Supporting Information

Cobalt(II) and (I) Complexes of Diphosphine-Ketone Ligands: Catalytic Activity in Hydrosilylation Reactions
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1. X-ray crystal structure determination

$\text{C}_4\text{H}_{36}\text{Cl}_2\text{CoOP}_2 \cdot \text{C}_4\text{H}_8 \text{O}$, Fw = 808.57, green needle, $0.60 \times 0.08 \times 0.08 \text{ mm}^3$, orthorhombic, Pbca (no. 61), $a = 18.5335(6)$, $b = 17.1819(4)$, $c = 25.6327(9) \text{ Å}$, $V = 8162.5(4) \text{ Å}^3$, $Z = 8$, $D_x = 1.316 \text{ g/cm}^3$, $\mu = 0.67 \text{ mm}^{-1}$. 90122 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $\sin(\theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1}$. The Eval15 software\cite{A1} was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS\cite{A2} (correction range 0.78-0.96). 9372 Reflections were unique ($R_{\text{int}} = 0.029$), of which 7569 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT\cite{A3}. Least-squares refinement was performed with SHELXL-2014\cite{A4} against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms of the metal complex were located in difference Fourier maps. Hydrogen atoms of the THF molecule were introduced in calculated positions. All hydrogen atoms were refined with a riding model. 473 Parameters were refined with no restraints. $R_1/wR_2$ [$I > 2\sigma(I)$]: 0.0313 / 0.0836. $R_1/wR_2$ [all refl.]: 0.0427 / 0.0906. $S = 1.012$. Residual electron density between -0.25 and 0.56 e/Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.\cite{A5}

CCDC 1871266 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Catalysis

All catalytic reactions were performed in duplo and given values are the average of the two runs, unless stated otherwise. Conversion and yield were determined by GC analysis, for which calibration curves were prepared for all substrates and products. The yields of product arising from 1-octene isomerization were determined using the calibration curve for 1-octene. Next to the characterized and quantified products, a number of small signals (GC area >1%) were generally obtained in GC analysis. These products could not be identified, and are therefore not described in the analysis.

**Hydrosilylation method 1** (Table 2): In a glovebox, catalyst (0.01 mmol) was added to a 6 mL vial. 1-Octene (0.160 mL, 1.0 mmol) was added. Addition of PhSiH$_3$ (0.135 mL, 1.1 mmol) while stirring caused bubbling of the mixture, and resulted in a clear brown solution after 1 minute. The solution was stirred for 1 h at room temperature and then taken out of the glovebox, where it was opened in air. The mixture was filtered over a plug of silica (~1 cm) using THF as eluent (total amount of mixture: 25 mL) to remove cobalt. From this a GC-MS sample was taken. For GC analysis, 1 mL of the prepared solution was added to 2.5 mL of a mesitylene (Mes) solution (internal standard, 0.017 M Mes solution: 102.4 mg Mes in 50 mL THF) and THF was added to a total volume of 10 mL.

**Hydrosilylation method 2** (Table 3, Entry 1-3): In a glovebox, 3$^p$Tol (7.0 mg, 0.01 mmol) was dissolved in THF (1 mL) resulting in a clear brown solution. A mixture of two substrates was added with a syringe while stirring. The solution was stirred for 4 h at room temperature and then taken out of the glovebox and opened in air. The mixture was filtered over a silica
plug (~1 cm) using THF as eluent (total amount of mixture: 25 mL) to remove cobalt. From this a GC-MS sample was taken. For GC analysis, 1 mL of the prepared solution was added to 2.5 mL of a mesitylene (Mes) solution (internal standard, 0.017 M Mes solution: 102.4 mg Mes in 50 mL THF) and THF was added to a total volume of 10 mL.

