Thermally Stable H_2 and N_2 Adducts of Cationic Ni(II)

Charlene Tsay, Jonas C. Peters*
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Supporting Information

Figure S8c. VT ^{1}H NMR spectra of [TP$^{i\mathrm{Pr}}$B]Ni under 1 atm H_2
Figure S8d. VT ^{31}P NMR spectra of [TP$^{i\mathrm{Pr}}$B]Ni under 1 atm H_2

Experimental Details.

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Solvents were degassed and dried by sparging with N_2 gas and passage through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. Reagents were purchased from commercial vendors and used without further purification unless otherwise noted. $[SiP^{Ph}_3]H$,[1] $[SiP^{iPr}_3]H$,[1] $[SiP^{iPr}_3]Ni\text{-}Cl$,[1, 2] $[TP^{iPr}B]Ni$,[3] and $H(BAr^F_4)\cdot 2Et_2O$ ($BAr^F_4 = B[3,5\text{-}(CF_3)_2C_6H_3]_4$),[4] were synthesized according to literature procedures. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

NMR Spectroscopy. ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were collected at room temperature, unless otherwise noted, on Varian 300 MHz, 400 MHz, and 500 MHz NMR spectrometers. ^1H and ^{13}C spectra were referenced to residual solvent resonances. ^{15}N spectra were referenced by using the "setref" protocol in Varian's VnmrJ software, which derives the chemical shifts from known frequency ratios of the ^{15}N standard (liq. NH_3 at 0 ppm) to the lock signal of the deuterated solvent.[5, 6] ^{19}F spectra were referenced to external C_6F_6 ($\delta = -164.9$ ppm). ^{31}P spectra were referenced to external 85% phosphoric acid ($\delta = 0$ ppm). $T1_{min}$ values were determined by fitting the pulse-recovery ^1H spectra at various temperatures using the T1 calculation protocols in either Varian's VnmrJ software or Mestrelab Research S. L.'s Mestrenova version 6.2.1.

IR Spectroscopy. IR measurements were obtained in KBr pellets or in a solution cell with salt plates using a Bio-Rad Excalibur FTS 3000 spectrometer with Varian Resolutions Pro software.

X-ray Crystallography. X-ray diffraction studies were carried out at the MIT Department of Chemistry X-ray Diffraction Facility on a Bruker three-circle Platform diffractometer coupled to a Bruker-AXS Smart Apex CCD detector and at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector. Data was collected at 100K using Mo Kα radiation ($\lambda = 0.71073$ Å). Structures were solved by direct or Patterson methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded. Some structures contained disorder in either the solvent molecules or the $–CF_3$ groups of the BAr^F_4 anions; these disorders were refined with the help of similarity restraints on equivalent 1-2 and 1-3 distances. Disordered $-CF_3$ groups were modeled as an idealized disorder over two positions rotated 60° from one another, with equivalent fluorine atoms constrained to have equal anisotropic displacement parameters.

For the structure of **2a**, checkCIF reports one level A alert (PLAT213_ALERT_2_A) due to a high ratio of maximum to minimum anisotropic displacement parameters (ADP) for atom C34B. As this atom is part of the benzene molecule that is highly disordered around a mirror plane and required the use of a rigid group constraint (AFIX 66), we did not deem it appropriate to model any further disorder.

Computational Details. All calculations were performed using the Gaussian03 suite.[8] The geometry optimizations were done without any symmetry restraints at the DFT level of theory using the B3LYP hybrid functional. The 6-31G (d) basis set was used for all atoms. The full ligand was used for each calculation, and the minimized structures were verified with frequency calculations. The starting coordinates for the metal and ligand were taken from the crystal structures of the corresponding N_2 adducts or the 4-coordinate Ni boratrane $[TP^{iPr}B]Ni$[3]; hydrogen atoms were placed in the apical binding site at an arbitrary initial distance of 1.5 Å from the metal and 0.9 Å from each other.

Note concerning lack of combustion data for the dihydrogen adducts 5a and 5b, and lack of satisfactory combustion data for methyl compound 1a. The cationic dihydrogen adducts **5a**, **5b**, in addition to their HD analogues, can be generated cleanly according to NMR spectroscopy by the methods described below; however, the fifth ligand is labile under vacuum, slow evaporative drying, or exposure to N_2, and this fact frustrates attempts to obtain reliable C,H,N data. In the case of compound **1a**, we have not yet been able to obtain satisfactory combustion analysis data. We are, however, confident in our assignment of the identity of this compound, as we can obtain spectroscopically clean samples. The NMR spectra are analogous to those of the previously reported[9] $[SiP^{iPr}_3]Pt\text{-}CH_3$ and $[SiP^{iPr}_3]Pd\text{-}CH_3$, and are indicative of the species shown in the crystal structure obtained for **1a**. The crystal selected for the X-ray diffraction study of compound **1a** was representative of the batch of crystals grown.

Preparation of $[SiP^{iPr}_3]Ni\text{-}CH_3$ (1a). Under a dinitrogen atmosphere, $[SiP^{iPr}_3]Ni\text{-}Cl$ (100 mg, 142 μmol) was dissolved in Et_2O and cooled to -78 °C. MeLi in Et_2O (2.7 mL of 0.16M solution, 427 μmol) was added dropwise at -78 °C. The red solution was allowed to warm to room temperature overnight then stirred at room temperature for 3 hr, resulting in a dark green solution. Volatiles were removed to yield dark green residue, which was dissolved in pentane and filtered through Celite. Volatiles were removed again; the resulting green solids were washed with Et_2O then dissolved in C_6H_6 and lyophilized to afford spectroscopically clean $[SiP^{iPr}_3]Ni\text{-}CH_3$ (58 mg, 60%) as an orange solid. ^1H NMR (C_6D_6, δ): 8.05 (d, J = 6.9 Hz, 3H), 7.21 (m, 6H), 7.07 (m, 3H), 2.51 (m, 6H), 1.12 (m, 18H), 0.66 (m, 18H), 0.33 (q, $^3J_{P\text{-}H}$ = 9.9 Hz, 3H, Ni-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 156.3 (m), 146.7 (m), 132.9 (m), 129.3 (s), 128.7 (s), 126.9 (s), 27.8 (m), 19.3 (s), 18.7 (s), -26.5 (q, $^2J_{P\text{-}C}$ = 15.6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 43.9 (s). Anal. Calcd. for $C_{37}H_{57}SiP_3Ni$: C, 65.20; H, 8.43. Found: C, 59.42; H, 8.47. (see note above)

Preparation of $[SiP^{Ph}_3]Ni\text{-}CH_3$ (1b). Under a dinitrogen atmosphere, $[SiP^{Ph}_3]H$ (100 mg, 124 μmol) and $NiCl_2{\cdot}DME$ (32 mg, 145 μmol) were weighed out into a vial, dissolved in THF, and cooled to -78 °C. MeMgCl in THF (4.4 mL of 0.3M solution, 1.24 mmol) was added slowly with stirring at -78 °C. The resulting red solution was allowed to warm to room temperature overnight, then stirred at room temperature for 1 hr, after which 5 mL 1,4-dioxane was added and the mixture was stirred at room temperature for another 2 hr. Volatiles were removed to yield brown residue, which was dissolved in C_6H_6 and filtered through a sintered glass frit. Volatiles were removed from the brown filtrate to yield brown residue, which was washed with Et_2O to afford spectroscopically clean $[SiP^{Ph}_3]Ni\text{-}CH_3$ as a mustard yellow solid (99 mg, 90%).

^{1}H NMR (C_6D_6, δ): 8.33 (d, J = 7.20 Hz, 3H), 7.59 (m, 6H), 7.07 (m, 12H), 6.96 (m, 3H), 6.84 (m, 6H), 6.71 (m, 12H), 0.55 (q, $^3J_{P\text{-}H}$ = 9.20 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 137.5 (m), 132.9 (m), 129.6 (s), 129.5 (s), 128.9 (m), 128.9 (s), 128.7 (s), 128.3 (s), 128.0 (m), 125.8 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 45.9 (s). (see note above concerning lack of EA data)

Preparation of $\{[SiP^{iPr}_3]Ni(N_2)\}\{BAr^F_4\}$ (2a). Under a dinitrogen atmosphere, $[SiP^{iPr}_3]Ni\text{-}CH_3$ (22 mg, 32 μmol) was dissolved in C_6H_6 and added to $HBAr^F_4{\bullet}2Et_2O$ (33 mg, 32 μmol). The resulting mixture was stirred at room temperature for 30 minutes, after which the orange precipitate was isolated from the yellow solution, washed with C_6H_6, and dried under vacuum to afford spectroscopically clean $\{[SiP^{iPr}_3]Ni\text{-}N_2\}\{BAr^F_4\}$ (40 mg, 80%). The complex decomposes over the course of days in CH_2Cl_2, but can be stored without decomposition in pentane at -30 °C. Orange crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, δ): 7.72 (m, 8H, *o*-BAr^F_4), 7.66 (m, 6H), 7.56 (s, 4H, *p*-BAr^F_4), 7.48 (m, 6H), 2.75 (br s, 6H), 1.04 (br s, 18H), 0.94 (br s, 18H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 162.3 (q, $^1J_{B\text{-}C}$ = 50 Hz), 150.4 (m), 139.9 (m), 135.4 (s), 132.9 (m), 131.6 (s), 130.7 (s), 129.5 (q, $^2J_{F\text{-}C}$ = 32 Hz), 128.9 (s), 125.2 (q, $^1J_{F\text{-}C}$ = 273 Hz, -CF_3), 118.0 (s), 28.2 (br s), 20.0 (br s), 18.9 (s). ^{1}H NMR (-70 °C, CH_2Cl_2, δ): 7.75 (m, 3H), 7.71 (m, 8H, *o*-BAr^F_4), 7.53 (s, 4H, *p*-BAr^F_4), 7.46 (m, 6H), 7.42 (m, 3H), 2.99 (s, 3H), 2.19 (m, 3H), 1.35 (s, 9H), 1.23 (s, 9H), 0.96 (s, 9H), -0.48 (s, 9H). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ): -61.3 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 46.2 (v br). $^{31}P\{^1H\}$ NMR (-70 °C, CH_2Cl_2, δ): 47.6 (s). IR (KBr, cm^{-1}) 2223 ($\nu_{N\text{-}N}$). Anal. Calcd. for $C_{68}H_{66}SiP_3NiN_2BF_{24}$: C, 52.43; H, 4.27; N, 1.80. Found: C, 52.62; H, 4.30; N, 1.62.

Preparation of $\{[SiP^{iPr}_3]Ni(^{15}N_2)\}\{BAr^F_4\}$ (2a'). Under a dinitrogen atmosphere, $\{[SiP^{iPr}_3]Ni(N_2)\}\{BAr^F_4\}$ (10 mg, 6 μmol) was dissolved in CD_2Cl_2 and transferred to a J. Young tube. The sample was freeze-pump-thawed five times, then exposed to ca. 0.2 atm $^{15}N_2$ while frozen. Upon thawing in the sealed tube, the solution retained the orange-brown color of the starting material. ^{1}H NMR (CD_2Cl_2, δ): 7.72 (m, 8H, *o*-BAr^F_4), 7.66 (m, 6H), 7.56 (s, 4H, *p*-BAr^F_4), 7.48 (m, 6H), 2.75 (br s, 6H), 1.06 (br s, 18H), 0.94 (br s, 18H). $^{15}N\{^1H\}$ NMR (-40 °C, CD_2Cl_2, δ): 361.8 (s), 310.4 (s, free $^{15}N_2$), 300.9 (s). $^{31}P\{^1H\}$ NMR (-30 °C, CH_2Cl_2, δ): 48.2 (s).

Preparation of $\{[SiP^{Ph}_3]Ni(N_2)\}\{BAr^F_4\}$ (2b). Under a dinitrogen atmosphere, $[SiP^{Ph}_3]Ni\text{-}CH_3$ (25 mg, 28 μmol) and $HBAr^F_4{\bullet}2Et_2O$ (29 mg, 28 μmol) were weighed out and suspended in abpit 5 mL n-pentane. About 0.5 mL benzene was added, and the resulting mixture was stirred at room temperature overnight, resulting in a pale orange solid suspension. The solid was isolated and dried under vacuum to afford analytically pure compound. ^{1}H NMR (C_6D_6, δ): 8.43 (s, 8H, *o*-BAr^F_4), 7.65 (s, 4H, *p*-BAr^F_4), 7.54 (d, J = 7.20 Hz, 3H), 7.10 (m, 3H), 6.96 (m, 3H), 6.87 (m, 9H), 6.73 (m, 24H). ^{1}H NMR (-20 °C, toluene-d_8, δ): 8.46 (s, 8H, *o*-BAr^F_4), 7.62 (s, 4H, *p*-BAr^F_4), 7.57 (d, J = 5 Hz, 2H), 7.51 (d, J = 5 Hz, 1H), 6.96 (br s, 3H), 6.90 (m, 6H), 6.84 (br s, 6H), 6.69 (m, 24H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 162.8 (q, $^1J_{B\text{-}C}$ = 49 Hz), 148.0 (m), 140.8 (m), 135.5 (s), 132.7 (m), 132.6 (m), 132.3 (m), 132.2 (s), 131.6 (s), 131.3 (s), 130.7 (s), 130.5 (s), 129.9 (q, $^2J_{F\text{-}C}$ = 31 Hz), 125.3 (q, $^2J_{F\text{-}C}$ = 272 Hz, -CF_3), 118.1 (s). $^{19}F\{^1H\}$ NMR (C_6D_6, δ): -60.6. $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 42.5 (s). $^{31}P\{^1H\}$ NMR (-20 °C, toluene-d_8, δ): 40.6. IR (KBr, cm^{-1}) 2234 ($\nu_{N\text{-}N}$). Anal. Calcd. for $C_{86}H_{54}SiP_3NiN_2BF_{24}$: C, 58.63; H, 3.09; N, 1.59. Found: C, 58.96; H, 3.29; N, 1.06.

Preparation of {[SiP$^{Ph}{}_3$]Ni($^{15}N_2$)}{BAr$^F{}_4$} (2b'). Under a dinitrogen atmosphere, [SiP$^{Ph}{}_3$]Ni-CH_3 (20 mg, 23 µmol) was dissolved in toluene-d_8 and added to HBAr$^F{}_4$•2Et_2O (23 mg, 23 µmol). The mixture was stirred at room temperature for 20 minutes, resulting in an orange-brown solution. The sample was freeze-pump-thawed seven times, then exposed to ca. 0.5 atm $^{15}N_2$ while frozen. Upon thawing in the sealed tube, the solution retained the orange-brown color of the starting material. ^{1}H NMR (toluene-d_8, δ): 8.34 (s, 8H, *o*-BAr$^F{}_4$), 7.65 (s, 4H, *p*-BAr$^F{}_4$), 7.61 (d, *J* = 6.80 Hz, 3H), 7.16 (m, 3H), 7.02 (m, 3H), 6.97 (m, 3H), 6.91 (m, 6H), 6.76 (s, 24H). ^{15}N{^{1}H} NMR (-20 °C, toluene-d_8, δ): 346.9 (s), 310.2 (s, free $^{15}N_2$), 296.9 (s). ^{31}P{^{1}H} NMR (-20 °C, toluene-d_8, δ): 40.6 (s).

