

Electronic Supporting Information

Selective hydration of nitriles to amides catalysed by PCP pincer supported nickel(II) complexes

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General Considerations. All manipulations were carried out in either an Innovative Technology Inc. inert atmosphere glovebox or on a greaseless dual manifold vacuum line using Teflon (Kontes) needle valves and swivel-frit type glassware. Tetrahydrofuran, toluene and hexanes were dried using a Grubbs/Dow solvent purification system and stored in evacuated thick glass vessels over sodium/benzophenone prior to use. Dichloromethane was dried over CaH₂, evacuated and transferred into a thick glass vessel over activated 4A molecular sieves prior to use. Toluene-d₈, benzene-d₆ and THF-d₈ were purchased from Aldrich, dried over sodium/benzophenone and vacuum transferred into sealed thick glass vessels prior to use. Proligands (C₆H₄PPr^{*i*})₂CH₂ and (C₆H₄PBu^{*t*})₂CH₂, and complex (C₆H₄PPr^{*i*})₂CHNiOH (**2^{iPr}**) were prepared according to published procedures.¹⁻² All other reagents were purchased from Aldrich and used as received. NMR spectra were obtained on Bruker Avance III 400 MHz and 600 MHz spectrometers. Elemental analyses were obtained by the Instrumentation Facility of the Department of Chemistry on a Perkin-Elmer CHNS/O series II analyzer 2400. X-ray crystallographic analyses were performed on a Nonius KappaCCD diffractometer with samples coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Full crystallography details can be found in independently uploaded (.cif) files.

Synthesis of di-cyclohexylphosphino substituted proligand.

To a flask charged with *bis*-(2-bromophenyl)methane (1.02g, 3.13 mmol), 60 mL of diethyl ether was added *via vac* transfer. The solution was cooled to -78 °C and *tert*-butyllithium (1.7 M in pentane, 7.36 mL, 12.5 mmol) was added drop-wise over 15 minutes. The mixture was left to stir for 3 hours while holding the temperature constant. Di-cyclohexylchlorophosphine (1.38 mL, 6.25 mmol) was then added quickly, and the solution was allowed to warm to room temperature with stirring overnight. The solution was filtered, and the solvent removed *in vacuo*. Acetonitrile (20 mL) and the crude product was triturated. The resulting solution was left at room temperature (2 hours) to recrystallize, then filtered. Colorless crystals were washed 3 times with acetonitrile. 1.635 g (2.92 mmol) of product was isolated (93% yield). ¹H NMR (600 MHz, C₆D₆): δ 7.48 (dt, ³J_{HH} = 7.4, ³J_{HP} = 2.4 Hz, 2H, ArH), 7.18 (m, 2H, ArH), 7.10 (m, 4H, ArH), 5.27 (t, ⁴J_{HP} = 3.2 Hz, 2H, CH₂), 2.02 (m, 4H, CH, Cy), 1.96 (m, 4H, CH₂, Cy), 1.72 (dtt, ³J_{HH} = 11.2, ³J_{HH} = 3.5, ³J_{HP} = 1.9 Hz, 8H, CH₂, Cy), 1.63 (m, 5H, CH₂, Cy), 1.56 (m, 5H, CH₂, Cy), 1.21 (m, 18H, CH₂, Cy). ³¹P{¹H} NMR (243 MHz, C₆D₆): δ -15 (s). ¹H NMR (600 MHz, THF): δ 7.53 – 7.44 (m, 2H), 7.22 – 7.05 (m, 4H), 6.98 – 6.86 (m, 2H), 4.80 (t, *J* = 3.2 Hz, 2H), 1.94 (tdd, *J* = 13.7, 8.8, 3.9 Hz, 4H), 1.84 – 1.69 (m, 6H), 1.71 – 1.54 (m, 6H), 1.44 – 0.98 (m, 28H). ¹³C{¹H} NMR (151 MHz, THF): δ 150.1 (d, ¹J_{CP} = 27.1 Hz, aryl CP), 135.3 (d, ²J_{CP} = 20.1 Hz, aryl C), 133.6 (d, ³J_{CP} = 2.9 Hz, aryl C), 131.4 (d, ²J_{CP} = 5.0 Hz, aryl C), 129.2 (s, aryl C), 126.1 (s, aryl C), 39.7 (t, ³J_{CP} = 26.3 Hz, CH₂), 35.2 (d, ¹J_{CP} = 14.6 Hz, C, Cy), 31.7 (d, ²J_{CP} = 17.7 Hz, C, Cy), 30.4 (d, ³J_{CP} = 9.1 Hz, C, Cy), 28.3 (d, ²J_{CP} = 12.0 Hz, C, Cy), 28.1 (d, ³J_{CP} = 7.6 Hz, C, Cy), 27.6 (s, C, Cy). ³¹P{¹H} NMR (243 MHz, THF): δ -15 (s). HRMS (ESI) calculated for C₃₇H₅₅P₂ (M⁺) 561.377351, found 561.376672; elemental analysis calcd (%) for C₃₇H₅₄P₂: C 79.25, H 9.71; found: C 79.25, H 10.24.

Synthesis of (C₆H₄PPr^{*i*})₂CHNiBr, **1^{iPr}**.

An improved synthesis than that previously reported was employed.¹ To a solid mixture of anhydrous NiBr₂ (0.546 g, 2.5 mmol) and the ligand precursor (C₆H₄PPr^{*i*})₂CH₂ (**1^{iPr}**) (1.0 g, 2.5 mmol) was added dichloromethane (50 mL) and triethylamine (0.71 mL, 5.1 mmol). The reaction mixture was stirred at room temperature for 1 day. The resulting brown solution was evacuated and the residue dissolved in toluene and filtered. The filtrate was concentrated to 3 mL. Hexanes were layered over the

toluene solution. The solution was stored at -30 °C for 2 days yielding large brown crystals of the product. The crystals were separated and dried under vacuum. Yield 1.25 g (93%). Spectroscopic data consistent with that previously reported was obtained.¹

Synthesis of $(C_6H_4PBu^t)_2CHNiCl$, **1^{tBu}**.

