Supporting Information for:

A Ni\(^{\theta}(\eta^2\text{-SiH})(\eta^2\text{-H}_2)\) Complex that Mediates Facile H Atom Exchange Between Two \(\sigma\)-Ligands

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**General Considerations.** Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under an N₂ atmosphere. Solvents were deoxygenated and dried by thoroughly sparging with N₂ gas followed by passage through an activated alumina column in a solvent purification system from SG Water, LLC, USA. Nonhalogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. NEt₃ was degassed and dried over activated 3 Å molecular sieves prior to use. KC₈¹ and [(SiP₂)₂O]H₂² were synthesized following literature procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 3 Å molecular sieves prior to use. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN.

**HD Gas Generation.** A Schlenk tube containing D₂O (0.3 mL) was freeze–pump–thawed three times and the D₂O was then vacuum transferred to an evacuated, cooled sample (77 K) of solid lithium aluminum hydride (200 mg) in a Schlenk tube. The Schlenk tube was slowly warmed to room temperature, filling an evacuated Schlenk line with the resulting HD gas (ca. 1 atm). A J-Young NMR tube containing a freeze–pump–thawed solution of 2 cooled to 77 K was exposed to the HD gas.

**NMR Spectroscopy.** ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectra were collected at room temperature, unless otherwise noted, on Varian 300 MHz, 400 MHz, and 500 MHz NMR spectrometers and Bruker 400 MHz NMR spectrometers. All spectra were referenced according to IUPAC recommendations.³

**IR Spectroscopy.** Thin-film and solid-state IR spectra were obtained on a Bruker Alpha spectrometer equipped with a diamond ATR probe.

**X-ray Crystallography.** XRD studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer (Mo Kα radiation). Structures were solved using SHELXS and refined against F² on all data by full-matrix least-squares with SHELXL. The crystals were mounted on a glass fiber under Paratone N oil.

**DFT Calculations.** Geometry optimizations, frequency calculations, and transition state IRC calculations were performed using the Gaussian09 package.⁴ The full structures of 3-2H and isomers I and II of 3-6H were optimized using the BP86 exchange-correlation functional with a 6-31G(d) basis set and the minimized structures were verified with frequency calculations. These calculations gave no evidence of metal-metal interaction so the monometallic analogues (with one half of the dimer substituted with an O-bound TMS group) were re-optimized and the minimized structures again verified with frequency calculations. A transition state search was begun using the optimized half-dimers ([SiHp₂O-TMS]Ni(H₂) and [SiP₂O-TMS]Ni(H₂)(H)) as inputs for starting and ending points for the Synchronous Transit-guided Quasi-Newton method (keyword QST3). Frequency calculations confirmed the optimization to a true saddle point indicating one imaginary frequency (–495.07 cm⁻¹). An intrinsic reaction coordinate calculation was then used to ensure that the identified transition state lies along the interconversion pathway of the two isomers.

In contrast to our experimental results, the BP86 exchange-correlation functional predicted isomer II to be 0.06 kcal/mol more stable than isomer I. We suspected that the M06L exchange-
correlation functional might give results more in-line with our experimental observations so we re-optimized the structures of isomers I and II using this functional and confirmed the minimized structures with frequency calculations.