**Hydrosilylation method 3** (Table 3, Entry 4; chemoselectivity experiment): In a glovebox, 3^P,Tot (7.0 mg, 0.01 mmol) was added to a small vial and dissolved in THF (1 mL) resulting in a clear brown solution. A mixture of two substrates was added with a syringe while stirring. The solution was stirred for 4 h at room temperature and taken out of the glovebox and opened in air. The reaction mixture was transferred to a separation funnel using Et₂O and quenched with a HCl solution (2.5 mL, 10%) to form the alcohol product. The aqueous layer was removed, and the organic layer was washed with H₂O (0.2 mL). The aqueous layer was washed Et₂O (3 x 2 mL). The Et₂O fractions were filtered over a silica plug (~1 cm, total volume after Et₂O addition: 25 mL). For GC analysis, 1 mL of the prepared solution was added to 2.5 mL of a mesitylene (Mes) solution (internal standard, 0.017 M Mes solution: 102.4 mg Mes in 50 mL THF) and THF was added to a total volume of 10 mL. For NMR analysis, the solvent and precursors were evaporated in vacuum resulting in a turbid white liquid.

**Analysis of 1-octene hydrosilylation products**

Hydrosilylation of 1-octene with PhSiH₃ by 3^P,Tot. In all cases hydrosilylation method 1 was used. t = time at GC chromatogram, yield is determined by GC analysis. If amounts are not specified below, according amounts were used following method 1.

Isolation for calibration curve: In a nitrogen-filled glovebox, 3^P,Tot (21.0 mg, 0.03 mmol) was dissolved in THF (1 mL). 1-Octene (0.470 mL, 3.0 mmol) and PhSiH₃ (0.405 mL, 3.3 mmol) were subsequently added, and bubbling occurred upon addition of the latter. The clear brown solution was stirred for 4 h and taken out of the glovebox. Air was bubbled through the solution for 20 min to quench the catalyst, turning the solution green. Cobalt was removed by filtration over a silica plug (~1 cm) with petroleum ether. The product was isolated by column chromatography using petroleum ether as the eluent. Evaporation of the solvents in vacuum resulted in a turbid white liquid (319 mg, 1.45 mmol, 48%). ¹H NMR (CD₂Cl₂): δ 7.52-7.43 (m, 3H, Ar–H), 7.18-7.01 (m, 2H, Ar–H), 4.48 (t, ³JHH = 3.7 Hz, ²JHH = 190.99 Hz, 2H, Si–H₂), 1.47-1.37 (m, 2H, –CH₂), 1.33-1.13 (m, 10H, –CH₂), 0.94-0.87 (t, ³JHH = 6.9 Hz, 3H, –CH₃), 0.87-0.79 (m, 2H, –CH₂). ¹³C NMR (CD₂Cl₂): δ 135.6 (Ar–CH), 132.9 (Ar–CH), 129.9 (Ar–CH), 128.4 (Ar–CH), 33.3 (octyl), 32.3 (octyl), 29.6 (octyl), 25.5 (octyl), 23.1 (octyl), 14.4 (–CH₃), 10.4 (SiH₂–CH₂). INEPT ²⁹Si-NMR (CD₂Cl₂): δ ~31.0. GC-MS: Octylphenylsilane: t: 15.9, m/z: [M-C₆H₄]⁺, obs: 142.2, calc: 142.1. GC: Octylphenylsilane t: 3.6.

Catalysis: **Table 2, Entry 1**: used amount: 3^P,Tot: 7.0 mg, 0.01 mmol. GC: Octyl(phenyl)silane: t: 3.63, 186.1 mg, 0.84 mmol, 84%. PhSiH₃: t: 3.58, 2.9 mg, 0.03 mmol, 2%, conv: 98%. 1-Octene: t: 3.63, 2.2 mg, 0.02 mmol, 2%, conv: 98%. Octane: t: 3.75, 2.3 mg, 0.02 mmol, 2%. 3-Octene: t: 3.82, 3.4 mg, 0.03 mmol, 3%. 2-Octene: t: 3.91, 3.5 mg, 0.03 mmol, 3%. Ph₂SiH₃: t: 7.23, 8.5 mg, 0.05 mmol, 5%.

**Table 2, Entry 2**: used amounts: PhSiH₃: 113.7 mg, 1.05 mmol. 1-Octene: 113.5 mg, 1.01 mmol. Reaction time: 1h15 min. NMR: no product formation.

**Table 2, Entry 3**: used amounts: CoCl₂: 1.3 mg, 0.01 mmol. CoCl₂ dissolved poorly resulting in a slightly blue mixture. GC: PhSiH₃: t: 3.61, 104.3 mg, 0.96 mmol, 84%, conv: 16%. 1-Octene: t: 3.68, 108.0 mg, 0.96 mmol, 96%, conv: 4%.