To a solid mixture of anhydrous $NiCl_2$ (0.143 g, 1.1 mmol) and the ligand precursor $(C_6H_4PBu^t)_2CH_2$ (**1^{tBu}**) (0.500 g, 1.1 mmol) was added dichloromethane (30 mL) and triethylamine (0.32 mL, 2.3 mmol). The reaction mixture was stirred at room temperature for 1 day. The resulting brown solution was evacuated and the residue dissolved in toluene and filtered. The filtrate was concentrated to 1 mL and the solution was slowly evaporated at -30 °C for 2 days yielding large brown crystals of the product. The crystals were separated and dried under vacuum. Yield 0.550 g (91%).

¹H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.51 (m, 2H, ArH), 7.25 (d, $J(H-H) = 8.0$ Hz, 2H, ArH), 7.01 (t, $J(H-H) = 7.6$ Hz, 2H, ArH), 6.91 (t, $J(H-H) = 7.2$ Hz, 2H, ArH), 5.49 (s, 1H, CHNi), 1.57 (app. dt, $J(H-H) = 15.2$ Hz, $J(P-H) = 6.4$ Hz, 36H, $C(CH_3)_3$). ³¹P{¹H} NMR (C_6D_6 , 161.9 MHz, 298 K): δ 55.4 (s). ¹³C{¹H} NMR (C_6D_6 , 100.6 MHz, 298 K): δ 160.4 (t, $J(P-C) = 18.1$ Hz, aryl C), 134.9 (s, aryl C), 134.4 (t, $J(P-C) = 16.1$ Hz, aryl C), 129.9 (s, aryl C), 127.3 (t, $J(P-C) = 7.0$ Hz, aryl C), 124.4 (t, $J(P-C) = 3.0$ Hz, aryl C), 43.4 (t, $J(P-C) = 8.1$ Hz, CHNi), 37.2 (app. dt, $J(P-C) = 66.4$ Hz, $J(P-C) = 5.0$ Hz, $C(CH_3)_3$), 31.0 (app. dt, $J(P-C) = 40.3$ Hz, $J(P-C) = 3.0$ Hz, $C(CH_3)_3$). Anal. Calcd. for $C_{29}H_{45}ClNiP_2$: C, 63.36; H, 8.25. Found: C, 63.47; H, 8.44. See Figure S1 for X-ray depiction of the molecular structure of **2^{tBu}** and Table S1 for relevant crystallographic data.

Synthesis of $(C_6H_4PCy_2)_2CHNiBr$, **1^{Cy}**.

To a solid mixture of anhydrous $NiBr_2$ (0.117 g, 0.54 mmol) and the ligand precursor $(C_6H_4PCy_2)_2CH_2$ (**1^{Cy}**) (0.300 g, 0.54 mmol) was added dichloromethane (50 mL) and triethylamine (0.15 mL, 1.09 mmol). The reaction mixture was stirred at room temperature for 1 day. The resulting dark orange solution was evacuated and the residue dissolved in toluene (5 mL) and filtered. Hexanes (5 mL) were layered over the toluene solution. The solution was stored at -30 °C for 2 days yielding small orange crystals of the product. The crystals were separated and dried under vacuum. Yield 0.340 g (90%).

¹H NMR (C_6D_6 , 600 MHz, 298 K): δ 7.31 (m, 4H, ArH), 7.07 (t, $J(H-H) = 7.2$ Hz, 2H, ArH), 6.97 (t, $J(H-H) = 7.8$ Hz, 2H, ArH), 5.57 (s, 1H, CHNi), 2.56 (m, 4H, Cy), 2.44 (m, 4H, Cy), 2.08 (m, 4H, Cy), 1.67 (m, 20H, Cy), 1.16 (m, 12H, Cy). ³¹P{¹H} NMR (C_6D_6 , 243.0 MHz, 298 K): δ 38.2 (s). ¹³C{¹H} NMR (C_6D_6 , 150.9 MHz, 298 K): δ 159.9 (t, $J(P-C) = 18.0$ Hz, aryl C), 135.5 (t, $J(P-C) = 18.0$ Hz, aryl C), 132.2 (s, aryl C), 130.4 (s, aryl C), 127.2 (t, $J(P-C) = 7.6$ Hz, aryl C), 125.4 (t, $J(P-C) = 3.0$ Hz, aryl C), 47.2 (t, $J(P-C) = 7.6$ Hz, CHNi), 35.2 (app. dt, $J(P-C) = 146.4$ Hz, $J(P-C) = 12$ Hz, $PCH(CH_2)_5$), 29.8 (app. d, $J(P-C) = 129.8$ Hz, Cy), 29.08 (app. d, $J(P-C) = 66.4$ Hz, Cy), 27.8 (m, Cy), 26.9 (app. d, $J(P-C) = 31.7$ Hz, Cy). Anal. Calcd. for $C_{37}H_{53}BrNiP_2$: C, 63.63; H, 7.65. Found: C, 63.89; H, 7.48. See Figure S2 for X-ray depiction of the molecular structure of **2^{Cy}** and Table S1 for relevant crystallographic data.

Synthesis of $(C_6H_4PBu^t)_2CHNi(OH)$, **2^{tBu}**.

To a solution of **2^{tBu}** (0.150 g, 0.27 mmol) in a mixture of THF (15 mL) and H_2O (0.2 mL) was added an excess of CsOH (0.200 g). The reaction mixture was sonicated at room temperature for 24 h. The reaction was monitored via ³¹P{¹H}NMR spectroscopy to ensure complete conversion had taken place prior to workup. The brown solution was filtered, and the filtrate was evaporated under vacuum. The residue was extracted with hexanes and concentrated to 0.5 mL under vacuum. Amorphous brown

crystals of the product were obtained after 2 days at -30°C . The crystals were separated by decantation and dried under vacuum. Yield 0.120 g (84%).