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\text{[(SiP}_2\text{O)]Ni}_2(\text{Cl})_2 (1-\text{Cl}). \text{[(SiP}_2\text{O)]H}_2 (95.3 \text{ mg, 0.112 mmol) was dissolved in THF (2 mL) and combined with a suspension of NiCl}_2\cdot\text{DME (81.5 mg, 0.371 mmol) in THF (2 mL). NEt}_3 (150 \text{ mg, 1.5 mmol) was added dropwise to the resulting stirred suspension. The reaction was stirred for 6 hours at room temperature then solvent was removed in vacuo and the product was taken up in benzene and filtered through Celite. Subsequent lyophilization and trituration with pentane yielded 1-Cl (92.5 mg, 89.5 \text{ \mu mol, 80\%}) as a yellow-orange powder. Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of 1-Cl in benzene. Elemental analysis was not conducted for 1-Cl; 1-Br was prepared and purified in an identical fashion and combustion analysis data was collected on this species.} \text{^1H NMR (CD}_6\text{D}_6, 300 \text{ MHz, 25 \degree C, ppm): \delta 7.45 (4H, m, Ar-H), 7.27 (4H, m, Ar-H), 7.13 (8H, m, Ar-H), 2.55 (4H, m, methine C-H), 2.24 (4H, m, methine C-H), 1.48 (12H, m, methyl C-H), 1.24 (24H, m, methyl C-H), 0.96 (12H, m, methyl C-H).} \text{^{31}P^{[1]}H NMR (CD}_6\text{D}_6, 121 \text{ MHz, 25 \degree C, ppm): \delta 60.20 (s).} \text{^{25}Si^{[1]}H NMR (CD}_6\text{D}_6, 79 \text{ MHz, 25 \degree C, ppm): \delta 43.55 (t, J_{Si,P} = 35.5 Hz).}
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\text{[(SiP}_2\text{O)]Ni}_2(\text{Br})_2 (1-Br). \text{[(SiP}_2\text{O)]H}_2 (105 mg, 0.124 mmol) was dissolved in THF (2 mL) and combined with a suspension of NiBr}_2\cdot\text{DME (81.5 mg, 0.264 mmol) in THF (2 mL). NEt}_3 (150 mg, 1.5 mmol) was added dropwise to the resulting stirred suspension causing a color change from greenish to orange. The reaction was stirred overnight at room temperature. Solvent was removed in vacuo and the product was taken up in benzene and filtered through Celite. Subsequent lyophilization and trituration with pentane yielded 1-Br (130.6 mg, 0.116 mmol, 94\%) as a yellow-orange powder.} \text{^1H NMR (CD}_6\text{D}_6, 400 \text{ MHz, 25 \degree C, ppm): \delta 7.53 (4H, m, Ar-H), 7.29 (4H, m, Ar-H), 7.13 (8H, m, Ar-H), 2.50 (8H, m, methine C-H), 1.46 (12H, m, methyl C-H), 1.21 (24H, m, methyl C-H), 0.89 (12H, m, methyl C-H).} \text{^{31}P^{[1]}H NMR (CD}_6\text{D}_6, 121 \text{ MHz, 25 \degree C, ppm): \delta 61.37 (s).} \text{^{25}Si^{[1]}H NMR (CD}_6\text{D}_6, 79 \text{ MHz, 25 \degree C, ppm): \delta 45.84 (t, J_{Si,P} = 34.0 Hz).} \text{Anal. Calc. for C}_{48}\text{H}_{72}\text{Br}_2\text{Ni}_2\text{O}_4\text{P}_4\text{Si}_2: C, 51.37; H, 6.47. Found: C, 51.24; H, 6.52.}
