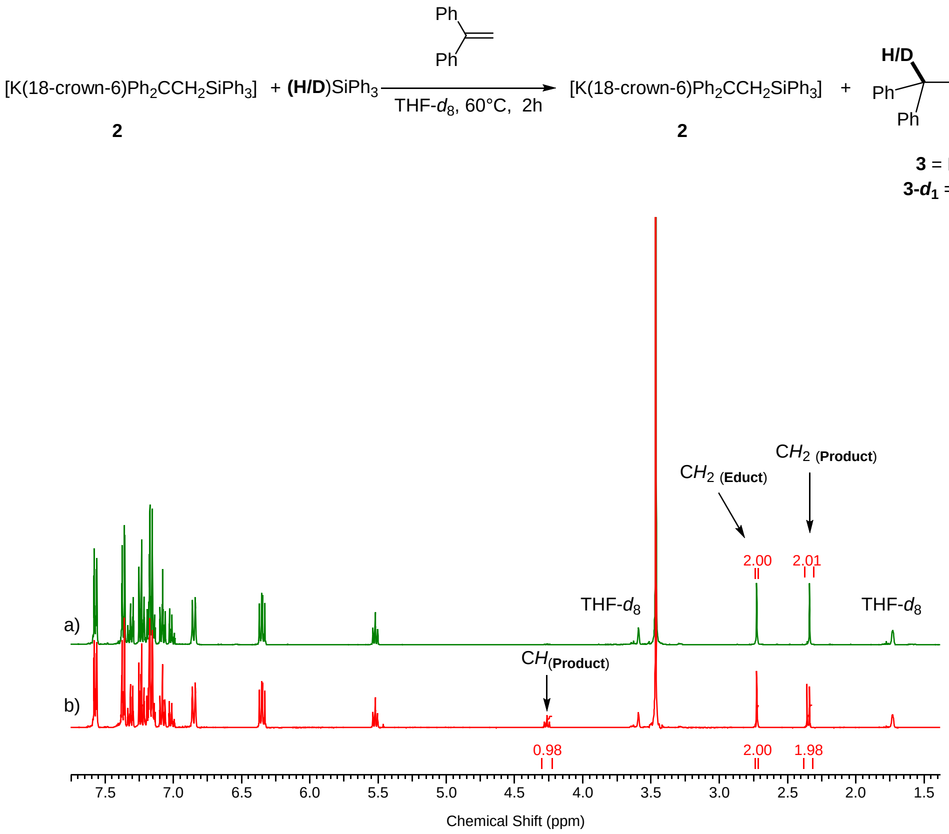

Figure S20. ^{1}H NMR Spectrum of the *in situ* reaction of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] with 1,1‘-DPE and a) $DSiPh_3$ or b) $HSiPh_3$ in THF-d_8 at 25 °C.

