# **Electronic Supplementary Information**

Boosting chemoselective hydrogention of olefins

with molecular hydrogen mediated by a bis(silylenyl)terphenyl-nickel(0) pre-catalyst

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### 1) General Considerations:

All experiments and manipulations were carried out under dry nitrogen using standard schlenk techniques or inside an MBraun glovebox. Solvents were dried by standard methods and freshly distilled prior to use. The NMR spectra were recorded on a Bruker spectrometers AV200 (<sup>1</sup>H, 200 MHz; <sup>13</sup>C, 50.32 MHz) or AV400 (<sup>1</sup>H, 400.13 MHz; <sup>13</sup>C {<sup>1</sup>H}, 100.61 MHz; <sup>29</sup>Si, 79.49 MHz) spectrometer. The <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} spectra were referenced to residual solvent signals as internal standards (<sup>1</sup>H NMR: benzene-d<sub>6</sub>, 7.16 ppm, THF-d<sub>8</sub>, 1.72; 3.58 ppm and  ${}^{13}C$  {<sup>1</sup>H} NMR: benzene-d<sub>6</sub>, 128.1 ppm, THF-d<sub>8</sub>, 77.2 ppm). <sup>29</sup>Si {<sup>1</sup>H} spectra were referenced by using SiMe<sub>4</sub> as external standard. Concentrated solutions of samples in deuterated solvent were sealed off in a NMR tube for measurements. Abbreviations: s = singlet; t = triplet; m = multiplet; br = broad. Signals were assigned by employing a combination of 2D NMR H,H-COSY, H,C-COSY (HMBC, HMQC) experiments and additional to DEPT experiments. High resolution APCI (atmospheric-pressure chemical ionization) or ESI (electrospray ionization) mass spectra were recorded on an Orbitrap LTQ XL of Thermo Scientific mass spectrometer. Elemental analyses were recorded in a Thermo FlashEA 1112 Organic elemental analyzer. The ATR/IR-spectroscopic Measurements were recorded on a Firma Thermo Fisher Scientific spectrometer inside a glovebox. Vibration Modes are given in wavenumbers (cm<sup>-1</sup>). Abbreviations: (vs) very strong, (s) strong, (m) middle, (w) weak and (br) broad. Commercially available reagents were purchased from SIGMA-Aldrich, Acros, Alfa-Assar or ABCR and used as received. 1,4-bis(2-bromophenyl)benzene (1) was synthesized according to reported procedures.<sup>[S1]</sup>

**Single crystal X-ray structure analyses:** Crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N<sub>2</sub> flow. The data for all compounds were collected on an Agilent Technologies SuperNova (single source) at 150 K (Cu-K<sub> $\alpha$ </sub> radiation,  $\lambda = 1.5418$  Å). All structures were solved by direct methods and refined on  $F^2$  with the SHELX-97 software <sup>[S2]</sup>. The positions of the H atoms were calculated and considered isotopically according to a riding model. The CCDC numbers 2025191 compound **2**), 2025192 (compound **3**), 2025193 (compound **4**) and 2025194 (compound **b**)

**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Cyclic Voltammetry Measurement:** Cyclic Voltammetry (CV) measurements were carried out at 295 K by using a Biologic SP-150 potentiostat and a three electrode setup. Pt-wire was used as an auxiliary electrode. A freshly polished glassy carbon disc (3 mm diameter) as a working electrode and a pseudo reference electrode Ag/Ag<sup>+</sup> was used. All cyclic voltammograms were referenced against the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> redox couple which was used as an internal standard. As an electrolyte, 0.3 M solutions of TBAPF<sub>6</sub> in THF was used. The iR-drop was determined and compensated by using the impedance measurement technique implemented in the EC-Lab Software V10.

#### Molecule-Index:



### 2) Synthesis and Characterisation:

**Synthesis of 1,4-bis(2-(phosphine)phenyl)benzene** (2). A mixture of 1,4-bis(2-bromophenyl)benzene (1, 200 mg, 0.515 mmol, 1.0 equiv.) and ether (10 mL) was cooled to - 78 °C and a solution of <sup>sec</sup>Buli (1.3 M in cyclohexane, 0.9 mL, 1.17 mmol, 2.2 equiv.) was added via syringe. After warming up to room temperature, the solution turned from slight yellow to a suspension containing a white precipitate. After stirring for 4 h at room temperature, the suspension was cooled to - 78 °C and 2-chloro-1,3-diisopropyl-1,3,2-diazaphospholidine (215 mg, 1.03 mmol, 2.0 equiv.) was added via syringe. After stirring for 1 h at room temperature, all volatiles were removed under reduced pressure and dissolved in 10 mL Et<sub>2</sub>O. After the solution was filtered and reduced to a volume of 1.0 ml, the solution was kept at -30 °C over night affording **2** as colorless crystals. After removal of Et<sub>2</sub>O, crystals were washed with 0.5 mL cold Et<sub>2</sub>O (-78 °C) to give **2** in 82 % (242 mg, 0.40 mmol) isolated yields. Single crystals suitable for an x-ray diffraction analysis were obtained from a concentrated hexane solution at room temperature overnight. Compound **2** is air stable and is well soluble in general organic solvents (Et<sub>2</sub>O, hexane, THF, toluene).

<sup>1</sup>**H NMR** (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 1.00 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 2.62 – 2.82 (mbr, 4 H, N(CH<sub>2</sub>)<sub>2</sub>N), 2.85 – 3.01 (mbr, 4 H, N(CH<sub>2</sub>)<sub>2</sub>N), 3.02 – 3.29 (m, 4 H, 4 x CH(CH<sub>3</sub>)),7.20 – 7.38 (m, 6 H, Ar*H*), 7.71 (s, 4 H, Ar*H*), 7.86 – 7.96 (m, 2 H, Ar*H*). <sup>1</sup>**H**{<sup>31</sup>**P**} **NMR** (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 1.00 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 2.83 (dm, 8 H, 4 x N(CH<sub>2</sub>)<sub>2</sub>N), 3.17 (sept, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 4 H, 4 x CH(CH<sub>3</sub>)), 7.20 – 7.38 (m, 6 H, Ar*H*), 7.71 (s, 4 H, Ar*H*), 7.86 – 7.96 (d, 2 H, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, Ar*H*). <sup>13</sup>**C NMR** (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 22.8 (s, 2 x CH(CH<sub>3</sub>)<sub>2</sub>), 22.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 22.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 47.9 (d, <sup>2</sup>J<sub>C,P</sub> = 7.0 Hz, 4 x N(CH<sub>2</sub>)<sub>2</sub>N), 51.0 (d, <sup>2</sup>J<sub>C,P</sub> = 25.3 Hz, 4 x CH(CH<sub>3</sub>)<sub>2</sub>), 126.2 (s, C<sub>Ar</sub>), 128.4 (s, C<sub>Ar</sub>), 130.3 (d, <sup>3</sup>J<sub>C,P</sub> = 4.5 Hz, C<sub>Ar</sub>), 130.7 (d, *J* = 3.6 Hz, C<sub>Ar</sub>), 130.9 (brs, C<sub>Ar</sub>), 141.4 (d, <sup>3</sup>J<sub>C,P</sub> = 3.6 Hz, C<sub>quart</sub>), 144.0 (d, <sup>1</sup>J<sub>C,P</sub> = 35.3 Hz, C<sub>quart</sub>), 146.3 (d, <sup>2</sup>J<sub>C,P</sub> = 23.5 Hz, C<sub>quart</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.00 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 92.55 (s, satellite: J<sub>P,C</sub> = 25.5 Hz). **FT-IR** (solid):  $\tilde{\nu}$ /cm<sup>-1</sup> = 3066 (w), 3047 (w), 2962 (s), 2920 (s), 2874 (s), 2841 (s), 1453 (s), 1301 (s), 1302 (s), 1210 (s), 1158 (s), 1041 (s), 1004 (s), 982 (s), 847 (s), 756 (vs). **ESI-MS** m/z (%): Calcd. for  $[M+H]^+ = C_{34}H_{49}N_4P_2^+$ : 575.3427, found. 575.3430. **Melting Point** T/°C: 102. **Elemental analysis**: Calcd. for  $C_{34}H_{48}N_4P_2$ : C, 71.05; H, 8.42; N, 9.75. Found: C, 71.23; H, 8.34; N, 9.43.

