Supporting Information

Regioselective Hydrosilylation of Epoxides catalyzed by Nickel(II)Hydrido Complexes

Jan Wenz, Hubert Wadepohl and Lutz H. Gade*

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I. General Information

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were predried over activated 4 Å molecular sieves and were refluxed over magnesium (methanol), sodium (toluene), potassium (hexane), sodium-potassium alloy (tetrahydrofurane, diethyl ether) or calcium hydride (dichloromethane) under an argon atmosphere and collected by distillation. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 600, Bruker Avance II 400 and Bruker DRX 200 spectrometer. $^1$H and $^{13}$C NMR spectra were referenced internally to residual protio-solvent ($^1$H) or solvent ($^{13}$C) resonances and are reported relative to tetramethylsilane. $^{19}$F NMR was measured at 376 MHz, and 1,4-bis(trifluoromethyl)benzene (−63.4 ppm) was used as an internal standard. All NMR spectra were recorded at room temperature (295 K). Mass spectra were recorded by the mass spectrometry service at the Organic Chemistry Laboratory of the University Heidelberg and the elemental analyses were measured by the analytical services of the University of Heidelberg Complexes [(S)iPr(PdmBox)NiCl], [(R)Ph(PdmBox)NiCl], [(S)iPr(PdmBox)NiH] 2a were synthesized according to the literature procedures. PhSiD$_3$ was prepared according to literature procedure. All other reagents were commercially available and used as received. Liquids were degassed by three freeze-pump-thaw cycles before use.
II. a) Preparation of precatalysts
1) [(S)\text{Pr}(PdmBox)NiF] (1a)

To a solution of complex [(S)\text{Pr}(PdmBox)NiCl] (1 g, 2.15 mmol) in 50 ml acetone an excess of CsF (1 g, 6.3 mmol) was added and stirred for 24 h. After removal of the solvents, the residue was treated with a toluene/pentane (1/10) mixture and filtrated. The solvents were removed in vacuo. The residue was treated with a toluene/pentane (1:3) mixture and the inorganic metal salts were filtered off. After the removal of the solvents, the product was recrystallized from a toluene/pentane mixture at room temperature to give the product in 90% yield.

\[
\begin{align*}
\text{N_2} & \quad \text{O} \\
\text{N} & \quad \text{7} \\
\text{O} & \quad \text{8} \\
\text{Ni} & \quad \text{F} \\
\text{H} & \quad \text{1} \quad \text{2} \quad \text{3} \\
\text{H} & \quad \text{7} \quad \text{8} \quad \text{9} \\
\text{H} & \quad \text{4} \quad \text{4'} \\
\text{H} & \quad \text{9} \quad \text{9'} \\
\end{align*}
\]

\(^1\text{H} \text{NMR (C}_6\text{D}_6, 600 \text{ MHz, 295 K}): \delta \text{ (ppm) } = 6.08 \text{ (s, 2 H, H}^1\text{)}, 3.90-3.84 \text{ (m, 2 H, H}^7\text{)}, 3.61-3.54 \text{ (m, 4 H, H}^6\text{)}, 2.66-2.52 \text{ (m, 2 H, H}^8\text{)}, 2.46 \text{ (s, 6 H, H}^4\text{)}, 1.53 \text{ (s, 6 H, H}^9\text{)}, 0.93 \text{ (d, } \frac{3}{2}J_{\text{H,H}} = 6.8 \text{ Hz, 6 H, H}^9\text{)}, 0.90 \text{ (d, } \frac{3}{2}J_{\text{H,H}} = 7.0 \text{ Hz, 6 H, H}^9\text{)}.

\(^{13}\text{C} \text{NMR (C}_6\text{D}_6, 150 \text{ MHz, 295 K}): \delta \text{ (ppm) } = 176.71 \text{ (C}^5\text{)}, 137.9 \text{ (C}^2\text{)}, 103.8 \text{ (C}^1\text{)}, 70.2 \text{ (C}^6\text{)}, 65.1 \text{ (C}^7\text{)}, 38.6 \text{ (C}^3\text{)}, 35.2 \text{ (C}^4\text{)}, 31.3 \text{ (C}^9\text{)}, 22.7 \text{ (C}^8\text{)}, 18.5 \text{ (C}^9\text{)}, 16.1 \text{ (C}^9\text{)}.