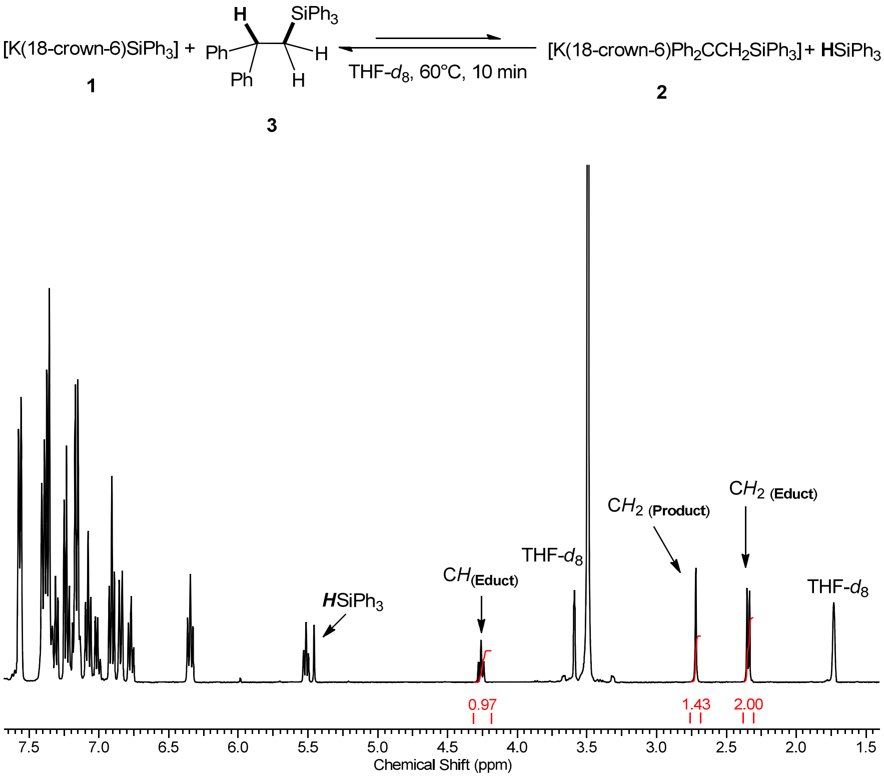

Figure S21. ^{1}H NMR Spectrum of the *in situ* reaction of [K(18-crown-6)$SiPh_3$] with (2,2’-diphenylethyl)triphenylsilane in THF-d_8 at 25 °C.

Crystallography

Crystal structure determination of [K(18-crown-6)$Ph_2CCH_2SiPh_3$] (2)

X-ray diffraction data of a single crystal of **2** (red block, 0.19 mm × 0.20 mm × 0.23 mm) were collected at –173 °C on a Bruker D8 goniometer with an APEX CCD area-detector in ω-scan mode. Mo-K_α radiation (multilayer optics, $\lambda = 0.71073$ Å) from an Incoatec microsource was used. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT;[S5] the absorption correction was applied with MULABS.[S6] The structure of $C_{44}H_{51}KO_6Si$ was solved in the monoclinic space group $P\ 2_1/c$ (no. 14) with $a = 9.3694(7)$ Å, $b = 24.0129(17)$ Å, $c = 19.4552(12)$ Å, $V = 3902.6(5)$ Å^3, $Z = 4$, $M = 743.04$ g.mol^{-1}, and $\mu = 0.215$ mm^{-1} by direct methods using SIR-92.[S7] The refinement was carried out with anisotropic displacement parameters for all non-hydrogen against F^2 with SHELXL-2013[S8] as implemented in the WinGX[S9] program system. Convergence was reached with $R1 = 0.0393$, $wR2 = 0.0775$ ($I > 2\sigma(I)$) and $R1 = 0.0592$, $wR2 = 0.0840$ (all data), $GoF = 0.907$. The program Diamond was used for the graphical representation.[S10] CCDC reference number 1454773, these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

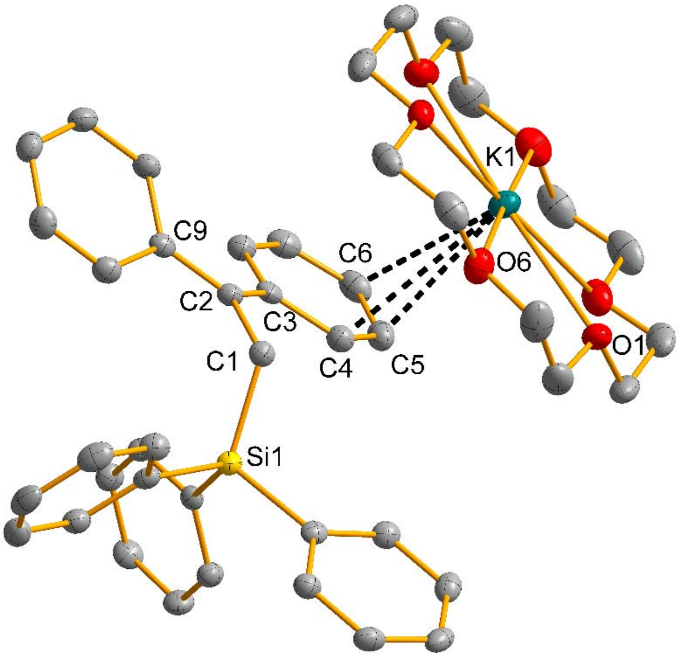

Figure S22. Molecular structure of **2** (cutout). Displacement ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