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\text{[(SiP}_2\text{O)]Ni}_2(2) (1-Br) (210.4 mg, 0.187 mmol) was dissolved in THF (6 mL) and combined with KCI (52.9 mg, 0.391 mmol). The reaction was stirred for 10 hours at room temperature and then filtered through Celite yielding a deep red-brown solution. Solvent was removed in vacuo and the product was washed with pentane (3 x 2 mL). Crystals (suitable for X-ray diffraction) were grown by diffusion of pentane into a THF solution of this material, yielding bright orange crystals of 2 (101.1 mg, 0.105 mmol, 56\%). The mother liquor was decanted, evaporated to dryness in vacuo and the residue was washed with pentane (3 x 2 mL). Subsequent recrystallization of the orange powder yielded an additional batch of crystals (15.1 mg, 15.7 \mu mol, 64\% overall yield).} \text{^1H NMR (CD}_6\text{D}_6, 400 \text{ MHz, 25 \degree C, ppm): \delta 8.46 (2H, d, J_{H,H} = 7.3 Hz, Ar-H), 8.41 (2H, d, J_{H,H} = 7.6 Hz, Ar-H), 7.43 (2H, m, Ar-H), 7.27 (2H, d, J_{H,H} = 7.9 Hz, Ar-H), 7.18 (2H, m, Ar-H), 7.06 (6H, m, Ar-H), 3.63 (2H, m, methine C-H), 2.44 (4H, m, methine C-H), 1.74 (8H, m, overlapping methine (2H) and methyl (6H) C-H), 1.64 (6H, dd, J_{H,H} = 7.41 Hz, J_{H,P} = 15.72 Hz, methyl C-H), 1.47 (6H, dd, J_{H,H} = 6.89 Hz, J_{H,P} = 9.10 Hz, methyl C-H), 1.29 (6H, m, methyl C-H), 0.87 (18H, m, methyl C-H), 0.13 (6H, m, methyl C-H).} \text{^1H–^{13}C HSQC (400 MHz, CD}_2\text{D}_2) \delta (8.46 (Ar-H), 135.42), (8.41 (Ar-H), 133.96), (7.43 (Ar-H), 129.04), (7.27 (Ar-H), 129.59), (7.18 (Ar-H), 129.38), (7.06 (Ar-H), 127.88), (3.63 (methine C-H), 37.32), (2.44 (methine C-H), 26.16), (2.45 (methyl C-H), 29.96), (1.74 (methine C-H), 31.08), (1.74 (methyl C-H), 31.08), (1.64 (methyl C-H), 26.16), (1.47 (methyl C-H), 22.30), (1.29
[(SiP₂)₂O]Ni₂(H)₂ (3-2H). 2 (7 mg, 7.27 µmol) was dissolved in C₆D₆ (0.5 mL) in a J. Young tube. The solution was freeze-pump-thawed twice to remove any N₂ and then exposed to 1 atm H₂. Over the course of six hours of stirring at room temperature, a gradual color change from bright orange to yellow was observed. After this time, the solution was freeze-pump-thawed three times cleanly yielding 3-2H as observed by ¹H and ³¹P NMR spectroscopy. It should be noted that this compound could also be accessed by exposure of 2 to higher pressures of H₂ followed by three freeze-pump-thaw cycles. Under these conditions, 2 reacted more rapidly with H₂ (2 hours under 3.9 atm, 3 hours under 2.1 atm). 3-2H was only stable under vacuum, preventing collection of elemental analysis data. An IR spectrum was obtained by lyophilizing a solution of 3-2H and quickly taking an IR of the solid under an N₂ atmosphere. ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 7.76 (4H, m, Ar-H), 7.40 (4H, m, Ar-H), 7.21 (8H, m, Ar-H), 2.39 (4H, m, methine C-H), 1.99 (4H, m, methine C-H), 1.48 (12H, m, methyl C-H), 1.07 (24H, m, methyl C-H), 0.65 (12H, m, methyl C-H), -4.00 (2H, br s, Ni-H). ¹H NMR (C₇D₇, 500 MHz, -90 °C, ppm): δ -3.83 (t, 2Jₚ-H = 45.25 Hz, Ni-H). ³¹P {¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 90.87 (s). ³¹P {¹H} NMR (C₆D₆, 202 MHz, -90 °C, ppm): δ 94.67 (m). ²⁹Si {¹H} NMR (C₆D₆, 99 MHz, -90 °C, ppm): δ 59.97 (t, 2Jₛ-P = 31.98 Hz). ²⁹Si NMR (C₆D₆, 99 MHz, -90 °C, ppm): δ 60.02 (br s). IR (solid): ν(NiH) = 1701 cm⁻¹, ν(NiD) = 1234 cm⁻¹.