**Synthesis of 1,4-bis(2-(silylene)phenyl)benzene (3)**. A diethylether suspension (20 mL) of 1,4-bis(2-bromophenyl)benzene (1, 500 mg, 1.29 mmol, 1.0 equiv.) was cooled to - 78 °C and a solution of <sup>sec</sup>Buli (1.3 M in cyclohexane, 2 mL, 2.58 mmol, 2.0 equiv.) was added via syringe. After warming up to room temperature, the solution turned from slight yellow to a suspension containing a white precipitate. After stirring for 4 h at room temperature, the suspension was cooled to - 78 °C and a solution (Et<sub>2</sub>O, 10 mL) of N,N'-di-tert-butyl(phenylamidinato)-phenylsilylene (750 mg, 2.58 mmol, 2.0 equiv.) was added via syringe. The cooling bath was removed and the suspension was stirred at room temperature over night to give a yellow suspension. Volatiles were removed under reduced pressure and the residue was washed twice with 4 mL Et<sub>2</sub>O. The title compound was extracted using hot toluene (60°C,  $3 \times 50$  ml) to give a yellow solution. After evaporation, **3** was isolated as pale yellow crystalline material in 68 % (650 mg, 0.87 mmol) isolated yields. Single crystals suitable for an xray diffraction analysis were obtained from a concentrated toluene solution at - 30 °C after 3 days. Compound **3** is not air stable and is generally not well soluble (THF > Et<sub>2</sub>O, toluene).

<sup>1</sup>H NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$ /ppm = 1.03 (s, 36 H, 4 x NC(CH<sub>3</sub>)<sub>3</sub>) 6.90 - 7.03 (m, 6 H, Ar*H*), 7.26 - 7.57 (m, 10 H, Ar*H*), 7.85 - 7.95 (m, 2 H, Ar*H*), 8.02 (s, 4H, Ar*H*<sub>central</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$ /ppm = 31.6 (s, 4 x NC(CH<sub>3</sub>)<sub>3</sub>), 53.1 (s, 4 x NC<sub>quart</sub>(CH<sub>3</sub>)<sub>3</sub>), 125.7 (s, 2 x Ar*C*), 127.4 (s, 2 x Ar*C*), 127.9 (s, 2 x Ar*C*), 128.1 (s, 2 x Ar*C*), 128.7 (s, 2 x Ar*C*), 128.9 (s, 2 x Ar*C*), 129.3 (s, 2 x Ar*C*), 130.7 (s, 2 x Ar*C*), 130.9 (s, 2 x Ar*C*), 135.1 (s, 2 x Ar*C*<sub>quart</sub>), 142.6 (s, 2 x Ar*C*<sub>quart</sub>), 145.2 (s, 2 x Ar*C*<sub>quart</sub>), 152.3 (s, 2 x Ar*C*<sub>quart</sub>), N*C*N not detected. <sup>29</sup>Si NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): +16.8 ppm (s). FT-IR (solid):  $\tilde{\nu}$ /cm<sup>-1</sup> = 3058 (w), 3041 (w), 2970 (s), 2928 (w), 2901 (w), 2885 (w), 1645 (w), 1612 (w), 1579 (w), 1416 (vs), 1663 (s), 1236 (s), 757 (vs). 616 (vs). APCI-MS

m/z (%): Calcd. for [M+OH]<sup>+</sup> = C<sub>48</sub>H<sub>59</sub>N<sub>4</sub>Si<sub>2</sub>O<sup>+</sup>: 763.4222, found. 763.4230. **Melting Point** T/°C: 240 (decomp.). **Elemental analysis:** Calcd. for C<sub>48</sub>H<sub>58</sub>N<sub>4</sub>Si<sub>2</sub>: C, 77.16; H, 7.82, N, 7.50. Found: C, 73.34; H, 7.36; N, 7.23. (Reduced C content due to SiC formation)

**Synthesis of [1,4-bis(2-(phosphine)phenyl)benzene]nickel(0)** (**4**). A mixture of 1,4-bis(2-(phosphine)phenyl)benzene (**2**, 100 mg, 0.17 mmol, 1.0 equiv) and Ni(cod)<sub>2</sub> (48 mg, 0.17 mmol, 1.0 equiv.) was dissolved in 10 mL Et<sub>2</sub>O and stirred for 4 h at room temperature upon which a dark red solution is formed. Then, all volatiles were removed and the title compound was extracted with 5 ml hexane. After reduction of the volume to 0.5 ml **4** could be obtained as dark red crystals in 84 % isolated yields (92 mg, 0.14 mmol) after 3 days at – 30 °C. Single crystals suitable for an x-ray diffraction analysis were obtained from a concentrated hexane solution at – 30 °C. Compound **2** is not air stable and is well soluble in general organic solvents (Et<sub>2</sub>O, hexane, THF, toluene, benzene). Complex **4** shows line-broadening in the <sup>1</sup>H-NMR at 298 K. <sup>1</sup>H, <sup>13</sup>C-NMR resonances of the coordinated arene were resolved at 233 K and assigned by a <sup>1</sup>H,<sup>13</sup>C-HSQC NMR spectra.