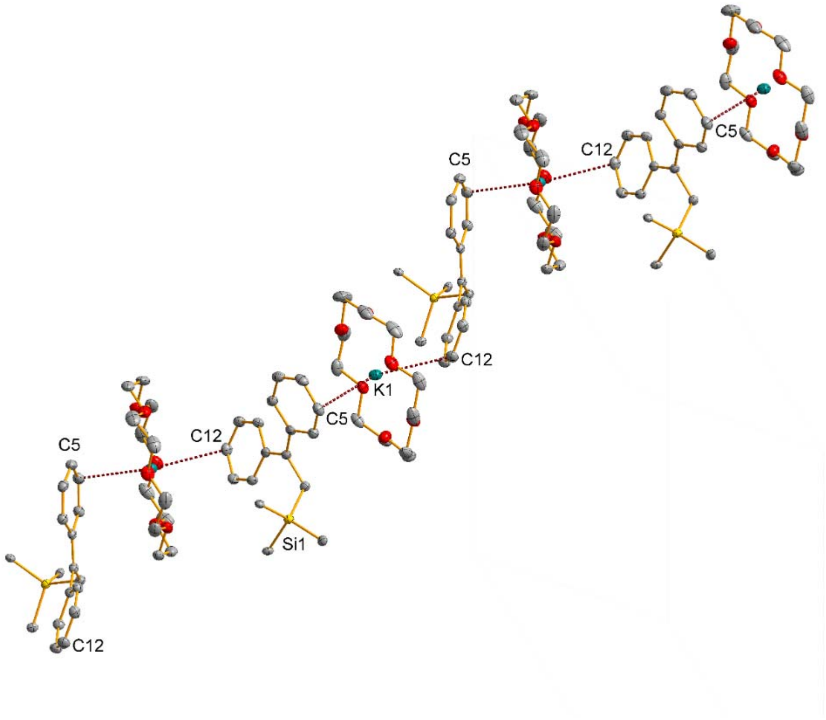

Figure S23. Molecular structure of **2** (extended structure). Displacement ellipsoids are shown at the 50% probability level; hydrogen atoms and phenyl rings at the Si1 atom are omitted for clarity.

Kinetic studies

A typical kinetic experiment was performed as follows. In a glovebox a solution of catalyst in THF-d_8 (0.1 mL) in a vial was treated with a solution of 1,1‘-DPE in THF-d_8 (0.2 mL). Immediately the reaction mixture turned deep red and a solution of HSiPh$_3$ in THF-d_8 (0.1 mL) was added. The reaction solution was then transferred to a J. Young type NMR tube, the vial was flushed twice with THF-d$_8$ (2 × 0.1 mL) and a solution of hexamethylbenzene (0.1 mL, 33.3 µmol) in THF-d_8 as internal standard was added to the NMR tube. The reaction mixture was heated at 60 °C for the indicated period of time and the NMR tube was cooled with an dry ice / ethnaol mixture subsequently. The conversions of the substrates were determined by ^{1}H NMR spectroscopy.

