Supporting Information for

The Hydrogenation of Molecules with Polar Bonds Catalyzed by a Ruthenium(II) Complex Bearing a Chelating *N*-Heterocyclic Carbene with a Primary Amine Donor

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Experimental Section

Synthesis. All of the preparations and manipulations, except where otherwise stated, were carried out under a nitrogen or argon atmosphere using standard Schlenk-line and glovebox techniques. Dry and oxygen-free solvents were always used. The synthesis of bis[1-(2-aminomethylphenyl)-3-methylimidazol-2-ylidene]nickel(II) hexafluorophosphate (**1a**) has been reported previously.[1] The syntheses of $RuCp^*(cod)Cl$[2] and 2-(diphenylphosphino)benzylamine ($P–NH_2$)[3] were reported in the literature. All other reagents and solvents were purchased from commercial sources and were used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and Sigma Aldrich and degassed and dried over activated molecular sieves prior to use. NMR spectra were recorded on a Varian 400 spectrometer operating at 400 MHz for ^1H, 100 MHz for ^{13}C, 161 MHz for ^{31}P and 376 MHz for ^{19}F. The ^1H and $^{13}C\{^1H\}$ NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All ^{19}F chemical shifts were measured relative to trichlorofluoromethane as an external reference. All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. The elemental analysis was performed at the Department of Chemistry, University of Toronto, on a Perkin-Elmer 2400 CHN elemental analyzer.

Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The CCD data were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using SHELXTL V6.1. Refinement was by full-matrix least-squares on F^2 using all data.

Crystal data for **2**: $C_{26}H_{33}F_6N_4PRu$, FW = 647.60, T = 150 K, λ = 0.71073 Å, triclinic, $P\bar{1}$, a = 12.973(1), b = 13.1208(7), c = 17.1470(14) Å, α = 73.954(4)°, β = 73.396(3)°, γ = 88.187(4)°, V = 2684.5(3)Å^3, Z = 4, ρ_{calc} = 1.602 Mg/m^3, μ = 0.709 mm^{-1}, data/restraints/parameters = 12107/7/719, R_1 = 0.0854, wR_2 (all data) = 0.2473.

Crystal data for **3a**: $C_{34}H_{38}F_6N_2P_2Ru$, FW = 751.67, T = 150 K, λ = 0.71073 Å, monoclinic, $P2_1/c$, a = 8.6982(2), b = 20.6135(8), c = 19.4091(7) Å, α = γ = 90°, β = 92.051(2)°, V = 3477.8(2)Å^3, Z = 4, ρ_{calc} = 1.436 Mg/m^3, μ = 0.601 mm^{-1}, data/restraints/parameters = 7870/0/411, R_1 = 0.0448, wR_2 (all data) = 0.1154.

Synthesis of [1-(2-Aminomethylphenyl)-3-methylimidazol-2-ylidene]-(η^5-pentamethyl cyclopentadienyl)(pyridine)ruthenium(II) Hexafluorophosphate ([$RuCp^*(C–NH_2)(py)$]PF_6, 2). A Schlenk flask was charged with **1a** (73 mg, 0.10 mmol) and $RuCp^*(cod)Cl$ (58 mg, 0.15 mmol). Dry acetonitrile (10 mL) was added to the reaction mixture, and it was refluxed under an argon atmosphere for 2.5 h. The colour of the solution turned from yellow to cloudy yellow and then to deep green. The solvent was evaporated under reduced pressure, and the residue was extracted with oxygen-free tetrahydrofuran (4 mL) and filtered through a pad of Celite under a nitrogen atmosphere. To the yellow-brown solution was added pyridine (1 mL), whereupon the colour of the solution turned into deep orange-red. The solution was evaporated under reduced pressure, and the solid residue was extracted with ice-cold acetone (2 mL) and filtered through a pad of Celite. Addition of diethyl ether (15 mL) to the acetone solution and slow cooling of the