\(^{19}\text{F} \text{NMR (C}_6\text{D}_6, 376 \text{ MHz, 295 K}): \delta \text{ (ppm)} = -448.6 \text{ (s)}.

\text{HR-FAB}^+: \text{Anal. Calcd for C}_{22}\text{H}_{34}\text{N}_3\text{NiO}_2\text{F: m/z 430.2003 (M}^+\text{-F).}

Elemental Anal. Calcd for C_{22}H_{34}N_3O_2NiF. C 58.69, H 7.61, N 9.33. Found C 58.77, H 7.44, N 9.36.
2) [(R)Pd(PdmBox)NiF] (1b)

According to procedure mentioned above. Yield 76% after crystallization from toluene pentane mixture.

\[
\begin{align*}
\text{H NMR (}^6\text{D}_6, 600 \text{ MHz, 295 K):} & \quad \delta (\text{ppm}) = 7.30 (\text{d}, J_{HH} = 7.4 \text{ Hz, 2 H, H}^{11}), 7.17 (\text{t}, J_{HH} = 7.5 \text{ Hz, 4 H, H}^{10}), 7.11 (\text{t}, J_{HH} = 7.3 \text{ Hz, 2 H, H}^{11}), 6.11 (\text{s, 2 H, H}^{1}), 4.83 (\text{dd}, J_{HH} = 6.2 \text{ Hz, } J_{HH} = 10.7 \text{ Hz, 2 H, H}^{7}), 3.69 - 3.63 (\text{m, 2 H, H}^{6}), 3.56-3.51 (\text{m, 4 H, H}^{6'}), 2.28 (\text{s, 6 H, H}^{4}), 1.54 (\text{s, 6 H, H}^{4'}). \\
\text{C NMR (}^6\text{D}_6, 150 \text{ MHz, 295 K):} & \quad \delta (\text{ppm}) = 176.6 (\text{C}^{5}), 141.9 (\text{C}^{8}), 137.5 (\text{C}^{2}), 129.1 (\text{C}^{9,10,11}), 128.6 (\text{C}^{9,10,11}), 127.4 (\text{C}^{9,10,11}), 103.6 (\text{C}^{1}), 75.6 (\text{d, } J_{CF} = 2.7 \text{ Hz, C}^{6}), 63.4 (\text{C}^{7}), 38.3 (\text{C}^{3}), 34.7 (\text{C}^{4}), 22.3 (\text{C}^{4'}). \\
\text{F NMR (}^6\text{D}_6, 376 \text{ MHz, 295 K):} & \quad \delta (\text{ppm})= -445.7 (\text{s}). \\
\text{HR-FAB}^+: \text{Anal. Caled for } C_{28}H_{30}N_3NiO_2F: m/z 533.1355 (M^+).
\end{align*}
\]

Elemental Anal. Caled for C_{22}H_{36}N_3O_2NiF. C, 64.89; H, 5.83; N, 8.11. Found: C 64.59; H 6.09; N 8.12.
II b) General Synthetic Procedure for stoichiometric epoxide activation.

To a solution of [(S)Pr(PdmBox)NiH]2a (120 mg, 0.28 mmol) in 0.5 ml d6-benzene the corresponding epoxide (0.28 mmol, 1.01 equiv.) was added in 0.5 ml d6-benzene. The reaction progress was monitored periodically using 1H NMR spectroscopy. After complete conversion the solvent was removed in vacuo the crude was recrystallized from a pentane mixture at −40 °C to give a red crystalline solid.