Preparation of {[SiP$^{iPr}{}_3$]Ni(NCMe)}{BAr$^F{}_4$} (3a). Under a dinitrogen atmosphere, {[SiP$^{iPr}{}_3$]Ni(N_2)}{BAr$^F{}_4$} (12 mg, 8 µmol) was dissolved in CD_2Cl_2 to form an orange-brown solution. Excess (192 µmol) MeCN was added, resulting in an orange solution. Volatiles were removed to yield spectroscopically clean material as an orange solid (12 mg, 100%). Analytically pure orange crystals suitable for X-ray diffraction were grown by slow diffusion of pentane vapors into a C_6H_6/minimal CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, δ): 7.78 (d, *J* = 6.0 Hz, 3H), 7.71 (s, 8H, *o*-BAr$^F{}_4$), 7.55 (s, 4H, *p*-BAr$^F{}_4$), 7.51 (m, 3H), 7.41 (m, 6H), 2.61 (br s, 6H), 2.31 (m, 3H, Ni-NCCH_3), 1.18 (m, 18H), 0.55 (br s, 18H). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 162.4 (q, $^1J_{B\text{-}C}$ = 50 Hz), 152.9 (m), 139.8 (m), 135.4 (s), 133.2 (m), 131.0 (s), 130.5 (s), 129.5 (q, $^2J_{F\text{-}C}$ = 32 Hz), 129.4 (s), 129.3 (m, Ni-N*C*CH$_3$), 125.2 (q, $^1J_{F\text{-}C}$ = 272 Hz, -*C*F$_3$), 118.0 (m), 27.1 (m), 18.9 (s), 18.7 (s), 5.7 (s, Ni-NC*C*H$_3$). ^{19}F{^{1}H} NMR (CD_2Cl_2, δ): -61.3 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 43.7 (s). Anal. Calcd. for $C_{70}H_{69}SiP_3NiN$: C, 53.52; H, 4.43; N, 0.89. Found: C, 53.22; H, 4.36; N, 0.93.

Preparation of {[SiP$^{iPr}{}_3$]Ni(CO)}{BAr$^F{}_4$} (4a). Under a dinitrogen atmosphere, {[SiP$^{iPr}{}_3$]Ni(N_2)}{BAr$^F{}_4$}(20 mg, 13 µmol) was dissolved in CH_2Cl_2 and transferred to a J. Young tube. The sample was freeze-pump-thawed once, then exposed to one atm CO, resulting in a bright yellow, spectroscopically clean solution. Analytically pure material was obtained by recrystallization by layering pentane on a benzene/minimal CH_2Cl_2 solution, isolating the resulting solid, and washing with pentane (12 mg, 60%). Yellow crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2, δ): 7.93 (d, *J* = 7.20 Hz, 3H), 7.73 (s, 8H, *o*-BAr$^F{}_4$), 7.56 (s, 4H, *p*-BAr$^F{}_4$), 7.50 (m, 9H), 2.62 (br s, 6H), 1.15 (m, 18H), 0.58 (br s, 18H). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 208.2 (q, $^2J_{P\text{-}C}$ = 12 Hz, Ni-*C*O), 162.3 (q, $^1J_{B\text{-}C}$ = 50 Hz), 152.3 (m), 139.1 (m), 135.4 (s), 133.7 (m), 132.3 (s), 130 7 (s), 130.2 (s), 129.5 (q, $^2J_{F\text{-}C}$ = 32 Hz), 125.2 (q, $^1J_{F\text{-}C}$ = 272 Hz, -*C*F$_3$), 118.0 (s), 28.0 (s), 18.8 (s), 18.2 (s). ^{19}F{^{1}H} NMR (CD_2Cl_2, δ): -61.4 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 63.6 (s). IR (KBr, cm^{-1}) 2036 ($\nu_{C\text{-}O}$). Anal. Calcd. for $C_{69}H_{66}SiP_3NiO$: C, 53.20; H, 4.27. Found: C, 52.32; H, 4.04.

Preparation of {[SiP$^{Ph}{}_3$]Ni(CO)}{BAr$^F{}_4$} (4b). Under a dinitrogen atmosphere, [SiP$^{Ph}{}_3$]Ni-CH_3 (25 mg, 28 µmol) was dissolved in C_6H_6 and added to HBAr$^F{}_4$•2Et_2O (29 mg, 28 µmol). The resulting mixture was stirred at room temperature for 30 minutes, resulting in a dark brown solution of {[SiP$^{Ph}{}_3$]Ni-N_2}{BAr$^F{}_4$}. The sample was transferred to a J. Young tube, freeze-pump-thawed twice, then exposed to one atm CO, resulting in a orange-yellow solution. Spectroscopically and analytically clean compound was obtained by layering pentane on a C_6H_6 solution, resulting in yellow microcrystals (28 mg, 57%). ^{1}H NMR (toluene-d_8, δ): 8.35 (s, 8H, *o*-BAr$^F{}_4$), 7.77 (d, *J* = 6.80 Hz, 3H), 7.65 (s, 4H, *p*-BAr$^F{}_4$), 7.23 (m, 3H), 6.98 (m, 6H), 6.85 (m, 6H), 6.70 (m, 24H). $^{13}C\{^1H\}$ NMR (toluene-d_8, δ): 203.0 (q, $^2J_{P\text{-}C}$ = 14 Hz, Ni-*C*O), 162.7 (q, $^1J_{B\text{-}C}$ = 50 Hz), 148.7 (m), 141.5 (m), 135.5 (s), 133.8 (s), 132.8 (m), 132.6 (s), 132.5 (m), 132.3 (m), 132.0 (s), 131.5 (s), 130.8 (s), 129.9 (q, $^2J_{F\text{-}C}$ = 31 Hz), 125.3 (q, $^1J_{F\text{-}C}$ = 273 Hz, -*C*F$_3$), 118.0 (s). $^{19}F\{^1H\}$ NMR (C_6D_6, δ): -60.5 (s). $^{31}P\{^1H\}$ NMR (toluene-d_8, δ): 50.6 (s). IR (KBr, cm^{-1}) 2046 ($\nu_{C\text{-}O}$). Anal. Calcd. for $C_{87}H_{54}SiP_3NiO$: C, 59.31; H, 3.09. Found: C, 59.20; H, 3.10.

Preparation of {[SiP$^{iPr}_3$]Ni(H$_2$)}{BAr$^F_4$} (5a). Under a dinitrogen atmosphere, {[SiP$^{iPr}_3$]Ni(N$_2$)}{BAr$^F_4$} (5 mg, 3 μmol) was dissolved in CD_2Cl_2 and transferred to a J. Young tube. The sample was freeze-pump-thawed five times, then exposed to one atm H_2 while frozen. Upon thawing in the sealed tube, the solution gradually turned bright yellow. Unsealing or diluting the sample results in gradual recovery of the four-coordinate starting material's color. ^1H NMR (CD_2Cl_2, δ): 7.93 (d, *J* = 7.20 Hz, 3H), 7.72 (m, 8H, *o*-BAr$^F_4$), 7.56 (s, 4H, *p*-BAr$^F_4$), 7.53 (m, 6H), 7.47 (m, 3H), 2.48 (br s, 6H), 1.06 (m, 18H), 0.47 (br s, 18H), -3.58 (br s, 2H). ^1H NMR (-70 °C, CH_2Cl_2, δ): 7.87 (d, *J* = 7.00 Hz), 7.71 (s, 8H, *o*-BAr$^F_4$), 7.53 (s, 4H, *p*-BAr$^F_4$), 7.45 (m, 9H), 4.55 (s, free H_2), 2.80 (s, 3H), 1.98 (s, 3H), 1.14 (m, 9H), 0.96 (s, 9H), 0.90 (s, 9H), -0.54 (s, 9H), -3.76 (s, 2H). $T_{1(min)}$ (500 MHz, -50 °C) = 20 ms. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 162.4 (q, $^1J_{B\text{-}C}$ = 50 Hz), 152.5 (m), 139.1 (m), 135.4 (s), 133.7 (m), 131.9 (s), 130.9 (s), 130 0 (s), 129.5 (q, $^2J_{F\text{-}C}$ = 31 Hz), 125.2 (q, $^1J_{F\text{-}C}$ = 272 Hz, -*C*F$_3$), 118.1 (s), 26.6 (br s), 18.6 (s), 18.3 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ): -61.3 (s). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 60.0 (s).

Preparation of {[SiP$^{iPr}_3$]Ni(HD)}{BAr$^F_4$} (5a'). A sample of {[SiP$^{iPr}_3$]Ni(N$_2$)}{BAr$^F_4$} (7 mg, 4 μmol) dissolved in CD_2Cl_2 in a J. Young tube was freeze-pump-thawed four times, then exposed to ca. 0.4 atm HD (generated from the reaction of excess $LiAlH_4$ and D_2O) while frozen. Upon thawing in the sealed tube, the solution gradually turned orange-yellow. ^1H NMR (CD_2Cl_2, δ): 7.92 (d, *J* = 7.50 Hz, 3H), 7.72 (m, 8H, *o*-BAr$^F_4$), 7.56 (s, 4H, *p*-BAr$^F_4$), 7.53 (m, 6H), 7.47 (m, 3H), 2.47 (br s, 6H), 1.05 (m, 18H), 0.46 (br s, 18H), -3.59 (m, 1H). ^1H NMR (-70 °C, CH_2Cl_2, δ): 7.87 (d, *J* = 6.99 Hz, 3H), 7.72 (m, 8H, *o*-BAr$^F_4$), 7.53 (s, 4H, *p*-BAr$^F_4$), 7.46 (m, 9H), 4.52 (t, $^1J_{H\text{-}D}$ = 42 Hz, free HD), 2.79 (s, 3H), 1.97 (s, 3H), 1.13 (s, 9H), 0.95 (s, 9H), 0.89 (s, 9H), -0.54 (s, 9H), -3.78 (t, $^1J_{H\text{-}D}$ = 35 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 60.1 (s).

Preparation of {[SiP$^{Ph}_3$]Ni(H$_2$)}{BAr$^F_4$} (5b). Under a dinitrogen atmosphere, [SiP$^{Ph}_3$]Ni-CH$_3$ (16 mg, 18 μmol) was dissolved in toluene-d_8 and added to HBAr$^F_4$•2Et$_2$O (18 mg, 18 μmol). The mixture was stirred at room temperature for 30 minutes, resulting in an orange-brown solution which was transferred to a J. Young tube. The sample was frozen, evacuated, and exposed to 1 atm H_2. Upon thawing the sealed tube and shaking, the solution turned red-orange. ^1H NMR (toluene-d_8, δ): 8.34 (s, 8H, *o*-BAr$^F_4$), 7.71 (m, 3H), 7.63 (s, 4H, *p*-BAr$^F_4$), 7.19 (m, 3H), 6.97 (m, 6H), 6.84 (br s, 6H), 6.68 br s, 24H), -2.55 (br s, 1H). ^1H NMR (-20 °C, toluene-d_8, δ): 8.47 (s, 8H, *o*-BAr$^F_4$), 7.69 (m, 3H), 7.62 (s, 4H, *p*-BAr$^F_4$), 7.18 (m, 3H), 6.92 (br s, 6H), 6.80 (m, 6H), 6.63 (br s, 24H), 4.53 (br s, free H_2), -2.91 (br s, 1H). $T_{1(min)}$ (500 MHz, -30 °C) = 24 ms. $^{13}C\{^1H\}$ NMR (toluene-d_8, δ): 162.7 (q, $^1J_{B\text{-}C}$ = 50 Hz), 148.8 (m), 141.1 (m), 135.5 (s), 133.1 (m), 132.8 (s), 132.7 (m), 132.5 (s), 132.1 (m), 131.7 (m), 131.2 (s), 130.4 (s), 129.9 (q m, $^2J_{F\text{-}C}$ = 31 Hz), 125.3 (q, $^1J_{F\text{-}C}$ = 272 Hz, -*C*F$_3$), 118.0 (s). $^{19}F\{^1H\}$ NMR (toluene-d_8, δ): -60.7. $^{31}P\{^1H\}$ NMR (toluene-d_8, δ): 44.8 (s).

Deprotonation of {[SiP$^{Ph}_3$]Ni(H$_2$)}{BAr$^F_4$} by triethylamine. Under a dinitrogen atmosphere, {[SiP$^{Ph}_3$]Ni(N$_2$)}{BAr$^F_4$} (10 mg, 6 μmol) was dissolved in C_6D_6 in a J. Young tube to form a orange solution. Excess (66 μmol) triethylamine was added with no visible color change. The sample was freeze-pump-thawed once, then exposed to one atm of H_2, resulting in a light orange solution. The major species in the ^1H and ^{31}P NMR spectra exhibited the characteristic resonances of $[SiP^{Ph}_3]Ni-H$; a minor impurity was not identified.

Preparation of $\{[SiP^{Ph}_3]Ni(HD)\}\{BAr^F_4\}$ (5b'). A sample of $\{[SiP^{Ph}_3]Ni(H_2)\}\{BAr^F_4\}$ dissolved in toluene-d_8 in a J. Young tube was freeze-pump-thawed twice, then exposed to ca. 1 atm HD (generated from the reaction of excess $LiAlH_4$ and D_2O) while frozen. Upon thawing in the sealed tube, the solution gradually turned red-orange. ^1H NMR (toluene-d_8, δ): 8.34 (s, 8H, *o*-BAr^F_4), 7.64 (br s, 7H, *p*-BAr^F_4 overlapped with 3H), 7.17 (m, 3H), 6.97 (br s, 6H), 6.87 (br s, 6H), 6.71 (br s, 24H), -2.70 (br s, 1H). ^1H NMR (-20 °C, toluene-d_8, δ): 8.46 (s, 8H, *o*-BAr^F_4), 7.68 (d, $J = 7$ Hz, 2H), 7.62 (s, 4H, *p*-BAr^F_4), 7.50 (d, $J = 7$ Hz, 1H), 7.17 (m, 3H), 6.92 (m, 6H), 6.79 (m, 6H), 6.73 (br s, 9H), 6.63 (s, 15H), 4.49 (t, $^1J_{H\text{-}D} = 42$ Hz, free HD), -2.93 (t, $^1J_{H\text{-}D} = 33$ Hz, 1H). $^{31}P\{^1H\}$ NMR (toluene-d_8, δ): 45.1 (s).