<sup>1</sup>**H** NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 0.87 (d, <sup>3</sup>J<sub>HH</sub> = 5.1 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 1.07 (d, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 12 H, 2 x CH(CH<sub>3</sub>)<sub>2</sub>, 2.86 (mbr, 4 H, N(CH<sub>2</sub>)<sub>2</sub>N), 3.13 (mbr, 4 H, N(CH<sub>2</sub>)<sub>2</sub>N), 3.57 (m, 4 H, 4 x CH(CH<sub>3</sub>)), 5.60 (br, 2H, central Aryl*H*), 7.17 – 7.36 (m, 6 H, Ar*H*), 7.47 – 7.60 (s, 2 H, Ar*H*), 7.67 – 7.78 (m, 2 H, Ar*H*). <sup>13</sup>C NMR (175 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 21.2 (s, 2 x CH(CH<sub>3</sub>)<sub>2</sub>), 22.0 (s, 2 x CH(CH<sub>3</sub>)<sub>2</sub>), 42.9 (br, 4 x N(CH<sub>2</sub>)<sub>2</sub>N), 47.1 (br, 4 x CH(CH<sub>3</sub>)<sub>2</sub>), 126.2 (s, C<sub>Ar</sub>), 127.0 (s, C<sub>Ar</sub>), 129.1 (s, C<sub>Ar</sub>), 128.2 (s, C<sub>Ar</sub>), 128.2 (s, C<sub>Ar</sub>), 130.6 (s, C<sub>Ar</sub>), 132.1 (t, <sup>3</sup>J<sub>C,P</sub> = 2.3 Hz, C<sub>quart</sub>), 138.9 (t, <sup>2</sup>J<sub>C,P</sub> = 7.4 Hz, C<sub>quart</sub>), 148.7 (t, <sup>1</sup>J<sub>C,P</sub> = 10.2 Hz, C<sub>quart</sub>). <sup>1</sup>H,<sup>13</sup>C-HSQC (125 MHz, d<sub>8</sub>-THF, 233 K): 4.7/ 62.4 (Ni-C<sub>2</sub>H<sub>2</sub>) 6.2/ 120.9 (*H*C<sub>Ar</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.00 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ/ppm = 103.6 (s). FT-IR (solid): λ/cm<sup>-1</sup> = 3043 (w), 2961 (s), 2925 (w), 2827 (s), 1583 (w), 1451 (s), 1357 (s), 1172 (vs), 1050 (vs), 955 (vs), 806 (vs), 742 (vs), 694 (vs). UV/VIS (THF):  $\tilde{\nu}$ /nm = 408. CV: E<sup>1/2</sup> (fc/fc<sup>+</sup>) = -0.938 (Ni<sup>0</sup>/Ni<sup>1</sup>); -0.472 (Ni<sup>1</sup>/Ni<sup>II</sup>) V (revers.). ESI-MS m/z (%): Calcd. for [C<sub>34</sub>H<sub>48</sub>N<sub>4</sub>P<sub>2</sub>Ni + H]<sup>+</sup>: 633.2780, found. 633.2781. Melting Point T/°C: 142. Elemental **analysis:** Calcd. for C<sub>34</sub>H<sub>48</sub>N<sub>4</sub>P<sub>2</sub>Ni: C: 64.47, H: 7.64, N: 8.85. Found: C, 64.12; H, 7.33; N, 8.34.

**Synthesis of [1,4-bis(2-(silylene)phenyl)benzene]nickel(0)** (5). A mixture of 1,4-bis(2-(silylene)phenyl)benzene (**2**, 200 mg, 0.27 mmol, 1.0 equiv) and Ni(cod)<sub>2</sub> (73.6 mg, 0.27 mmol, 1.0 equiv.) was dissolved in 4 mL Et<sub>2</sub>O and stirred for 4 h at room temperature upon which dark red crystals are formed. The suspension was cooled to -78 °C and the upper solution was removed via cannula filtration. After additional washing with 0.7 ml cold Et<sub>2</sub>O (-78 °C) Ni(0) complex **5** was isolated in 64 % (140 mg, 0.17 mmol) as small dark-red crystals. Single crystals suitable for an x-ray diffraction analysis were obtained from a concentrated toluene solution at – 30 °C. Compound **2** is not air stable and smokes off to a black solid. **2** is highly soluble in THF and toluene > Et<sub>2</sub>O > benzene. Complex **5** shows line-broadening in the <sup>1</sup>H-NMR at 298 K. <sup>1</sup>H, <sup>13</sup>C-HSQC NMR spectra.

<sup>1</sup>**H** NMR (500 MHz, d<sub>8</sub>-THF, 298 K): δ/ppm = 1.11 (br s, 36 H, 4 x NC(CH<sub>3</sub>)<sub>3</sub>), 4.21 (br s, 2 H, Ar*H*<sub>central</sub>), 5.91 (br s, 2 H, Ar*H*<sub>central</sub>), 7.22 - 7.29 (m, 4 H, Ar*H*), 7.35 - 7.40 (m, 4 H, Ar*H*), 7.50 - 7.58 (m, 8 H, Ar*H*), 7.76 - 7.78 (s, 2H, Ar*H*). <sup>13</sup>**C** NMR (125 MHz, d<sub>8</sub>-THF, 298 K): δ/ppm = 32.2 (s, 4 x NC(CH<sub>3</sub>)<sub>3</sub>), 54.4 (s, 4 x NC<sub>quart</sub>(CH<sub>3</sub>)<sub>3</sub>), 126.3 (s, 2 x Ar*C*), 126.5 (s, 2 x Ar*C*), 128.8 (s, 2 x Ar*C*), 128.8 (s, 2 x Ar*C*), 129.0 (s, 2 x Ar*C*), 129.1 (s, 2 x Ar*C*), 130.8 (s, 2 x Ar*C*), 131.6 (s, 2 x Ar*C*), 131.7 (s, 2 x Ar*C*), 135.1 (s, 2 x Ar*C*<sub>quart</sub>), 135.6 (s, 2 x Ar*C*), 131.6 (s, 2 x Ar*C*), 131.7 (s, 2 x Ar*C*), 135.1 (s, 2 x Ar*C*<sub>quart</sub>), 135.6 (s, 2 x Ar*C*<sub>quart</sub>), 137.0 (s, 2 x Ar*C*<sub>quart</sub>), 155.1 (s, 2 x Ar*C*<sub>quart</sub>), 166.5 (s, 2 x C<sub>quart</sub>, NCN). <sup>1</sup>H,<sup>13</sup>C-HSQC (125 MHz, d<sub>8</sub>-THF, 233 K): 4.14/54.5 (Ni-C<sub>2</sub>H<sub>2</sub>) 6.00/ 118.6 (*H*C<sub>Ar</sub>). <sup>29</sup>Si NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): + 51.0 ppm (s). FT-IR (solid): λ/cm<sup>-1</sup> = 3042 (w), 2971 (s), 2930 (w), 2867 (w), 1579 (s), 1417 (vs), 1389 (s), 1277 (s), 1236 (vs) 754 (vs), 707 (vs), 624 (vs). UV/VIS (THF):  $\tilde{\nu}$  /nm = 442. CV: E<sup>1/2</sup> (fc/fc<sup>+</sup>) = -1.341 (Ni<sup>0</sup>/Ni<sup>1</sup>); -1.227 (Ni<sup>1</sup>/Ni<sup>II</sup>) V (revers.). ESI-MS m/z (%): Calcd. for [M+H]<sup>+</sup> = C<sub>48</sub>H<sub>59</sub>N<sub>4</sub>Si<sub>2</sub>Ni<sup>+</sup>: 805.3627, found. 805.3626. Melting Point T/°C: > 300 (decomp.). Elemental analysis: Calcd. for C<sub>48</sub>H<sub>58</sub>N<sub>4</sub>Si<sub>2</sub>Ni: C, 71.54; H, 7.25; N, 6.95. Found: C, 68.20; H, 7.13; N, 6.63.