^1H NMR (C_6D_6 , 600 MHz, 298 K): δ 7.54 (m, 2H, ArH), 7.35 (d, $J(\text{H-H}) = 7.8$ Hz, 2H, ArH), 7.04 (t, $J(\text{H-H}) = 7.8$ Hz, 2H, ArH), 6.93 (t, $J(\text{H-H}) = 7.2$ Hz, 2H, ArH), 4.83 (s, 1H, CHNi), 1.55 (app. dt, $J(\text{P-H}) = 6.0$ Hz, $J(\text{P-H}) = 1.2$ Hz, 36H, $\text{C}(\text{CH}_3)_3$), -3.22 (t, $J(\text{P-H}) = 5.2$ Hz, 1H, NiOH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 243.0 MHz, 298 K): δ 51.8 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz, 298 K): δ 162.0 (t, $J(\text{P-C}) = 18.1$ Hz, aryl C), 135.1 (t, $J(\text{P-C}) = 16.6$ Hz, aryl C), 134.2 (s, aryl C), 129.7 (s, aryl C), 127.4 (t, $J(\text{P-C}) = 7.6$ Hz, aryl C), 123.9 (t, $J(\text{P-C}) = 3.0$ Hz, aryl C), 39.6 (t, $J(\text{P-C}) = 10.6$ Hz, CHNi), 36.9 (app. dt, $J(\text{P-C}) = 69.4$ Hz, $J(\text{P-C}) = 6.0$ Hz, $\text{C}(\text{CH}_3)_3$), 30.7 (app. dt, $J(\text{P-C}) = 42.3$ Hz, $J(\text{P-C}) = 3.0$ Hz, $\text{C}(\text{CH}_3)_3$). Anal. Calcd. for $\text{C}_{29}\text{H}_{46}\text{NiOP}_2$: C, 65.56; H, 8.73. Found: C, 65.49; H, 8.55.

Synthesis of $(\text{C}_6\text{H}_4\text{PCy}_2)_2\text{CHNi}(\text{OH})$, 2^{Cy} .

To a solution of 2^{Cy} (0.100 g, 0.14 mmol) in a mixture of THF (15 mL) and H_2O (0.2 mL) was added CsOH (0.200 g). The reaction mixture was sonicated at room temperature for 24 h. The reaction was monitored via $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy to ensure complete conversion had taken place prior to workup. The brown solution was filtered, and the filtrate was evaporated under vacuum. The residue was extracted with hexanes and dried under vacuum. The obtained solid was washed with cold pentanes and dried under vacuum. Yield 0.085 g (96%).

^1H NMR (C_6D_6 , 600 MHz, 298 K): δ 7.29 (d, $J(\text{H-H}) = 8.4$ Hz, 2H, ArH), 7.26 (m, 2H, ArH), 7.07 (t, $J(\text{H-H}) = 7.8$ Hz, 2H, ArH), 6.97 (t, $J(\text{H-H}) = 7.2$ Hz, 2H, ArH), 4.84 (s, 1H, CHNi), 2.46 (m, 4H, Cy), 2.24 (m, 4H, Cy), 1.90 (m, 4H, Cy), 1.68 (m, 20H, Cy), 1.16 (m, 12H, Cy), -2.94 (t, $J(\text{P-H}) = 6.2$ Hz, 1H, NiOH). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 243.0 MHz, 298 K): δ 31.6 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz, 298 K): δ 161.8 (t, $J(\text{P-C}) = 18.1$ Hz, aryl C), 135.2 (t, $J(\text{P-C}) = 18.1$ Hz, aryl C), 131.9 (s, aryl C), 129.9 (s, aryl C), 127.3 (t, $J(\text{P-C}) = 7.5$ Hz, aryl C), 124.8 (s, aryl C), 38.3 (t, $J(\text{P-C}) = 9.1$ Hz, CHNi), 34.4 (app. dt, $J(\text{P-C}) = 10.6$ Hz, $J(\text{P-C}) = 7.5$ Hz, $\text{PCH}(\text{CH}_2)_5$), 29.7 (app. d, $J(\text{P-C}) = 144.9$ Hz, Cy), 28.9 (app. d, $J(\text{P-C}) = 33.2$ Hz, Cy), 27.8 (m, Cy), 26.9 (app. d, $J(\text{P-C}) = 36.2$ Hz, Cy). Anal. Calcd. for $\text{C}_{37}\text{H}_{54}\text{NiOP}_2$: C, 69.93; H, 8.57. Found: C, 70.00; H, 8.53.

Synthesis of free $(\text{C}_6\text{H}_4\text{PPr}^i)_2\text{CHNiNHC}(\text{O})\text{Ph}$, 3^{iPr}

To a solution of $(\text{C}_6\text{H}_4\text{PPr}^i)_2\text{CNiNCBu}^t$ (20 mg, 0.037 mmol) in toluene (0.6 mL) was added dry $\text{PhC}(\text{O})\text{NH}_2$ (4 mg, 0.033 mmol). The reaction mixture was stirred for 1 h at room temperature and evaporated under vacuum. The residue was extracted with toluene. The toluene fractions were combined and concentrated. Hexanes were layered over the toluene solution. Orange crystals of the title product were obtained after 1 day at -30°C . Yield 12 mg (60%).

^1H NMR (C_6D_6 , 400 MHz, 298 K): δ 8.12 (d, $J(\text{H-H}) = 7.9$ Hz, 2H, ArH), 7.25 (m, 4H, ArH), 7.15 (m, 1H, ArH), 7.11 (m, 2H, ArH), 7.05 (t, $J(\text{H-H}) = 7.5$ Hz, 2H, ArH), 6.92 (t, $J(\text{H-H}) = 7.5$ Hz, 2H, ArH), 5.42 (s, 1H, NiCH), 3.50 (br s, 1H, NiNH), 2.44 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 2.31 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.47 (dt, $J(\text{H-H}) = J(\text{P-H}) = 7.8$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.22 (dt, $J(\text{H-H}) = J(\text{P-H}) = 7.4$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.09 (m, 12H, $\text{CH}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz, 298 K): δ 45.8 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz, 298 K): δ 173.0 (s, $\text{C}(\text{O})\text{Ph}$), 160.3 (t, $J(\text{P-C}) = 18.1$ Hz, aryl C), 141.1 (s, aryl C), 134.7 (t, $J(\text{P-C}) = 18.0$ Hz, aryl C), 131.5 (s, aryl CH), 130.1 (s, aryl CH), 128.7 (s, aryl CH), 128.2 (s, aryl CH), 127.4 (s, aryl CH), 127.0 (t, $J(\text{P-C}) = 6.9$ Hz, aryl CH), 124.6 (t, $J(\text{P-C}) = 2.7$ Hz, aryl CH), 43.3 (t, $J(\text{P-C}) = 10.0$ Hz, NiCH), 25.8 (t, $J(\text{P-C}) = 9.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 24.6 (t, $J(\text{P-C}) = 10.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.6 (t, $J(\text{P-C}) = 2.5$

