Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

"Rational Design of Efficient Rhodium Catalysts for the Anti-Markovnikov Oxidative Amination of Styrene"

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S-1 Experimental Details and Synthesis of the Complexes

Scientific Equipment. C, H and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on Bruker Avance 300 MHz spectrometers. ^{1}H (300.13 MHz), $^{31}P\{^{1}H\}$ (121.48 MHz) and $^{13}C\{^{1}H\}$ (75.48 MHz) NMR chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances for ^{1}H and ^{13}C, and H_3PO_4 (85%) for ^{31}P. Coupling constants (*J*) are given in Hertz. Conductivities were measured in *ca.* 5 10^{-4} M acetone solutions of the complexes using a Philips PW 9501/01 conductimeter. Electrospray mass spectra (ESI-MS) were recorded in methanol on a Bruker MicroTof-Q using sodium formiate as reference. MALDI-Tof mass spectra were obtained on a Bruker Miocroflex mass spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) or dithranol as matrix. FT-IR spectra were collected on a Nicolet Nexus 5700 FT spectrophotometer equipped with a Nicolet Smart Collector diffuse reflectance accessory.

Organic compounds were identified by Gas Chromatography-Mass Spectrometry (GC-MS) recorded in the mass range 1-1000 m/z on a Agilent 6890 GC-Agilent 5973 MS, equipped with a polar capillary column HP-5MS (30m x 0.25 mm d.i. x 0.25 μm). The catalytic reactions were analyzed on a GC HP 6890N with an ionization detector fitted up to a HP Ultra-1 (25m x 0.32 mm d.i. x 0.17 μm). Calibration was made with the internal standard tetradecane.

Synthesis. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Solvents were obtained from a Solvent Purification System (Innovative Technologies). $CDCl_3$, CD_2Cl_2, THF-d_8 (Euriso-top) were dried using activated molecular sieves. Standard literature procedures were used to prepare the starting materials $[Rh(\mu\text{-}Cl)(cod)]_2$[i] and $[Rh(\mu\text{-}Cl)(coe)_2]_2$[ii]. The functionalized ether phosphine (3-ethoxypropyl)diphenylphosphine, $Ph_2P(CH_2)_3OEt$, was prepared following published methods[iii]

Synthesis of $[Rh(cod)\{Ph_2P(CH_2)_3OEt\}]BF_4$ (1). A suspension of $[Rh(\mu\text{-}Cl)(cod)]_2$ (246 mg, 0.500 mmol) in acetone (10 mL) at 0 ºC was treated with $AgBF_4$ (194 mg, 1.00 mmol). The AgCl formed was removed by filtration and the resulting yellow solution was poured into a solution of $Ph_2P(CH_2)_3OEt$ (272 mg, 1.00 mmol) in acetone (3 cm^3) at 0 ºC and stirred for 40 min. The solvent was removed under vacuum and the crude compound was dissolved in acetone (2 cm^3) and layered with diethyl ether (10 cm^3) at room temperature for 12 h to give the compound **1** as yellow crystals, which were filtered off, washed with diethyl ether (2 x 5 cm^3), and dried in vacuo (353 mg, 62%; Anal. Found: C, 52.89; H, 5.10. $C_{25}H_{33}BF_4OPRh$ requieres C, 52.66; H, 5.83); δ_H (300.13 MHz; 298 K; $CDCl_3$; Me_4Si): 7.61–7.43 (10H, m, 2 x Ph), 5.22 (2H, br, =CH cod), 4.04 (2H, m, CH_2) , 3.44 (2H, q, *J* 7.2, CH_2CH_3) , 3.19 (2H, br, =CH cod) , 2.68 (2H, m, CH_2), 2.58–2.42 (4H, m, CH_2 cod) , 2.08–1.18 (6H, m, CH_2 cod and CH_2), 1.04 (3H, t, *J* 7.2, CH_2CH_3); δ_P (121.48 MHz; 298 K; $CDCl_3$; H_3PO_4): 20.69 (d, $J_{P\text{-}Rh}$ 147.6); δ_C (75.48 MHz; 298 K; $CDCl_3$; Me_4Si): 132.81 (d, $J_{C\text{-}P}$ 10.7, C_o), 131.23 (d, $J_{C\text{-}P}$ 2.1, C_p), 129.30 (d, $J_{C\text{-}P}$ 40.5, C_i),