1) [(S)Pr(PdmBox)Ni(OC8H10)] (3a)

a) Preparation of the 2-Phenylethanolate complex [(S)Pr(PdmBox)Ni(OC8H10)] (2a). After 6 hours, 1H NMR spectrum of the crude reaction mixture showed complete conversion. Yield 68%.

b) For identification purposes complex was also independently generated from the metathesis reaction between [(S)Pr(PdmBox)NiCl] and PhCH2CH2ONa.

To a stirring solution of 2-phenylethan-1-ol (40 mg, 0.321 mmol, 1.5 equiv.) in 10 mL of THF was added NaH (8 mg, 0.332 mmol, 1.55 equiv.) at room temperature over a period of 30 min. [(S)PrPdmBox]NiCl (100 mg, 0.215 mmol, 1 equiv.) was then added and the reaction mixture was stirred for additional 2 h. The volatiles were removed under vacuum, the residue extracted with pentane and filtered through a pad of Celite. The red residue was washed two times with 1 ml of cold pentane. Yield (35 %). Single crystals of 3a were grown by slow cooling a saturated pentan solution to -40°C.

1H NMR (C6D6, 600 MHz, 295 K): δ (ppm) = 7.39 (d, 3J_H,H = 7.0 Hz, 2 H, H13), 7.24 (t, 3J_H,H = 7.7 Hz, 2 H, H14), 7.08 (tt, 3J_H,H = 7.3 Hz, 2.3 Hz, 1 H, H15), 6.10 (s, 2 H, H1), 4.16 (ddd, 3J_H,H = 8.8 Hz, 7.1 Hz, 6.0 Hz, 1 H, H10), 3.81 (dt, 3J_H,H = 9.9 Hz, 4.0 Hz, 2 H, H7), 3.72 (dd, 3J_H,H = 9.1 Hz, 4.4 Hz, 2 H, H6), 3.56 (dd, 3J_H,H = 9.6 Hz, 9.3 Hz, 23.37 (dt, 3J_H,H = 8.9 Hz, 6.9 Hz, 1 H, H10), 3.00- 2.85 (m, 4 H, H8, H11), 2.61 (s, 3 H, H4), 1.60 (s, 3 H, H14), 0.73 (d, 3J_H,H = 2.1 Hz, 6 H, H9), 0.72 (d, 3J_H,H = 1.4 Hz, 6 H, H9).

13C NMR (C6D6, 150 MHz, 295 K): δ (ppm) = 175.0 (C5), 141.4 (C12), 136.7 (C2), 128.4 (C13,14,15), 127.5 (C13,14,15), 124.5 (C13,14,15), 101.6 (C1), 68.3 (C10), 67.9 (C9), 64.3 (C7), 42.3 (C11), 37.4 (C5), 33.8 (C4), 30.3 (C9), 21.2 (C5), 17.4 (C9), 13.6 (C9).
2) [(S)Pr(PdmBox)Ni(OC\textsubscript{14}H\textsubscript{15})] (4a)

Preparation of the 2,2-Diphenylethanolate complex [(S)Pr(PdmBox)Ni(OC\textsubscript{14}H\textsubscript{15})] (4a). After 36 hours, \textsuperscript{1}H NMR spectrum of the crude reaction mixture showed complete conversion. Red solid. Yield 74%.

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 600 MHz, 295 K): \(\delta\) (ppm) = 7.46-7.42 (m, 4 H, H\textsubscript{15,18}), 7.20-7.13 (m, 4 H, H\textsubscript{13,17}), 7.01-7.00 (m, 2 H, H\textsubscript{15,19}), 6.05 (s, 2 H, H\textsubscript{1}), 4.42 (dd, \(\text{J}_{\text{HH}} = 9.1\) Hz, 5.6 Hz, 1 H, H\textsubscript{10}), 4.09 (dd, \(\text{J}_{\text{HH}} = 6.3\) Hz, 6.3 Hz, 1 H, H\textsubscript{11}), 3.77 (dd, \(\text{J}_{\text{HH}} = 9.0\) Hz, 7.6 Hz, 1 H, H\textsubscript{10}), 3.70-3.66 (m, 2 H, H\textsubscript{7}), 3.61 (dd, \(\text{J}_{\text{HH}} = 9.0\) Hz, 4.6 Hz, 23.44 (dd, \(\text{J}_{\text{HH}} = 9.4\) Hz, 9.0 Hz, 2 H, H\textsubscript{6}), 2.94 (ds, \(\text{J}_{\text{HH}} = 6.9\) Hz, 3.7 Hz, 2 H, H\textsubscript{8}), 2.58 (s, 6 H, H\textsubscript{6}), 1.54 (s, 6 H, H\textsubscript{8}), 0.64 (d, \(\text{J}_{\text{HH}} = 2.1\) Hz, 6 H, H\textsubscript{9}), 0.63 (d, \(\text{J}_{\text{HH}} = 1.8\) Hz, 6 H, H\textsubscript{9}).

\textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}, 150 MHz, 295 K): \(\delta\) (ppm) = 175.1 (C\textsubscript{5}), 144.5 (C\textsubscript{12,16}), 144.4 (C\textsubscript{12,16}), 136.7 (C\textsubscript{2}), 128.2 (C\textsubscript{13,14,17,18}), 127.8 (C\textsubscript{13,14,17,18}), 127.2 (C\textsubscript{13,14,17,18}), 127.1 (C\textsubscript{13,14,17,18}), 124.9 (C\textsubscript{15,19}), 124.8 (C\textsubscript{15,19}), 101.6 (C\textsubscript{1}), 72.0 (C\textsubscript{10}), 67.8 (C\textsubscript{6}), 64.3 (C\textsubscript{3}), 56.4 (C\textsubscript{11}), 37.5 (C\textsubscript{3}), 33.8 (C\textsubscript{4}), 30.3 (C\textsubscript{8}), 21.2 (C\textsubscript{4}), 17.3 (C\textsubscript{9}), 13.6 (C\textsubscript{9}).

Elemental Anal. Calcd. for C\textsubscript{36}H\textsubscript{47}N\textsubscript{3}NiO\textsubscript{3}: C 68.80, H 7.54, N 6.69. Found: C 69.13, H 7.41, N 6.45.
II. c) General Procedure for the Synthesis of Epoxides

All epoxides that were not commercially available were synthesized under standard Corey Chaykovsky conditions as follows. A oven-dried 100 ml flask was charged with a stir bar, trimethyl sulfonium iodide (9.8 g, 48 mmol, 2 equiv.), and sodium hydride (60% dispersion in oil, 1.9 g, 48 mmol, 2 equiv). The flask was evacuated and refilled 3x with argon, and anhydrous DMSO (30 ml) and THF (22 ml) were added and the reaction was stirred for 20 minutes at room temperature. The solution was then cooled to 0 °C and the aldehyde (24 mmol, 1 equiv.) in THF (10 ml) was added at 0 °C and allowed to stir until consumption of aldehyde by TLC. The reaction was diluted with water (40 ml) and extracted with Et₂O (30 ml x 4). The combined organic layers were washed with water (20 ml) and brine (20 ml x 2), dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was either purified by vacuum distillation or column chromatography (Aluminum oxide). Epoxides were stored under Ar.

III. Catalytic Hydrosilylation of Epoxides

a) Screening of Silanes in the Hydrosilylation of Styrene oxide

![Diagram of cat. hydrosilane reaction]

**Table 1** Reaction conditions: Substrate (0.25 mmol) in 0.5 ml C₆D₆. a) Conversion was determined by ¹H NMR analysis of crude reaction mixture using 1,4-dimethoxybenzene as the internal standard. b) Isolated yield of purified product after column chromatography. c) Isolated without workup as stable PhCH₂CH₂OSiPh₃. In case of this sterically demanding triphenylsilane the nickel alkoxido complex was identified as the resting state instead of the nickel hydrido complex.