Preparation of $[SiP^{iPr}_3]Ni-H$ (6a). Under a dinitrogen atmosphere, $H[SiP^{iPr}_3]$ (29 mg, 48 μmol) and $Ni(COD)_2$ (16 mg, 58 μmol) were dissolved in about 3 mL Et_2O, stirred for about 24 hours at room temperature, then pumped down. The residue was dissolved in pentane and filtered, resulting in an orange solution. Volatiles were removed under vacuum to afford an orange solid (yield, %). Though we have not yet been able to obtain spectroscopically and analytically pure compound (NMR shows around 2% $[SiP^{iPr}_3]Ni-Cl$ impurity), the major species observed in the ^1H and ^{31}P NMR spectra has an upfield ^1H resonance with a chemical shift and $^2J_{H\text{-}P}$ consistent with the analogous $[SiP^R_3]$ Pt hydrides previously reported,[9] and corresponds to the product obtained in the deprotonation of $\{[SiP^{iPr}_3]Ni-H_2\}\{BAr^F\}$ with triethylamine (vide infra). Orange crystals suitable for X-ray diffraction were grown by cooling a saturated pentane solution to -35 °C; the crystal structure showed about 2.5 % occupancy of the chloride. ^1H NMR (C_6D_6, δ): 8.11 (d, $J = 8$ Hz, 3H), 7.25 (m, 6H), 7.07 (m, 3H), 2.26 (m, 6H), 0.98 (m, 18H), 0.63 (br s, 18H), -8.05 (q, $^2J_{H\text{-}P} = 36$ Hz, 1H). ^{13}C NMR (C_6D_6, δ): 156.4 (m), 148.7 (m), 133.2 (m), 129.4 (s), 128.8 (s), 126.7 (s), 26.4 (s), 18.74 (s), 18.65 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 67.8 (s). IR (C_6H_6, cm^{-1}) 1732 ($\nu_{Ni\text{-}H}$).

Reaction of $[SiP^{iPr}_3]Ni-H$ with 1-octene. Under a dinitrogen atmosphere, $[SiP^{iPr}_3]Ni-H$ (5 mg, 7 μmol) was dissolved in C_6D_6 in a J. Young tube to form a forest green solution. Excess (64 μmol) 1-octene was added with no visible color change. After one day at room temperature in the sealed tube, the major Ni-containing species was still $[SiP^{iPr}_3]Ni-H$, with a ^{31}P chemical shift of 67.2 ppm; a new species had also grown in, with a ^{31}P chemical shift of 35.2 ppm. ^1H and ^{13}C NMR spectra showed almost complete consumption of 1-octene (characteristic ^1H peaks: 5.01 (m, 1H), 5.79 (m, 1H); ^{13}C peaks: 139.3 (s), 114.5 (s)) and formation of both *cis*- and *trans*- 2-octene (characteristic 1H peaks: 5.43 (m, 2H); 13C peaks: 131.1 (s) and 123.8 (s) for *cis*-, 132.0 (s) and 124.8 (s) for *trans*-)

Preparation of $[SiP^{Ph}_3]Ni-H$ (6b). Under a dinitrogen atmosphere, $H[SiP^{Ph}_3]$ (40 mg, 49 μmol) and $Ni(COD)_2$ (13 mg, 49 μmol) were dissolved in around 5 mL C_6H_6 and stirred at room temperature until the initial clear, yellow solution turned orange and then brown-yellow. Volatiles were removed under vacuum and the remaining sample was washed with minimal C_6H_6 and Et_2O to yield a yellow solid. Though we have not yet been able to obtain spectroscopically and analytically pure compound, the major species observed in the ^{1}H and ^{31}P NMR spectra has an upfield ^{1}H resonance with a chemical shift and $^2J_{\mathrm{H\text{-}P}}$ consistent with analogous $[\mathrm{SiP}^{\mathrm{R}}_3]$ Pt hydrides previously reported,[7] and corresponds to the product obtained in the deprotonation of $\{[\mathrm{SiP}^{\mathrm{Ph}}_3]\mathrm{Ni\text{-}H_2}\}\{\mathrm{BAr^F}\}$ with triethylamine (vide infra). ^{1}H NMR (C_6D_6, δ): 8.54 (d, J = 8 Hz, 3H), 7.36 (m, 6H), 7.23 (br s, 12H), 7.05 (m, 3H), 6.73 (m, 6H), 6.58 (m, 12H), 5.36 (q, $^2J_{\mathrm{H\text{-}P}}$ = 36 Hz, 1H). ^{31}P{^{1}H} NMR (C_6D_6, δ): 62.1 (s). IR (C_6H_6, cm^{-1}) 1736 ($\nu_{\mathrm{Ni\text{-}H}}$).

Reaction of $[\mathrm{SiP}^{\mathrm{Ph}}_3]$Ni-H with 1-octene. Under a dinitrogen atmosphere, 5 µmol $[\mathrm{SiP}^{\mathrm{Ph}}_3]$Ni-H in C_6D_6 was added to a J. Young tube, resulting in an orange solution. One equivalent of 1-octene in C_6D_6 was added with no visible color change. After one day at 60 °C in the sealed tube, the major Ni-containing species was still $[\mathrm{SiP}^{\mathrm{Ph}}_3]$Ni-H, with a ^{31}P chemical shift of 62.1 ppm; a new species had also grown in, with a ^{31}P chemical shift of 33.9 ppm. The ^{1}H spectrum showed complete consumption of 1-octene (characteristic ^{1}H peaks: 5.01 (m, 1H), 5.79 (m, 1H) and formation of both *cis*- and *trans*- 2-octene (characteristic 1H peaks: 5.43 (m, 2H))

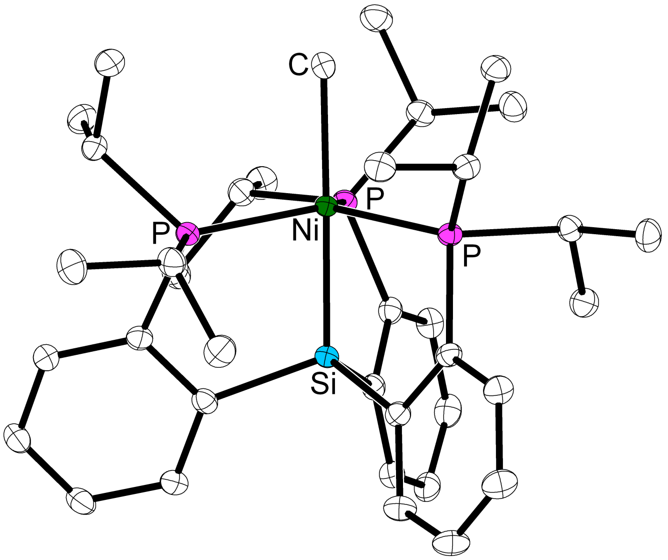

Figure S1. Solid-state structures of **1a**. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms omitted for clarity.

Table S1a. Crystal data and structure refinement for **1a**.

Identification code	09401	
Empirical formula	C37 H57 Ni P3 Si	
Formula weight	681.54	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 16.1008(13) Å	α = 90°.

	b = 16.9634(13) Å	β = 90°.
	c = 25.931(2) Å	γ = 90°.
Volume	7082.4(10) $Å^3$	
Z	8	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.742 mm^{-1}	
F(000)	2928	
Crystal size	0.50 x 0.40 x 0.25 mm^3	
Theta range for data collection	1.57 to 30.51°.	
Index ranges	-22<=h<=23, -24<=k<=24, -37<=l<=37	
Reflections collected	152436	
Independent reflections	10796 [R(int) = 0.0595]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8362 and 0.7079	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10796 / 309 / 392	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0848	
R indices (all data)	R1 = 0.0482, wR2 = 0.0939	
Largest diff. peak and hole	0.697 and -0.360 e.$Å^{-3}$	

Table S1b. Selected bond lengths [Å] and angles [°] for **1a**.

Ni(1)-C(100)	2.0643(15)
Ni(1)-Si(1)	2.2247(5)
Ni(1)-P(1)	2.2686(5)
Ni(1)-P(2)	2.2764(4)
Ni(1)-P(3)	2.2346(4)
C(100)-Ni(1)-Si(1)	177.33(4)
P(1)-Ni(1)-P(2)	116.192(16)
P(3)-Ni(1)-P(1)	118.530(16)
P(3)-Ni(1)-P(2)	121.683(17)
C(100)-Ni(1)-P(1)	98.09(4)
C(100)-Ni(1)-P(2)	96.68(4)
C(100)-Ni(1)-P(3)	94.29(4)

Si(1)-Ni(1)-P(1)	84.196(16)
Si(1)-Ni(1)-P(2)	83.484(16)
Si(1)-Ni(1)-P(3)	83.376(17)

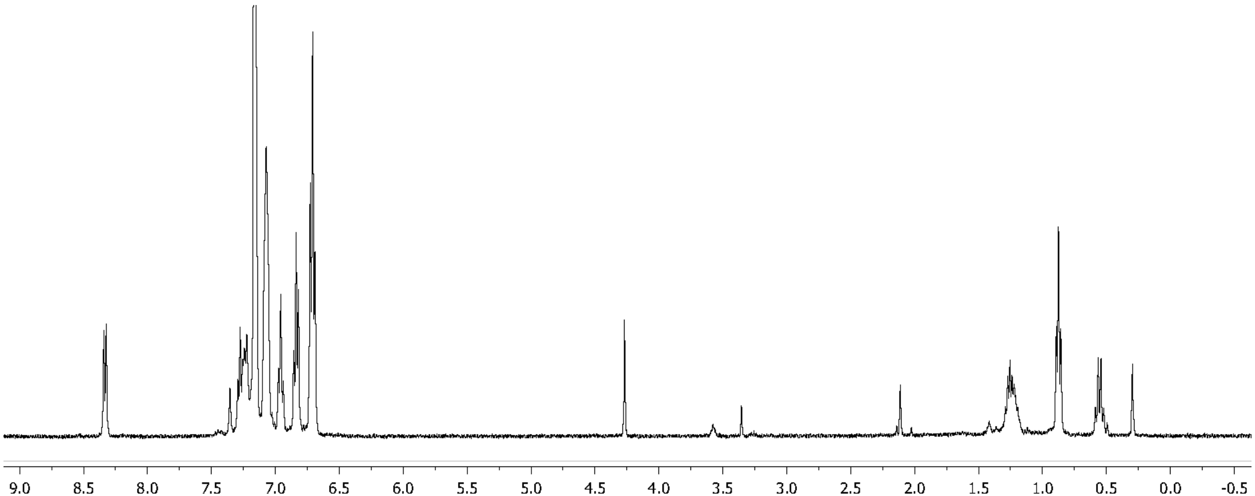

Figure S2a. ^{1}H NMR spectrum of **1b** in C_6D_6 at 25 °C.

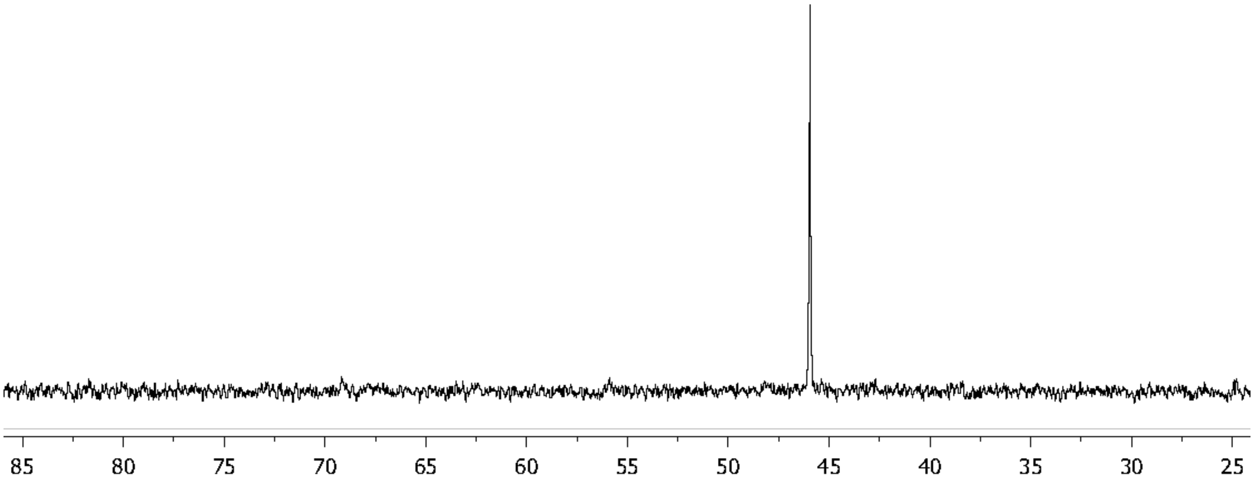

Figure S2b. ^{31}P NMR spectrum of **1b** in C_6D_6 at 25 °C.

Table S2a. Crystal data and structure refinement for **2a**.

Identification code	09450
Empirical formula	C77.75 H75.75 B F24 N2 Ni P3 Si
Formula weight	1684.67
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 47.534(4) Å	α = 90°.
	b = 13.9003(11) Å	β = 128.6300(10)°.
	c = 30.423(2) Å	γ = 90°.
Volume	15703(2) Å^3	
Z	8	
Density (calculated)	1.425 Mg/m^3	
Absorption coefficient	0.425 mm^{-1}	
F(000)	6914	
Crystal size	0.50 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.10 to 30.03°.	
Index ranges	-66<=h<=66, -19<=k<=19, -42<=l<=42	
Reflections collected	211753	
Independent reflections	22976 [R(int) = 0.0677]	
Completeness to theta = 30.03°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9199 and 0.8158	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22976 / 48 / 1037	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1140	
R indices (all data)	R1 = 0.0680, wR2 = 0.1291	
Largest diff. peak and hole	1.202 and -0.833 e.Å^{-3}	

Table S2b. Selected bond lengths [Å] and angles [°] for **2a**.

Ni(1)-N(1)	1.9049(16)
N(1)-N(2)	1.087(2)
Ni(1)-Si(1)	2.2452(5)
Ni(1)-P(1)	2.3064(5)
Ni(1)-P(2)	2.3340(6)
Ni(1)-P(3)	2.3099(5)

N(1)-Ni(1)-Si(1)	178.63(5)
N(2)-N(1)-Ni(1)	179.8(2)
P(1)-Ni(1)-P(2)	120.044(19)

P(1)-Ni(1)-P(3)	118.03(2)
P(3)-Ni(1)-P(2)	117.31(2)
N(1)-Ni(1)-P(1)	95.84(5)
N(1)-Ni(1)-P(2)	97.18(5)
N(1)-Ni(1)-P(3)	98.53(5)
Si(1)-Ni(1)-P(1)	83.11(2)
Si(1)-Ni(1)-P(3)	82.757(19)
Si(1)-Ni(1)-P(2)	82.613(19)

Table S3a. Crystal data and structure refinement for **2b**.

Identification code	ct07	
Empirical formula	C86 H54 B F24 N2 Ni P3 Si	
Formula weight	1761.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.2952(6) Å	α = 74.996(3)°.
	b = 15.4595(7) Å	β = 84.981(3)°.
	c = 20.2687(10) Å	γ = 83.775(3)°.
Volume	3992.6(3) $Å^3$	
Z	2	
Density (calculated)	1.466 Mg/m^3	
Absorption coefficient	0.422 mm^{-1}	
F(000)	1784	
Crystal size	0.23 x 0.15 x 0.08 mm^3	
Theta range for data collection	1.81 to 28.28°.	
Index ranges	-17<=h<=17, -20<=k<=20, -25<=l<=27	
Reflections collected	72851	
Independent reflections	19649 [R(int) = 0.0712]	
Completeness to theta = 28.28°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9671 and 0.9093	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19649 / 1036 / 1073	
Goodness-of-fit on F^2	1.011	

Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1037
R indices (all data)	R1 = 0.0963, wR2 = 0.1203
Largest diff. peak and hole	1.215 and -0.987 e.Å^{-3}

Table S3b. Bond lengths [Å] and angles [°] for **2b**.