129.04 (d, $J_{C\text{-}P}$ 10.0, C_m), 107.22 (dd, $J_{C\text{-}Rh}$ 10.4, $J_{C\text{-}P}$ 7.2, =CH cod), 72.54 (CH_2CH_3), 70.58 (d, $J_{C\text{-}Rh}$ 15.2, =CH cod), 69.68 (CH_2O), 32.60, 27.71 (CH_2 cod), 23.87 (d, $J_{C\text{-}P}$ 24.9, CH_2P), 22.83 (CH_2), 14.65 (CH_2CH_3); MS (MALDI-Tof, DCTB, MeOH) *m/z*: 483 (M^+).

Synthesis of [Rh(cod)($Ph_2P(CH_2)_3OEt$)(PPh_3)]BF_4 (2). To a yellow solution of [Rh(cod){$Ph_2P(CH_2)_3OEt$}]BF_4 (**1**) (100 mg, 0.170 mmol) in dichloromethane (5 cm^3) a solution of PPh_3 (44.6 mg, 0.170 mmol) in the same solvent (2 cm^3) was added slowly and the resulting solution was stirred for 30 min. The solution was concentrated under vacuum at *ca.* 1 cm^3 and the slow addition of diethyl ether gave the compound **2** as a yellow solid that was filtrated, washed with diethyl ether (2 x 5 cm^3) and dried in vacuo (141 mg, 84%; Anal. Found: C, 62.84; H, 5.98. $C_{43}H_{48}BF_4OP_2Rh$ requieres C, 62.04; H, 5.81); δ_H (300.13 MHz; 298 K; $CDCl_3$; Me_4Si): 7.70–7.27 (25H, m, Ph), 4.66 (2H, br, =CH cod), 4.60 (2H, br, =CH cod), 3.16 (2H, q, *J* 7.0, CH_2CH_3), 3.89 (2H, t, *J* 5.9, OCH_2), 2.40 (4H, m, CH_2 cod), 2.24 (4H, m, CH_2 cod), 1.45 (2H, m, CH_2), 1.30 (2H, m, CH_2), 0.94 (3H, t, *J* 7.0, CH_2CH_3); δ_P (121.48 MHz; 298 K; $CDCl_3$; H_3PO_4): 27.32 (dd, $J_{P\text{-}Rh}$ 146.2, $J_{P\text{-}P}$ 30.4), 15.76 (dd, $J_{P\text{-}Rh}$ 141.4, $J_{P\text{-}P}$ 30.4); δ_C (75.48 MHz; 298 K; $CDCl_3$; Me_4Si): 134.35 (d, $J_{C\text{-}P}$ 12.1, C_o), 133.28 (d, $J_{C\text{-}P}$ 9.9, C_o), 131.54, 131.19 (C_p), 130.46, (d, $J_{C\text{-}P}$ 42.3, C_i), 129.74, (d, $J_{C\text{-}P}$ 41.2, C_i), 129.01 (d, $J_{C\text{-}P}$ 9.3, C_m), 128.94 (d, $J_{C\text{-}P}$ 10.4, C_m), 99.68 (dd, $J_{C\text{-}Rh}$ 8.8, $J_{C\text{-}P}$ 8.2, =CH cod), 97.32 (dd, $J_{C\text{-}Rh}$ = $J_{C\text{-}P}$ 8.8, =CH cod), 69.82 (d, $J_{C\text{-}P}$ 12.6, CH_2O), 65.95 (CH_2CH_3), 30.55, 30.43, 30.06 (CH_2 cod), 25.59 (d, $J_{C\text{-}P}$ 6.0, CH_2), 23.66 (dd, $J_{C\text{-}P}$ 24.8, $J_{C\text{-}Rh}$ 2.7, CH_2P), 14.87 (CH_2CH_3); MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 637 (M^+ - cod), 483 (Rh{P–O}$^+$), 473 (Rh{PPh_3}$^+$).

Synthesis of [Rh(cod){$Ph_2P(CH_2)_3OEt$}$_2$][X] (X = BF_4, 3a; PF_6, 3b; SbF_6, 3c). The compounds [Rh(cod){$Ph_2P(CH_2)_3OEt$}$_2$][X] (**3a-3c**) were obtained from the solvato [Rh(cod)(Me_2CO)$_x$][X] (0.250 mmol) species obtained by reaction of complex [Rh(μ-Cl)(cod)]$_2$ (61.6 mg, 0.125 mmol) with the appropriate silver salt AgX (0.250 mmol) in acetone (5 cm^3).