**Synthesis of [E(Terp)E]Ni(CO)**<sup>2</sup> (**E** = **P,Si**). A J. Young NMR tube was charged with 4 mg of the Ni(0) complex and 0.45 mL THF was added into the NMR tube. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar CO gas at room temperature with an immediate color change from dark red to pale yellow. After 2 minutes at room temperature, volatiles were removed under reduced pressure and the obtained pale yellow solid was subjected to an FT-IR spectroscopic analysis revealing the formation of the corresponding [Ni]CO<sub>2</sub> complexes **4-CO** and **5-CO** as indicated by two very strong IR-absorption bands. The other minor absorption band, which is observed for both complexes (**4-CO** and **5-CO**) possibly corresponds to the related 18VE Tricarbonylcomplex which is formed in small quantities in the presence of an excess CO.

### **Characterization by FT-IR spectroscopy (solid, cm<sup>-1</sup>, S1):**

**4-CO:** *ν* = 1997, 1939 (vs, CO).

**5-CO:**  $\tilde{v}$  = 1970, 1881 (vs, CO).



Fig. S1: FT-IR spectra of 4-CO (top) and 5-CO (bottom).

## 3) NMR spectra:



Fig. S2: <sup>1</sup>H NMR spectrum of bis(phosphine) 2 in C<sub>6</sub>D<sub>6</sub> at 298 K.



Fig. S3: <sup>13</sup>C NMR spectrum of bis(phosphine) 2 in C<sub>6</sub>D<sub>6</sub> at 298 K.



Fig. S5: <sup>1</sup>H NMR spectrum of bis(silylene) 3 in  $C_6D_6$  at 298 K.



Fig. S7: <sup>29</sup>Si NMR spectrum of bis(silylene) 3 in C<sub>6</sub>D<sub>6</sub> at 298 K.



Fig. S9:  $^{13}\text{C}$  NMR spectrum of Ni(0) complex 4 in  $\text{C}_6\text{D}_6$  at 298 K .



Fig. S11: <sup>1</sup>H,<sup>13</sup>C-HSQC NMR spectrum of Ni(0) complex 4 in d<sub>8</sub>-THF at 233 K .







Fig. S12:  ${}^{31}P{}^{1}H$  NMR spectrum of Ni(0) complex 4 in C<sub>6</sub>D<sub>6</sub> at 298 K.



Fig. S13: <sup>1</sup>H NMR spectrum of Ni(0) complex 5 in d<sub>8</sub>-THF at 298 K.



Fig. S14: VT-<sup>1</sup>H NMR spectrum of Ni(0) complex 5 at variable temperature in d<sub>8</sub>-THF (500 MHz).



Fig. S15:  ${}^{1}$ H, ${}^{13}$ C-HSQC NMR spectrum of Ni(0) complex 5 in d<sub>8</sub>-THF at 233 K .



Fig. S16:  $^{\rm 13}C$  NMR spectrum of Ni(0) complex 5 in d\_8-THF at 298 K .



Fig. S17: <sup>29</sup>Si NMR spectrum of Ni(0) complex 5 in d<sub>8</sub>-THF at 298 K.

## 4) UV/VIS Spectra:



Fig. S18: UV/ VIS spectra recorded in THF at 298 K of 4 and 5.

Compound	λ <sub>max</sub> [nm]
Bis(phosphine) Ni(0)-complex 4	408
Bis(silylene) Ni(0)-complex 5	442

# 5) FT-IR Spectra:







Fig. S22: FT-IR spectrum of compound 5.

## 6) ESI-MS Spectra:





### 7) Cyclic Voltammetry Measurements



Fig. 24: Top: CV of complex 4 (1 mM in THF/ 0.3 M TBAPF<sub>6</sub>) recorded at a scan rate  $v = 100 \text{ mV} \cdot \text{s}^{-1}$ showed two reversible redox events. Bottom: Reversible redox event at E<sup>1/2</sup> = -0.938 V and E<sup>1/2</sup> = - 0.472 V (vs Fc/Fc<sup>+</sup>) measured with scan rates v = 50-800 mVs<sup>-1</sup>.



Fig. 25: Top: CV of complex 5 (1 mM in THF/ 0.3 M TBAPF<sub>6</sub>) recorded at a scan rate  $v = 100 \text{ mV} \cdot \text{s}^{-1}$ showed two reversible redox events. Bottom: Reversible redox event at E<sup>1/2</sup> = -1.227 V and E<sup>1/2</sup> = -1.344 V (vs Fc/Fc<sup>+</sup>) measured with scan rates v = 50-800 mVs<sup>-1</sup>.

### 8) Reversible H<sub>2</sub>-activation by bis(silylene)Ni( $\eta^2$ -arene) 5

A J. Young NMR tube was charged with 5 mg of the Ni(0) complex and 0.45 mL d<sub>8</sub>-THF was added into the NMR tube. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> gas at room temperature upon which no color change did occur. <sup>1</sup>H-proton NMR analysis revealed the partial formation of **5**-H<sub>2</sub> with a characteristic singlet resonance at  $\delta = -1.50$  ppm (2 H) and  $\delta = +5.77$  ppm for the central arene protons (4 H). A mixture of initial Ni(0) complex **5** and **5**-H<sub>2</sub> exist in an equilibrium under these conditions. Removal of H<sub>2</sub> by successive freeze–pump– thaw cycles regenerates **5** quantitatively. This process was repeated and identical results were obtained with no indication of decomposition (S26). The <sup>29</sup>Si-NMR shifts were assigned by a <sup>1</sup>H,<sup>29</sup>Si-HMQC NMR spectrum optimized for <sup>1</sup>*J*<sub>Si,H</sub> = 45 Hz as obtained from <sup>29</sup>Si-satelites (<sup>1</sup>*J*<sub>Si,H</sub> = 44.6 Hz, S27).



Ni(0) complex **5** quantitatively.



Fig. S27: <sup>1</sup>H NMR spectrum of 5 in  $d_8$ -THF under 1 bar H<sub>2</sub> at 298 K (\* = solvent).