<table>
<thead>
<tr>
<th>entry</th>
<th>Cat.</th>
<th>Silane (equiv)</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Conv. [%]</th>
<th>workup</th>
<th>Yield [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>2a 5 mol%</td>
<td>PhSiH₃ (1)</td>
<td>16 h</td>
<td>50</td>
<td>100</td>
<td>-</td>
<td>-</td>
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<tr>
<td>2</td>
<td>2a 5 mol%</td>
<td>(EtO)₃SiH (2)</td>
<td>24 h</td>
<td>50</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>2a 5 mol%</td>
<td>PhMe₂SiH (2)</td>
<td>16 h</td>
<td>50</td>
<td>0</td>
<td>-</td>
<td>-</td>
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<tr>
<td>4</td>
<td>2a 5 mol%</td>
<td>Ph₂SiH₂ (1)</td>
<td>16 h</td>
<td>50</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>2a 5 mol%</td>
<td>PMHS (5)</td>
<td>16 h</td>
<td>50</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2a 5 mol%</td>
<td>(EtO)₃MeSiH (2)</td>
<td>16 h</td>
<td>50</td>
<td>&lt;10</td>
<td>-</td>
<td>-</td>
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<tr>
<td>7</td>
<td>2a 5 mol%</td>
<td>(TMS)₃SiH (2)</td>
<td>16 h</td>
<td>50</td>
<td>0</td>
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<td>8</td>
<td>2a 5 mol%</td>
<td>PhSiH</td>
<td>120 h</td>
<td>50</td>
<td>100</td>
<td>HCl⁷</td>
<td>90⁶</td>
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<tr>
<td>9</td>
<td>2a 5 mol%</td>
<td>Et₂SiH (2)</td>
<td>16 h</td>
<td>50</td>
<td>0</td>
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<td>-</td>
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<tr>
<td>10</td>
<td>2a 5 mol%</td>
<td>PhMe₂SiH</td>
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<tr>
<td>11</td>
<td>2a 5 mol%</td>
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<td>24 h</td>
<td>30</td>
<td>100</td>
<td>K₂CO₃, MeOH⁸</td>
<td>50</td>
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<tr>
<td>12</td>
<td>2a 5 mol%</td>
<td>PhSiH₃ (1)</td>
<td>24 h</td>
<td>30</td>
<td>100</td>
<td>TBAF, H₂O</td>
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<td>NaOH (5%), H₂O³</td>
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</tr>
<tr>
<td>13</td>
<td>1b 5 mol%</td>
<td>PhSiH₃ (1)</td>
<td>24 h</td>
<td>30</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>All above</td>
<td>120 h</td>
<td>80</td>
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</table>
General Procedure for the Catalytic Hydrosilylation of Epoxides

A J-Young NMR tube was charged with the precatalyst 1a or 1b (5 mol%), epoxide (0.25 mmol), hydrosilane (1 equiv.) and 1,4-dimethoxybenzene as internal standard in 0.5 ml benzene-d<sub>6</sub>. The conversion and the NMR yield of the corresponding silyl ether were determined directly from <sup>1</sup>H NMR Spectra of the reaction mixture after the reaction. After complete conversion 1 ml of MeOH was added followed by 1 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 2 ml). The combined organic layers were washed with brine dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude was purified by flash column chromatography on silica gel.

The reaction products were identified by comparison to authentic, commercially available samples. If the alcohols were not commercially available, they were synthesized using LiAlH<sub>4</sub> or NaBH<sub>4</sub> to reduce the corresponding aldehyde or ketone.

1) 2-phenylethan-2-d-1-ol

![2-phenylethan-2-d-1-ol structure]

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 295 K): δ (ppm) = 7.35-7.30 (m, 2 H, H<sup>4</sup>), 7.25-7.21 (m, 3 H, H<sup>5</sup>, H<sup>6</sup>), 3.85 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 2 H, H<sup>1</sup>), 2.84 (m, 1 H, H<sup>2</sup>).

