Supporting Information

Facile Conversion of Alcohols into Esters and Dihydrogen Catalyzed by New Ruthenium Complexes

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General Procedures. All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glovebox over 4Å molecular sieves. The ligand 2,6-bis(di-iso-propylphosphinomethyl)pyridine (iPr-PNP), and RuHCl(CO)(PPh₃)₃ were prepared according to literature procedures.

¹H, ¹³C and ³¹P NMR spectra were recorded at 250 or 400, 100, and 162 MHz, respectively, using a Bruker AMX-250 and AMX-400 NMR spectrometers. ¹H and ¹³C {¹H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ³¹P NMR chemical shifts are reported in parts per million downfield from H₃PO₄ and referenced to an external 85% solution of phosphoric acid in D₂O. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, v, virtual. Elemental analyses were performed at Kolbe Laboratorium, Mulheim, Germany.

Synthesis of PNN (2-(di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine

(1) 2-Diethylaminomethyl-6-methylpyridine
To a dry 500 mL round-bottom flask were added 20 mL (172 mmol) 2,6-dimethylpyridine, 30.61 g (172 mmol) NBS and 300 mL CCl₄. The mixture was refluxed for seven hours during which 0.5 g AIBN (2,2'-Azobisisobutyronitrile) was added every hour. After cooling to room temperature, the mixture was filtered and the solvent was under vacuum, yielding crude 2-bromomethyl-6-methylpyridine as a pink-red oil. It was pure enough for the next step.
A solution of the pink-red oil in 120 mL of dry THF was cooled to 0°C and a pre-cooled solution (0°C) of 40 mL diethylamine (386 mmol) in THF (120 mL) was added to it dropwise. The mixture was allowed to slowly warm up to room temperature and stirred overnight. The solvent was removed under vacuum and the residue was dissolved in 1.2L of diethyl ether and washed with 2 × 200 mL of a 10% aqueous KOH solution. The ethereal solution was dried over Na₂SO₄ and the ether was removed under vacuum. The residue was distilled under vacuum, yielding 17.5g of 2-diethylaminomethyl-6-methylpyridine (66% yield) as a yellow oil, bp: 76 °C (0.3 mmHg). ¹H NMR (CDCl₃): 1.06 (t, J_HH = 7.0 Hz, 6H, N(CH₂CH₃)₂), 2.54 (s, 3H, py-CH₃), 2.60 (q, J_HH = 7.0Hz, 4H, N(CH₂CH₃)₂), 3.70 (s, Py-CH₂-N), 6.96 (d, J_HH = 7.5 Hz, 1H, py-H5), 7.28 (d, J_HH = 7.5
209.62 (t, 1H, py-H4). $^{13}$C-$^1$H NMR (CDCl$_3$): 13.15 (s, N(CH$_2$CH$_3$)$_2$), 25.8 (s, py-CH$_3$), 48.66 (s, N(CH$_2$CH$_3$)$_2$), 61.05 (s, py-CH$_2$-N), 121.00 (s, py-C5), 122.00 (s, py-C3), 138.00 (s, py-C4), 156.00 (s, py-C6), 162.00 (s, py-C2).