Ni(1)-N(1)	1.891(2)
N(1)-N(2)	1.083(3)
Ni(1)-Si(1)	2.2396(8)
Ni(1)-P(1)	2.2352(8)
Ni(1)-P(2)	2.2770(8)
Ni(1)-P(3)	2.2465(7)
N(1)-Ni(1)-Si(1)	172.87(7)
N(2)-N(1)-Ni(1)	175.2(2)
P(1)-Ni(1)-P(2)	116.33(3)
P(1)-Ni(1)-P(3)	125.29(3)
P(3)-Ni(1)-P(2)	113.84(3)
N(1)-Ni(1)-P(1)	96.32(7)
N(1)-Ni(1)-P(2)	102.30(8)
N(1)-Ni(1)-P(3)	93.14(7)
Si(1)-Ni(1)-P(1)	83.64(3)
Si(1)-Ni(1)-P(2)	84.02(3)
Si(1)-Ni(1)-P(3)	81.16(3)

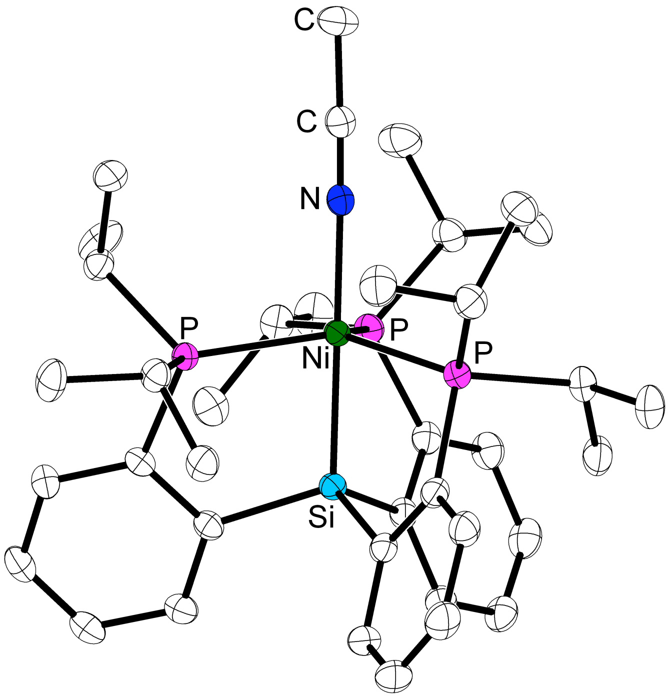

Figure S3a. Solid-state structures of **3a**. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms and BAr$^F{}_4$ anion omitted for clarity.

Table S4a. Crystal data and structure refinement for **3a**.

Identification code	09453	
Empirical formula	C70 H69 B F24 N Ni P3 Si	
Formula weight	1570.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.8286(8) Å	α = 90°.
	b = 14.9103(10) Å	β = 96.7790(10)°.
	c = 38.095(3) Å	γ = 90°.
Volume	7235.7(8) Å^3	
Z	4	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	0.454 mm^{-1}	
F(000)	3216	
Crystal size	0.50 x 0.25 x 0.25 mm^3	
Theta range for data collection	1.08 to 30.54°.	
Index ranges	-18<=h<=18, -21<=k<=21, -53<=l<=53	

Reflections collected	198282
Independent reflections	22112 [R(int) = 0.0664]
Completeness to theta = 30.54°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8949 and 0.8047
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22112 / 46 / 943
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1096
R indices (all data)	R1 = 0.0708, wR2 = 0.1239
Largest diff. peak and hole	0.812 and -0.563 e.Å^{-3}

Table S4b. Selected bond lengths [Å] and angles [°] for **3a**.

Ni(1)-N(1)	1.9359(16)
N(1)-C(1)	1.140(3)
C(1)-C(2)	1.461(3)
Ni(1)-Si(1)	2.2297(6)
Ni(1)-P(1)	2.3229(6)
Ni(1)-P(2)	2.3054(5)
Ni(1)-P(3)	2.3154(5)

N(1)-Ni(1)-Si(1)	179.26(5)
C(1)-N(1)-Ni(1)	178.49(17)
N(1)-C(1)-C(2)	178.7(2)
P(2)-Ni(1)-P(1)	119.52(2)
P(3)-Ni(1)-P(1)	117.75(2)
P(2)-Ni(1)-P(3)	117.94(2)
N(1)-Ni(1)-P(1)	97.53(5)
N(1)-Ni(1)-P(2)	96.85(5)
N(1)-Ni(1)-P(3)	97.58(5)
Si(1)-Ni(1)-P(1)	82.23(2)
Si(1)-Ni(1)-P(2)	82.68(2)
Si(1)-Ni(1)-P(3)	83.15(2)

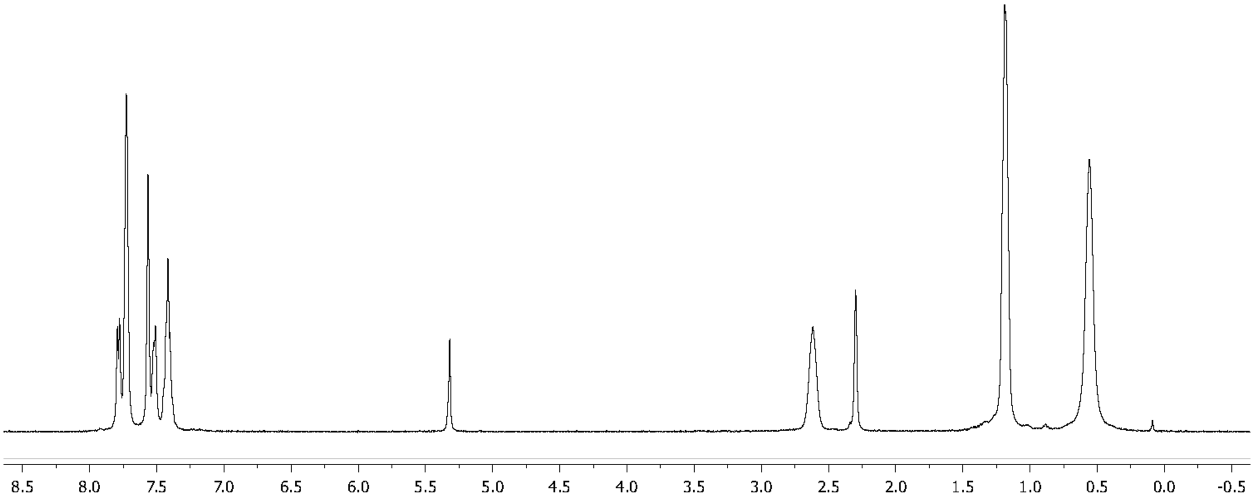

Figure S3b. ^{1}H NMR spectrum of **3a** in CD_2Cl_2 at 25 °C.

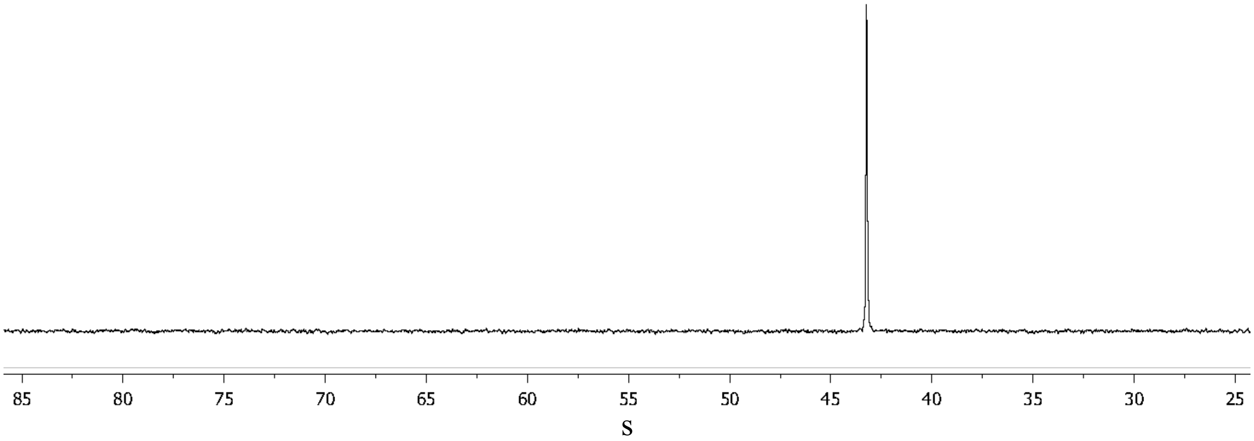

Figure S3c. ^{31}P NMR spectrum of **3a** in CD_2Cl_2 at 25 °C.

Table S5a. Crystal data and structure refinement for **4a**.

Identification code	ct03	
Empirical formula	C69 H66 B Cl F24 Ni O P3 Si	
Formula weight	1593.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 26.3375(11) Å	α = 90°.
	b = 19.5435(8) Å	β = 90°.
	c = 27.2078(10) Å	γ = 90°.

Volume	14004.6(10) Å^3
Z	8
Density (calculated)	1.511 Mg/m^3
Absorption coefficient	0.508 mm^{-1}
F(000)	6504
Crystal size	0.26 x 0.18 x 0.15 mm^3
Theta range for data collection	1.86 to 30.54°.
Index ranges	-35<=h<=37, -26<=k<=27, -33<=l<=38
Reflections collected	190453
Independent reflections	21390 [R(int) = 0.0698]
Completeness to theta = 30.54°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9277 and 0.8792
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21390 / 970 / 923
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1278
R indices (all data)	R1 = 0.0832, wR2 = 0.1443
Largest diff. peak and hole	2.027 and -0.826 e.Å^{-3}

Table S5b. Selected bond lengths [Å] and angles [°] for **4a**.

Ni(1)-C(1)	1.787(4)
C(1)-O(1)	1.157(8)
Ni(1)-Cl(1)	2.303(15)
Ni(1)-Si(1)	2.2578(6)
Ni(1)-P(1)	2.2909(6)
Ni(1)-P(2)	2.3201(6)
Ni(1)-P(3)	2.3006(6)
C(1)-Ni(1)-Si(1)	178.87(15)
O(1)-C(1)-Ni(1)	178.7(4)
P(1)-Ni(1)-P(2)	119.52(2)
P(1)-Ni(1)-P(3)	117.71(2)
P(3)-Ni(1)-P(2)	117.68(2)
C(1)-Ni(1)-P(1)	97.61(15)
C(1)-Ni(1)-P(2)	96.75(15)

C(1)-Ni(1)-P(3)	98.29(14)
Si(1)-Ni(1)-P(1)	82.39(2)
Si(1)-Ni(1)-P(2)	82.29(2)
Si(1)-Ni(1)-P(3)	82.69(2)
Si(1)-Ni(1)-Cl(1)	175.8(4)
P(1)-Ni(1)-Cl(1)	96.4(3)
P(3)-Ni(1)-Cl(1)	94.4(4)
Cl(1)-Ni(1)-P(2)	101.8(4)

Table S6a. Crystal data and structure refinement for **4b**.

Identification code	ct10	
Empirical formula	C87 H54 B F24 Ni O P3 Si	
Formula weight	1761.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.2892(5) Å	α = 74.8510(10)°.
	b = 15.4570(6) Å	β = 85.1070(10)°.
	c = 20.2883(7) Å	γ = 83.8420(10)°.
Volume	3992.3(3) Å^3	
Z	2	
Density (calculated)	1.466 Mg/m^3	
Absorption coefficient	0.422 mm^{-1}	
F(000)	1784	
Crystal size	0.32 x 0.16 x 0.08 mm^3	
Theta range for data collection	1.91 to 30.47°.	
Index ranges	-18<=h<=18, -22<=k<=22, -26<=l<=28	
Reflections collected	93327	
Independent reflections	24174 [R(int) = 0.0490]	
Completeness to theta = 30.47°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9670 and 0.8768	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24174 / 1147 / 1090	
Goodness-of-fit on F^2	1.019	

Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1140
R indices (all data)	R1 = 0.0733, wR2 = 0.1289
Largest diff. peak and hole	1.423 and -0.857 e.Å^{-3}

Table S6b. Bond lengths [Å] and angles [°] for **4b**.

Ni(1)-C(1)	1.796(2)
C(1)-O(1)	1.137(3)
Ni(1)-Si(1)	2.2631(6)
Ni(1)-P(1)	2.2271(6)
Ni(1)-P(2)	2.2385(5)
Ni(1)-P(3)	2.2661(6)
C(1)-Ni(1)-Si(1)	172.56(7)
O(1)-C(1)-Ni(1)	175.9(2)
P(1)-Ni(1)-P(2)	124.87(2)
P(1)-Ni(1)-P(3)	116.53(2)
P(2)-Ni(1)-P(3)	113.63(2)
C(1)-Ni(1)-P(1)	96.32(7)
C(1)-Ni(1)-P(2)	93.33(7)
C(1)-Ni(1)-P(3)	103.13(7)
P(1)-Ni(1)-Si(1)	83.23(2)
P(2)-Ni(1)-Si(1)	80.95(2)
Si(1)-Ni(1)-P(3)	83.62(2)

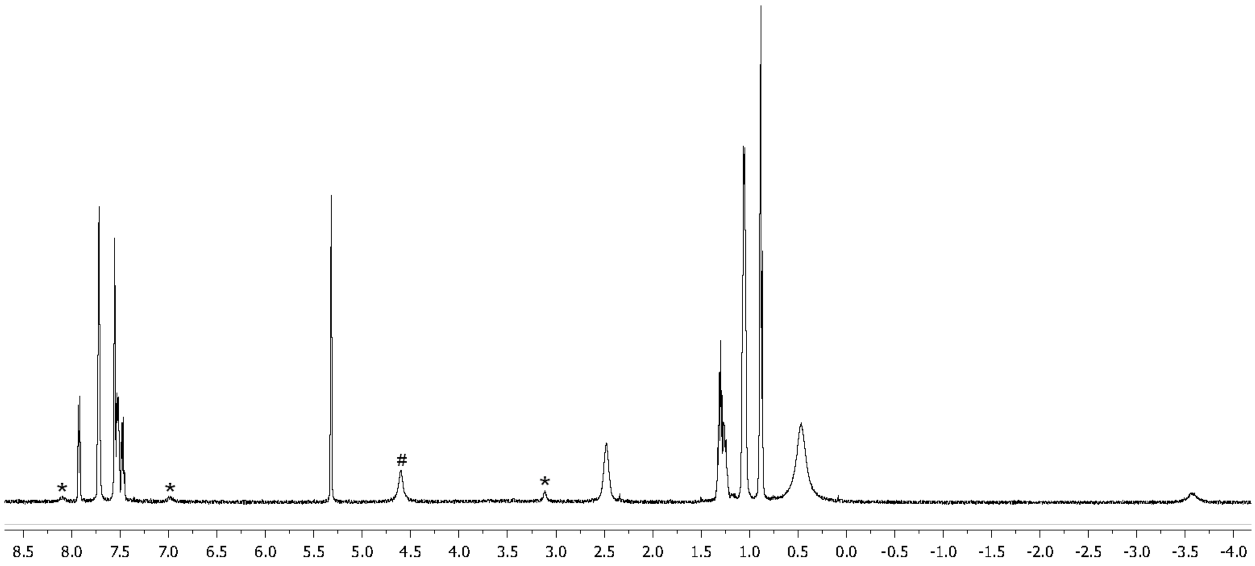

Figure S4a. ^{1}H NMR spectrum of **5a** in CD_2Cl_2 at 25 °C. Peak marked with a '#' symbol is from free H_2 in solution; peaks marked with a '*' symbol correspond to {[SiP$^{iPr}{}_3$]Ni-Cl}{BAr$^F{}_4$} from decomposition of the {[SiP$^{iPr}{}_3$]Ni(N_2)}{BAr$^F{}_4$} starting material.