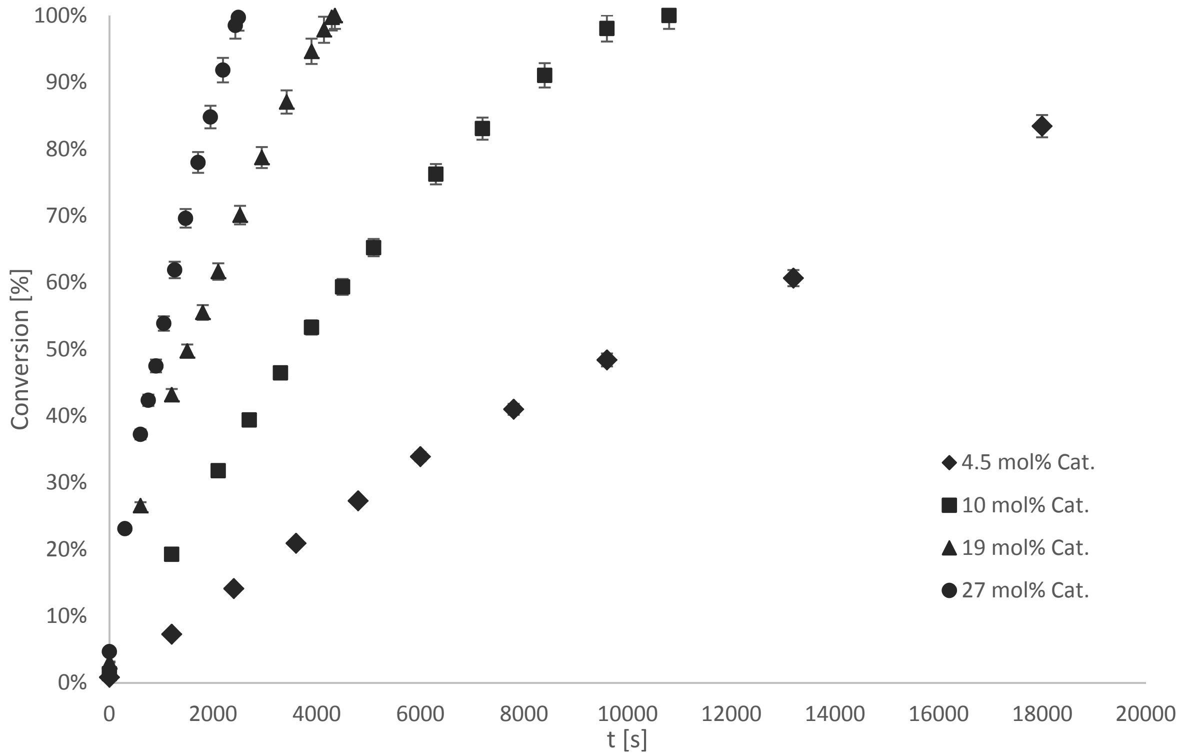

Figure S24. Time conversion plot (only formation of the hydrosilylation product) of the hydrosilylation of 1,1-DPE with $HSiPh_3$ with different catalyst concentrations.

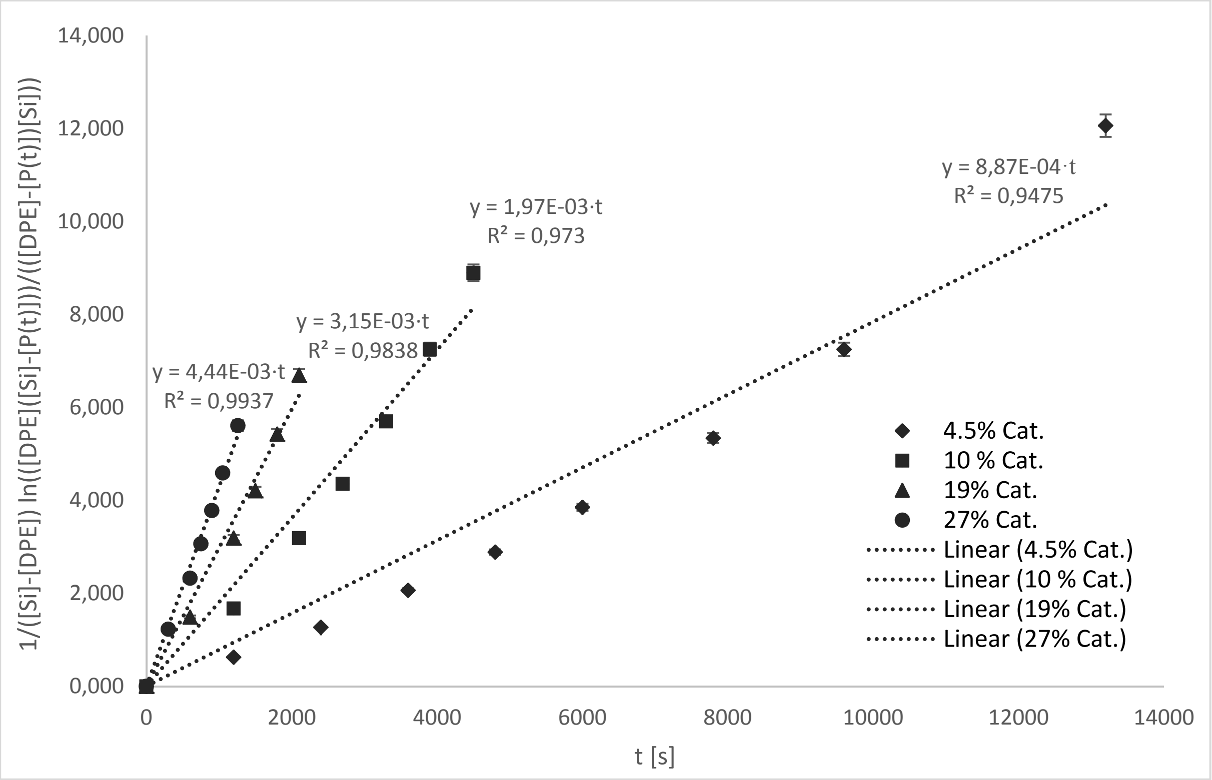

Figure S25. Semi-logarithmic plot of product formation (up to 60% conversion) with different catalyst concentrations.