(2) Synthesis of 2-(di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine (PNP) To an oven-dried, argon flushed, 3-neck round bottom flask equipped with an argon-inlet tube, an “egg” magnetic bar and a rubber septum was placed 3.85 g (20 mmol) of 2-diethylaminomethyl-6-methylpyridine in 70 mL dry ether. The solution was cooled to 0 °C and a solution of n-BuLi (22 mmol) in hexane was added with a syringe during a few minutes. The mixture was stirred for 2 hrs at 0°C and then cooled to –78 °C and a solution of 3.96 g (22mmol) di-tert-butylchlorophosphine in 25 mL dry ether was added dropwise to it. The mixture was allowed slowly to warm up to room temperature and stirred overnight. To this reaction mixture was added 50 mL of degassed water and the ether phase was separated under N$_2$ atmosphere. The aqueous phase was extracted with ether (2 × 100 mL). The combined ether solutions were dried over anhydrous Na$_2$SO$_4$, filtered, and the solvent was removed under vacuum. The residue was distilled under high vacuum (0.02 mmHg), yielding 4.5 g (70%) of PNN as a pale-yellow oil, bp: 130 °C (0.02 mmHg). $^3$P-$^1$H NMR (CDCl$_3$): 37.0 (s). $^1$H NMR (CDCl$_3$): 1.03 (t, J$_{HH}$ = 7.0 Hz, 6H, N(CH$_2$CH$_3$)$_2$), 1.34 (d, J$_{PH}$ = 11.0 Hz, 18H, P(CH$_3$)$_3$)$_2$, 2.55 (q, J$_{HH}$ = 7.0 Hz, 4H, N(CH$_2$CH$_3$)$_2$), 3.05 (d, J$_{PH}$ = 3.2 Hz, 2H, P-CH$_2$), 3.68 (s, Py-CH$_2$-N), 7.22 (d, J$_{HH}$ = 7.5 Hz, 1H, py-H5), 7.31 (d, J$_{HH}$ = 7.5 Hz, 1H, py-H3), 7.52 (t, J$_{HH}$ = 7.5 Hz), 1H, py-H4). $^{13}$C-$^1$H NMR (CDCl$_3$): 11.80 (s, N(CH$_2$CH$_3$)$_2$), 29.60 (d, J$_{PC}$ = 13.1 Hz, P(CH$_3$)$_3$)$_2$, 31.50 (d, J$_{PC}$ = 23.5 Hz, P-CH$_2$-Py), 31.80 (d, J$_{PC}$ = 21.2, P(CH$_3$)$_3$)$_2$, 47.20 (s, N(CH$_2$CH$_3$)$_2$), 59.50 (s, py-CH$_2$-N), 119.50 (s, py-C5), 121.70 (d, J$_{PC}$ = 10.3 Hz, py-C3), 136.20 (s, py-C4), 159.20 (s, py-C6), 161.60 (d, J$_{PC}$ = 12.5 Hz, py-C2).