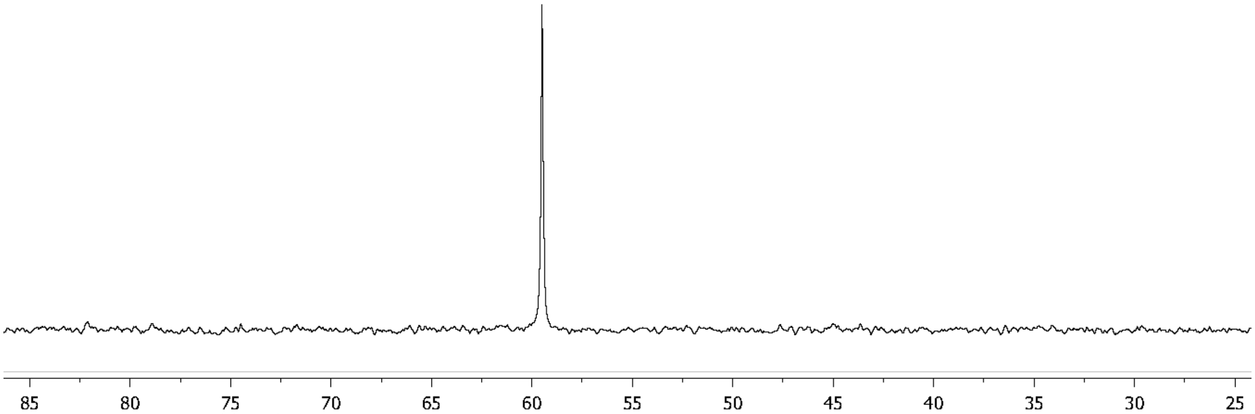

Figure S4b. $^{31}P\{^1H\}$ NMR spectrum of **5a** in CH_2Cl_2 at 25 °C.

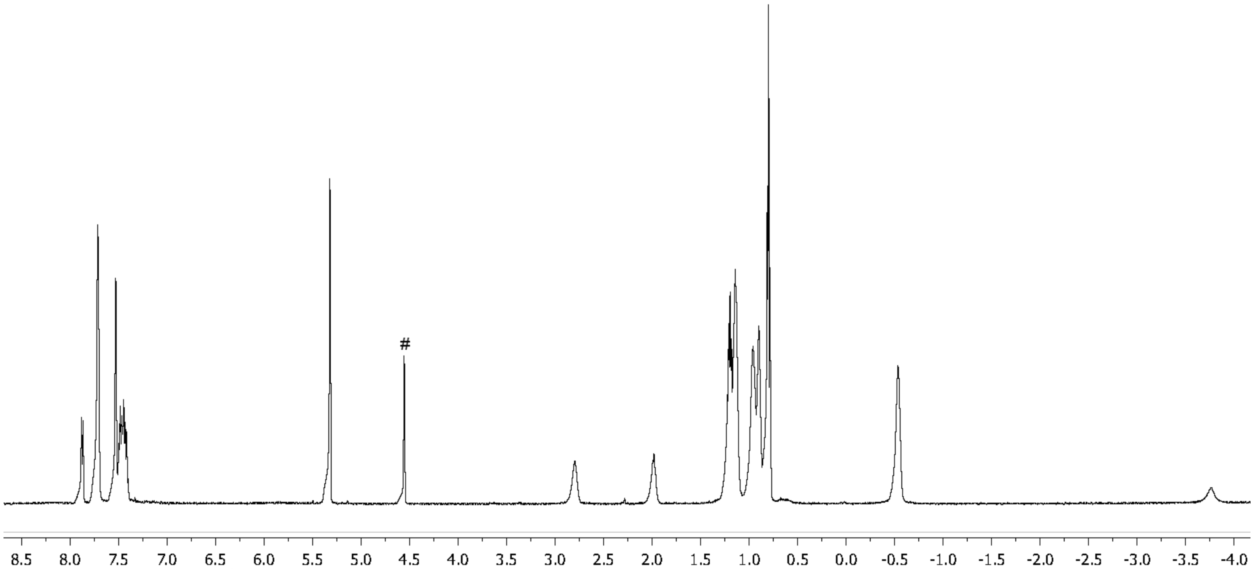

Figure S4c. ^{1}H NMR spectrum of **5a** in CD_2Cl_2 at -70 °C. Peak marked with a '#' symbol is from free H_2 in solution.

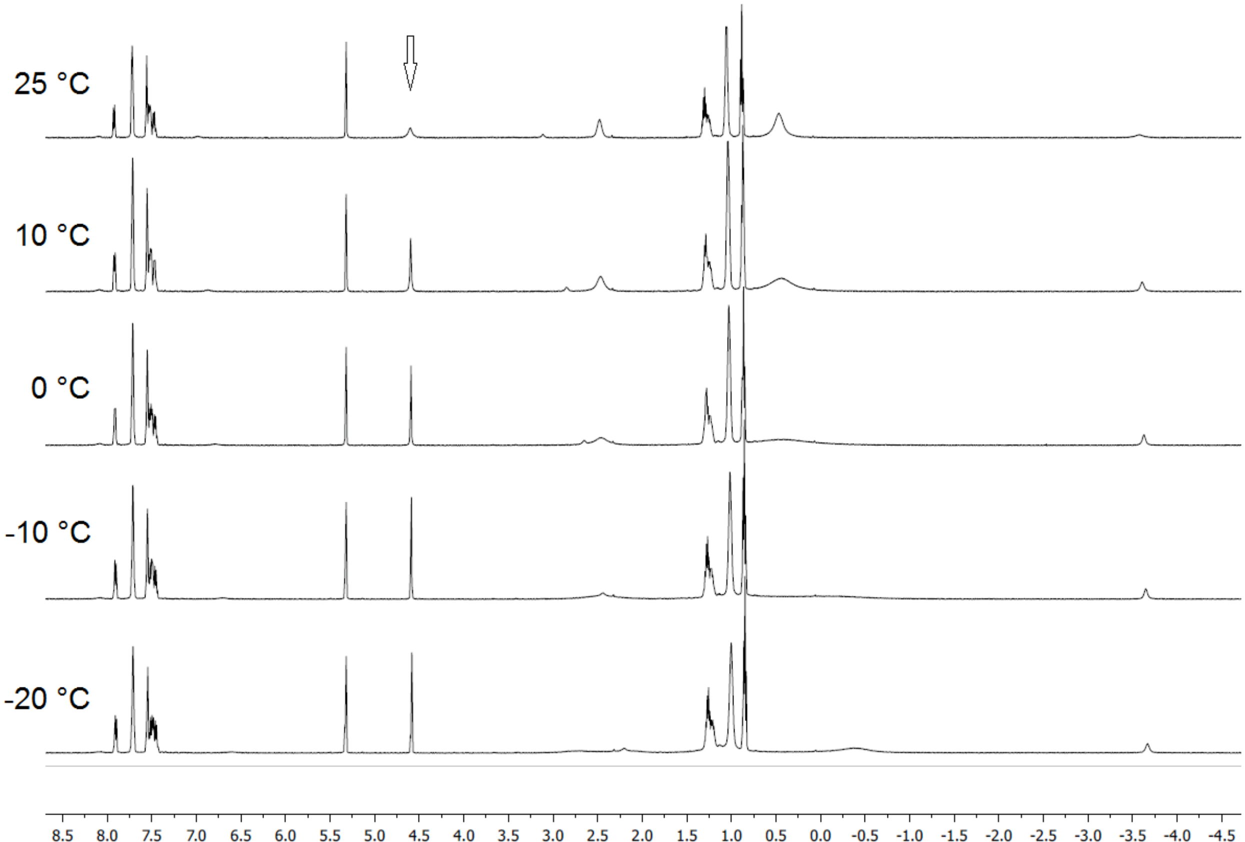

Figure S4d. VT ^1H NMR spectra of **5a** in CD_2Cl_2. Peaks marked with an arrow are from free H_2 in solution.

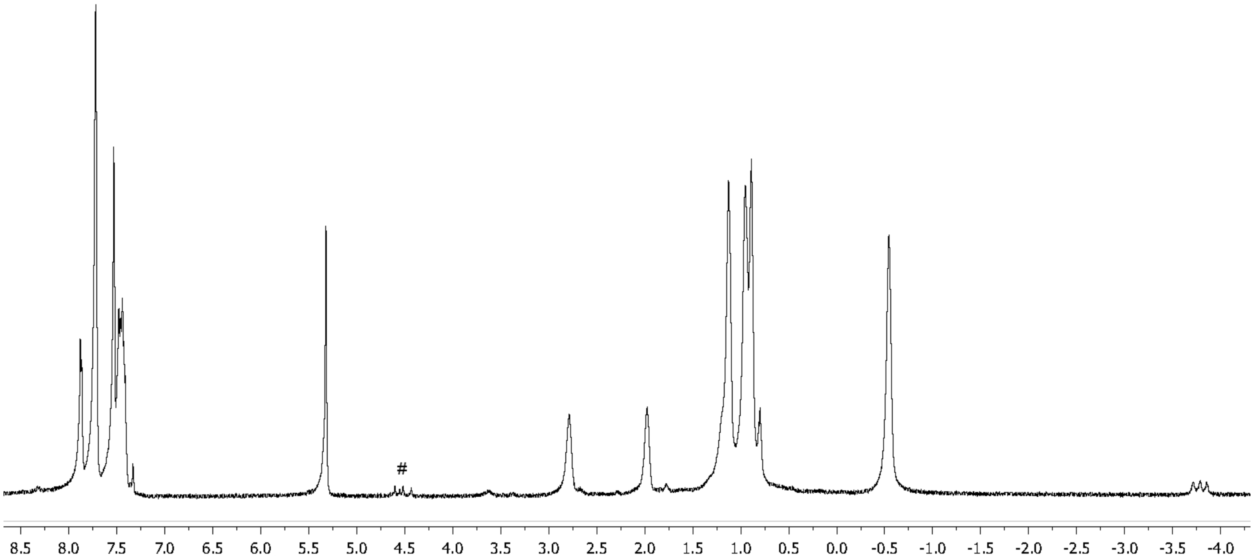

Figure S4e. VT ^1H NMR spectrum of **5a'** in CD_2Cl_2 at -70 °C. Peaks marked with a '#' symbol are from free H_2 (singlet) and HD (three-line pattern) in solution.

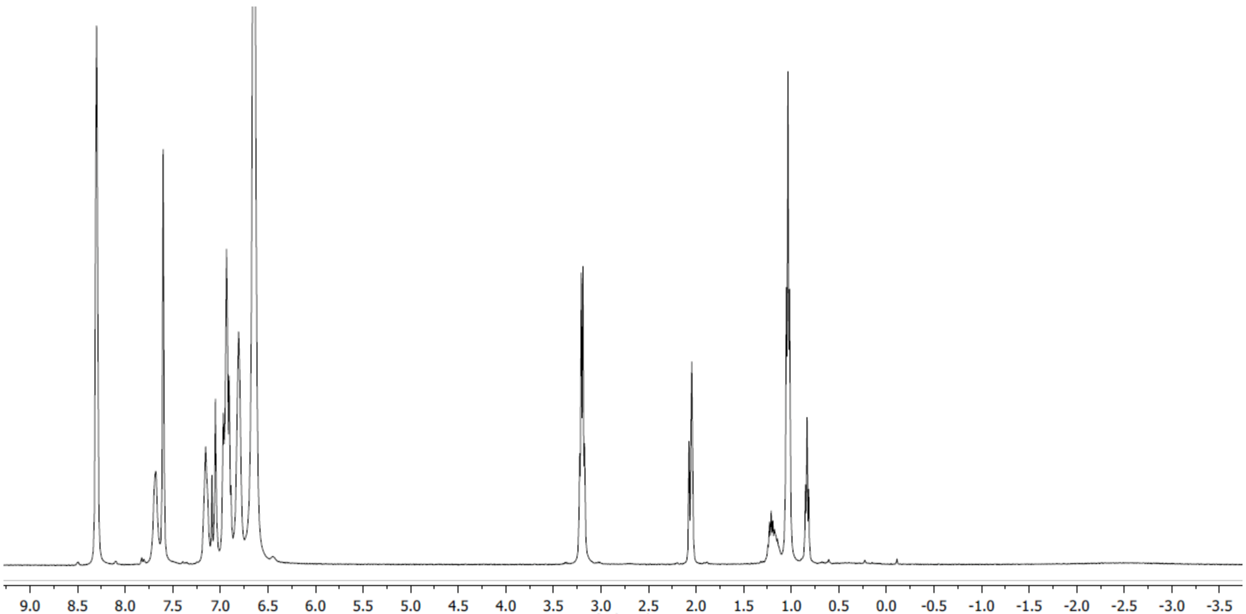

Figure S5a. ^{1}H NMR spectrum **of 5b** in toluene-d_8 at 25 °C.

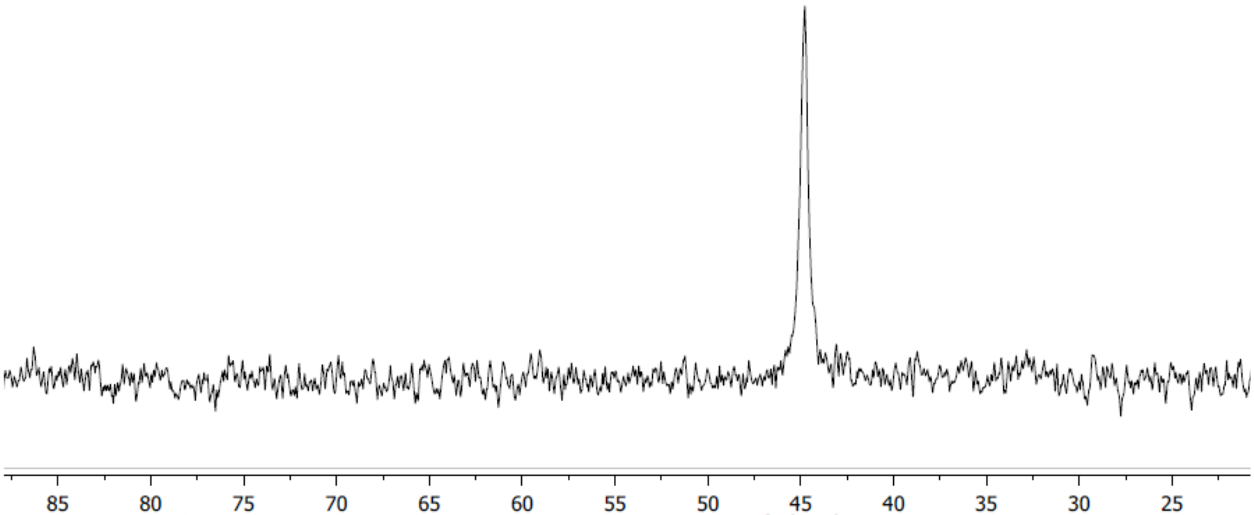

Figure S5b. ^{31}P{^{1}H} NMR spectrum of **5b** in toluene-d_8 at 25 °C.