Hz, CH(CH₃)₂), 18.6 (m, CH(CH₃)₂), 17.8 (s, CH(CH₃)₂). IR (NaCl): 1677 cm⁻¹ (C=O). Anal. Calcd. For C₃₂H₄₃NNiOP₂: C, 66.46; H, 7.49; N, 2.42. Found: C, 65.99; H, 7.45; N, 2.28.

Synthesis of 3^{iPr}•NH₂C(O)Ph under catalytic conditions

To a solution of PhCN (0.010 mL, 0.097 mmol) and (PCP-Prⁱ)NiOH (5 mg, 0.010 mmol) in THF (0.6 mL) was added H₂O (0.010 mL, 0.55 mmol). The reaction mixture was stored for 1 day at room temperature. Color change from orange to yellow was observed. The reaction mixture was evaporated and dried under vacuum. The residue was extracted with hexanes. The hexanes fractions were combined and concentrated under vacuum. A few yellow crystals (~2-3 mg) were obtained overnight at -30°C, which were separated from the solution by decantation and analyzed by X-ray crystallography.

Synthesis of (C₆H₄PPrⁱ)₂CHNiOC(O)CH₃, 4^{iPr}.

To a solution of 2^{iPr} (20 mg, 0.04 mmol) in EtOH (0.6 mL) was added KOC(O)CH₃ (73 mg, 0.75 mmol). The reaction mixture was stirred for 1 h at room temperature and evaporated under vacuum. The residue was extracted with toluene and concentrated under vacuum. Hexanes were layers over the toluene solution. Brown crystals of the title product were obtained after 3 days at -30°C. Yield 20 mg (97%).

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.17 (d, overlaps with solvent peak, 2H, Ar-*H*), 7.07 (m, 2H, Ar-*H*), 7.01 (t, *J*(H-H) = 7.4 Hz, 2H, Ar-*H*), 6.91 (t, *J*(H-H) = 7.1 Hz, 2H, Ar-*H*), 5.17 (s, 1H, NiCH), 2.29 (m, 4H, CH(CH₃)₂), 2.12 (s, 3H, C(O)CH₃), 1.49 (dt, *J*(H-H) = *J*(P-H) = 7.7 Hz, 6H, CH(CH₃)₂), 1.31 (dt, *J*(H-H) = *J*(P-H) = 7.5 Hz, 6H, CH(CH₃)₂), 1.19 (dt, *J*(H-H) = *J*(P-H) = 7.2 Hz, 6H, CH(CH₃)₂), 1.13 (dt, *J*(H-H) = *J*(P-H) = 6.9 Hz, 6H, CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆, 162.0 MHz, 298 K): δ 42.0 (s). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K): δ 175.9 (s, OC(O)), 160.2 (t, *J*(P-C) = 18.2 Hz, aryl C), 133.7 (t, *J*(P-C) = 18.4 Hz, aryl C), 131.6 (s, aryl CH), 130.0 (s, aryl CH), 126.8 (t, *J*(P-C) = 7.0 Hz, aryl CH), 124.8 (t, *J*(P-C) = 2.8 Hz, aryl CH), 37.2 (t, *J*(P-C) = 10.2 Hz, NiCH), 25.0 (t, *J*(P-C) = 9.2 Hz, CH(CH₃)₂), 23.9 (t, *J*(P-C) = 10.1 Hz, CH(CH₃)₂), 19.1 (t, *J*(P-C) = 2.6 Hz, CH(CH₃)₂), 18.4 (m, CH(CH₃)₂), 17.7 (s, C(O)CH₃). Anal. Calcd. For C₂₇H₄₀NiO₂P₂: C, 62.70; H, 7.79. Found: C, 62.22; H, 7.82. See below for X-ray depiction of the molecular structure of 4^{iPr}.

Synthesis of (C₆H₄PPrⁱ)₂CHNiCN, 5^{iPr}.

To a solution of 3^{iPr} (20 mg) in THF (0.6 mL) was added (CH₃)₂C(OH)(CN) (30 μL). Full conversion into (C₆H₄PPrⁱ)₂CHNiCN 5^{iPr} was observed by NMR spectroscopy. The solvent was evacuated and the residue dried under vacuum for 3h at 60°C. The dry solids were dissolved in toluene (2 mL) and layered with hexanes (1 mL). Yellow crystals of the title complex were obtained after 24h at -30°C. The crystals were separated by decantation and dried under vacuum. Yield 14 mg (68%).