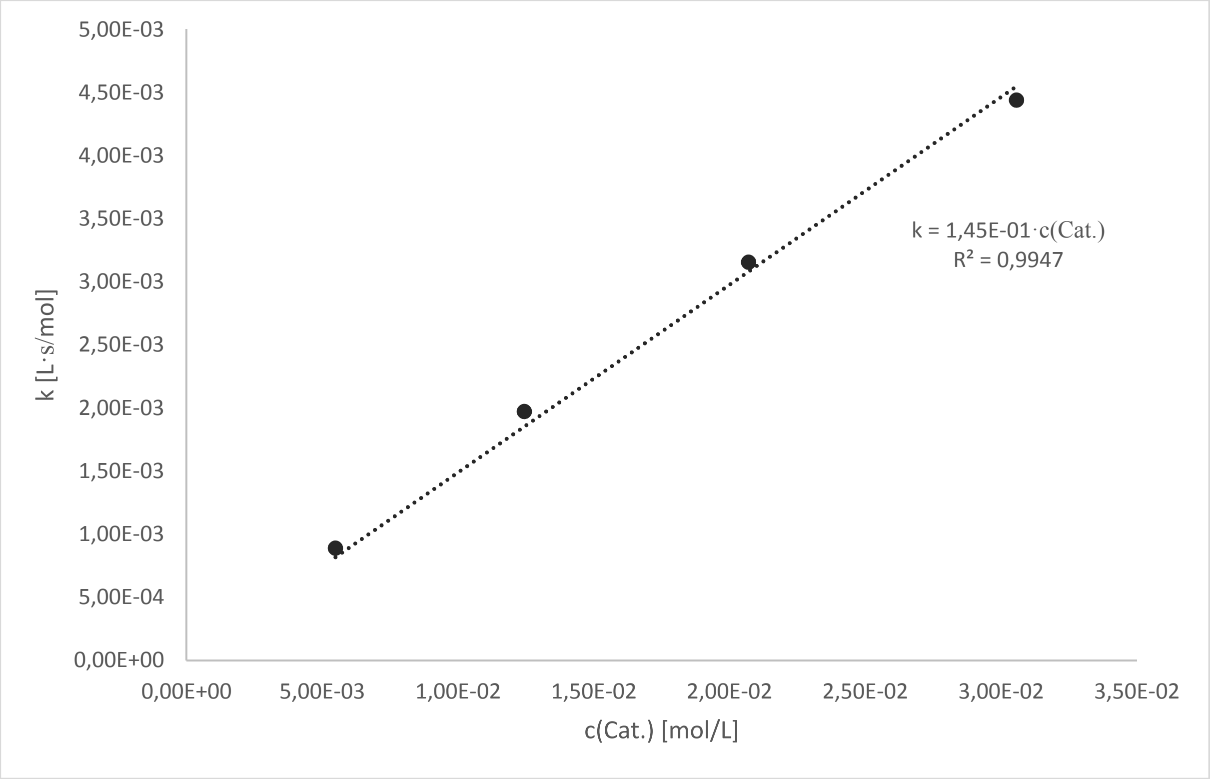

Figure S26. Rate constants *k* versus catalyst concentration.