Fig. S28: Left:  ${}^{1}H$ ,  ${}^{29}Si$ -HMQC NMR spectra of 5 in d<sub>8</sub>-THF under 1 bar H<sub>2</sub> at 298 K.



Fig. S29: <sup>1</sup>H,<sup>13</sup>C-HSQC NMR spectrum of 5 under 1 bar H<sub>2</sub> at 193 K.



Fig. S30: <sup>29</sup>Si NMR spectra of 5 in d<sub>8</sub>-THF under 1 bar H<sub>2</sub> at 298 K.

The equilibrium constant  $k_1/k_1$  was determined using ferrocene as internal standard and was found to be  $k_1/k_1 = 0.66$ . Addition of D<sub>2</sub> at - 80 °C to a solution of **5/5-H**<sub>2</sub> inside a J. Young NMR tube resulted in fast H-D scrambling ( $\delta = 4.50$  ppm, <sup>1</sup>*J*<sub>H,D</sub> = 43 Hz) and the appearance of an additional triplet resonance signal at  $\delta = -1.24$  ppm, <sup>2</sup>*J*<sub>H,D</sub> = 4.88 Hz) corresponding to **5-HD** (S31).



Fig. S32: <sup>1</sup>H, <sup>29</sup>Si-HMQC NMR spectrum (optimized for  $J_{Si,H} = 45$  Hz) of 5 + H<sub>2</sub>/D<sub>2</sub> in d<sub>8</sub>-THF.

H,H-EXSY NMR additionally shows the expected cross-signal for the hydride-signal and dissolved H<sub>2</sub> gas in  $d_8$ -THF (S33).



Fig. S33: H,H-EXSY NMR spectrum of 5 in d<sub>8</sub>-THF under 1 bar H<sub>2</sub> at 298 K.

### T1 Time Measurement:

 $T_1$  values were measured at 298 K and 193 K on a 500 MHz spectrometer of the corresponding hydride Signal in the <sup>1</sup>H proton NMR at  $\delta$  = - 1.50 ppm in d<sub>8</sub>-THF.

Temperature [K]	<i>T</i> <sub>1</sub> [ms]
298	1080
193	930

Variable temperature <sup>1</sup>H NMR analysis was performed of **5** in the range of T = 298 K to T = 198 K in d<sub>8</sub>-THF under 1 bar H<sub>2</sub> pressure (left) and in the presence of a mixture of H<sub>2</sub>/D<sub>2</sub> (right). The temperature dependency of the hydride resonance signal at  $\delta$  = -1.50 ppm is shown in Fig. 34. Coalescence was observed at T<sub>c</sub> = 233 K. At T = 198 K two doublets resonances are obtained corresponding to two inequivalent H atoms (H<sup>A</sup>, H<sup>B</sup>) at low temperature which equilibrate at higher temperature.







Fig. S34: VT <sup>1</sup>H NMR spectrum of 5 under 1 bar H<sub>2</sub> (left) and additional D<sub>2</sub> (right) in d<sub>8</sub>-THF.



Fig. S35: <sup>1</sup>H NMR spectrum of  $5 + H_2$  and  $D_2$  gas in d<sub>8</sub>-THF at 193 K.



Fig. S36: <sup>1</sup>H NMR spectrum of 5 in d<sub>7</sub>-toluene under 1 bar H<sub>2</sub> at 298 K.

Calculation of the free energy of activation  $\Delta G^{\#}$ 



The exchange nuclei have mutual coupling ( $J_{H,H}$ ) and the following expression was used to calculate  $k_{233}$  with  $\Delta v = 99.5$  Hz and  $J_{H,H} = 30.9$  Hz from the <sup>1</sup>H NMR spectra obtained at 193 K on a 500 MHz spectrometer:

$$k_{233} = 2.22 \sqrt{\Delta v^2 + 6(J_{\rm H,H})^2}$$
  
 $k_{233} = 275 \, {\rm s}^{-1}$ 

The free energy of activation  $\Delta G^{\#}$  was calculated based on the following expression with T<sub>c</sub> = 233 K and  $k_{233}$  = 275 s<sup>-1</sup>:

$$\Delta G^{\#} = 4.58 \cdot T_c \cdot \left(10.32 + \log \frac{T_c}{k_{233}}\right)$$
$$\Delta G^{\#} = 10.9 \text{ kcal/mol} (44.6 \text{ kj/mol})$$

### 9) Hydrogenation of Olefins

**General Procedure for Olefin Hydrogenation.** A stock solution was used containing ferrocene (0.022 mmol/0.45 mL) and catalyst **5** (1.1  $\mu$ mol/0.45 mL, 2 mol%). From the stock solution, 0.45 mL were taken and transferred into a sealed J. Young NMR tube and olefin (0.054 mmol) was added. Prior to H<sub>2</sub> addition, a <sup>1</sup>H NMR was recorded. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The reaction progress was further monitored by <sup>1</sup>H NMR analysis.

**Mercury Drop Test.** In a 3 mL vial, norbornene (21.0 mg, 0.223 mmol), ferrocene (17 mg, 0.091 mmol) and catalyst **5** were dissolved in 2 mL C<sub>6</sub>D<sub>6</sub>. The red solution was transferred into a 25 mL Schlenk tube containing a stir bar. The solution was frozen in liquid nitrogen and mercury (250 mg, 1.15 mmol) was added under a N<sub>2</sub> atmosphere. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature and stirred for 14 h. Conversion was determined by <sup>1</sup>H NMR analysis. A full conversion (>99 %) was achieved in the presence of Hg, indicating a homogeneous reaction. However, decomposition was observed resulting in decoloration and formation of a black solid. When Ni(0) complex **5** is exposed to mercury (exc.) inside a sealed J. Young NMR tube. Slow decomposition was observed in the absence and presence of 1 bar H<sub>2</sub> gas in d<sub>8</sub>-THF resulting in decoloration and the formation of a black solid. In the absence of mercury, **5** and **5-H**<sub>2</sub> are stable in solution and show no decomposition within 7 days at room temperature.

**Hydrogenation of 1,1-diphenylethylene.** In a 3 mL vial, 1,1-diphenylacetylene (48.0 mg, 0.27 mmol) and catalyst **5** (0.5 mol%, 1.1 mg, 1.35  $\mu$ mol) were dissolved in 2 mL C<sub>6</sub>D<sub>6</sub>. The red solution was transferred into a 25 mL Schlenk tube containing a stir bar. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature and stirred for 24 h. The mixture was filtered through silica and rinsed with additional Et<sub>2</sub>O (1 mL). The solvent was removed affording 1,1-diphenylethane as colorless oil (43 mg, 0.24 mmol, 89 %).