Synthesis of [RuH(Cl)(iPr-PNP)(CO)] 1. To a suspension of RuHCl(PPh$_3$)$_3$(CO) (95.3 mg, 0.1 mmol) in THF (5 ml) was added iPr-PNP (34 mg, 0.1 mmol), and the mixture was stirred at room temperature for 12 hrs. The pale-yellow solution was filtered and the filtrate was evaporated to dryness under vacuum. The yellow residue was dissolved in minimum THF (0.5 mL) and pentane (5 mL) was added slowly to precipitate the off-white solid, which was filtered and dried under vacuum (46mg, 91%). $^3$P-$^1$H NMR (THF-d$_8$): 73.6 (s). $^1$H NMR (THF-d$_8$): -14.59 (t, J$_{PH}$ = 18.0 Hz, 1H, Ru-H), 0.94 (q, J$_{PH}$ = J$_{HH}$ = 8.0 Hz, 6H, P(CH(CH$_3$)$_2$)$_2$, 1.17 (q, J$_{PH}$ = J$_{HH}$ = 8.0 Hz, 6H, P(CH(CH$_3$)$_2$)$_2$, 1.32 (q, J$_{PH}$ = J$_{HH}$ = 8.0 Hz, 6H, P(CH(CH$_3$)$_2$)$_2$, 1.33 (q, J$_{PH}$ = J$_{HH}$ = 8.0 Hz, 6H, P(CH(CH$_3$)$_2$)$_2$, 2.17 (m, 2H, P(CH(CH$_3$)$_2$)$_2$, 2.76 (m, 2H, P(CH(CH$_3$)$_2$)$_2$, 3.45 (dt, J$_{HH}$ = 16.0 Hz, J$_{PH}$ = 4.0 Hz, 2H, -CHHP), 3.81 (dt, J$_{HH}$ = 16.0 Hz, J$_{PH}$ = 4.0 Hz, 2H, -CHHP), 7.20 (d, J$_{HH}$ = 8.0 Hz, 2H, pyridine-H3, 5), 7.48 (t, J$_{HH}$ = 8.0 Hz, 1H, pyridine-H4). $^{13}$C-$^1$H NMR (THF-d$_8$): 18.34 (s, P(CH(CH$_3$)$_2$)$_2$), 19.17 (s, P(CH(CH$_3$)$_2$)$_2$), 20.37 (t, J$_{PC}$ = 3.5 Hz, P(CH(CH$_3$)$_2$)$_2$), 20.47 (s, P(CH(CH$_3$)$_2$)$_2$), 25.85 (t, J$_{PC}$ = 12.5 Hz, P(CH(CH$_3$)$_2$)$_2$), 26.88 (t, J$_{PC}$ = 11.0 Hz, P(CH(CH$_3$)$_2$)$_2$), 41.23 (t, J$_{PC}$ = 9.5Hz, CH$_2$P), 120.57 (t, J$_{PC}$ = 5.0 Hz, Py-C3,5), 137.53 (s, Py-C4), 163.86 (t, J$_{PC}$ = 5.5 Hz, Py-C2,6), 209.62 (t, J$_{PC}$ = 12.0 Hz, Ru-CO). IR (KBr, pellet): 1994.2 (vRuH), 1903.3 (vCO) cm$^{-1}$. Anal. Calcd. for C$_{20}$H$_{36}$NOP$_2$ClRu: C, 47.57; H, 7.19. Found: C, 47.48; H, 7.12.
Synthesis of [RuH(Cl)(PNN)(CO)] 2. To a suspension of HClRu(PPh₃)₃(CO) (95.3 mg, 0.1 mmol) in THF (2 ml) was added PNN (32 mg, 0.1 mmol), and the mixture was stirred and heated at 65°C for 12 hrs, then cooled to room temperature. The pale yellow solid thus obtained was filtered and washed with ether (3 x 3mL), then dried under vacuum (44mg, 90%). 31P {1H} NMR (Acetone-d₆): 108.7 (s); 1H NMR (Acetone-d₆): -15.25 (d, J_pH = 27.5 Hz, 1H, Ru-H), 1.12 (t, J_HH = 7.5 Hz, 3H, N(CH₂CH₃)₂), 1.25 (t, J_HH = 7.5 Hz, 3H, N(CH₂CH₃)₂), 1.33 (d, J_pH = 9.0 Hz, 9H, P(C(CH₃)₃)₂), 1.26 (d, J_pH = 9.0 Hz, 9H, P(C(CH₃)₃)₂), 2.71 (m, 1H, N(CHHMe₂)), 2.81 (m, 1H, N(CHHMe₂)), 3.34 (dd, J_HH = 17.5 Hz, J_pH = 8.5 Hz, 1H, -CHHP), 3.48 (m, 1H, N(CHHMe₂)), 3.70 (dd, J_HH = 17.5 Hz, J_pH = 10Hz, 1H, -CHHP), 3.86 (m, 1H, N(CHHMe₂)), 3.90 (d, J_HH = 14.0 Hz, 1H, -CHHN), 5.28 (d, J_HH = 14.0 Hz, 1H, -CHHN), 7.37 (d, J_HH = 8.0 Hz, 1H, pyridine-H3), 7.52 (d, J_HH = 8.0 Hz, 1H, pyridine-H5), 7.78 (t, J_HH = 8.0 Hz, 1H, pyridine-H4). 13C {1H} NMR (Acetone-d₆): 10.72 (s, N(CH₂CH₃)₂), 13.38 (s, N(CH₂CH₃)₂), 32.40 (s, P(C(CH₃)₃)₂), 37.55 (d, J_pC = 25.2 Hz, P(C(CH₃)₃)₂), 39.90 (d, J_pC = 21.4 Hz, PCH₂-), 51.70 (s, N(CH₂CH₃)₂), 56.59 (s, N(CH₂CH₃)₂), 66.80 (s, pyCH₂N), 123.15 (s, Py-C₃), 131.69 (s, Py-C₅), 140.15 (s, Py-C₄), 163.34 (d, J_pC = 2.5 Hz, Py-C₆), 164.55 (d, J_pC = 3.9 Hz py-C₂), 211.30 (d, J_pC = 16.4 Hz); IR (KBr, pellet): 2042 (vRu=H), 1901 (vCO) cm⁻¹. Anal. Calcd. for C₂₀H₃₆N₂OPClRu: C, 53.20; H, 7.44. Found: C, 53.20; H, 7.84.