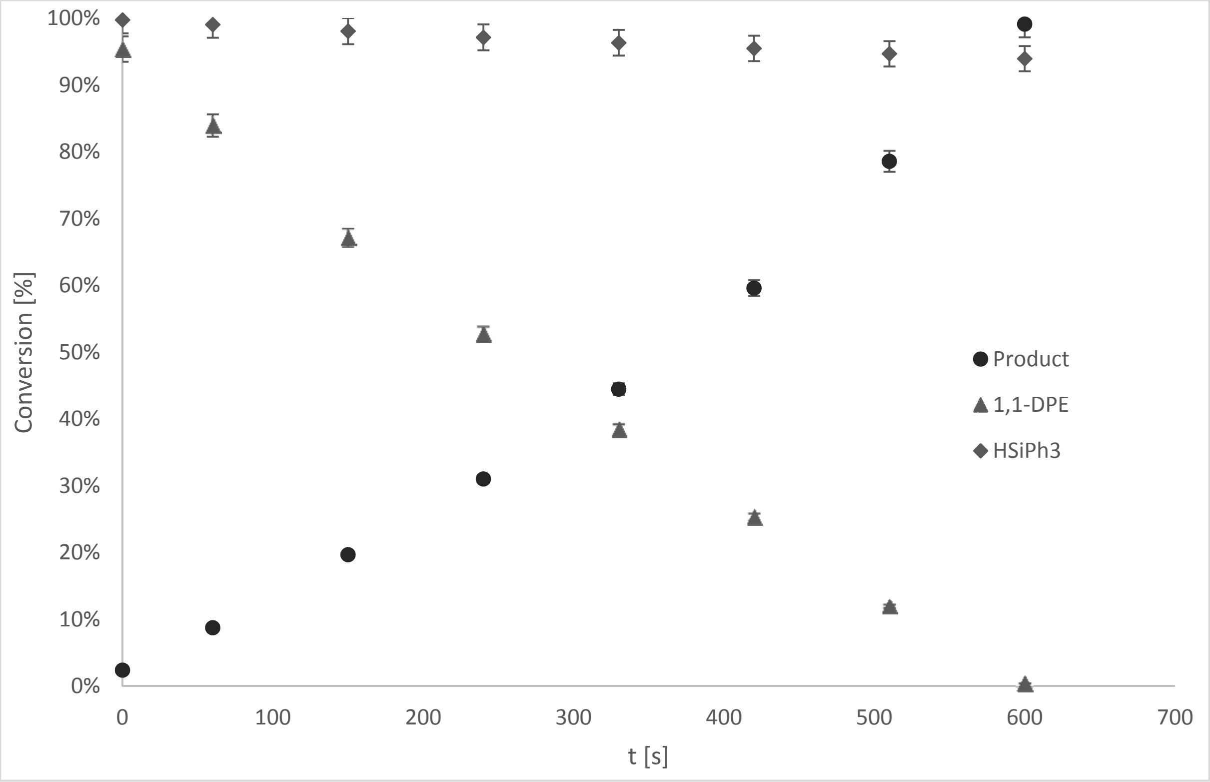

Figure S27. Time conversion plot of the hydrosilylation of 1,1-DPE with $HSiPh_3$ (excess).