¹H NMR (C₆D₆, 400 MHz, 298 K): δ 7.32 (d, *J*(H-H) = 8.3 Hz, 2H, Ar-*H*), 7.07 (t, *J*(H-H) = 7.4 Hz, 2H, Ar-*H*), 6.89 (t, *J*(H-H) = 7.4 Hz, 2H, Ar-*H*), 5.31 (s, 1H, NiCH), 2.35 (m, 4H, CH(CH₃)₂), 1.40 (m, 12H, CH(CH₃)₂), 1.03 (m, 12H, CH(CH₃)₂). ³¹P{¹H} NMR (C₆D₆, 162.0 MHz, 298 K): δ 60.0 (s). ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 298 K, CN carbon was not found/overlaps with solvent peak): δ 159.3 (t, *J*(P-C) = 17.4 Hz, aryl C), 134.8 (t, *J*(P-C) = 18.0 Hz, aryl C), 131.5 (s, aryl CH), 130.5 (s, aryl CH), 127.3 (t, *J*(P-C) = 7.4 Hz, aryl CH), 124.9 (t, *J*(P-C) = 2.9 Hz, aryl CH), 51.9 (t, *J*(P-C) = 8.3 Hz, NiCH), 25.9 (t, *J*(P-C) = 11.1 Hz, CH(CH₃)₂), 25.1 (t, *J*(P-C) = 12.7 Hz, CH(CH₃)₂), 19.5 (br s, CH(CH₃)₂), 18.4 (br s, CH(CH₃)₂), 18.3 (br s, CH(CH₃)₂). IR (NaCl): 2099 cm⁻¹ (CN). Anal. Calcd. For C₂₆H₃₇NNiP₂: C, 64.49; H, 7.70; N, 2.89. Found: C, 63.91; H, 7.46; N, 3.18. See below for X-ray depiction of the molecular structure of 5^{iPr}.

Catalytic Hydration of Nitriles to Amides

A typical small scale nitrile hydration was carried out as follows. Nitrile (0.2 mmol), H₂O:iPrOH 1:1 (0.5 mL) and catalyst (0.1-0.5 mol%) were placed in a J. Young NMR tube and heated inside the NMR spectrometer at the desired temperature. The progress of the reaction was monitored via ¹H NMR spectroscopy.

A typical large scale nitrile hydration was carried out as follows. Nitrile (2 mmol), H₂O:iPrOH 1:1 (10 mL) and catalyst (0.05-0.5 mol%) were placed in a thick walled vessel and heated in an oil bath at 80 °C. The progress of the reaction was monitored via ¹H NMR spectroscopy of quenched aliquots. Once the reaction was deemed complete, all the volatiles were removed under vacuum. The resulting solids were washed with hexane (3 x 20 mL) and dried under vacuum to yield the desired product amide.

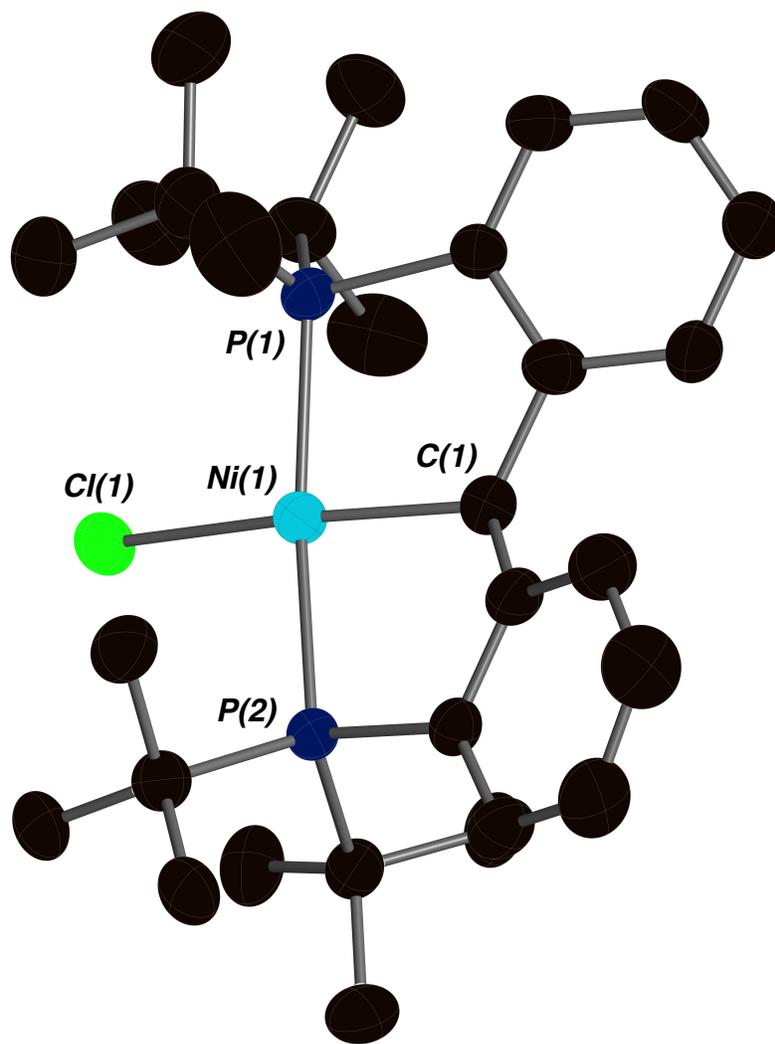


Figure S1. Molecular structure of $(C_6H_4PtBu_2)_2CHNiCl$, 2^{tBu} . Two independent molecules were present in the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cl1-Ni1 2.2300(15), Ni1-C1 1.982(1), Ni1-P1 2.2116(15), Ni1-P2 2.2090(14), Cl1-Ni1-C1 163.2(3), P1-Ni1-P2 167.89(6), Cl2-Ni2 2.2332(15), Ni2-C30 1.960(5), Ni2-P3 2.1968(15), Ni2-P4 2.2262(14), Cl2-Ni2-C30 168.6(2), P3-Ni2-P4 165.84(6).