**General procedure for the generation of mixtures of 3-2H, 3-4H, and 3-6H.** 2 (7 mg, 7.27 µmol) was dissolved in C₆D₆ (0.5 mL) in a J. Young tube. The solution was freeze-pump-thawed twice to remove any N₂ and then exposed to the desired pressure of H₂ (1 atm, 2.1 atm, 3.9 atm, 12.6 atm). Pressures of 2.1 atm and 3.9 atm were achieved by cooling the J. Young tube to -131 °C and -196 °C, respectively, and then exposing to a constant flow of H₂ for 1 min. A pressure of 12.6 atm was achieved using a high pressure sapphire NMR tube. The reaction was stirred until completion—6 hours for 1 atm, 3 hours for 2.1 atm, 2 hours for 3.9 atm, and 1 hour for 12.6 atm. It should be noted that an equilibrium mixture of 3-2H, 3-4H, and 3-6H was also accessible through re-exposure of 3-2H to H₂ pressure. It should be noted that since 3-4H and 3-6H only exist under H₂ pressure, we were unable to collect elemental analysis data.

**2 + 1 atm H₂.** ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 7.89 (4H, m, Ar-H), 7.37 (4H, m, Ar-H), 7.18 (8H, m, Ar-H), 2.32 (4H, m, methine C-H), 2.05 (4H, m, methine C-H), 1.28 (12H, m, methyl C-H), 1.05 (24H, m, methyl C-H), 0.73 (12H, m, methyl C-H), -2.27 (4.36H, br s, averaged hydrides and free H₂). ¹H NMR (C₇D₇, 500MHz, -90 °C, ppm): δ -1.86 (br s, Ni-H₂), -3.03 (br s, Ni-H-Si), -3.81 (t, 2Jₚ-H = 45.1 Hz, Ni-H). ³¹P {¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 82.97 (s). ³¹P {¹H} NMR (C₆D₆, 202 MHz, -90 °C, ppm): δ 90.54 (m), 64.75 (br s), 57.61 (br s). ²⁹Si {¹H} NMR (C₆D₆, 99 MHz, -90 °C, ppm): δ 59.82 (br s), 1.76 (s).

**2 + 2.1 atm H₂.** ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 8.00 (4H, d, ³¹J_H-H = 7.1Hz, Ar-H), 7.35 (4H, d, ³¹J_H-H = 7.1Hz, Ar-H), 7.1-7.21 (8H, m, Ar-H), 2.25 (4H, m, methine C-H), 2.08 (4H, m, methine C-H), 1.09 (24H, m, methyl C-H), 0.98 (12H, m, methyl C-H), 0.80 (12H, m, methyl C-H), -1.27 (5.54H, br s, averaged hydrides and free H₂). ³¹P {¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 77.23 (s).
2 + 3.9 atm H₂. ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 8.08 (4H, d, J₃H-H = 7.0 Hz, Ar-H), 7.33 (4H, d, J₃H-H = 7.4 Hz, Ar-H), 7.08-7.34 (8H, m, Ar-H), 2.21 (4H, m, methine C-H), 2.07 (4H, m, methine C-H), 1.08 (12H, m, methyl C-H), 0.96 (24H, m, methyl C-H), 0.85 (12H, m, methyl C-H), -0.20 (7.60H, br s, averaged hydrides and free H₂). ¹H NMR (C₆D₆, 500 MHz, 90 °C, ppm): δ 4.56 (br s, free H₂), -1.84 (br s, Ni-H₂), -3.01 (br s, Ni-H-Si). ³¹P{¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 72.57 (s). ³¹P{¹H} NMR (C₆D₆, 202 MHz, 90 °C, ppm): δ 67.02 (br s, 57.10 (br s), ²⁹Si NMR (C₆D₆, 99 MHz, 25 °C, ppm): δ 21.31 (br s). ²⁹Si{¹H} NMR (C₆D₆, 99 MHz, -90 °C, ppm): δ 1.69 (s). ²⁹Si NMR (C₆D₆, 99 MHz, -90 °C, ppm): δ 1.68 (d, J₁J₅-H = 102.0 Hz).

2 + 3.9 atm HD. ¹H NMR (C₆D₆, 500 MHz, -90 °C, ppm): δ 4.52 (br s, free H₂, HD), -1.86 (m, Ni-H₂, Ni-HD), -3.06 (br t, J₂P-H = 22.2 Hz, Ni-H-Si). ¹H{³¹P} NMR (C₆D₆, 500 MHz, -90 °C, ppm): δ -1.84 (t, J₁H-D = 34.2 Hz, Ni-H₂, Ni-HD), -3.05 (br s, Ni-H-Si). ¹H{³¹H} NMR (C₆D₆, 500 MHz, -90 °C, ppm): δ -1.86 (br s, Ni-H₂, Ni-HD), -3.06 (br t, J₂H-P = 22.3 Hz, Ni-H-Si).

2 + 12.6 atm H₂. ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 8.14 (4H, d, J₃H-H = 7.3 Hz, Ar-H), 7.31 (4H, d, J₃H-H = 7.5 Hz, Ar-H), 7.02-7.23 (8H, m, Ar-H), 2.12 (8H, m, methine C-H), 1.64 (10.56H, br s, averaged hydrides and free H₂), 1.09 (12H, m, methyl C-H), 0.89 (36H, m, methyl C-H). ³¹P{¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 67.47 (s).