**Table 2, Entry 4**: used amounts: CoCl₂: 1.3 mg, 0.01 mmol, PPh₃: 5.2 mg, 0.02 mmol. CoCl₂ dissolved poorly resulting in a slightly blue mixture. GC: PhSiH₃: t: 3.56, 6.1 mg, 0.06 mmol, 5%.
conv: 95%. 1-Octene: t: 3.64, 109.0 mg, 0.97 mmol, 97%. Octane: t: 3.75, 1.2 mg, 0.01 mmol, 1%. 3-Octene: t: 3.82, 2.7 mg, 0.02 mmol, 2%. 2-Octene: t: 3.91, 5.4 mg, 0.05 mmol, 5%.

**Table 2, Entry 5:** Used amount: 3\text{Tot} \text{mmol}. GC: Octyl(phenyl)silane: t: 7.62, 71.0 mg, 0.32 mmol, 32%. PhSiH₃: t: 3.66, 65.6 mg, 0.64 mmol, 40%, conv: 60%. 1-Octene: t: 3.66, 65.6 mg, 0.58 mmol, 58%, conv: 42%. Octane: t: 3.75, 1.7 mg, 0.01 mmol, 1%. 3-Octene: t: 3.82, 2.3 mg, 0.02 mmol, 2%. 2-Octene: t: 2.91, 2.3 mg, 0.02 mmol, 2%

**Table 2, Entry 6:** Used amount: 3\text{Ph} \text{mmol}. The catalyst dissolved poorly resulting in a brown turbid mixture. GC: Octyl(phenyl)silane: t: 7.62, 165.1 mg, 0.75 mmol, 75%. PhSiH₃: t: 3.58, 1.0 mg, 0.01 mmol, 1%, conv: 99%. 1-Octene: t: 3.63, 2.2 mg, 0.02 mmol, 2%, conv: 98%. Octane: t: 3.74, 2.1 mg, 0.02 mmol, 2%. 3-Octene: t: 3.82, 3.0 mg, 0.03 mmol, 3%. 2-Octene: t: 2.90, 2.8 mg, 0.02 mmol, 2%. Ph₂SiH₂: t: 7.22, 6.1 mg, 0.04 mmol, 3%

**Table 2, Entry 7:** Used amount: 3\text{Ph} \text{mmol}, 0.01 mmol. The catalyst was dissolved before addition of substrates resulting in a clear brown solution. GC: Octyl(phenyl)silane: t: 7.63, 189.3, 0.86 mmol, 86%; Octane: t: 3.77, 1.7 mg, 0.01 mmol, 1%. 3-Octene: t: 3.84, 3.3 mg, 0.03 mmol, 3%. 2-Octene: t: 3.93, 3.0 mg, 0.03 mmol, 3%. Ph₂SiH₂: t: 7.24, 6.6 mg, 0.04 mmol, 3%

**Analysis of styrene and allylbenzene hydrosilylation products**

*In all cases hydrosilylation method 2 was used. t = time at GC chromatogram, yield is determined by GC analysis. If amounts are not specified below, according amounts were used following method 2.*

**Table 3, Entry 1:**
Isolation for calibration curve: Amounts: 3\text{FTot} \text{mmol} (14.0 mg, 0.02 mmol), THF (1 mL), 1.9 mL of a PhSiH₃/allylbenzene mixture (0.961 mL, 7.8 mmol/0.939 mL, 7.1 mmol). Substrate addition caused bubbling and the mixture instantly turned to a clear brown solution. It was stirred further for 72 h. The product was isolated by column chromatography with petroleum ether as eluent. Evaporation of the solvents in vacuum resulted in a turbid white liquid (1.044 g, 4.61 mmol, 65%). ¹H NMR (C₆D₆): δ 3.88-6.98 (m, 12H, Ar–H), 4.46 (t, 2\text{JHH} = 3.7 Hz, 2\text{JHHS} = 191.6 Hz, 2\text{H}), 2.74 (t, 3\text{JHH} = 7.6 Hz, 2\text{JHHS} = 126.0 Hz, 2\text{H}), 1.65 (m, 2\text{JHS} = 127.4, 2\text{H}), 0.77 (m, 2\text{JHS} = 120.5, 2\text{H}). ¹³C NMR (C₆D₆): δ 141.84, 135.14, 132.19, 129.45, 128.41, 128.20, 127.93, 125.71, 38.84 (CH₂), 26.92 (CH₂), 9.56 (CH₂). INEPT ²⁹Si-NMR (C₆D₆): δ –31.10.