#### Catalyst comparison in nbe hydrogenation.

Two 3 mL vials were charged with Ni(0) catalyst (1.1  $\mu$ mol, 2 mol%), ferrocene (0.022 mmol) and norbornene (0.054 mmol). The mixture was dissolved in 0.45 mL C<sub>6</sub>D<sub>6</sub> and transferred into a sealed J. Young NMR tube. Prior to H<sub>2</sub> addition, a <sup>1</sup>H NMR was recorded. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The reaction progress was further monitored by <sup>1</sup>H NMR analysis. Data points were fitted with a linear function (R<sup>2</sup> = 0.97).



**Fig. S37**: Reaction profile of Ni(0) catalyzed nbe hydrogenation inside a sealed J. Young NMR tube under 1 bar H<sub>2</sub> at 298 K.

Bis(silylene) complex **5** catalyzes the hydrogenation of norbornene 12 times faster compared to bis(phosphine) complex **4** under identical reaction conditions. Thus, 120 h were needed to reach full conversion using 2 mol% of **4**.



**Fig. S39:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 3,3-dimethyl1-1butene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 3h (bottom).



**Fig. S40:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing allylbenzene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 5 h (bottom).



**Fig. S41:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 3-methylenepentane, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 18 h (bottom).



**Fig. S42:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 2,3-dimethyl-1,3butadiene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 22 h (bottom).



**Fig. S43:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing norbornene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 14 h (bottom).



**Fig. S44:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing tetramethylethylene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 22 h (bottom).



**Fig. S45:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 2-cyclohexen-1-one, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 12 h (bottom).



**Fig. S46:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing methyl methacrylate, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 12 h (bottom).



**Fig. S47:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 5-hexen-2-one, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 12 h (bottom).



**Fig. S48:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing *trans*-stilbene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 72 h (bottom).



**Fig. S49:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing  $\beta$ -methylstilbene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 96 h (bottom).







**Fig. S51:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 4-methoxystyrene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 3 h (bottom).



**Fig. S52:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing styrene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 8 h (bottom).



**Fig. S53:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 4-chorostyrene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 14 h (bottom).



**Fig. S54:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing4-(trifluoromethyl)styrene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 16 h (bottom).



**Fig. S55:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 4-(cyano)styrene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 7 h (bottom).



**Fig. S56:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 1,4-cyclohexadiene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 28 h (bottom).



**Fig. S57:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing 1*H*-Indene, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 42 h (bottom).



**Fig. S58:** <sup>1</sup>H NMR spectrum of the reaction mixture prior H<sub>2</sub> addition containing benzofurane, ferrocene and 2 mol% catalyst **5** (top). <sup>1</sup>H NMR spectrum under 1 bar H<sub>2</sub> after 72 h (botto

### 10) Mechanistic study / kinetic analysis:

### Sub-stoichiometric experiments using 5 and norbornene.

A J. Young NMR tube was charged with 5.6 mg of the Ni(0) complex, 3.3 mg of norbornene (Nbe) and 0.45 mL d<sub>8</sub>-THF was added into the NMR tube resulting in a homogeneous dark red solution. <sup>1</sup>H-proton NMR analysis revealed the partial formation of **5-nbe** with a characteristic pattern in the hydride region at  $\delta = -0.32$  ppm and  $\delta = -0.52$  ppm similar to those of literature known Ni(nbe) adducts. <sup>[S2]</sup>



Fig. S59: <sup>1</sup>H NMR spectrum of 5 + 5 equiv. norbornene in d<sub>8</sub>-THF at 298 K (\* = solvent).

After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> gas at room temperature upon which no color change did occur. <sup>1</sup>H-proton NMR analysis revealed the partial formation of **5-H**<sub>2</sub>. Hydrogenation reaction under these conditions is very slow and 2 hours were needed to reach full conversion. Integration of the resonances indicates a ratio of **5(nbe)** ( $\sigma$  = - 0.32/-0.52 ppm, 2H) and **5(H**<sub>2</sub>) (2H) of 3:1 (S63) suggesting **5-nbe** as catalytic active resting state. The hydride-shift was obtained at  $\delta$  = - 1.49 ppm (**5-H**<sub>2</sub>) exhibiting sharp <sup>29</sup>Si satellites (<sup>1</sup>*J*<sub>Si,H</sub> = 44.6 Hz) after full conversion.



Fig. S60: <sup>1</sup>H NMR spectrum of 5 + 5 equiv. norbornene in d<sub>8</sub>-THF at 298 K under 1 bar H<sub>2</sub> pressure.



**Fig. S61:** Hydridic region of the <sup>1</sup>H NMR spectrum of **5** + 5 equiv. norbornene in d<sub>8</sub>-THF at 298 K under 1 bar H<sub>2</sub> pressure.

Then, 20 equiv. of Nbe was added and the experiment was repeated. After full conversion, the same results were obtained with no observable catalyst degradation.



Fig. S62: <sup>1</sup>H NMR spectrum of 5 + 20 equiv. norbornene in d<sub>8</sub>-THF at 298 K under 1 bar H<sub>2</sub> pressure.



**Fig. S63:** <sup>1</sup>H, <sup>29</sup>Si HMQC NMR spectrum (optimized for  $J_{Si,H} = 4$  Hz) after hydrogenation of 25 equiv. of norbornene with catalyst **5** as only detectable specie.



**Fig. S64:** <sup>1</sup>H NMR spectrum of norbornene hydrogenation using 2 mol% of catalyst **5** after full conversion showing no decomposition and the appearance of **5-H**<sub>2</sub>.

### Kinetic isotope effect:

Two NMR-samples were prepared, each containing 2 mol% of **5** (0.8 mg, 1.1  $\mu$ mol) from a stock solution in C<sub>6</sub>D<sub>6</sub> containing ferrocene as internal standard (0.022 mmol, 4 mg) and norbornene (0.054 mmol, 5 mg). <sup>1</sup>H-NMR spectra were obtained at regular intervals approx. 1 h and the NMR tubes were shaken after each measurement. The concentration of norbornene was plotted against time and the data points were fitted with a linear function (R<sup>2</sup> = 0.98/0.99).



Fig. S65: Reaction profile of nbe reduction using  $H_2/D_2$  for KIE determination.

The KIE was calculated using the following equation:

$$KIE = \frac{k_H}{k_D} = \frac{-9.96}{-11.78} = 0.85$$

#### **TOF / TON measurement**

A mixture of norbornene (**9f**, 1.07 mmol), ferrocene (0.43 mmol, internal standard) and **5** (1.07  $\mu$ mol) was prepared inside a 3 mL vial and dissolved in 3 mL C<sub>6</sub>D<sub>6</sub>. The obtained red solution was transferred to a 25 mL Schlenk tube containing a stir bar. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The stir bar rotation was set at 1400 min<sup>-1</sup>. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy by removal of 0.1 mL from the reaction mixture.



Fig. S66: Reaction profile of nbe hydrogenation using 0.1 mol% cat. 5 in C<sub>6</sub>D<sub>6</sub> inside a Schlenk tube.