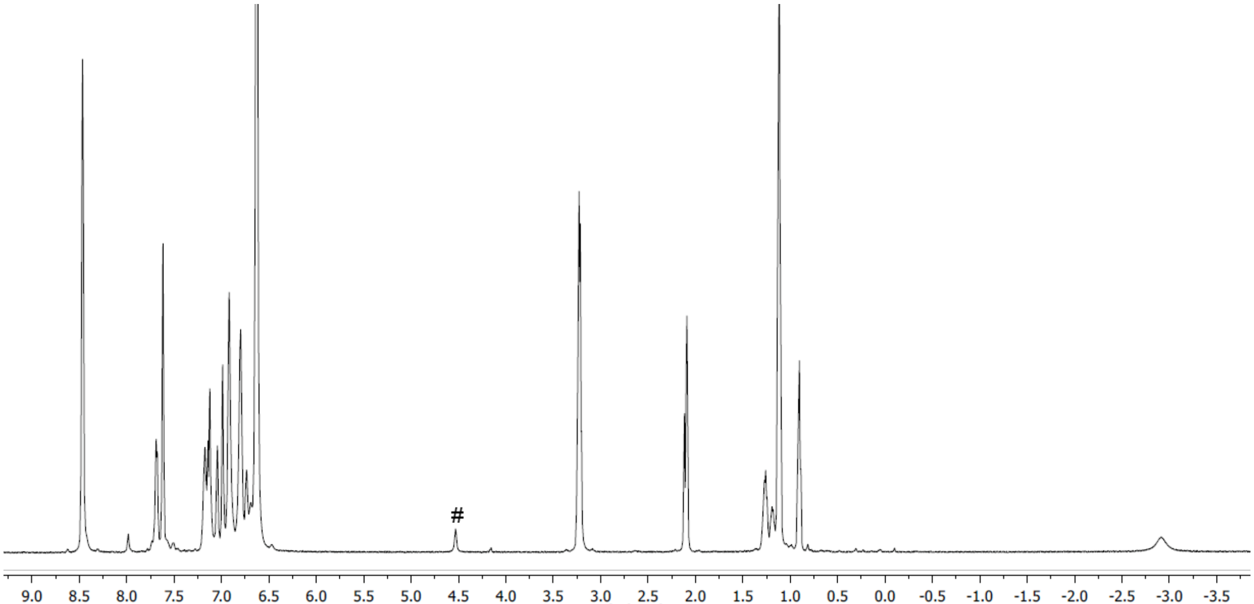

Figure S5c. ^{1}H NMR spectrum of **5b** in toluene-d_8 at -20°C. Peak marked with a '#' symbol is from free H_2 in solution.

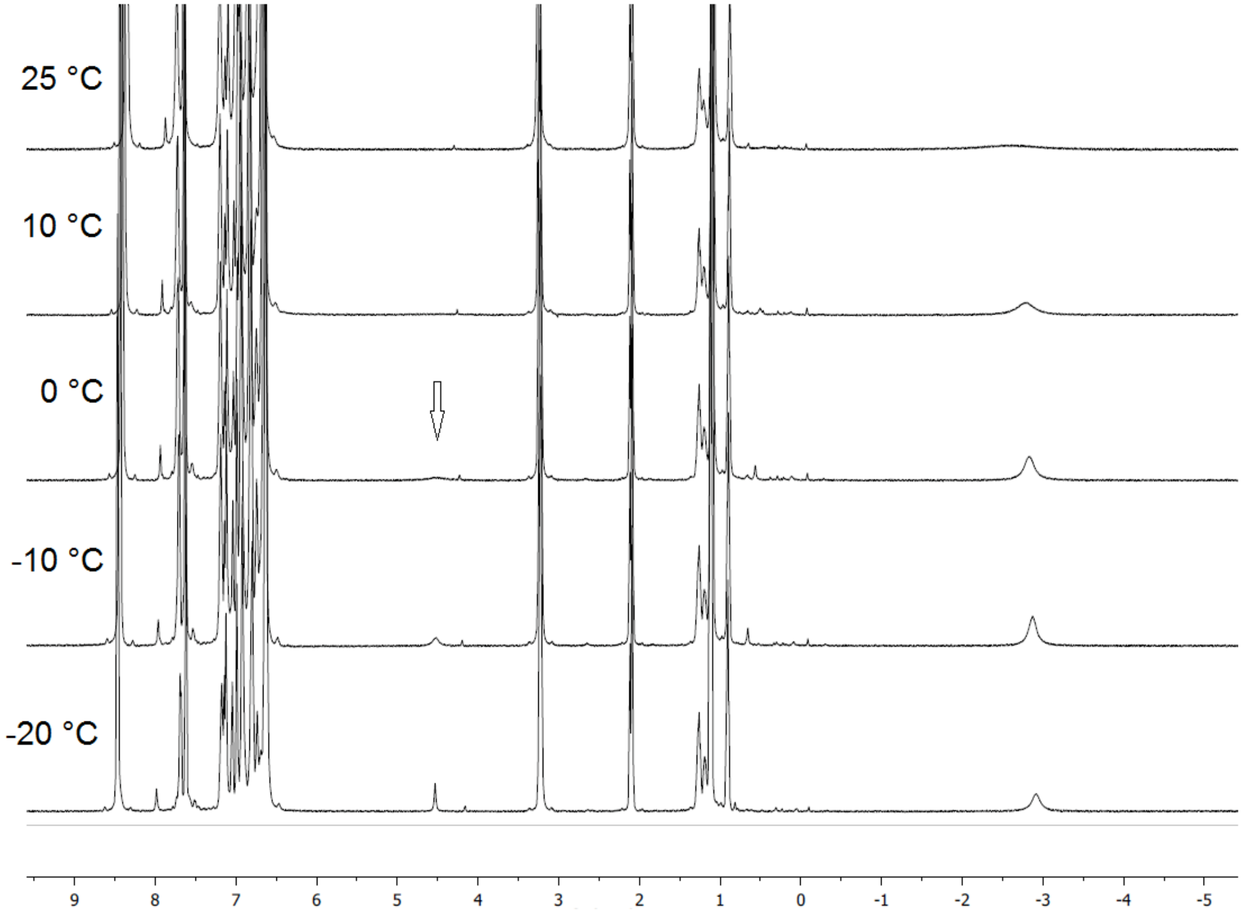

Figure S5d. ^{1}H NMR spectra of **5b** in toluene-d_8. Peaks marked with an arrow are from free H_2 in solution.

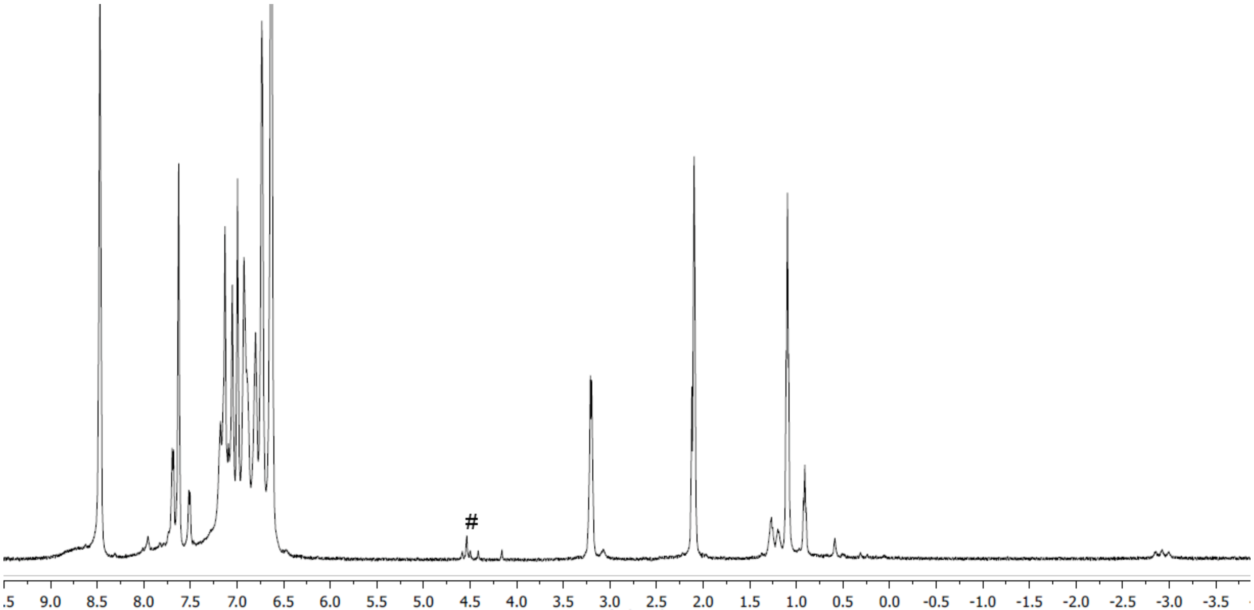

Figure S5e. ^{1}H NMR spectrum of **5b'** in toluene-d_8 at -20°C. Peak marked with a '#' symbol is from free H_2 (singlet) and HD (three-line pattern) in solution.

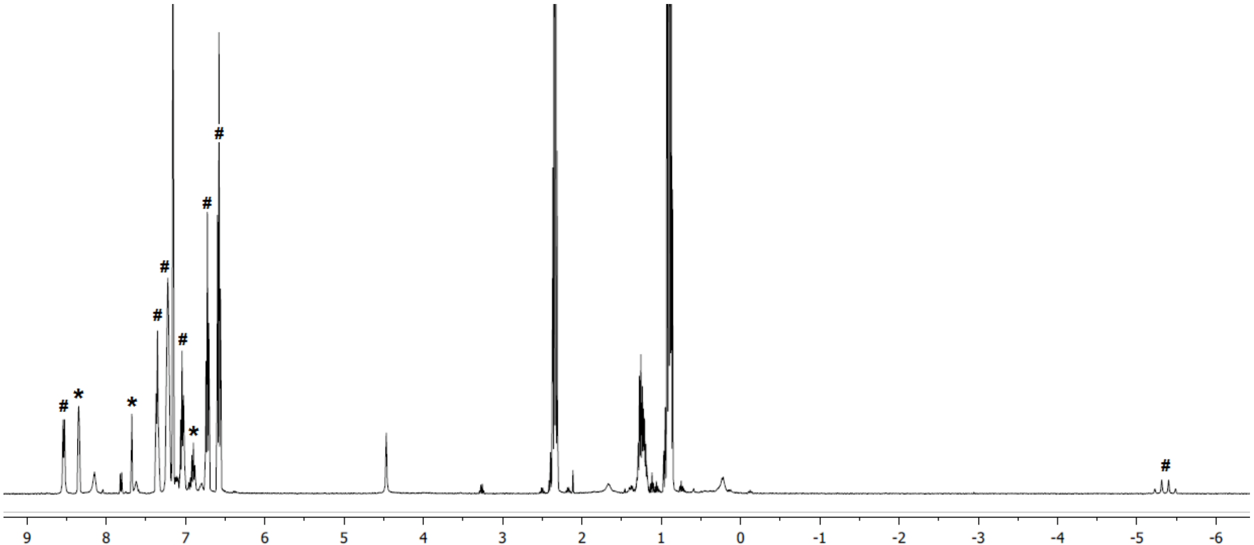

Figure S5f. ^{1}H NMR spectrum of deprotonation of **5b** in C_6D_6 at 25 °C. Peaks marked with a '#' symbol are from the resulting hydride, **6b**; peaks marked with a '*' symbol are from remaining **5b**. The large peaks at 2.34 and 0.91 are from excess triethylamine.

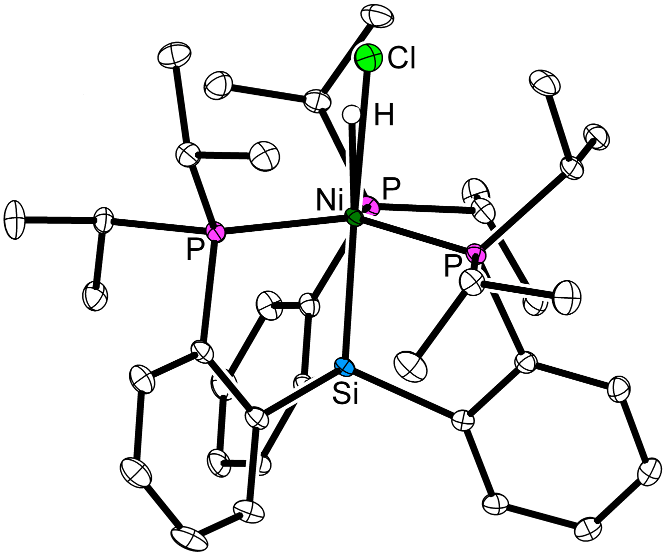

Figure S6a. Solid-state structures of **6a**. Partially-occupied (2.6%) chloride position also shown. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms omitted for clarity.

Table S7a. Crystal data and structure refinement for **6a**.

Identification code	ct15	
Empirical formula	C36 H55 Cl Ni P3 Si	
Formula weight	702.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9905(7) Å	α = 78.237(3)°.
	b = 11.1304(7) Å	β = 79.052(3)°.
	c = 16.8144(11) Å	γ = 61.648(2)°.
Volume	1761.8(2) Å^3	
Z	2	
Density (calculated)	1.325 Mg/m^3	
Absorption coefficient	0.821 mm^{-1}	
F(000)	750	
Crystal size	0.36 x 0.35 x 0.04 mm^3	
Theta range for data collection	1.24 to 36.32°.	
Index ranges	-18<=h<=18, -18<=k<=18, -28<=l<=28	
Reflections collected	82069	
Independent reflections	16765 [R(int) = 0.0631]	
Completeness to theta = 36.32°	98.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9679 and 0.7564
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16765 / 0 / 390
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1045
R indices (all data)	R1 = 0.0750, wR2 = 0.1168
Largest diff. peak and hole	1.065 and -0.544 e.Å^{-3}

Table S7b. Selected bond lengths [Å] and angles [°] for **6a**.