[(SiP₂)₂O][Ni₂(CO)₂(H₂)] (4). 2 (29.0 mg, 28.4 μmol) was dissolved in benzene (6 mL). The solution was freeze-pump-thawed two times to remove any N₂ and then exposed to 3.9 atm H₂. After stirring at room temperature for 2.5 hours the consumption of 2 was complete as determined by NMR spectroscopy and the reaction was freeze-pump-thawed four times and then exposed to 1 atm CO. After stirring vigorously for 15 minutes, the solution was freeze-pump-thawed two times. Subsequent lyophilization and trituration with pentane yielded 4 (26.2 mg, 25.7 μmol, 85%) as a white powder. Elemental analysis data was not collected for 4 as it isomerizes to 5 in solution; Combustion analysis data for 5 is provided below. ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 8.26 (4H, d, J₃H-H = 7.2 Hz, Ar-H), 7.15 (8H, m, Ar-H), 6.97 (4H, m, Ar-H), 2.16 (8H, m, methine C-H), 1.16 (24H, m, methyl C-H), 0.75 (12H, m, methyl C-H), 0.65 (12H, m, methyl C-H), -6.94 (2H, t, J₂P-H = 42.3 Hz, Ni-H). ³¹P{¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 88.35 (s). ²⁹Si NMR (C₆D₆, 79 MHz, 25 °C, ppm): δ 69.65 (m). ¹H{²⁹Si} HMBC (400 MHz, C₆D₆) δ [-6.94 (Ni-Hi), 70.19 (Si)] (dt, J₂Si-H = 67.9 Hz, J₂P-H = 42.3 Hz). IR (thin film): ν(CO) = 1966 cm⁻¹, ν(NH) = 1769 cm⁻¹, ν(NiD) = 1279 cm⁻¹.

[(SiH₃P₂)₂O][Ni₃(CO)₃] (5). 4 (26.2 mg, 25.7 μmol) was dissolved in benzene (0.6 mL) and heated at 45°C for 12 hours. The solution was filtered through Celite and solvent was removed in vacuo, yielding 5 (25.1 mg, 24.6 μmol, 96%) as a yellowish-white powder. ¹H NMR (C₆D₆, 300 MHz, 25 °C, ppm): δ 8.11 (4H, d, J₃H-H = 7.3 Hz, Ar-H), 7.27 (4H, m, Ar-H), 7.15 (4H, m, Ar-H), 7.04 (4H, m, Ar-H), 2.17 (8H, hept, J₃H-H = 6.9 Hz, methine C-H), 1.17 (12H, m, methyl C-H), 1.02 (12H, m, methyl C-H), 0.94 (12H, m, methyl C-H), 0.70 (12H, m, methyl C-H), -2.40 (2H, t, J₂P-H = 22.1 Hz, J₁J₅-H = 122.5 Hz, Ni-H-Si). ³¹P{¹H} NMR (C₆D₆, 121 MHz, 25 °C, ppm): δ 67.66 (s). ¹H{²⁹Si} HMBC (400 MHz, C₆D₆) δ (-2.40 (Ni-H-Si), 8.98 (Si)) (dt, J₂Si-H = 122.5 Hz, J₂P-H = 22.1 Hz). IR (thin film): ν(CO) = 1956 cm⁻¹. Anal. Calc. for C₉₀H₄₅Ni₉O₁₅P₄Si₂: C, 58.84; H, 7.31. Found: C, 58.39; H, 7.20.