Synthesis of [RuH(PNN)(CO)] 3. To a suspension of complex 2 (49 mg, 0.1 mmol) in THF (5 ml) was added t-BuOK (11.2 mg, 0.1 mmol) at room temperature for 20min until the color of the solution changed to yellow. 31P {1H} NMR indicated 100% conversion to the trans dihydride complex 4. (b) to a solution of complex 3 (49 mg, 0.1 mmol) was added NaHBEt₃ (0.1 mL of a 1M toluene solution; 0.1 mmol) and the mixture was stirred at room temperature for 2 hrs, then filtered. The yellow filtrate was carefully dried under vacuum to 0.5 mL and 5 mL pentane was added to precipitate a brown-red solid, which was filtered and washed with pentane (3 x 2mL), then dried under vacuum (40mg, 89%). 31P {1H} NMR (C₆D₆): 94.7 (s); 1H NMR (C₆D₆): -26.45 (d, J_pH = 25.5 Hz, 1H, Ru-H), 0.78 (t, J_HH = 7.3 Hz, 3H, N(CH₂CH₃)₂), 0.94 (t, J_HH = 7.0 Hz, 3H, N(CH₂CH₃)₂), 1.43 (d, J_pH = 6.0 Hz, 9H, P(C(CH₃)₃)₂), 1.46 (d, J_pH = 5.5 Hz, 9H, P(C(CH₃)₃)₂), 2.13 (m, 1H, N(CHHMe₂)), 2.35 (m, 1H, N(CHHMe₂)), 2.48 (m, 1H, N(CHHMe₂)), 2.66 (d, J_HH = 13.5 Hz, 1H, -CHHN), 2.76 (m, 1H, N(CHHMe₂)), 3.49 (d, J_HH = 13.5 Hz, 1H, -CHHN), 3.66 (s, 1H, =CHP), 5.34 (d, J_HH = 7.5 Hz, 1H, pyridine-H3), 6.50 (d, J_HH = 8.0 Hz, 1H, pyridine-H5), 6.59 (vτ, J_HH = 8.0 Hz, J_HH = 7.5 Hz, 1H, pyridine-H4). 13C {1H} NMR (C₆D₆): 10.87 (s, N(CH₂CH₃)₂), 11.30 (s, N(CH₂CH₃)₂), 29.14 (s, P(C(CH₃)₃)₂), 35.25 (d, J_pC = 27.7 Hz, P(C(CH₃)₃)₂), 38.08 (d, J_pC = 26.4 Hz, P(C(CH₃)₃)₂), 50.63 (s, N(CH₂CH₃)₂), 55.31 (s, N(CH₂CH₃)₂), 64.44 (s, CH₂N), 65.25 (d, J_pC = 50.3 Hz, =CHP), 96.52 (s, Py-C₅), 114.27 (d, J_pC = 16.4 Hz, Py-C₃), 132.09 (s, Py-C₄), 156.88 (d, J_pC = 2.5 Hz, Py-C₆), 169.12 (d, J_pC = 15.1 Hz, py-C₂), 206.90 (d, J_pC = 11.3 Hz, Ru-CO) ppm; IR (KBr, pellet): 1899 (vCO) cm⁻¹. Anal. Calcd. for C₂₀H₃₅N₂OPClRu: C, 53.20; H, 7.82. Found: C, 53.31, H, 7.94.
concentrated to 0.5 mL with H$_2$ gas, then 5 mL pentane was added to precipitate a yellow solid, which was filtered and washed with pentane (3 × 1 mL), then dried with H$_2$ flow (30mg, 63% yield). The compound is stable only under an atmosphere of H$_2$. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): 124.9 (s); $^1$H NMR (C$_6$D$_6$): -4.06 (d, $J_{PH} = 17.0$ Hz, 2H, Ru-H), 1.10 (t, $J_{HH} = 6.5$ Hz, 6H, N(CH$_2$CH$_3$)$_2$), 1.50 (d, $J_{PH} = 5.5$ Hz, 18H, P(CH$_3$)$_3$)$_2$, 3.05 (m, 2H, N(CHHMe)$_2$), 3.12 (d, $J_{PH} = 8.5$ Hz, 2H, -CH$_2$P), 3.14 (m, 2H, N(CHHMe)$_2$), 3.83 (s, 2H, py-CH$_2$N), 6.42 (d, $J_{HH} = 8.0$ Hz, 1H, pyridine-H3), 6.59 (d, $J_{HH} = 8.0$ Hz, 1H, pyridine-H5), 6.59 (t, $J_{HH} = 8.0$ Hz, 1H, pyridine-H4), $^{13}$C{$^1$H} NMR (C$_6$D$_6$): 10.82 (s, N(CH$_2$CH$_3$)$_2$), 29.64 (s, P(CH$_3$)$_3$)$_2$, 35.34 (d, $J_{PC} = 17.6$ Hz, P(CH$_3$)$_3$)$_2$, 37.89 (d, $J_{PC} = 17.6$ Hz, py-CH$_2$P), 54.97 (s, N(CH$_2$Me)$_2$), 67.62 (s, CH$_2$N), 117.62 (s, Py-C5), 119.06 (d, $J_{PC} = 8.8$ Hz, Py-C3), 133.27 (s, Py-C4), 158.12 (s, Py-C6), 160.51 (s, py-C2), 214.03 (d, $J_{PC} = 17.0$ Hz, Ru-CO) ppm.