<sup>2</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 295 K): δ (ppm) = 2.88 (bs).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 295 K): δ (ppm) = 138.5 (C<sup>6</sup>), 129.17 (C<sup>5</sup>), 128.7 (C<sup>4</sup>), 126.6 (C<sup>3</sup>), 63.6 (C<sup>1</sup>), 38.9 (t, <sup>1</sup>J<sub>C,D</sub> = 19.4 Hz, C<sup>2</sup>).

HR-EI<sup>+</sup>: for C<sub>8</sub>H<sub>9</sub>DO m/z: 123.08024 (M<sup>+</sup>), 92.06156 (M<sup>+</sup>-CH<sub>3</sub>O).
Solvent free conditions

A J-Young NMR tube was charged with the precatalyst 1a (19 mg, 42.2 μmol, 1 mol%), styrene oxide (500 mg, 4.22 mmol) and phenylsilane (205 mg, 1.9 mmol, 0.45 equiv.). After 4 hours 1H NMR spectra of the reaction mixture showed complete conversion. 5 ml of MeOH was added followed by 5 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 10 ml). The combined organic layers were washed with brine dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The crude was purified by vacuum distillation to give 2-phenylethan-1-ol in 95% yield.

Solvent free ball milling conditions:

A ball milling vessel (Achat, 20 ml) was charged with the precatalyst 1a (20 mg, 44.42 μmol, 3 mol%), 2-(4-Biphenylyl)oxirane (290 mg, 1.48 mmol), phenylsilane (81 mg, 0.74 mmol, 0.5 equiv.) and 10 grinding balls (Achat, diameter: 0.5 cm). The ball milling vessel was then transferred to a mixer mill and milled at 8 Hz for 90 min. The crude reaction mixture was isolated by washing the vessel and the ball with Et₂O (5 x 10 ml). The reaction mixture was concentrated to approx. 5 ml, then 5 ml of MeOH was added followed by 5 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 10 ml). The combined organic layers were washed with brine dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. 2-(4-Biphenylyl)ethanol was then isolated by flash column chromatography in 89% Yield.
Mechanistic studies

Determination of the $^1$H-$^2$H Kinetic Isotope Effect using Competition Experiments

A J-Young NMR tube was charged with Nickel complex $1a$ or $1b$ (5 mol%) and styrene oxide (1 eq) in 0.4 ml benzene-$d_6$. A preformed 1:1 mixture of 1 equiv. PhSiD$_2$ and 1 equiv. PhSiH$_3$ was added in 0.1 ml benzene-$d_6$. The reaction was monitored by $^1$H NMR spectroscopy. After 16 h at room temperature the reaction showed complete conversion and 1 ml of MeOH was added followed by 1 ml of 5% NaOH aqueous solution with vigorous stirring. The reaction mixture was further stirred for 24 h at room temperature and was extracted with diethyl ether (3 x 2 ml). The combined organic layers were washed with brine dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The crude was purified by flash column chromatography on silica gel. The ratio of deuterated to normal product was determined by $^{13}$C NMR spectroscopy and averaged over two independent runs.

Figure S1 Exemplary $^{13}$C-NMR spectrum of the competition hydrosilylation of styrene oxide with hydrosilane and deuterosilane.

<table>
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<th>Catalyst</th>
<th>Epoxide</th>
<th>Silane</th>
<th>$k_H/k_D$</th>
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<tr>
<td>$1a$</td>
<td>Styrene oxide</td>
<td>Ph$_2$SiD$_2$/Ph$_2$SiH$_2$</td>
<td>1.56</td>
</tr>
<tr>
<td>$1a$</td>
<td>Styrene oxide</td>
<td>PhSiD$_3$/PhSiH$_3$</td>
<td>1.58</td>
</tr>
<tr>
<td>$1b$</td>
<td>Styrene oxide</td>
<td>PhSiD$_3$/PhSiH$_3$</td>
<td>1.47</td>
</tr>
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</table>

Stoichiometric reaction between [(S)(iPrPdmBox)NiH] 2a, styrene oxide and Ph$_2$SiD$_2$.