Catalysis: Amounts: 0.267 mL of a PhSiH₃/allylbenzene mixture (0.135 mL, 1.1 mmol/0.132 mL, 1.0 mmol). Upon addition, minor bubbling was observed and a color change form brown to yellow-brown was observed during reaction. GC-MS: phenyl(1-phenylethyl)silane: t: 17.99, m/z: [M-C₆H₅]⁺ 143.1, calcld. 148.1. PhSiH₃: t: 3.48, m/z: [M]⁺ 108.0, calcld. 108.0. Styrene: t: 8.01, m/z: [M]⁺ 118.1, calcld. 118.1. Ph₂SiH₂: t: 14.08, m/z: [M]⁺ 184.1, calcld. 184.1. GC: phenyl(1-phenylethyl)silane: t: 8.18, 190.5 mg, 0.84 mmol, 84%. PhSiH₃: t: 3.60, 3.4 mg, 0.03 mmol, 3%, conv: 97%. Allylbenzene: t: 5.57, 4.8 mg, 0.04 mmol, 4%, conv: 96%. Ph₂SiH₂: t: 7.24, 7.5 mg, 0.04 mmol, 4%.

**Table 3, Entry 2:** 0.250 mL of a PhSiH₃/styrene mixture (0.135 mL, 1.1 mmol/0.115 mL, 1.0 mmol) was used. Upon addition, minor bubbling was observed and a color change from brown to yellow-brown was observed during reaction. Markovnikov product: ¹H NMR (C₆D₆): δ 3.75-6.98 (m, 12H, Ar–H), 4.45 (t, 2\text{JHH} = 3.6 Hz, 2\text{JHHS} = 193.1 Hz, 2\text{H}, 1\text{a}), 2.41 (m, 1H, 2\text{a}), 1.33 (d, 3\text{JHH} = 7.5, 2\text{JHHS} = 127.6, 3\text{H}, 3\text{a}). ¹³C NMR (C₆D₆): δ 144.36-109.98 (Ar–C), 25.26 (CH₃, 1\text{a}). INEPT ²⁹Si-NMR (C₆D₆): δ –21.27 (1\text{a}). GC-MS: t: 15.80, m/z: [M]⁺ 212.0, calcld. 212.1. anti-Markovnikov product: ¹H NMR (C₆D₆): δ 7.52-6.98 (m, 12H, Ar–H), 4.48 (m, 2\text{JHH} = 3.5 Hz, 2\text{JHHS} = 195.8 Hz, 2\text{H}, 1\text{b}), 2.62 (m, 3\text{JHH} = 8.4 Hz, 2\text{H}, 2\text{b}), 1.10 (m, 2\text{H}, 3\text{b}). ¹³C NMR (C₆D₆): δ
144.36-09.98 (Ar–C), 30.98 (CH₂, 2b), 11.94 (CH₂, 3b). INEPT²⁹Si-NMR (CD₂Cl₂): δ –31.40 (1b). GC-
MS: t: 16.80, m/z: [M-C₅H₅]⁺ obs. 134.1, calcd. 134.1. GC: Markovnikov product: t: 7.69, 6.1 mg,
0.03 mmol, 3%. Anti-Markovnikov product: t: 7.93, 8.4 mg, 0.04 mmol, 4%. PhSiH₃: t: 3.61, 89.8
mg, 0.83 mmol, 69%, conv: 31%. Styrene: t: 4.65, 86.7 mg, 0.83 mmol, 83%, conv: 17%. Ph₂SiH₂: t:
7.24, 10.1 mg, 0.05 mmol, 5%.