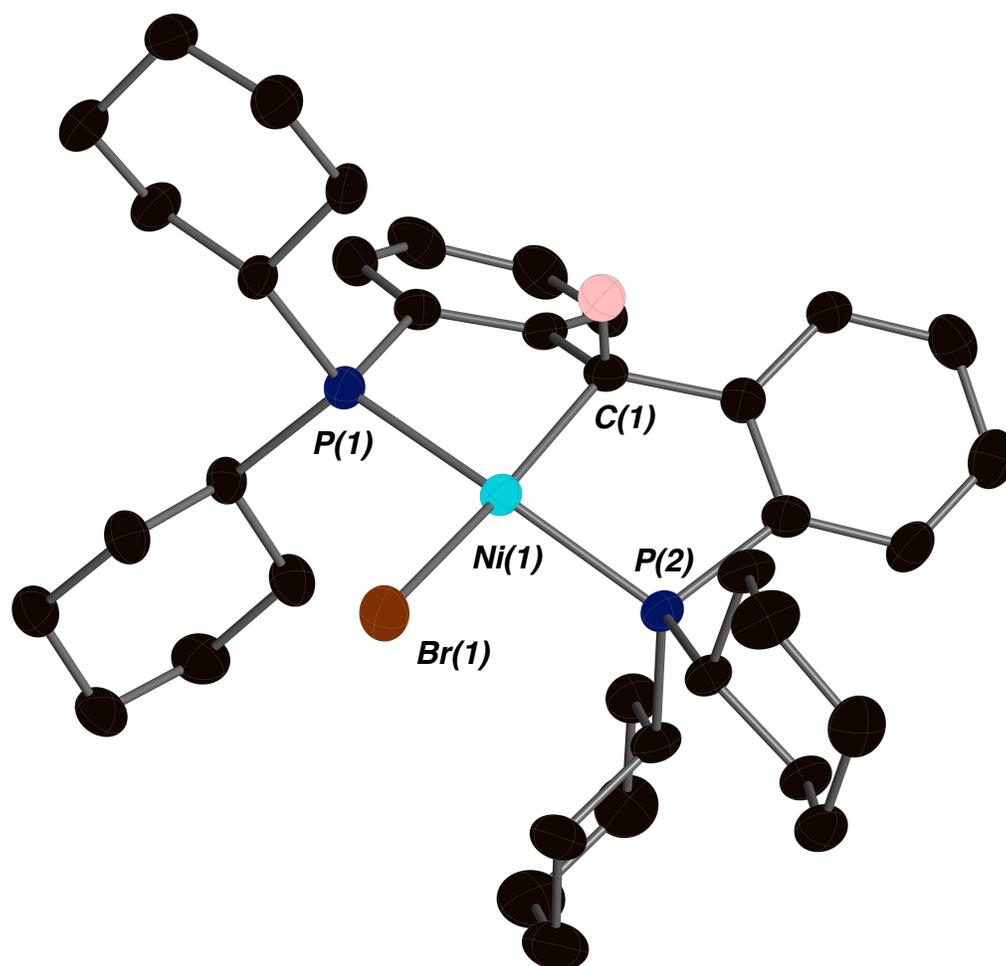


Figure S2. Molecular structure of $(\text{C}_6\text{H}_4\text{PCy}_2)_2\text{CHNiBr}$, 2^{Cy} . Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms (except for that attached to C1) have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Br1-Ni1 2.3501(8), Ni1-C1 1.975(5), Ni1-P1 2.1499(14), Ni1-P2 2.1911(14), Br1-Ni1-C1 167.62(14), P1-Ni1-P2 159.63(6).

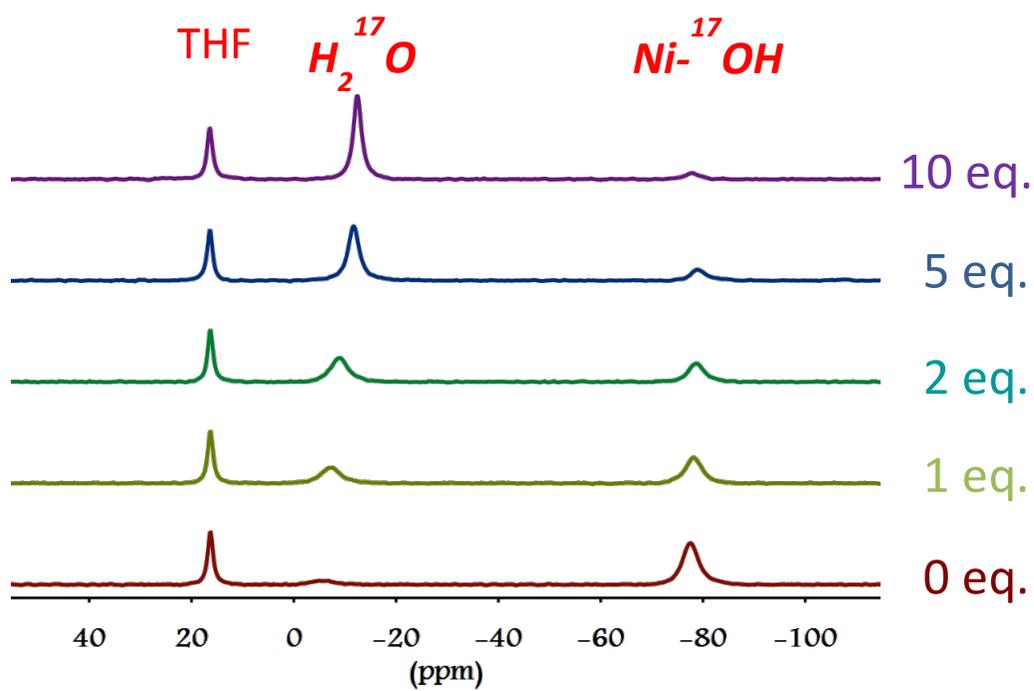


Figure S3. ^{17}O NMR spectra obtained upon treatment of ^{17}O labeled 2^{iPr} (bottom spectrum) with 1-10 equivalents of unlabeled H_2O , demonstrating the rapid exchange of the coordinated hydroxo group with the oxygen in free water.