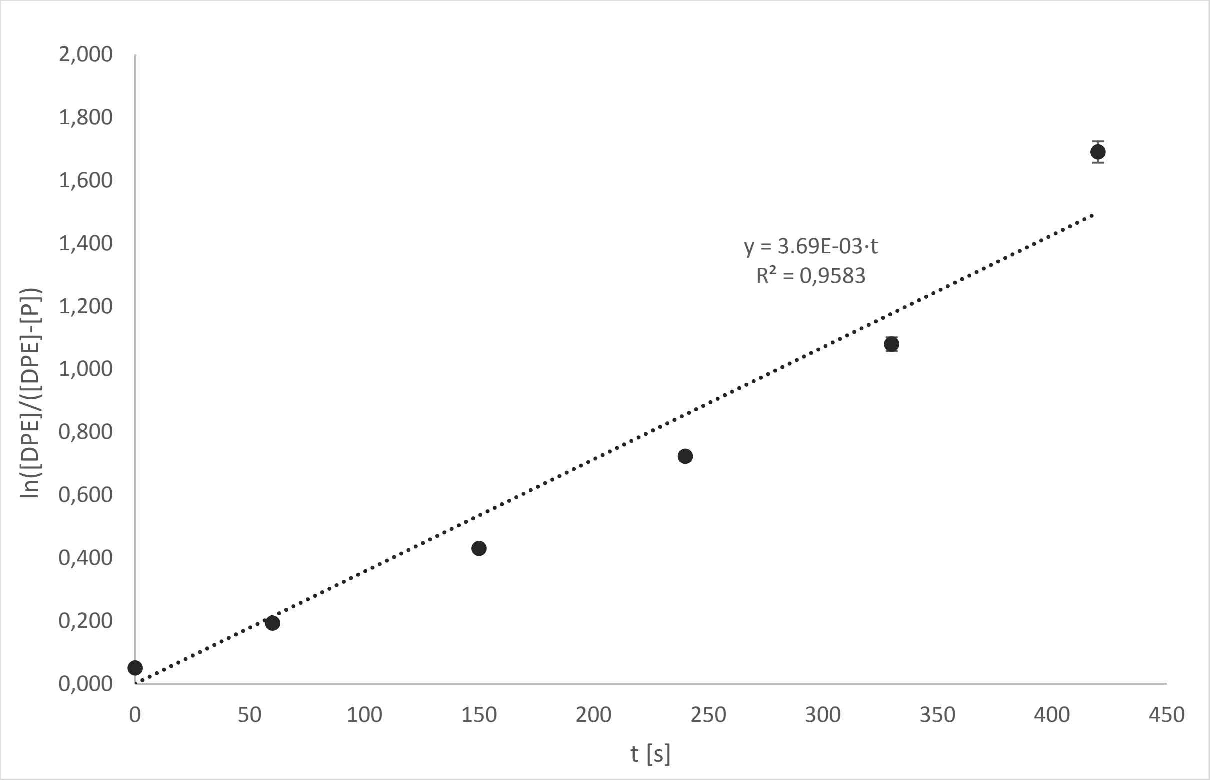

Figure S28. Logarithmic plot of product formation (up to 60% conversion) with excess of $HSiPh_3$.

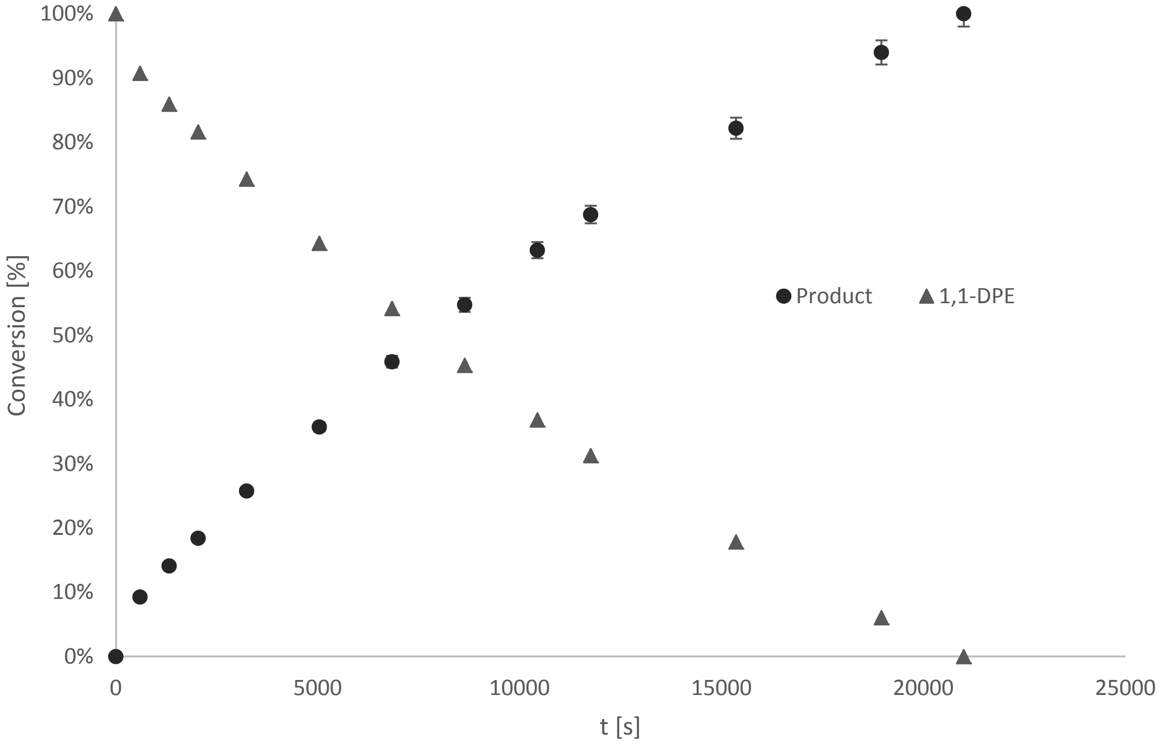

Figure S29. Time conversion plot of the hydrosilylation of 1,1-DPE with $DSiPh_3$.