solution at -25°C afforded orange-red needles, which were collected on a glass frit, washed with diethyl ether (1 mL) and dried in vacuo. Yield: 63 mg, 64%. Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated solution of **2** in acetone under a nitrogen atmosphere. ^{1}H NMR (acetone-d_6, 233K, δ): 8.49 (m, 4-CH of py, 1H), 7.88 (m, 2-CH of py, 2H), 7.77 (m, 3-CH of Ph, 1H), 7.67 (d, J_{HH} = 1.99 Hz, 5-CH of imid.,1H), 7.63 (m, 4-CH and 5-CH of Ph, 2H), 7.60 (d, J_{HH} = 1.99 Hz, 4-CH of imid., 1H), 7.49 (m, 6-CH of Ph, 1H), 7.42 (m, 3-CH of py, 2H), 4.23 (t, J_{HH} = 13.37 Hz, CH_2, 1H), 3.48 (s, CH_3, 3H), 3.30 (t, J_{HH} = 9.22 Hz, CH_2, 1H), 2.83 (m, br, NH_2, 1H), 2.59 (m, br, NH_2, 1H), 1.23 (s, CH_3 of Cp^*, 15H). ^{19}F NMR (acetone-d_6, 233K, δ): -72.0 (d, J_{PF} = 708 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, 233K, δ): 198.0 (Ru–$C_{carbene}$), 156.0 (C_{py}), 141.8 (C_{py}), 136.3 (C_{Ph}), 132.9 (C_{Ph}), 132.5 (C_{Ph}), 130.0 (C_{Ph}), 128.3 (C_{Ph}), 127.1 (C_{Ph}), 126.6 (C_{py}), 124.8 ($C_{imid.}$), 124.3 ($C_{imid.}$), 80.7 ($C_{Ar\text{-}Cp^*}$), 48.7 (CH_2), 37.6 (CH_3), 9.6 (CH_3 of Cp^*). MS (ESI, methanol/water; *m/z*): 456.1 $[M - py + CH_3OH]^+$, 424.1 $[M - py]^+$. Anal. Calcd for $C_{26}H_{33}F_6N_4PRu$: C, 48.22; H, 5.14; N, 8.65. Found: C, 47.73; H, 4.20; N, 9.25.

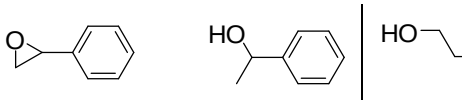
Synthesis of [2-(Diphenylphosphino)benzylamine]-(η^5-pentamethylcyclopentadienyl)-(pyridine)ruthenium(II) Hexafluorophosphate ([RuCp*(P–NH$_2$)(py)]PF$_6$, 3a). A scintillation vial with a threaded screw cap was charged with RuCp*(cod)Cl (40 mg, 0.11 mmol) in dry dichloromethane (3 mL) under a nitrogen atmosphere. A solution of 2-(diphenylphosphino)-benzylamine (32 mg, 0.10 mmol) in dry dichloromethane (3 mL) was added to the aforementioned yellow solution and stirred for 1 h at room temperature (25°C), whereupon the reaction mixture turned into orange in colour. Silver hexafluorophosphate (27 mg, 0.11 mmol) in dry acetonitrile (1 mL) was added to the reaction mixture, and a yellow-brown suspension was obtained. After stirring the reaction mixture for 0.5 h, it was filtered through a pad of Celite under a nitrogen atmosphere. To the yellow solution was added pyridine (1 mL), and the colour of the solution turned into deep orange-yellow. Addition of pentane (15 mL) yielded an orange-yellow precipitate, which was washed with pentane (3 mL) and dried in vacuo. Alternatively, the crude product can be recrystallized with acetone and pentane or acetone and diethyl ether mixtures at -25°C to afford an orange-yellow solid. Yield: 53 mg, 67%. Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated of **3a** in acetone under a nitrogen atmosphere. ^{1}H NMR (CD_2Cl_2, 233K, δ): 7.76 (d, J_{HH} = 5.20 Hz, 2-CH of py, 2H), 7.56 (m, 6-CH of Ph, 1H), 7.47 (m, 5-CH of Ph, 1H), 7.45 (m, 4-CH of py, 1H), 7.42 (m, Ar-CH of PPh_2, 10H), 7.19 (t, J_{HH} = 8.32 Hz, 4-CH of Ph, 1H), 7.07 (dd, J_{HH} = 7.44, 7.37 Hz, 3-CH of Ph, 1H), 6.93 (t, J_{HH} = 7.40 Hz, 3-CH of py, 1H), 3.91 (m, CH_2, 1H), 3.67 (m, CH_2, 1H), 3.54 (m, br, NH_2, 1H), 3.32 (m, br, NH_2, 1H), 1.21 (s, CH_3 of Cp^*, 15H). ^{19}F NMR (CD_2Cl_2, 233K, δ): -72.4 (d, J_{PF} = 712 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 233K, δ): 44.7 (s), -144.6 (sept, J_{PF} = 709 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 233K, δ): 154.7 (C_{py}), 136.0 (C_{py}), 134.9 (C_{Ph}), 132.9 (t, J_{CP} = 11.61 Hz, C_{Ph}), 130.4 (d, J_{CP} = 8.64 Hz, C_{Ph}), 130.0 (C_{Ph}), 129.6 (d, J_{CP} = 17.86 Hz, C_{Ph}), 128.7 (d, J_{CP} = 9.05 Hz, C_{Ph}), 128.3 (m, C_{PPh}), 124.8 (C_{py}), 84.0 ($C_{Ar\text{-}Cp^*}$), 46.6 (CH_2), 9.0 (CH_3 of Cp^*). MS (ESI, methanol/water; *m/z*): 528.1 $[M - py]^+$. Anal. Calcd for $C_{34}H_{38}F_6N_2P_2Ru$: C, 54.33; H, 5.10; N, 3.73. Found: C, 54.00; H, 5.30; N, 3.75.