**Typical procedures for the catalytic dehydrogenation of primary alcohols:** (a) Complex 1 (0.01 mmol) or 2 (0.01 mmol) were dissolved in the primary alcohol (10 mmol) and KOH (0.01 mmol) was added. The flask was equipped with a condenser and the solution was heated with stirring in an open system under an argon flow at the specified temperature and time (Table 1 in the paper). After cooling to room temperature, the aldehydes and esters were determined by GC with mesitylene or benzene (for 1-butanol) as internal standard, using a Carboxen 1000 column on a HP 690 series GC system; (b) complex 3 (0.01 mmol) was heated under an argon flow in different alcohols (10 mmol) at the specified temperatures and times (Table 1). After cooling to room temperature, the aldehydes and esters were determined by GC with mesitylene or benzene (for 1-butanol) as internal standards using a Carboxen 1000 column on a HP 690 series GC system; (c) the reactions were performed as above, except that 2ml of toluene solvent were added to the reactants and the solution was refluxed under argon for the specified period. Reaction follow up in the case of benzyl alcohol is presented in the Figure.
X-ray Crystal Structure Determination of 2. A crystal was mounted on a nylon loop and flash frozen in a nitrogen stream at 120K. Data were collected on a Nonius Kappa CCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The four structures were solved using direct methods with SHELXS-97 based on $F^2$. Complex 2: C$_{20}$H$_{36}$N$_2$OPClRu + 0.5×C$_5$H$_{12}$, pale-yellow plate, 0.40×0.40×1.00 mm$^3$, monoclinic, $C2/c$ (No.15), $a = 32.672(6)$ Å, $b = 10.770$ (2) Å, $c = 15.855$ (2) Å, $β = 116.19(3)^°$, $V = 5006$ (2) Å$^3$, $Z = 8$, fw = 524.07, $F(000) = 2200$, $D_c = 1.391$ Mg/m$^3$, $µ = 0.813$ mm$^{-1}$. The final cycle of refinement based on $F^2$ gave an agreement factor $R = 0.028$ for data with $I > 2σ(I)$ and $R = 0.035$ for all data (4269 reflections) with a goodness-of-fit of 1.074. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1RU, which was located in the difference map and refined independently.

References