**Table 3, Entry 3:** 0.250 mL of a PhSiH₃/styrene mixture (0.135 mL, 1.1 mmol/0.115 mL, 1.0 mmol)
and a reaction time of 24h were used. Upon addition, minor bubbling was observed. A color change
from brown to yellow-brown was observed during reaction. GC: Markovnikov product: t: 7.69, 6.2
mg, 0.03 mmol, 3%. Anti-Markovnikov product: t: 7.92, 9.3 mg, 0.04 mmol, 4%. PhSiH₃: t: 3.60,
79.2 mg, 0.73 mmol, 61%, conv: 39%. Styrene: t: 4.64, 83.5 mg, 0.80 mmol, 80%, conv: 20%. Ph₂SiH₂: t:
7.23, 13.2 mg, 0.07 mmol, 7%.

**Analysis of acetophenone and 5-hexen-2-one hydrosilylation products**

Hydrosilylation of acetophenone with PhSiH₃ catalyzed by 2²Total. *Hydrosilylation method 3 was used. t =
* = time at GC chromatogram, yield is determined by GC analysis.*

**Table 3, Entry 4:**
Isolation for calibration curve: The product of the reaction, 1-phenylethanol, was purchased from
commercial sources and was used for the calibration curve and as reference for the GC response time.
Catalysis: Amounts: 0.252 mL of a PhSiH₃/acetophenone mixture (0.135 mL, 1.1 mmol/0.117 mL,
1.0 mmol). GC-MS: 1-Phenylethanol: t: 8.76, m/z: [M]+ obs. 122.1, calcd. 122.1. GC: 1-
phenylethanol: t: 5.74, 126.5 mg, 1.04 mmol, >99%. PhSiH₃: t: 3.59, 10.4 mg, 0.10 mmol, 8%, conv:
92%. Ph₂SiH₂: t: 7.23, 8.5 mg, 0.05 mmol, 4%.

Chemo-selectivity experiments: hydrosilylation of 5-hexen-2-one with PhSiH₃ catalyzed by 2²Total.
*Hydrosilylation method 3 was used. t = time at GC chromatogram, product assignment is based in
GC-MS analysis, conversions determined by GC analysis. Calibration curves for these products are
lacking due to problems in the isolation of single components, therefore yields are not specified.*

5-hexen-2-one, 2.1 eq. PhSiH₃, 4h: Amounts: 0.375 mL of a PhSiH₃/5-hexen-2-one mixture (0.259
mL, 2.1 mmol/0.116 mL, 1.0 mmol). GC-MS: prod A: t: 3.59, m/z: [M-H₂O]⁺: obs. 82.0, calcd. 82.1.
prod B: t: 15.82, m/z: [M-H]⁺ obs. 205.2, calcd. 205.1. prod C: t: 15.95, m/z: [M-2H]⁺ obs. 206.1,
calcd. 206.1. GC: prod A: t: 3.79; prod B: t: 24.41; prod C: t: 24.55. 5-Hexen-2-one: t: 3.61. PhSiH₃: t:
3.61, 69.2 mg, 0.64 mmol, 28%, conv: 72%.

5-hexen-2-one, 2.1 eq. PhSiH₃, 24h: Amounts: 0.375 mL of a PhSiH₃/5-hexen-2-one mixture (0.259
mL, 2.1 mmol/0.116 mL, 1.0 mmol). Reaction time of 24h. GC-MS: prod C: t: 15.95, m/z: [M-2H]⁺
obs. 206.1, calcd. 206.1. GC: prod C: t: 24.55. PhSiH₃: t: 3.74, 13.6 mg, 0.13 mmol, 5%, conv: 95%.

5-hexen-2-one, 1 eq. PhSiH₄, 4h: Amounts: 0.239 mL of a PhSiH₄/5-hexen-2-one mixture (0.123
mL, 1.0 mmol/0.116 mL, 1.0 mmol). GC-MS: prod A: t: 3.59, m/z: [M-H₂O]⁺ obs. 82.0, calcd. 82.1.
prod B: t: 15.82, [M-H]⁺ obs. 205.2, calcd. 205.1. prod C: t: 15.95, m/z: [M-2H]⁺ obs. 206.1, calcd.
206.1. GC: prod A: t: 3.79, prod B: t: 24.41, prod C: t: 24.55. 5-hexen-2-one: t: 3.60. PhSiH₄: t: 3.74,
7.1 mg, 0.07 mmol, 5%, conv: 95%.

