Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Efficient Homogeneous Catalytic Hydrogenation of Esters to Alcohols

Jing Zhang, Gregory Leitus, Yehoshoa Ben-David and David Milstein*

[*] Dr. J. Zhang, Y. Ben-David, Prof. D. Milstein*

Department of Organic Chemistry, Weizmann Institute of Science

76100 Rehovot (Israel)

E-mail: david.milstein@weizmann.ac.il

Dr. G. Leitus

Chemical Research Support, Weizmann Institute of Science

76100 Rehovot (Israel)

Experimental section.

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 purifer 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. Complexes [RuHCl(^{i}Pr-PNP)(CO)] (^{i}Pr-PNP = 2,-6-bis-(di-iso-propylphosphinomethyl)pyridine) and [RuH(PNN(-))(CO)] (PNN = 2-(di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine) were prepared according to our previous paper.[1]

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 400 or 500, 100 or 126, and 162 or 202 MHz, respectively, using a Bruker AMX-400 and AMX-500 NMR spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. 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 RuH (^{i}Pr-PNP(-))(CO) 1. To a solution of complex RuHCl(^{i}Pr-PNP)(CO)[1] (51 mg, 0.1 mmol) in THF (5 ml) was added KOBu^{t} (11.2 mg, 0.1 mmol) at –32 °C. The mixture was stirred at room temperature for 4 hrs, then filtered. The orange filtrate was concentrated under vacuum to 0.5 mL and 5 mL of pentane were added. The mixture was cooled at –32 ^{0}C overnight and the yellow crystals that formed were isolated by filtration, washed with pentane (3 × 2mL) and dried under vacuum to give 40mg (85% yield) of pure **1**.

$^{31}P\{^{1}H\}$ (C_6D_6): AB system, δ_A: 67.0 (d, J_{PP} = 256.0 Hz; δ_B: 66.3 (d, J_{PP} = 256.0 Hz). ^{1}H (C_6D_6): -13.04 (t, 1H, J_{PH} = 24.0 Hz, Ru-H), 0.84 (overlapped dq, 6H, P(CH(C*H*$_3$)$_2$)$_2$), 1.04 (t, 3H, J_{PH} = J_{HH} = 8.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.26 (q, 3H, J_{PH} = J_{HH} = 6.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$)), 1.44 (q, 3H, J_{PH} = J_{HH} = 6.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$, 1.56 (q, 3H, J_{PH} = J_{HH} = 6.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.63 (q, 3H, J_{PH} = J_{HH} = 6.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.71 (t, 3H, J_{PH} = J_{HH} = 6.0 Hz, P(CH(C*H*$_3$)$_2$)$_2$), 1.94 (m, 1H, P(C*H*(CH$_3$)$_2$)$_2$), 2.26 (m, 1H, P(C*H*(CH$_3$)$_2$)$_2$), 2.36 (m, 1H, P(C*H*(CH$_3$)$_2$)$_2$), 2.64 (dd, 1H, J_{HH} = 18.0 Hz, J_{PH} = 10.0 Hz, -CH*H*P), 2.86 (dd, J_{HH} = 16.0 Hz, J_{PH} = 6.0 Hz, 1H, -C*H*HP), 3.60 (m, 1H, P(C*H*(CH$_3$)$_2$)$_2$), 3.85 (d, 1H, J_{PH} = 12.0 Hz, =CH-P), 5.64 (d, 1H, J_{HH} = 4.0 Hz, pyridine-H3 or H5), 6.33 (vt, J_{HH} = 8.0 Hz, J_{HH} = 4.0 Hz, 1H, pyridine-H4), 6.52 (d, J_{HH} = 8.0 Hz, 1H, pyridine-H3 or H5). $^{13}C\{^{1}H\}$ NMR (C_6D_6): 17.1 (d, J_{PC} = 5.0 Hz, P(CH(*C*H$_3$)$_2$)$_2$),