Ni(1)-H(100)	1.49(3)
Ni(1)-Cl(1)	2.345(16)
Ni(1)-Si(1)	2.2014(5)
Ni(1)-P(1)	2.2045(5)
Ni(1)-P(2)	2.2096(4)
Ni(1)-P(3)	2.2085(4)

Si(1)-Ni(1)-H(100)	174.3(9)
Si(1)-Ni(1)-Cl(1)	178.6(4)
P(1)-Ni(1)-P(2)	119.831(16)
P(1)-Ni(1)-P(3)	118.269(17)
P(3)-Ni(1)-P(2)	119.496(17)
P(1)-Ni(1)-H(100)	91.3(9)
P(2)-Ni(1)-H(100)	93.2(9)
P(3)-Ni(1)-H(100)	101.0(9)
P(1)-Ni(1)-Cl(1)	96.0(4)
P(2)-Ni(1)-Cl(1)	95.4(4)
P(3)-Ni(1)-Cl(1)	94.1(4)
Si(1)-Ni(1)-P(1)	85.076(16)
Si(1)-Ni(1)-P(2)	84.776(16)
Si(1)-Ni(1)-P(3)	84.652(16)

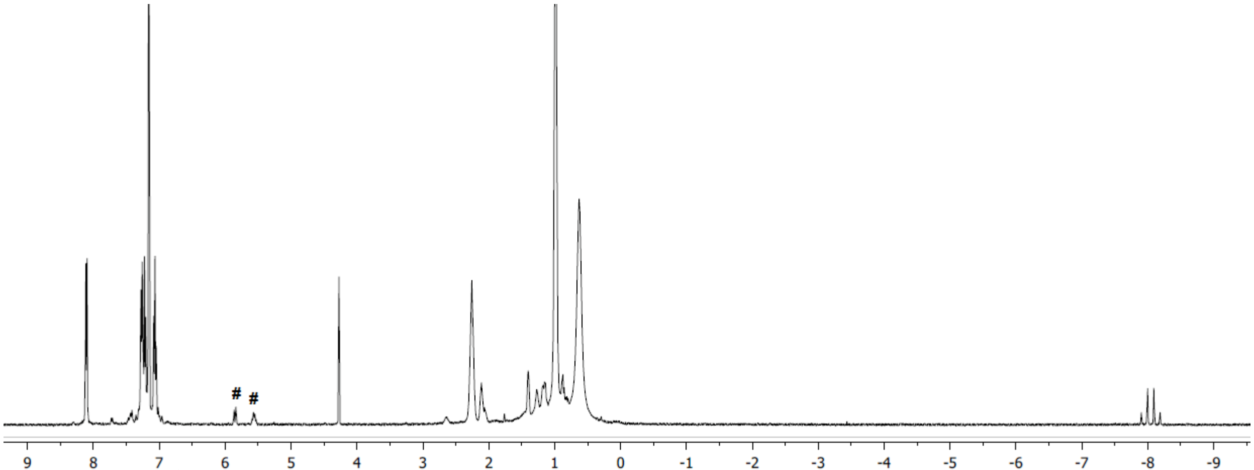

Figure S6b. ^{1}H NMR spectrum of **6a** in C_6D_6 at 25 °C. Peaks marked with a '#' symbol correspond to remaining COD; peaks for the free H[SiP$^{iPr}{}_3$] ligand are observed among the small impurity peaks.

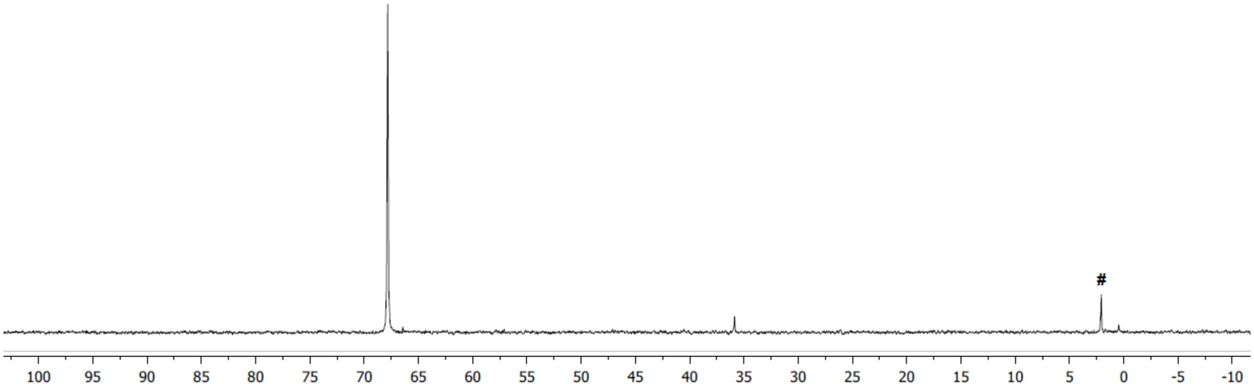

Figure S6c. ^{31}P{^{1}H} NMR spectrum of **6a** in C_6D_6 at 25 °C. The peak marked with a '#' symbol corresponds to free H[SiP$^{iPr}{}_3$] ligand; two other small impurities have not been identified.

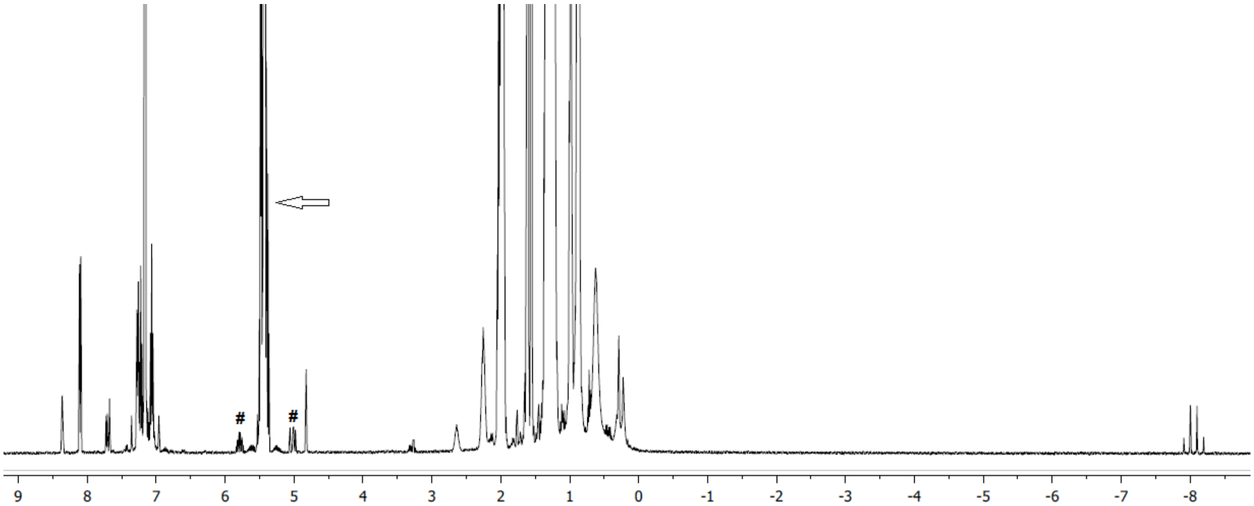

Figure S6d. ^{1}H NMR spectrum of reaction of **6a** with 1-octene in C_6D_6 at 25 °C. Peaks marked with an arrow correspond to *cis*- and *trans*- 2-octene; peaks marked with a '#' symbol correspond to 1-octene.

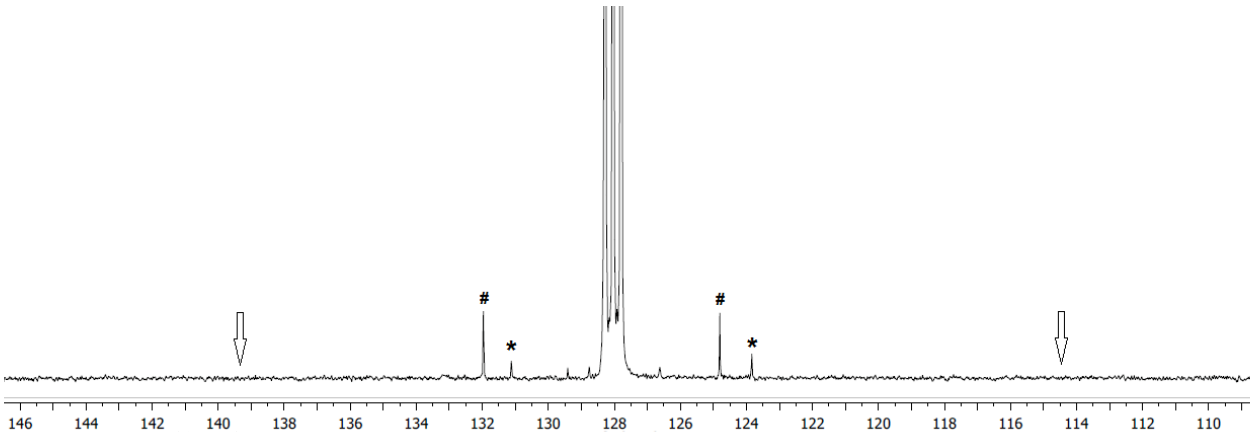

Figure S6e. $^{13}C\{^{1}H\}$ NMR spectrum of reaction of **6a** with 1-octene in C_6D_6 at 25 °C. The peaks marked with a '#' symbol correspond to *trans*-2-octene while those marked with a '*' symbol correspond to *cis*-2-octene; the arrows indicate where the resonances for 1-octene should occur.

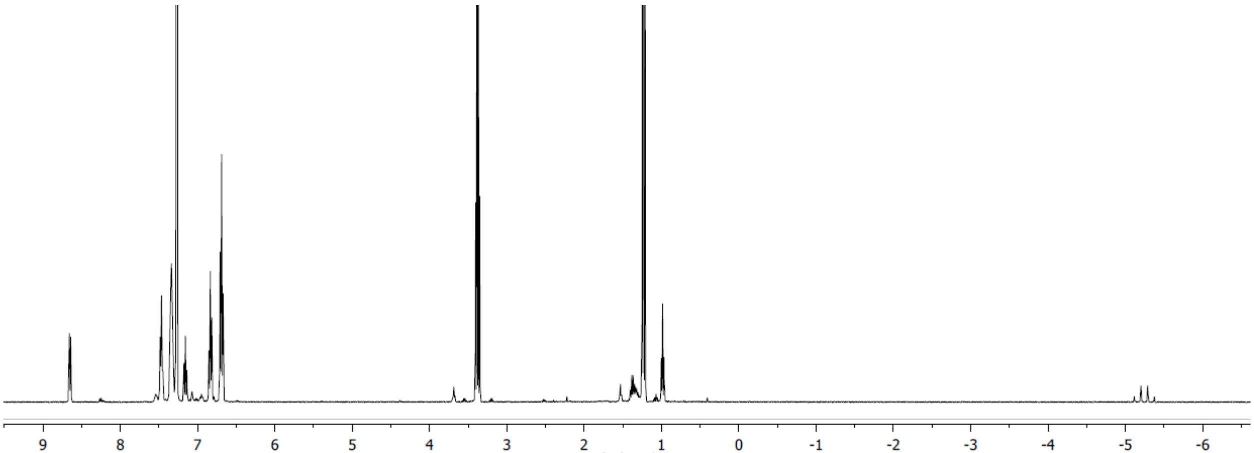

Figure S7a. ^{1}H NMR spectrum of **6b** in C_6D_6 at 25 °C.

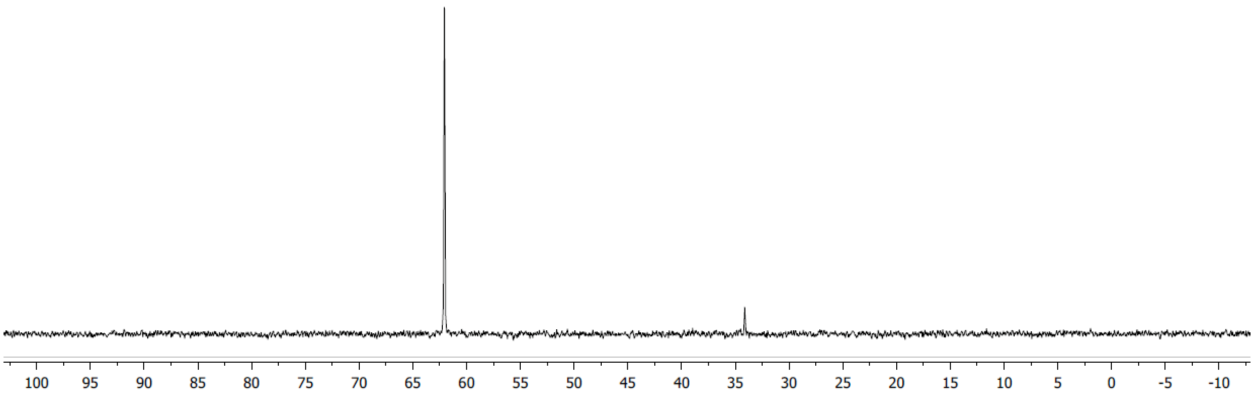

Figure S7b. $^{31}P\{^{1}H\}$ NMR spectrum of **6b** in C_6D_6 at 25 °C. The small impurity at 34.1 ppm has not been identified.

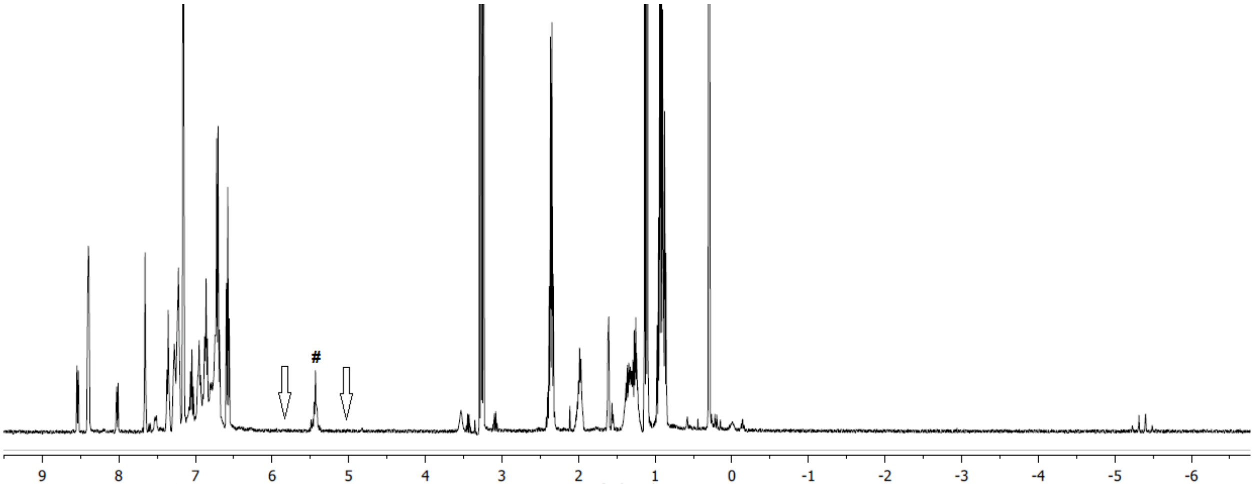

Figure S7c. ^{1}H NMR spectrum of reaction of **6b** with 1-octene in C_6D_6 at 25 °C. Peaks marked with a '#' symbol correspond to *cis*- and *trans*- 2-octene; the arrows indicate where the resonances of 1-octene should occur.