A J-Young NMR tube was charged with [(S)(iPrPdmBox)NiH] 2a (20 mg, 46 μmol, 1 equiv.) and Ph$_2$SiD$_2$ (8.5 mg, 45.5 μmol, 1 equiv.) in 0.4 ml C$_6$D$_6$. No H/D exchange was observed at room temperature after 24 h. Then styrene oxide (5.5 mg, 45.8 μmol, 1 equiv.) dissolved in 0.1 ml C$_6$D$_6$ was added. After additional 24 h $^1$H NMR indicated that Nickel hydrido complex 2a was fully converted to the nickel-deuteride compound accompanied by the formation of silyl ether products of the epoxide. After alkaline hydrolysis no deuterium incorporation of the product alcohol could be monitored by NMR.

Mercury Test$^8$

To a solution of [(S)(iPrPdmBox)NiH] 2a (5.0 mg, 11.6 μmol) and styrene oxide (30 ml, 250 μmol) in 0.5 ml C$_6$D$_6$, Hg(0) (350 mg, 1.75 mmol). After 15 minutes PhSiH$_3$ (27 mg, 250 μmol) was added. The reaction was monitored periodically by NMR yielded the same conversion and selectivity as a sample without addition of Hg(0).
Details for Kinetic Experiments

![Reaction diagram]

<table>
<thead>
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<th>Reaction conditions</th>
<th>Standard conditions</th>
</tr>
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<td>[Catalyst]</td>
<td>0.011 - 0.034 M</td>
<td>5 mg, 5 mol% (0.02 M)</td>
</tr>
<tr>
<td>[[Epoxide]]</td>
<td>0.21 - 0.65 M</td>
<td>30 mg (0.44 M)</td>
</tr>
<tr>
<td>[Silane]</td>
<td>0.1 - 0.74 M</td>
<td>30 mg 1.2 equiv. (0.55 M)</td>
</tr>
</tbody>
</table>

\[(S)\text{PdmBox}NiF\] (1a), 4'-fluorostyrene oxide, PhSiH₃, and 1,4- bis(trifluoromethyl)benzene as internal standard were dissolved in 0.5 ml benzene-d₆ in a J. Young NMR tube. The sample was measured at ambient conditions (23 °C) and ¹⁹F NMR spectra were recorded until at least 50 % conversion were observed. For analysis of the spectra, the integral of the internal standard was set to 1 in each spectrum and the values for the starting material as well as the products were used without further manipulation.

**Figure S2** Typical ¹⁹F{'H} NMR spectra recorded during a kinetic measurement run.

**Figure S3** Typical reaction profile for the catalytic hydrosilylation using 1a as catalyst.
Figure S4 Determining the rate law for the catalytic hydrosilylation.
X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-Kα radiation, microfocus X-ray tubes, multilayer mirror optics). Detector frames (typically \( \omega \)-, occasionally \( \varphi \)-scans, scan width 0.4...1°) were integrated by profile fitting.\(^1\) Data were corrected for air and detector absorption, Lorentz and polarization effects\(^2\) and scaled essentially by application of appropriate spherical harmonic functions.\(^2,3,4\) Absorption by the crystal was treated numerically (Gaussian grid).\(^4,5\) An illumination correction was performed as part of the numerical absorption correction.\(^4\) The structures were solved by direct methods with dual-space recycling (VLD-procedure, compound 1b)\(^6\) or by the charge flip procedure (compound 3a:Ph(CH\(_2\))\(_3\)OH)\(^7\) and refined by full-matrix least squares methods based on \( F^2 \) against all unique reflections.\(^8\) All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. The position of the hydroxyl hydrogen in 3a:Ph(CH\(_2\))\(_3\)OH was taken from a difference Fourier synthesis and refined.