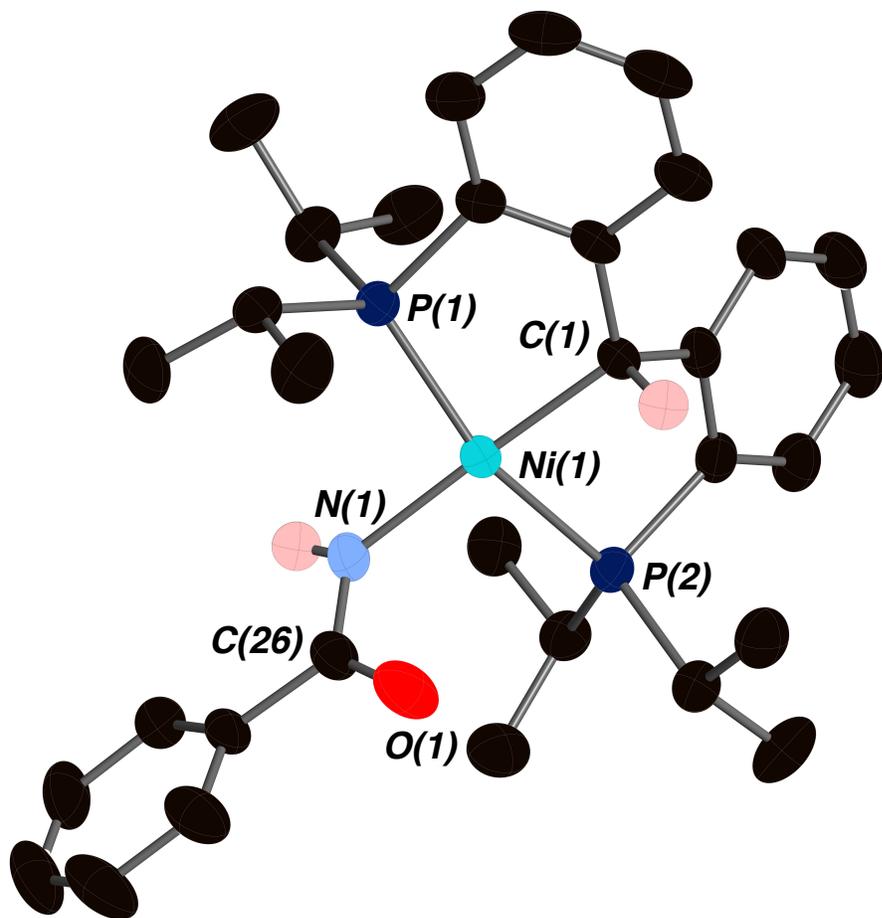


Figure S4. Molecular structure of 3^{iPr} . Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. For selected bond lengths (Å) and angles (°) see main text, Figure 1 (numbers in ***bold italic*** in square brackets).

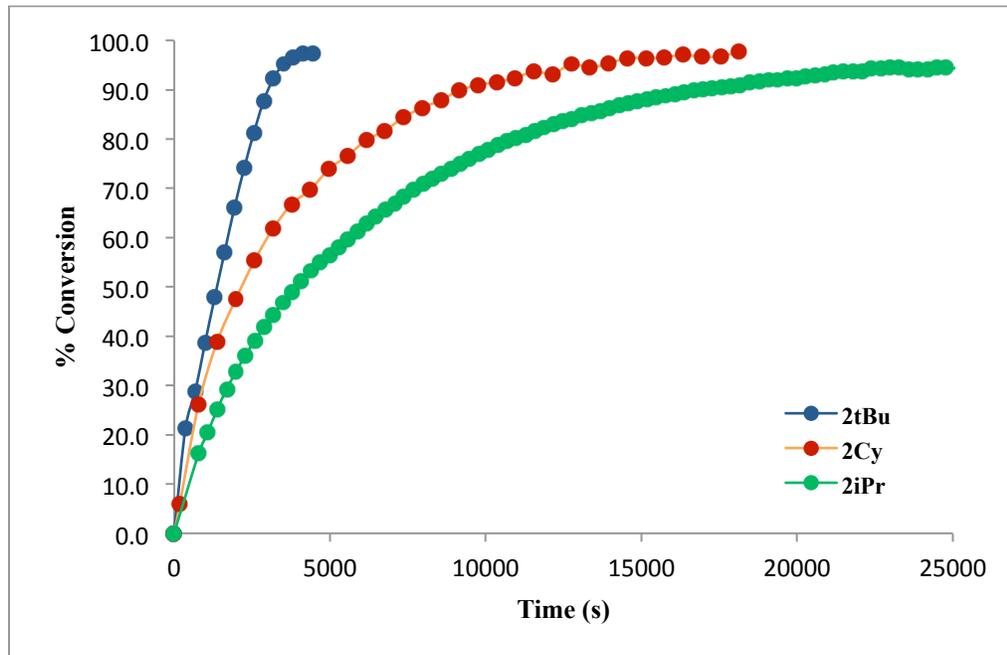


Figure S5. Percent conversion vs time for the hydration of benzonitrile at 80 °C catalyzed by 2^{iPr} , 2^{tBu} and 2^{Cy} (0.1 % catalyst loading, 1:1 iPrOH/H₂O), see also Table 1, main text.