A full conversion was achieved after 5.8 h using 0.1 mol% of catalyst **5** resulting in an TON of TON = 1000 and TOF = 170 h<sup>-1</sup>, respectively. The same experiment was conducted using 3.72 mmol norbornene in a 100 mL Schlenk tube resulting in a full conversion after 22 h (TON = 3700) with a comparable turn over frequency of TOF = 160 h<sup>-1</sup>.

When 3,3-dimethyl-1-butene (**9a**) is employed as olefin (4.35 mmol, 250 mL Schlenk tube), a TON value of TON = 4350 was achieved within 14 h (conv. >99 %, TOF =  $320 h^{-1}$ ). For the TON<sub>MAX</sub> determination, 1.2 mL (9.31 mmol) 3,3-dimethyl-1-butene (**9a**) in d<sub>8</sub>-THF (1.0 mL) was exposed to 1 bar H<sub>2</sub>. After 48 h, a TON value of TON<sub>MAX</sub> = 9800 was achieved (conv. 98 %).

### Determination of Reaction order in [olefine], [Ni]

Two NMR-samples were prepared, each containing 2 mol% of **5** (0.8 mg, 1.1  $\mu$ mol) from a stock solution in C<sub>6</sub>D<sub>6</sub> containing ferrocene as internal standard (0.022 mmol, 4 mg) and 5 / 2.5 mg of norbornene. Prior to H<sub>2</sub> addition, a <sup>1</sup>H NMR was recorded. After addition of H<sub>2</sub>, <sup>1</sup>H-NMR spectra were obtained at intervals of approx. 1 h. The concentration of norbornene was plotted against time (8 hours) and the data points were fitted with a linear function (R<sup>2</sup> > 0.98).

c₀ (Nbe)	TON
104 mM	27
51 mM	25

For both concentrations of nbe, a very similar TON was observed within 8 hours. We conclude, that the reaction is 0. order in [Olefin]. The TOF value after >99% conversion was the same  $(3.2 h^{-1})$ . We conclude, that the reaction is 1. order in [**5**].



Fig. S67: Rate dependence on the olefin concentration c(olefin) which is 0. order and 1. Order in [5].

#### Determination of Reaction order in [H<sub>2</sub>]

Three solutions were prepared, each containing 0.5 mol% of **5** (1.1 µmol) from a stock solution in C<sub>6</sub>D<sub>6</sub> (1.5 mL) containing ferrocene as internal standard (0.088 mmol, 16 mg) and 20 mg of norbornene. The solutions were subjected to different H<sub>2</sub> pressures (1.0, 2.0, 3.0 bar) inside a Schlenk tube containing a stir bar after three freeze-pump-thaw cycles. During hydrogenation, the H<sub>2</sub>-cylinder was directly attached to the Schlenk tube to ensure a constant H<sub>2</sub> pressure. After t = 10 min, 0.1 mL of the reaction mixture were removed and analyzed by <sup>1</sup>H NMR spectroscopy. The conversion of norbornene was plotted against the H<sub>2</sub>-pressure and the data points were fitted with a linear function. A linear correlation was obtained (R<sup>2</sup> = 0.98). We conclude, that the reaction is 1. order in [H<sub>2</sub>].



Fig. S68: Obtained alkane concentration at different H<sub>2</sub> pressure after t = 10 min.

### Calculation of the experimental date law:

The overall reaction rate can be expressed by the following equation based on our experimental findings discussed above:

$$[Alkane]_t = -k[Ni][H_2]$$

The Henry's constant used for the calculation of [H<sub>2</sub>] in benzene is  $k_{\rm H} = 341$  Mpa.<sup>[21]</sup>

Pressure [Mpa]	Xi	Conc. H <sub>2</sub> [mol/L]
0.1	2,931·10 <sup>-4</sup>	3.42·10 <sup>-3</sup>
0.2	5,86·10 <sup>-4</sup>	6.84·10 <sup>-3</sup>
0.3	8,79·10 <sup>-4</sup>	10.26·10 <sup>-3</sup>

With [Ni] = 0.00018 mol/L and k = 0.7451 L/mol·min.



Fig. S69: Obtained data using different H<sub>2</sub> pressure after 10 min.

The overall experimental rate law is  $v = k[\mathbf{5}][H_2]$  where k = 69 M<sup>-1</sup>·sec<sup>-1</sup>.

### Hammet-Plot analysis

Four solutions were prepared in a vial, each containing 0.5 mol% of **5** (1.1 µmol) from a stock solution in C<sub>6</sub>D<sub>6</sub> (1.5 mL) containing ferrocene as internal standard (0.088 mmol, 16 mg) and *para*-substituted styrene derivatives (0.216 mmol). The solutions were transferred into a 10 mL Schlenk tube containing a stir bar. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy by removal of 0.1 mL from the reaction mixture within the first 3 hours. Data points were fitted with a linear function ( $R^2 = 0.99$ ).



Fig. S70: Generated Hammet-Plot from conversion of different substituted para-styrene derivatives.

#### Solvent effect

Two vials were prepared, each containing 0.5 mol% of **5** (0.8 mg, 1.1 µmol) and ferrocene as internal standard (0.088 mmol, 16 mg). After dissolving the mixture in C<sub>6</sub>D<sub>6</sub> / d<sub>8</sub>-THF (1.5 mL), 4-methoxystyrene (0.216 mmol) was added and the solutions were transferred into a 10 mL Schlenk tube containing a stir bar. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy by removal of 0.1 mL from the reaction mixture. Full conversion was indicated by a color change from orange to red as the catalyst is regenerated after full conversion. <sup>1</sup>H NMR analysis revealed a full hydrogenation of the olefin. [olefin] was plotted against time and the data points were fitted with a linear function (R<sup>2</sup> = 0.99).

Solv.	Time [min], conv. > 99%	TON	TOF [h <sup>-1</sup> ]
$C_6D_6$	62	200	200
dଃ-THF	43	200	334



Fig. S71: Determination of solvent effect using benzene and THF on 4-methoxystyrene hydrogenation.

### Cycling Experiment on 3,3-dimethyl-1-butene hydrogenation

A stock solution was used containing ferrocene (0.022 mmol/0.45 mL) and catalyst **5** (1.1  $\mu$ mol/0.45 mL, 2 mol%). From the stock solution, 0.45 mL were taken and transferred into a sealed J. Young NMR tube and 3,3-dimethyl-1-butene (6.9  $\mu$ L, 0.054 mmol) was added. Prior to H<sub>2</sub> addition, a <sup>1</sup>H NMR spectrum was recorded. After three freeze-pump-thaw cycles, the solution was subjected to 1 bar H<sub>2</sub> at room temperature. The reaction progress was further monitored by <sup>1</sup>H NMR analysis. After 3 h, full conversion was achieved (Cycle 1). The experiment was repeated upon addition of another portion of 3,3-dimethyl-1-butene (6.9  $\mu$ L, 0.054 mmol) (Cycle 2) resulting in a quantitative hydrogenation after 3 h. After the second portion, no catalyst degradation was observed leading to the observation of **5-H**<sub>2</sub>.