**Additional catalytic tests**

3²Total + 1-octene, 1-octene isomerization: Hydrosilylation method 2 used, only 1-octene added
(112.22 mg, 1.0 mmol). Stirred for 1 h. GC: no conversion of 1-octene
3^Tol + PhSiH₃, silane scrambling, 1 h: Hydrosilylation method 2 used, only PhSiH₃ added (0.119 mg, 1.1 mmol). Stirred for 1 h. GC: PhSiH₃: t: 3.60, 66.5 mg, 0.61 mmol, 51%, conv: 49%. Ph₂SiH₂: t: 7.23, 8.7 mg, 0.05 mmol, 4%.

3^Tol + PhSiH₃, silane scrambling, 4 h: Hydrosilylation method 2 used, only PhSiH₃ added (0.119 mg, 1.1 mmol). Stirred for 4 h. GC: PhSiH₃: t: 3.59, 62.4 mg, 0.58 mmol, 48%, conv: 52%. Ph₂SiH₂: t: 7.22, 8.9 mg, 0.05 mmol, 4%.

3^Tol + PhSiH₃, silane scrambling, 4 days: Hydrosilylation method 2 used, only PhSiH₃ added (0.119 mg, 1.1 mmol). Stirred for 4 days. GC: PhSiH₃: t: 3.62, 49.8 mg, 0.46 mmol, 38%, conv: 62%. Ph₂SiH₂: t: 7.24, 14.6 mg, 0.08 mmol, 7%.

2.1 Calibration curves

Two representative examples of the calibration curves are given below. Others were prepared similarly. General procedure: 1-octene or PhSiH₃ (representative amounts for catalytic runs: amounts between 0-100 %) and 2.5 mL of a Mes solution in THF (102.4 mg Mes in 50 mL, 0.017 M) were added in a volumetric flask. THF was added to a total volume of 25 mL. 1 mL of each sample was diluted another 10 times with THF before GC analysis.

![Figure S1. Calibration curve of 1-octene.](image1)

![Figure S2. Calibration curve of PhSiH₃.](image2)
3. NMR spectra

**Figure S3.** $^1$H NMR spectrum of $^{p\text{Tol}}$dpbp (C$_6$D$_6$).

**Figure S4.** $^{13}$C NMR spectrum of $^{p\text{Tol}}$dpbp (C$_6$D$_6$).
Figure S5. $^{31}$P NMR spectrum of $^{\rho}$Toldpbp ($C_6D_6$).

Figure S6. $^1$H NMR spectrum of ($^{\rho}$Toldpbp)CoCl$_2$ (CH$_2$Cl$_2$).
Figure S7. $^{1}$H NMR spectrum of $(p^{\text{Tol}} \text{dpb})\text{CoCl} (\text{CsD}_{6})$.

Figure S8. APT $^{13}$C NMR spectrum after hydrosilylation of 1-octene with PhSiH$_{3}$ by 3$p^{\text{Tol}}$ forming octylphenylsilane, containing one signal (*) with the opposite phasing in the aliphatic region.
Figure S9. APT $^{13}$C NMR spectrum (C$_6$D$_6$) of the hydrosilylation product of allylbenzene (positive phase: CH, CH$_3$; negative phase: Cq, CH$_2$).

Figure S10. 2D $^1$H-$^1$H COSY NMR spectrum of the styrene hydrosilylation reaction.
Figure S11. APT $^{13}$C NMR (C$_6$D$_6$) spectrum of styrene hydrosilylation (pos. phase: CH, CH$_3$; neg. phase: Cq, CH$_2$).

Figure S12. Product mixture of styrene hydrosilylation with PhSiH$_3$. Simulated spectrum of the anti-Markovnikov product by Mestrenova (top) and measured $^1$H NMR spectrum (in C$_6$D$_6$, bottom).
Figure S13. Product mixture of styrene hydrosilylation with PhSiH₃. Simulated spectrum of the Markovnikov product by Mestrenova (top) and measured ¹H NMR spectrum (in C₆D₆, bottom).

Figure S14. ¹H NMR spectrum (C₆D₆) of the reaction mixture of 3PyTol + PhSiH₃, silane activation.
Figure S15. $^{31}$P NMR spectrum (CdD$_6$) of the reaction mixture of $3^{\text{Ptd}} +$ PhSiH$_3$, silane activation.
4. References

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