Catalysis. Oxygen-free tetrahydrofuran used for all of the catalytic runs was stirred over sodium for 2-3 days under argon, and freshly distilled from sodium benzophenone ketyl prior to use. Acetophenone was vacuum distilled over phosphorus pentoxide (P_2O_5) and stored under nitrogen prior to use. All of the other substrates were vacuum distilled, dried over activated molecular sieves, and stored under nitrogen prior to use. All of the hydrogenation reactions were performed at constant pressures using a stainless steel 50 mL Parr hydrogenation reactor. The temperature was maintained at 25℃ using a constant temperature water bath. The reactor was flushed several times with hydrogen gas at 2-4 bar prior to the addition of catalyst and substrate, and base solutions.

In a typical run (**Table 2**, Entry 4), the catalyst **2** (3 mg, 4.6 μmol) and 4'-bromoacetophenone (1.383 g, 6.9 mmol), and potassium tert-butoxide (4 mg, 0.036 mmol) were dissolved in tetrahydrofuran (4 mL and 2 mL, respectively) under a nitrogen atmosphere. The catalyst/substrate and base solutions were taken up by means of two separate syringes and needles in a glovebox. The needles were stoppered and the syringes were taken to the reactor. The solutions were then injected into the reactor against a flow of hydrogen gas. The hydrogen gas was adjusted to the desired pressure. Small aliquots of the reaction mixture were quickly withdrawn with a syringe and needle under a flow of hydrogen at timed intervals by venting the Parr reactor at reduced pressure. Alternatively, small aliquots of the reaction mixture were sampled from a stainless steel sampling dip tube attached to a modified Parr reactor. The dip tube was 30 cm in length with an inner diameter of 0.01 inches, and a swing valve was attached to the end of the sampling tube. Other technical details were previously reported.[4] Two small aliquots of samples were thereby withdrawn quickly at timed intervals by opening the swing valve, and the first two aliquots were discarded. All samples for gas chromatography (GC) analyses were diluted to a total volume of approximately 0.75 mL using oxygenated tetrahydrofuran.

A Perkin–Elmer Clarus 400 chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m x 2.5 mm) with an auto-sampling capability was used for GC analyses. Hydrogen was used as a mobile phase at a column pressure of 5 psi with a split flow rate of 50 mL/min. The injector temperature was 250℃ and the FID temperature was 275℃. The oven temperatures and the retention times (t_R, t_p, /min) for all of the substrates and alcohol products are given in Table S1. All conversions were reported as an average of two GC runs. The reported conversions were reproducible.

Table S1. The oven temperatures, retention times (t_R, t_p, /min) for all the substrates and alcohol products reported from GC analyses.

Substrates/Alcohol Products	Oven Temperature (^oC)	t_R (min)	t_P (min)
	130	4.56	7.58, 8.03
	145	4.63	10.34, 12.16
	140	6.46	14.81, 16.05
	145	5.96	11.03, 12.09
	155	7.02	12.79, 13.72
	140	10.61	13.50, 14.28
	140	5.19	10.06 (rac)
	170	9.67	14.43, 14.76
	180	7.94	12.57
	60	5.62	17.64, 18.79
	130	3.53	7.31
	130	4.81, 4.95	8.15, 8.65; 9.47
	140	3.83	5.70, 5.93(tridecane)