**Fig. S72:** <sup>1</sup>H NMR spectrum of the reaction mixture prior  $H_2$  addition containing 3,3-dimethyl-1-butene, ferrocene and 2 mol% catalyst **5** (top). After complete hydrogenation (t = 3 h), 50 equiv. of olefin was added and hydrogenated within 3 hours.

## 11) Crystallographic Data



Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

### Volume Z

Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges **Reflections collected** Independent reflections Completeness to theta = 67.42° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

C38 H48 N4 P2 574.70 150(2) K 1.54184 Å triclinic P-1 a = 7.5552(5) Å  $\alpha = 76.651(5)^{\circ}$ . b = 9.5169(6) Å  $\beta = 84.110(5)^{\circ}$ . c = 11.8279(6) Å  $\gamma = 72.543(6)^{\circ}$ . 788.85(9) Å<sup>3</sup> 1 1.210 Mg/m<sup>3</sup> 1.463 mm<sup>-1</sup> 310 0.640 x 0.220 x 0.120 mm<sup>3</sup> 3.843 to 67.486°. -8<=h<=8, -10<=k<=11, -14<=l<=14 4857 2831 [R(int) = 0.0156] 99.7 % Semi-empirical from equivalents 1.00000 and 0.45220 Full-matrix least-squares on F<sup>2</sup> 2831 / 0 / 185 1.050  $R_1 = 0.0377$ ,  $wR_2 = 0.1020$  $R_1 = 0.0396$ ,  $wR_2 = 0.1039$ 0.339 and -0.364 e.Å<sup>-3</sup>



Empirical formula C<sub>48</sub> H<sub>58</sub> N<sub>4</sub> Si<sub>2</sub> 747.16 Formula weight 150(2) K Temperature Wavelength 0.71073 Å Crystal system monoclinic C2/c Space group Unit cell dimensions a = 25.0720(15) Å  $\alpha = 90^{\circ}$ . b = 9.1667(4) Å  $\beta = 99.889(6)^{\circ}$ . c = 19.7603(11) Å  $v = 90^{\circ}$ . 4716.67(13) Å<sup>3</sup> Volume Ζ 4 1.109 Mg/m<sup>3</sup> Density (calculated) 0.115 mm<sup>-1</sup> Absorption coefficient F(000) 1608 0.210 x 0.060 x 0.030 mm<sup>3</sup> Crystal size 2.092 to 26.230° Theta range for data collection Index ranges -31<=h<=30, -11<=k<=11, -23<=l<=24 **Reflections collected** 16755 Independent reflections 4440 [R(int) = 0.0793 Completeness to theta = 67.42° 99.9 % Absorption correction Semi-empirical from equivalents 1.00000 and 0.45220 Max. and min. transmission Full-matrix least-squares on F<sup>2</sup> Refinement method Data / restraints / parameters 4440 / 66 / 302 Goodness-of-fit on F<sup>2</sup> 1.023 Final R indices [I>2sigma(I)]  $R_1 = 0.0632$ ,  $wR_2 = 0.1412$  $R_1 = 0.1185$ ,  $wR_2 = 0.1746$ R indices (all data) 0.337 and -0.198 e.Å-3 Largest diff. peak and hole



Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges **Reflections collected** Independent reflections Completeness to theta =  $67.42^{\circ}$ Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F<sup>2</sup> Final R indices [I>2sigma(I)] R indices (all data) Largest diff. peak and hole

C55 H66 N4 Ni Si2 898.01 150.00(10) K 1.54184 Å monoclinic P21/m a = 9.1662(5) Å  $\alpha = 90^{\circ}$ . b = 26.4418(13) Å  $\beta = 90.567(5)^{\circ}$ . c = 9.8935(6) Å $y = 90^{\circ}$ . 2397.8(2) Å<sup>3</sup> 2 1.244 Mg/m<sup>3</sup> 1.366 mm<sup>-1</sup> 960 0.32 x 0.08 x 0.08 mm<sup>3</sup> 4.47 to 67.49°. --10<=h<=10, -29<=k<=31, -7<=l<=11 7952 4355 [R(int) = 0.0390] 98.8 % Semi-empirical from equivalents 0.8986 and 0.6721 Full-matrix least-squares on F<sup>2</sup> 4355 / 549 / 529 1.194  $R_1 = 0.0982$ ,  $wR_2 = 0.2212$  $R_1 = 0.1221$ ,  $wR_2 = 0.2417$ 3.847 and -0.989 e.Å<sup>-3</sup>



Empirical formula Formula weight Temperature Wavelength	C <sub>34</sub> H <sub>48</sub> N <sub>4</sub> Ni P <sub>2</sub> 633.41 150(2) K 1.54184 Å		
Crystal system Space group	triclinic P-1		
Unit cell dimensions	a = 10.1955(3) Å b = 10.3773(3) Å c = 16.0898(6) Å	$\begin{split} \alpha &= 76.412(3)^\circ.\\ \beta &= 80.446(3)^\circ.\\ \gamma &= 88.451(3)^\circ. \end{split}$	
Volume Z	1631.60(9) Å <sup>3</sup> 2		
Density (calculated)	1.289 Mg/m <sup>3</sup>		
Absorption coefficient F(000)	1.998 mm <sup>-1</sup> 676		
Crystal size	0.340 x 0.320 x 0.190 r	nm <sup>3</sup>	
Theta range for data collection Index ranges 19<=I<=19Reflections collected Independent reflections	2.864 to 67.499°. -12<=h<=12, -12<=k<= 10913 5876 [R(int) = 0.0211]	12, -	
Completeness to theta = $67.42^{\circ}$	99.8 %		
Absorption correction Max. and min. transmission	orption correction Semi-empirical from equivalents 1.00000 and 0.45220		
Refinement method Data / restraints / parameters	Full-matrix least-squares on F <sup>2</sup> 5876 / 0 / 390		
Goodness-of-fit on F <sup>2</sup>	1.050		
Final R indices [I>2sigma(I)] R indices (all data)	$\begin{array}{l} R_1 = 0.0326, \ wR_2 = 0.0 \\ R_1 = 0.0348, \ wR_2 = 0.0 \end{array}$	0.0326, wR <sub>2</sub> = 0.0856 0.0348, wR <sub>2</sub> = 0.0870	
Largest diff. peak and hole	0.311 and -0.417 e.Å <sup>-3</sup>		

## 12) References:

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[S2] J. S. Bair, Y. Schramm, A. G. Sergeev, E. Clot, O. Eisenstein, J. F. Hartwig, *J. Am. Chem. Soc.* 2014, 136, 13098-13101.