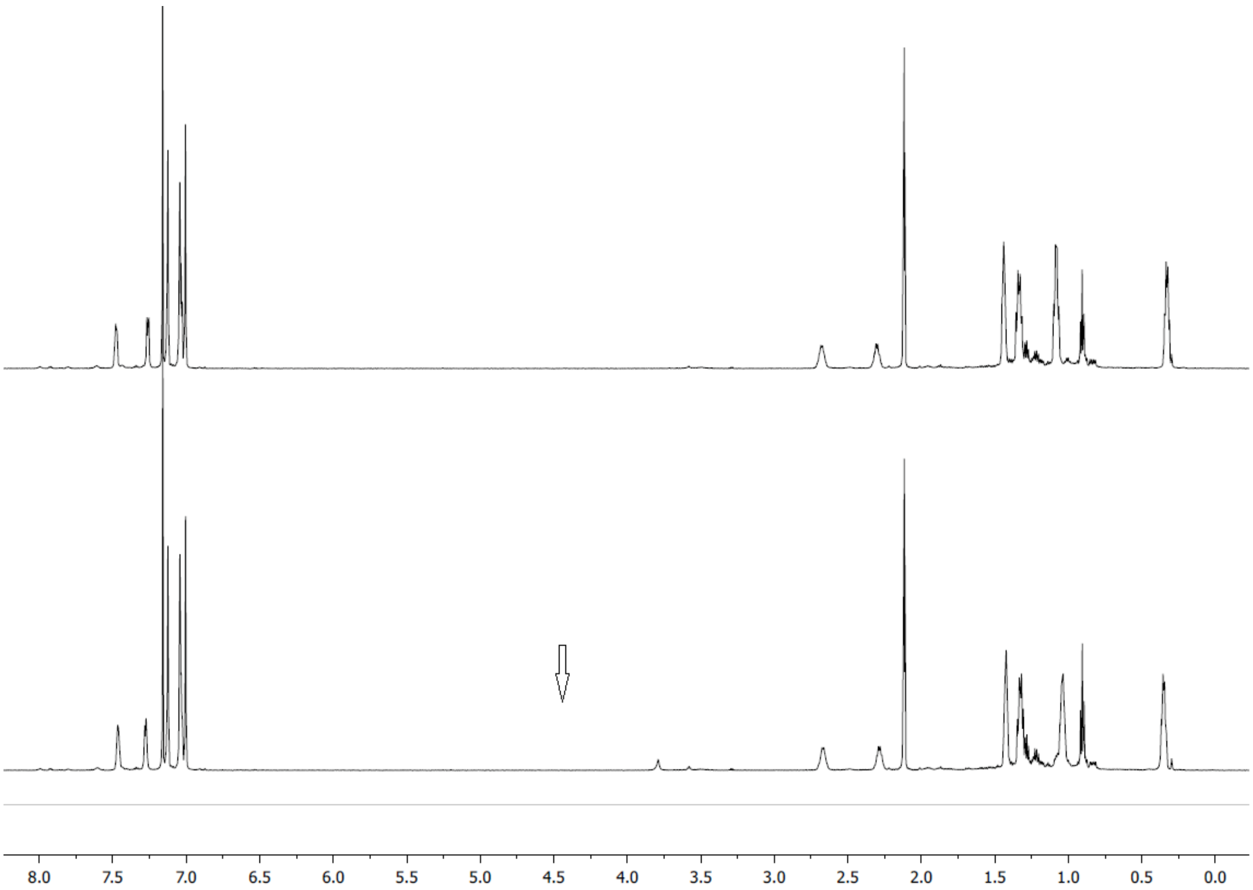

Figure S8a. ^{1}H NMR spectra of [TP$^{i\text{Pr}}$B]Ni in toluene-d$_8$ (top) and [TP$^{i\text{Pr}}$B]Ni under 1 atm H_2 in tolune-d$_8$ (bottom). The arrow indicates where the resonance of free H_2 in solution should occur.

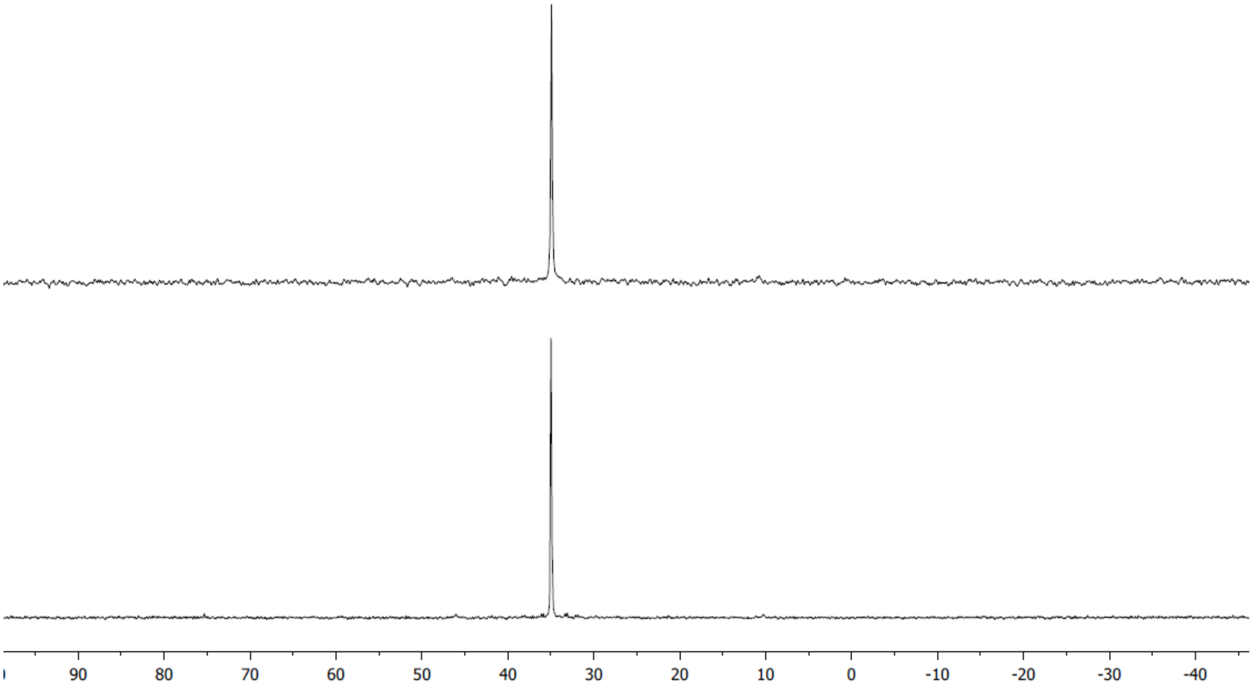

Figure S8b. ^{31}P NMR spectra of [TP$^{i\text{Pr}}$B]Ni in toluene-d$_8$ (top) and [TP$^{i\text{Pr}}$B]Ni under 1 atm H_2 in toluene-d$_8$ (bottom).

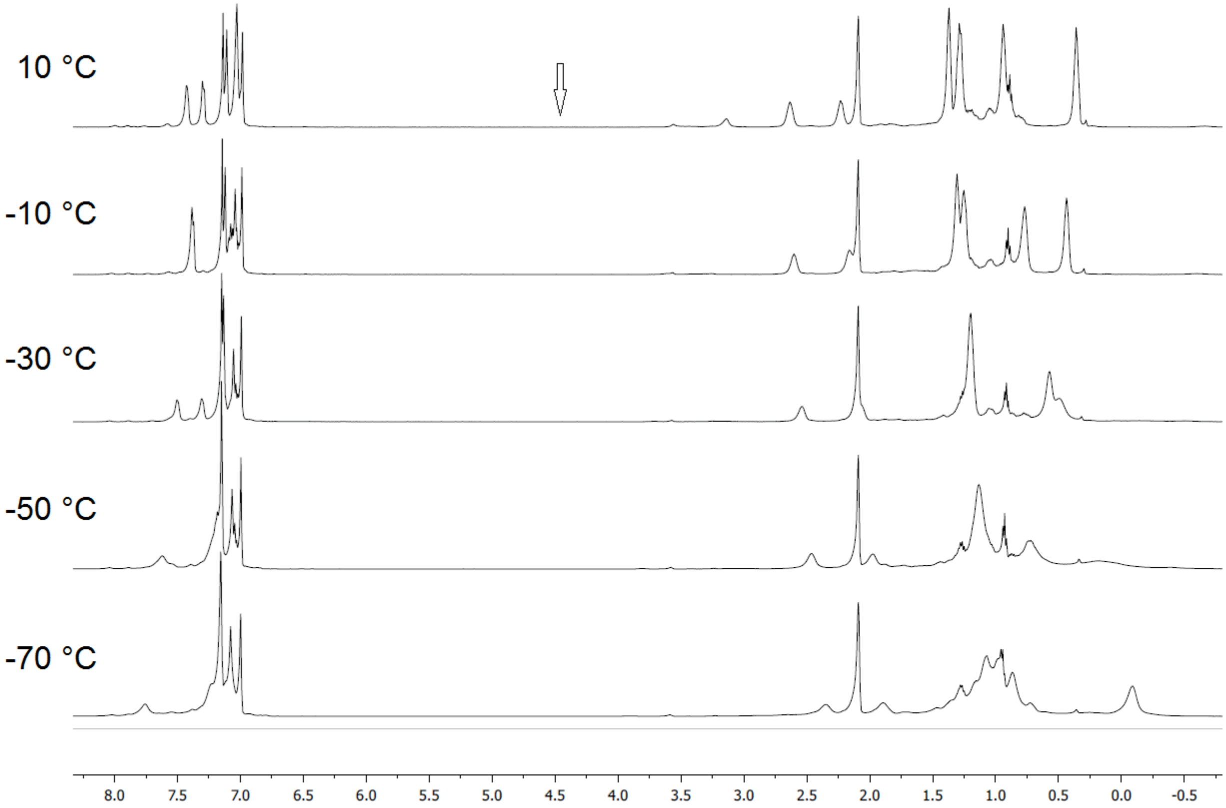

Figure S8c. VT ^{1}H NMR spectra of [TP^{iPr}B]Ni in toluene-d_8 under 1 atm H_2. The arrow indicates where the resonance of free H_2 in solution should occur.

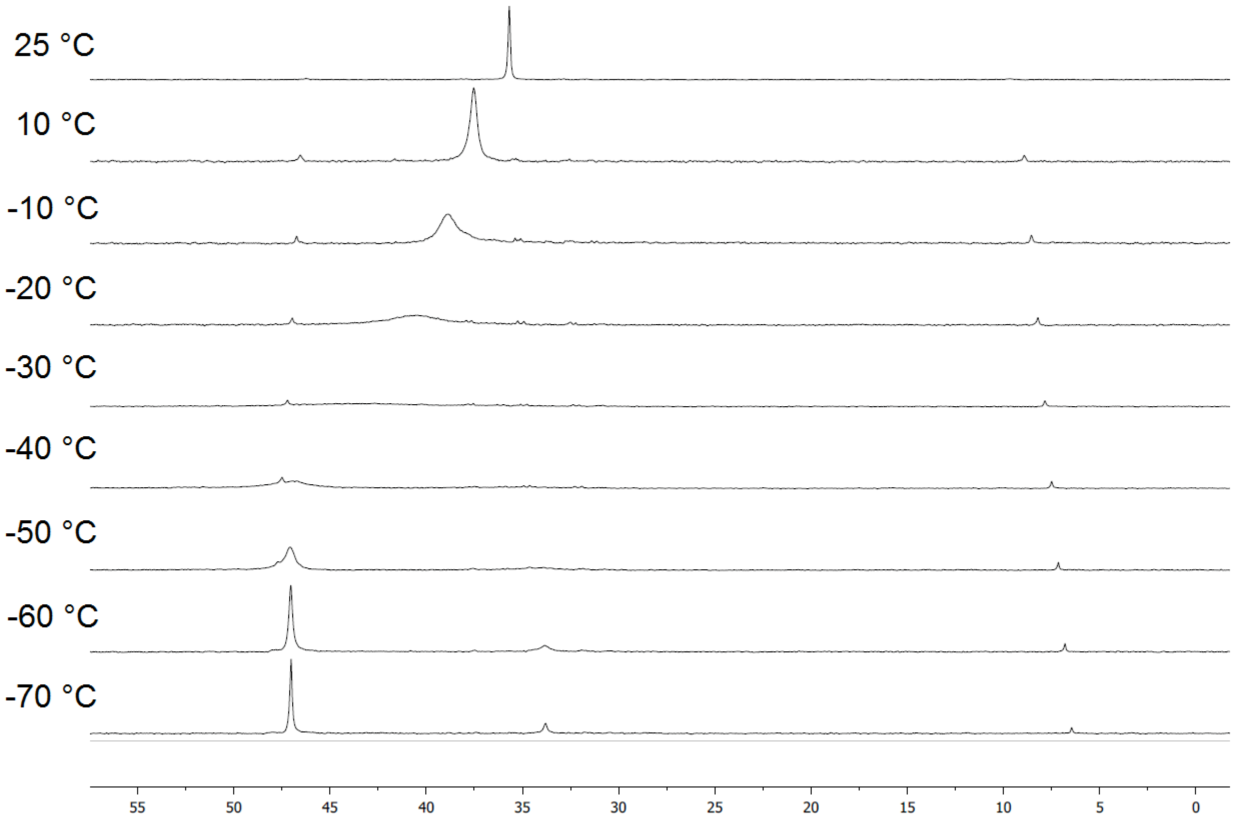

Figure S8d. VT ^{31}P NMR spectra of [TP^{iPr}B]Ni in toluene-d$_8$ under 1 atm H$_2$.

---

1 M. T. Whited, N. P. Mankad, Y. H. Lee, P. F. Oblad, and J. C. Peters, *Inorg. Chem.,* 2009, **48**, 2507.

2 Minor alterations to literature procedure: NiCl$_2$·DME was used instead of NiCl$_2$ and the reaction was done at room temperature in benzene instead of at reflux in THF.

3 M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffron, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, and D. Bourissou, *J. Am. Chem. Soc.,* 2008, **130**, 16729.

4 (a) M. Brookhart, B. Grant, and A. F. Volpe, Jr., *Organometallics,* 1992, **11**, 3920. (b) A solution of 1.2 M HCl in Et$_2$O was used instead of gaseous HCl.

5 Implementation of "setref" is detailed in the Vnmr file found at /vnmr/nuctables/nuctabref.

6 R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, and P. Granger, *Pure Appl. Chem.,* 2001, **73**, 1795.

7 G. M. Sheldrick, *SHELXTL 2000*, Universität Göttingen: Göttingen, Germany, 2000.

8 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03; Revision B.05 ed.; Gaussian, Inc: Pittsburgh, PA, 2003.

9 C. Tsay, N. P. Mankad, and J. C. Peters, *J. Am. Chem. Soc.,* 2010, **132**, 13975.