18.7 (s, $P(CH(CH_3)_2)_2$), 19.2 (s, $P(CH(CH_3)_2)_2$), 20.2 (s, $P(CH(CH_3)_2)_2$), 20.3 (s, $P(CH(CH_3)_2)_2$), 21.5 (d, J_{PC} = 7.0 Hz, $P(CH(CH_3)_2)_2$), 21.8 (s, $P(CH(CH_3)_2)_2$), 22.1 (s, $P(CH(CH_3)_2)_2$), 27.0 (d, J_{PC} = 26.1 Hz, $P(CH(CH_3)_2)_2$), 29.8 (d, J_{PC} = 9.0 Hz, $P(CH(CH_3)_2)_2$), 30.6 (d, J_{PC} = 9.0 Hz, $P(CH(CH_3)_2)_2$), 31.2 (d, J_{PC} = 22.1 Hz, $P(CH(CH_3)_2)_2$), 39.0 (s, =CH-P), 42.7 (d, J_{PC} = 15.1 Hz, CH_2P), 108.3 (d, J_{PC} = 10.0 Hz, Py-C3 or C5), 116.6 (d, J_{PC} = 12.1 Hz, Py-C3 or C5), 132.5 (s, Py-C4), 159.5 (d, J_{PC} = 7.0 Hz, Py-C2 or C6), 178.6 (d, J_{PC} = 7.0 Hz, py-C2 or 6), 210.0 (t, J_{PC} = 11.1 Hz, Ru-CO). IR (KBr, pellet): 2024 (ν_{RuH}), 1888.2 (ν_{CO}) cm,$^{-1}$ Anal. Calcd. for $C_{20}H_{35}NOP_2Ru$: C, 51.27; H, 7.53. Found: C, 51.38; H, 7.59.

Synthesis of [*trans*-$(H)_2$Ru(^{i}Pr-PNP)(CO)] 3. (a) To a solution of [*trans*-(H)(Cl)Ru(^{i}Pr-PNP)(CO)] (25.3 mg, 0.05 mmol) in THF (5 ml) was added $NaHBEt_3$ (50µL of 1M in toluene, 0.05 mmol), and the mixture was stirred at room temperature for 2 hrs. The yellow solution was filtered and the filtrate was evaporated under vacuum to dryness. The residual yellow oil was treated with pentane (5 mL), the pale-yellow solid thus obtained was filtered and dried under vacuum (21mg, 90%); (b) Complex **1** (9.4 mg, 0.02 mmol) was dissolved in 1 mL benzene-d_6 and the solution was bubbled with H_2 for 20 min. $^{31}P\{^1H\}$ NMR of the solution shows 100 % conversion to complex **3**. $^{31}P\{^1H\}$ (C_6D_6): 91.2 (s,). ^1H (C_6D_6): -4.96 (t, 2H, J_{PH} = 20.0 Hz, Ru-H), 1.14 (q, 12H, J_{PH} = J_{HH} = 8.0 Hz, $P(CH(CH_3)_2)_2$), 1.32 (q, 12H, J_{PH} = J_{HH} = 8.0 Hz, $P(CH(CH_3)_2)_2$), 1.97 (m, 4H, $P(CH(CH_3)_2)_2$), 2.97 (t, 4H, J_{PH} = 4.0 Hz, $-CH_2P$), 6.36 (d, 2H, J_{HH} = 8.0 Hz, pyridine-H3, 5), 6.68 (t, 1H, J_{HH} = 8.0 Hz, pyridine-H4). $^{13}C\{^1H\}$ NMR (C_6D_6): 18.9 (s, $P(CH(CH_3)_2)_2$), 27.7 (t, $P(CH(CH_3)_2)_2$), 41.0 (t, J_{PC} = 9.0Hz, CH_2P), 119.4 (t, J_{PC} = 4.0 Hz, Py-C3,5), 134.7 (s, Py-C4), 162.2 (t, J_{PC} = 6.0Hz, py-C2,6), 211.5 (t, J_{PC} = 13.0 Hz, Ru-CO). Anal. Calcd. for $C_{20}H_{37}NOP_2Ru$: C, 51.05; H, 7.93. Found: C, 51.07; H, 7.66.

X-ray Crystal Structure Determination of 1. The 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 structure was solved using direct methods with SHELXS-97 based on F^2.

Complex 1: 2 × $C_{20}H_{35}NOP_2Ru$, yellow plate, 1.20 × 0.10×0.05 mm^3, monoclinic, $P2_1/n$ (No.14), a = 12.827 (3) Å, b = 17.961 (4) Å, c = 19.501 (4) Å, β = 101.62 (3)°, V = 4401 (2) $Å^3$, Z = 4, fw = 937, $F(000)$ = 1952, D_c = 1.414 Mg/m^3, μ = 0.866 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R = 0.057 for data with $I > 2\sigma(I)$ and R = 0.072 for all data (6051 reflections) with a goodness-of-fit of 1.047. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H1r which was located in the difference map and refined independently.

General procedure for catalytic hydrogenation of esters: A 90 mL Fischer-Porter tube was charged under nitrogen with the catalyst **2** (0.02 mmol), ester (2 mmol) and dioxane (2mL) and then filled with H_2 (75 psi). The solution was heated at 115 ºC (actual solution temperature) with stirring for the specified period. After cooling to room temperature, the product alcohols 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.

Reference:

[1] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein *J Am. Chem. Soc.* **2005**, *127*, 10840.