CCDC 1532348 and 1532349 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

References

\(^3\) R. H. Blessing, Acta Cryst. 1995, A51, 33;
\(^7\) (a) L. Palatinus, SUPERFLIP, EPF Lausanne, Switzerland and Fyzikální ústav AV ČR, v. v. i., Prague, Czech Republic, 2007-2014; (b) L. Palatinus, G. Chapuis, J. Appl. Cryst. 2007, 40, 786.
\(^8\) (a) G. M. Sheldrick, SHELXL-20xx, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2012-2016; (b) G. M. Sheldrick, Acta Cryst. 2008, A64, 112; (c) G. M. Sheldrick, Acta Cryst. 2015, C71, 3.
**Figure S5** Molecular structure of 1b. Hydrogen atoms are omitted for clarity; thermal ellipsoids displayed at 50% probability. Only one of the three independent molecules is shown. Selected bond lengths [Å] and angles [°]: Ni–F 1.814(3) ... 1.828(3), Ni–N1 1.875(4) ... 1.894(4), Ni–N2 1.860(4) ... 1.867(4), Ni–N3 1.892(4) ... 1.892(5), N(1)–Ni–N(2) 90.21(18) ... 91.42(18), N(1)–Ni–F 88.58(16) ... 88.96(16).

**Table S1** Details of the crystal structure determinations of 1b and 3a·C₈H₁₀O.
<table>
<thead>
<tr>
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<th>[1b]</th>
<th>[3a]-C₃₈H₅₃N₃NiO₈F</th>
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<tr>
<td><strong>formula</strong></td>
<td>C₂₈H₃₀Ni₃O₂F</td>
<td>C₃₈H₅₃N₃NiO₈</td>
</tr>
<tr>
<td><strong>Mr</strong></td>
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<td>674.54</td>
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<tr>
<td><strong>space group</strong></td>
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<td>P 2₁₂₂₂</td>
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<tr>
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<td>9.93003(15)</td>
</tr>
<tr>
<td><strong>b /Å</strong></td>
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<td>10.15945(19)</td>
</tr>
<tr>
<td><strong>c /Å</strong></td>
<td>54.0604(8)</td>
<td>35.2869(6)</td>
</tr>
<tr>
<td><strong>V /Å³</strong></td>
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<td>3559.88(11)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
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<td>4</td>
</tr>
<tr>
<td><strong>F₀₀₀</strong></td>
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<td>1448</td>
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<tr>
<td><strong>dC /Mg·m⁻³</strong></td>
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<td>1.259</td>
</tr>
<tr>
<td><strong>X-radiation, λ /Å</strong></td>
<td>Mo-Kα, 0.71073</td>
<td>Cu-Kα, 1.54184</td>
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<tr>
<td><strong>μ /mm⁻¹</strong></td>
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<td>1.118</td>
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<td>0.974, 0.901</td>
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<tr>
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<td>120(1)</td>
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<tr>
<td><strong>θ range /°</strong></td>
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<td>4.5 to 71.0</td>
</tr>
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<td>-12 ... 12, -12 ... 12, -43 ... 40</td>
</tr>
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<td><strong>reflections measured</strong></td>
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<td>122869</td>
</tr>
<tr>
<td><strong>unique [Rint]</strong></td>
<td>13494 [0.1099]</td>
<td>6862 [0.0845]</td>
</tr>
<tr>
<td><strong>observed [I≥2σ(I)]</strong></td>
<td>11850</td>
<td>6225</td>
</tr>
</tbody>
</table>
NMR Spectra of New Compounds

$^1$H NMR (C$_6$D$_6$, 600 MHz, 295 K):

$^{13}$C NMR (C$_6$D$_6$, 150 MHz, 295 K):
$^1$H NMR (C$_6$D$_6$, 600 MHz, 295 K):

$^{13}$C NMR (C$_6$D$_6$, 150 MHz, 295 K):
$^1$H NMR (C$_6$D$_6$, 600 MHz, 295 K):

$^{13}$C NMR (C$_6$D$_6$, 150 MHz, 295 K):
$^1$H NMR (CDCl$_3$, 600 MHz, 295 K):

$^2$H NMR (CDCl$_3$, 92 MHz, 295 K):

$^{13}$C NMR (CDCl$_3$, 150 MHz, 295 K):