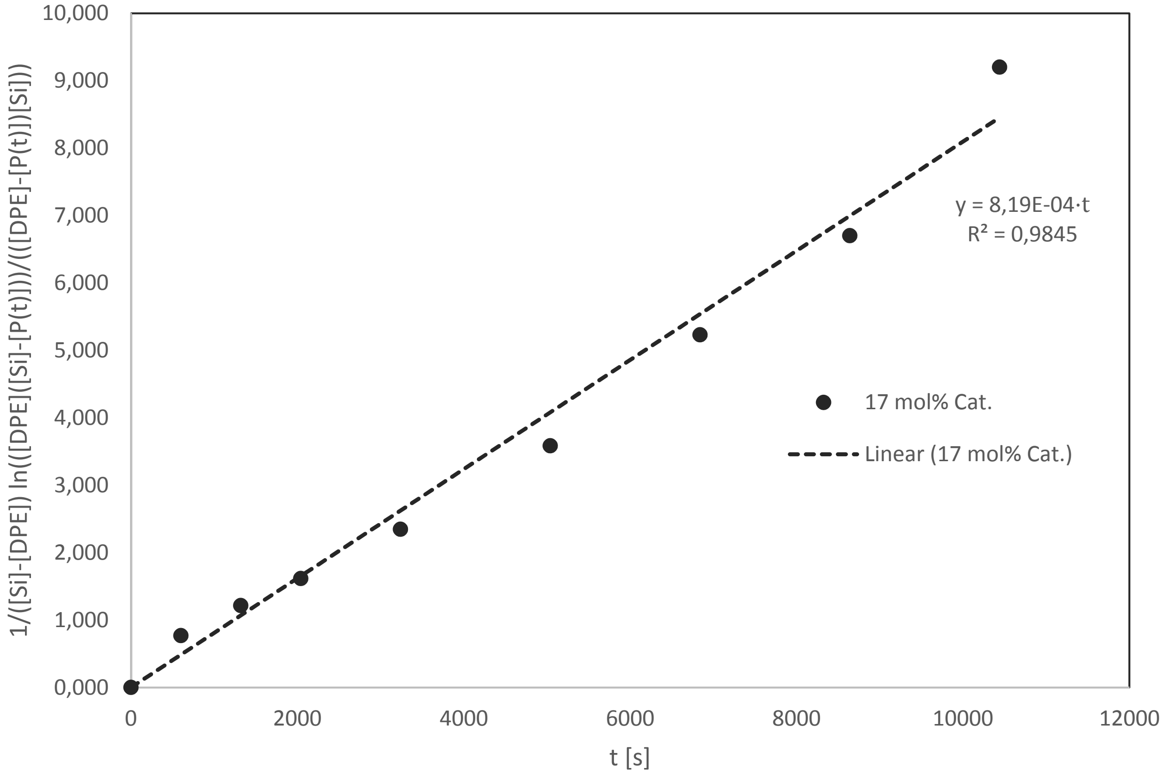

Figure S30. Logarithmic plot of product formation (up to 60% conversion) with $DSiPh_3$.

References

(S1) Leich, V.; Lamberts, K.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2014**, *43*, 14315-14321.
(S2) Smart, K. A.; Mothes-Martin, E.; Annaka, T.; Grellier, M.; Sabo-Etienne, S. *Adv. Synth. Catal.* **2014**, *356*, 759-764.
(S3) Wu, T. C.; Wittenberg, D.; Gilman, H. *J. Org. Chem.* **1960**, *25*, 596-598.
(S4) Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wang, Q. *Organometallics* **1991**, *10*, 3574-3581.
(S5) *Bruker, SAINT+ (Version 7.68)*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
(S6) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7-13.
(S7) Altomare, A. Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435-436.
(S8) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112-122.
(S9) Farrugia, L. J. *J. Appl. Crystallogr.* **2012**, 45, 849-854.
(S10) *Diamond 4.0.3*, Crystal Impact GbR: Bonn, Germany, **2015**.