Catalytic deuteration studies. Three C₆D₆ solutions of 2 (100 μL, 10.4 mM in C₆D₆), excess Ph₂SiH₂ (see Table S1), and 1,3,5-trimethoxybenzene (100 μL, 0.281 M in C₆D₆) were prepared (total volume 0.6 mL) in NMR tubes. The exact ratios of 2 : Ph₂SiH₂ : 1,3,5-trimethoxybenzene
were determined by integration of the $^1$H NMR spectra. The solutions were then transferred to separate 25 mL Schlenk tubes and freeze-pump-thawed twice. The Schlenk tubes, submerged in liquid nitrogen, were exposed to an external pressure of 1 atm D$_2$ (3.9 atm internal pressure, $\sim$15,000 eq. D$_2$) and stirred vigorously for 12 hours. The solutions were freeze-pump-thawed twice to remove D$_2$ then transferred to NMR tubes. 30 $\mu$L of a 1:1 THF:THF-d$_8$ in C$_6$D$_6$ was added to each tube as a deuterium standard. Integration of the Ph$_2$SiHD and Ph$_2$SiH$_2$ $^1$H NMR signals relative to 1,3,5-trimethoxybenzene gave the yields in Table S1. Formation of the expected amount of deuterated product was confirmed by integration of the Ph$_2$SiHD and Ph$_2$SiD$_2$ signal in the $^2$H spectrum (5.1 ppm (s)). The reported catalyst loading (0.54 mol %) and corresponding yields of Ph$_2$SiD$_2$ (85%) and Ph$_2$SiHD (14%) were obtained by averaging the values for runs 1-3. It is important to note that the $^2$H and $^{29}$Si (-34 ppm (quintet)) NMR spectra both displayed just one product signal indicating clean formation of deuterated silane. To test for heterogenous catalysis, one run was conducted in the presence of Hg (1.0 g). No significant difference was observed between this run and the others (Table S1). Runs with no catalyst added and with Ni(CO)$_2$(PPh$_3$)$_2$ were conducted in a similar fashion as for runs 1-3. In the absence of any Ni species, no deuterium was incorporated into Ph$_2$SiH$_2$ as evidenced by $^2$H NMR. In the presence of Ni(CO)$_2$(PPh$_3$)$_2$ (4.8 mol%), a small amount of deuterium was incorporated as evidenced by $^2$H NMR but the amount was so small that accurate quantification was not feasible.

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**Table S1:** Data for the catalytic deuteration of silanes by 2.
Figure S1: $^1$H NMR spectrum (300 MHz, 25 °C) of 1-Cl in C$_6$D$_6$.

Figure S2: $^{31}$P{$_^1$H} NMR spectrum (121 MHz, 25 °C) of 1-Cl in C$_6$D$_6$.

Figure S3: $^{29}$Si{$_^1$H} NMR spectrum (79 MHz, 25 °C) of 1-Cl in C$_6$D$_6$. 
Figure S4: $^1$H NMR spectrum (400 MHz, 25 °C) of 1-Br in C$_6$D$_6$.

Figure S5: $^{31}$P$^{'\{^1\}H}$ NMR spectrum (121 MHz, 25 °C) of 1-Br in C$_6$D$_6$. 
Figure S6: $^{29}$Si-$^1$H NMR spectrum (79 MHz, 25 ºC) of 1-Br in C$_6$D$_6$.

Figure S7: $^1$H NMR spectrum (300 MHz, 25 ºC) of 2 in C$_6$D$_6$. 
**Figure S8:** $^1$H–$^{13}$C HSQC spectrum (400MHz, C$_6$D$_6$) of 2 in C$_6$D$_6$.

**Figure S9:** $^{31}$P–$^1$H NMR spectrum (121 MHz, 25 °C) of 2 in C$_6$D$_6$. 
Figure S10: $^{29}$Si $^{1}$H NMR spectrum (79 MHz, 25 °C) of 2 in C$_6$D$_6$.

Figure S11: $^1$H NMR spectrum (300 MHz, 25 °C) of 3-2H in C$_6$D$_6$. 
**Figure S12**: $^{29}\text{Si} \{^1\text{H}\}$ NMR spectrum (99 MHz, -90 °C) of 3-2H in C$_7$D$_8$.

**Figure S13**: Overlaid solid IR spectrum of 3-2H and 3-2H-$d_2$. 
Figure S14: $^1$H NMR spectrum (300 MHz, 25 °C) of 3-2H and the reactions of 2 with 1, 2.1, 3.9, and 12.6 atm H$_2$ in C$_6$D$_6$.

Figure S15: $^{31}$P$^{1}$H NMR spectrum (121 MHz, 25 °C) of 3-2H and the reactions of 2 with 1, 2.1, 3.9, and 12.6 atm H$_2$ in C$_6$D$_6$. 
Table S2: Chemical shift and integration data for the NMR spectra in Figure S14 and Figure S15.