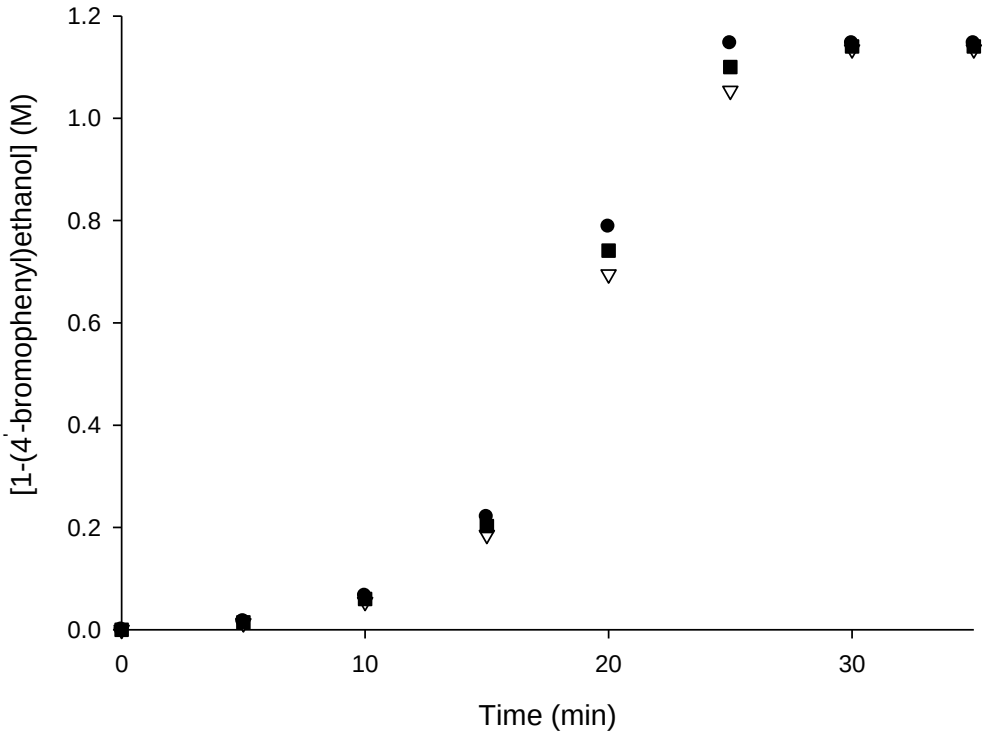


Figure S1. Catalytic H_2-hydrogenation of 4'-bromoacetophenone to 1-(4'-bromophenyl)ethanol (Table 2, Entry 4) in the presence of catalyst **2**, KO^{t}Bu, and THF (6 mL) in 8 bar of H_2 pressure at 25^{o}C (C/B/S = 1/8/1500).

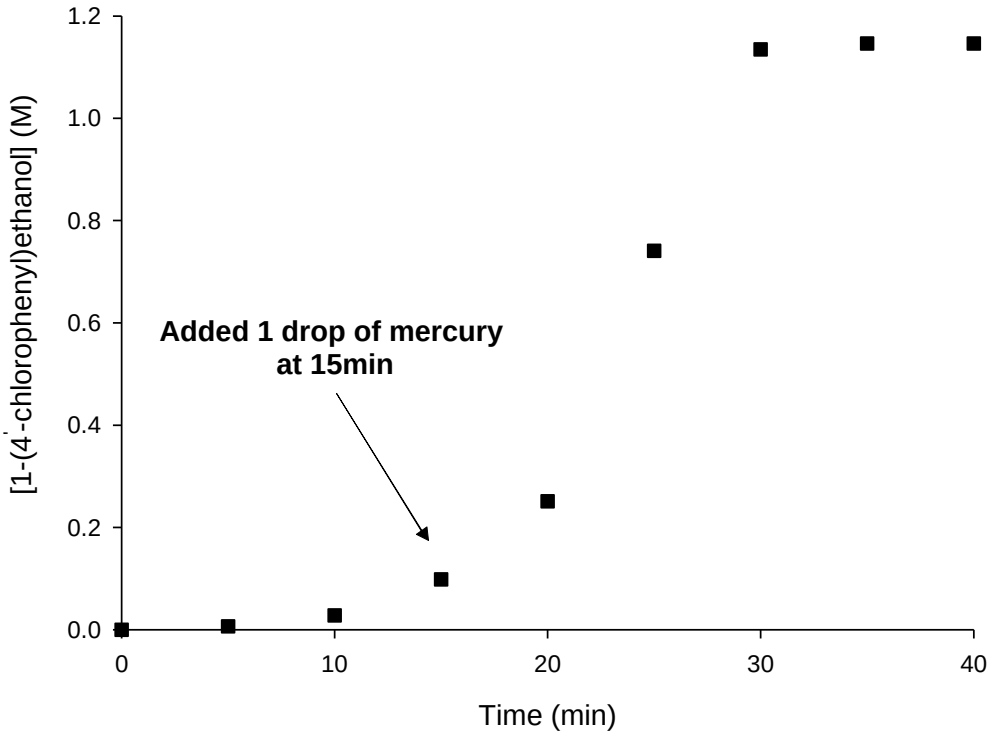


Figure S2. Catalytic H_2-hydrogenation of 4'-chloroacetophenone to 1-(4'-chlorophenyl)ethanol in the presence of catalyst **2**, KO^{t}Bu, and THF (6 mL) in 8 bar of H_2 at 25^{o}C (C/B/S = 1/14/2250). Mercury poisoning test was conducted by adding a drop of mercury to the reaction mixture against a flow of hydrogen at 15 min.

References

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