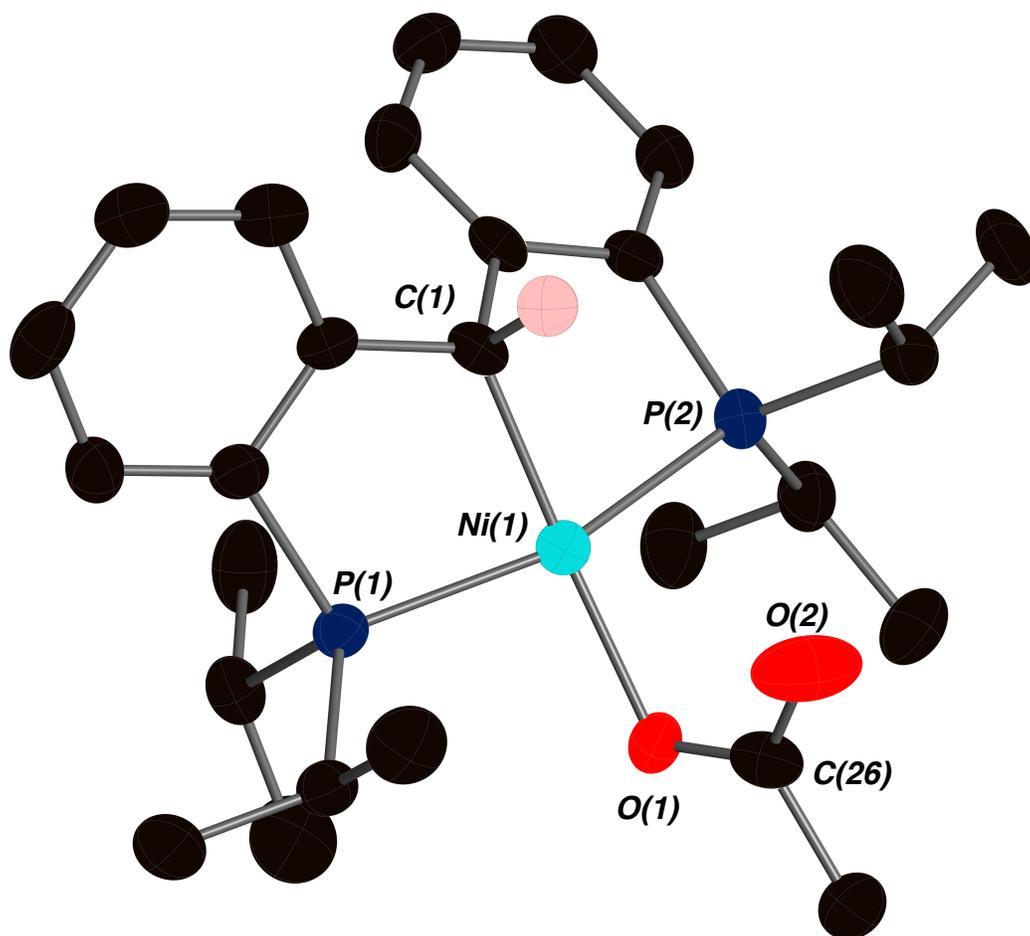


Figure S6. Molecular structure of $(C_6H_4PiPr_2)_2CHNiOC(O)CH_3$, 4^{iPr} . Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Ni1-O1 1.926(4), Ni1-O2 2.842(6), Ni1-C1 1.965(5), Ni1-P1 2.1501(16), Ni1-P2 2.2061(16), O1-C26 1.277(7), O2-C26 1.219(7), O1-Ni1-C1 172.5(2), P1-Ni1-P2 157.36(6), Ni1-O1-C26 113.2(4), O1-C26-O2 124.8(6).

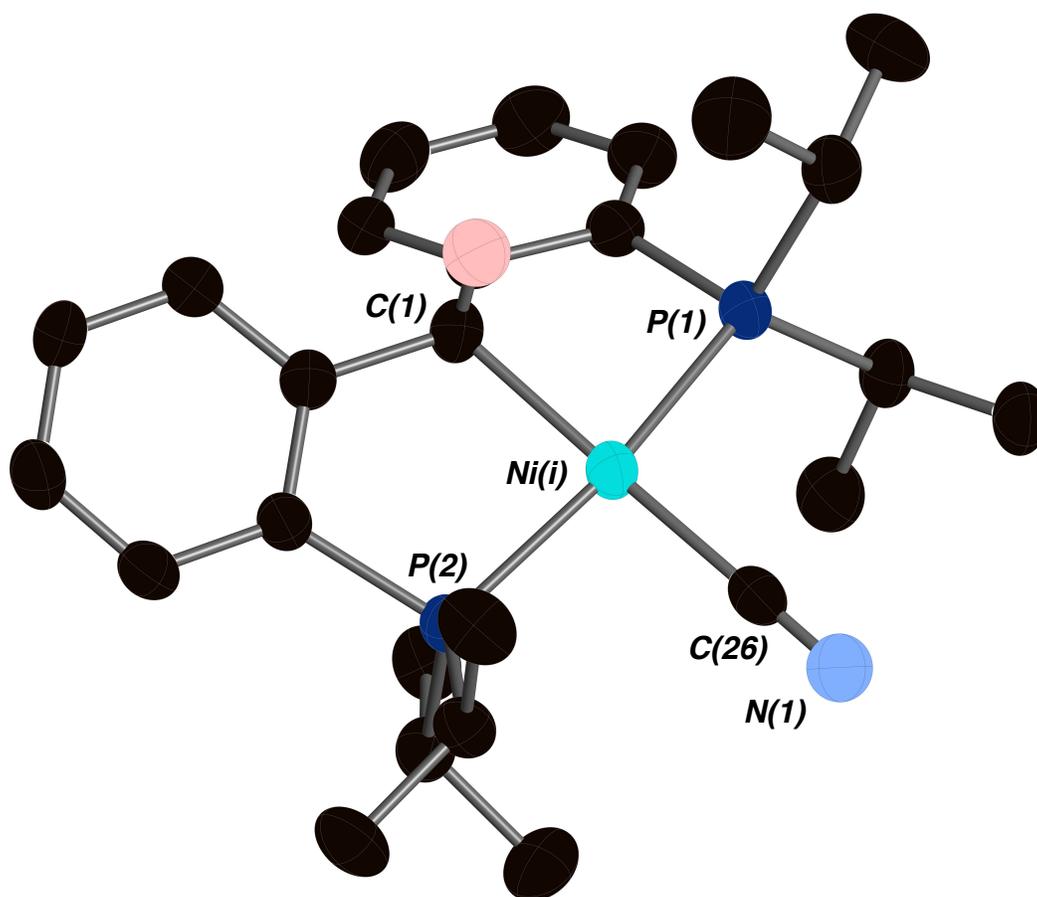


Figure S7. Molecular structure of $(\text{C}_6\text{H}_4\text{PiPr}_2)_2\text{CHNiCN}$, 5^{iPr} . Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ni1-C1 1.979(5), Ni1-C26 1.888(5), Ni1-P1 2.1681(13), Ni1-P2 2.1390(13), C26-N1 1.104(6), C1-Ni1-C26 171.3(2), P1-Ni1-P2 161.99(5), Ni1-C26-N1 175.5(5).

References

- 1) Burford, R. J.; Piers, W. E.; Parvez, M., *Organometallics*, **2012**, *31*, 2949-2952.
- 2) Gutsulyak, D. V.; Piers, W. E.; Borau-Garcia, J.; Parvez, M., *J. Amer. Chem. Soc.*, **2013**, *135*, 11776-11779.