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Figure S16: Variable Temperature $^1$H NMR (500 MHz, methylcyclohexane-$d_{22}$) of the reaction of 2 with 3.9 atm H₂. At -100 °C the resonance ascribable to bound H₂ becomes too broad to observe.
Figure S17: Variable Temperature $^1$H NMR (500 MHz, C$_7$D$_8$) of the reaction of 2 with 3.9 atm H$_2$ near the decoalescence point of the hydride signals.

Figure S18: $^{31}$P{${^1}$H} NMR spectrum (202 MHz, -90 °C) of 3-2H and the reactions of 2 with 1 and 3.9 atm H$_2$ in C$_7$D$_8$. 
Figure S19: $^{29}\text{Si}$_{1}{	ext{H}}^{1}$ NMR spectrum (99 MHz, -90 °C) of 3-2H and the reactions of 2 with 1 and 3.9 atm H$_2$ in C$_7$D$_8$.

Figure S20: $^{29}\text{Si}$ NMR spectrum (99 MHz, 25 °C) of 3-6H in C$_7$D$_8$. 
Figure S21: $^{29}$Si {$^1$H} NMR spectrum (99 MHz, -90 °C) of 3-6H in C$_7$D$_8$.

Figure S22: $^{29}$Si NMR spectrum (99 MHz, -90 °C) of 3-6H in C$_7$D$_8$.

Figure S23: $^1$H NMR spectrum (300 MHz, 25 °C) of 4 in C$_6$D$_6$. 
Figure S24: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, 25 °C) of 4 in C$_6$D$_6$.

Figure S25: $^{29}\text{Si}$ NMR spectrum (79 MHz, 25 °C) of 4 in C$_6$D$_6$. 
Figure S26: $^1$H–$^{29}$Si HMBC spectrum (400 MHz, 25 °C) of 4 in C$_6$D$_6$. Asterisks denote the $^{29}$Si satellites.

Figure S27: Overlaid thin film IR spectra of 4 and 4-$d_2$ deposited from C$_6$D$_6$ solutions.
**Figure S28:** $^1$H NMR spectrum (300 MHz, 25 °C) of 5 in $\text{C}_6\text{D}_6$. Inset: enlargement of the hydride signal showing $^{29}\text{Si}$ satellites.

**Figure S29:** $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, 25 °C) of 5 in $\text{C}_6\text{D}_6$. 
Figure S30: $^1$H–$^{29}$Si HMBC spectrum (400 MHz, 25 °C) of 5 in C$_6$D$_6$. Asterisks denote the $^{29}$Si satellites.

Figure S31: Thin film IR spectrum of 5 deposited from C$_6$D$_6$. 
Table S3: Energy data for the various optimized monomeric and dimeric structures.

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Table S4. Optimized coordinates (Å) for [(SiP$_2$)$_2$O]Ni$_2$(H)$_2$ (3-2H) (BP86/6-31G(d)).

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**Table S7.** Optimized coordinates (Å) for [SiP₂O-TMS]Ni(H) (monomeric 3-2H) (BP86/6-31G(d)).
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Table S8. Optimized coordinates (Å) for [SiH₂P₂O-TMS]Ni(H₂) (monomeric Isomer I) (BP86/6-31G(d)).

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S35
Table S9. Optimized coordinates (Å) for [SiP₂O-TMS]Ni(H₂)(H) (monomeric Isomer II) (BP86/6-31G(d)).

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Table S11. Optimized coordinates (Å) for monomeric \([\text{Si}^\text{H}^\text{P}_2\text{O}]\text{Ni}_2(\text{H}_2)_2\) (3-6H, Isomer I) (M06L/6-31G(d)).
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**Table S12.** Optimized coordinates (Å) for monomeric [(SiP$_2$)$_2$O]Ni$_2$(H$_2$)$_2$(H) (3-6H, Isomer II) (M06L/6-31G(d)).
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<td>wR(F²) (all)</td>
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<td>0.0914</td>
</tr>
<tr>
<td>GOF</td>
<td>1.035</td>
<td>1.040</td>
</tr>
</tbody>
</table>

**Table S13:** X-Ray Diffraction table for 1-Cl and 2.
Cited References