Work up as described above for the synthesis of **1** gave the compounds **3a** (162 mg, 77%; Anal. Found: C, 60.02; H, 6.49. $C_{42}H_{54}BF_4O_2P_2Rh$ requieres C, 59.87; H, 6.46), **3b** (182 mg, 81%; Anal. Found: C, 56.32; H, 6.14. $C_{42}H_{54}F_6O_2P_3Rh$ requieres C, 56.01; H, 6.04), and **3c** (166 mg, 67%; Anal. Found: C, 50.55; H, 5.40. $C_{42}H_{54}F_6O_2P_2RhSb$ requieres C, 50.88; H, 5.49), as yellow crystals. **[Rh(cod){$Ph_2P(CH_2)_3OEt$}$_2$]PF_6 (3b).** Spectroscopic data: δ_H (300.13 MHz; 298 K; $CDCl_3$; Me_4Si): 7.54–7.39 (20H, m, 4 x Ph), 4.69 (4H, br, 2 x =CH cod), 3.34 (4H, q, *J* 7.0, 2 x CH_2CH_3), 3.23 (4H, t, *J* 5.5, 2 x CH_2), 2.45 (4H, br, CH_2 cod), 2.17 (4H, br, CH_2 cod), 1.95 (4H, br, 2 x CH_2), 1.71 (4H, br, 2 x CH_2), 1.00 (6H, t, *J* 7.0, 2 x CH_2CH_3); δ_P (121.48 MHz; 298 K; $CDCl_3$; H_3PO_4): 18.50 (d, $J_{P\text{-}Rh}$ 143.1); δ_C (75.48 MHz; 298 K; $CDCl_3$; Me_4Si): 133.27 (d, $J_{C\text{-}P}$ 5.2, C_o), 131.13 (C_p), 130.42 (d, $J_{C\text{-}P}$ 41.9, C_i), 129.04 (d, $J_{C\text{-}P}$ 4.8, C_m), 97.78 (m, =CH cod), 70.25 (d, $J_{C\text{-}P}$ 6.5, CH_2), 66.25 (CH_2CH_3), 30.61, 26.44 (CH_2 cod), 24.22 (dd, $J_{C\text{-}P}$ 13.4, CH_2), 24.22 (CH_2), 15.17 (CH_2CH_3); MS (ESI+, MeOH) *m/z*: 755 (M^+).

Synthesis of [Rh{$Ph_2P(CH_2)_3OEt$}$_2$]PF_6 (4). A suspension of [Rh(μ-Cl)(coe)$_2$]$_2$ (71.7 mg, 0.100 mmol) in acetone (10 cm^3) was treated with $AgPF_6$ (50.6 mg, 0.200 mmol) and allowed to react for 1h at 0 ºC. The AgCl formed was removed by filtration and the resulting yellow solution was poured into a solution of $Ph_2P(CH_2)_3OEt$ (108 mg, 0.40 mmol) in acetone (1 cm^3) to give a red solution. The solvent was removed under vacuum and the residue washed with diethyl ether (3 x 5 cm^3). The resulting orange solid was dissolved in THF (1 cm^3) and layered with diethylether (10 cm^3) at room temperature to render orange crystals of **4** which were filtered, washed with diethyl ether and dried in vacuo (158 mg, 72%; Anal. Found: C, 51.62; H, 5.38. $C_{34}H_{42}F_6O_2P_3Rh$ requieres C, 51.53; H, 5.34.); δ_H (300.13 MHz; 258 K; THF-d^8; Me_4Si): 7.53–7.15 (20H, m, 4 x Ph), 4.09 (4H, br, 2 x CH_2O), 3.68 (4H, q, *J* 6.8, 2 x CH_2CH_3), 2.49 (4H, br, 2 x CH_2), 1.80 (4H, m, 2 x CH_2) 1.50 (6H, t, *J* 6.8, 2 x CH_2CH_3); δ_P (121.48 MHz; 258 K; $CDCl_3$; H_3PO_4): 46.45 (d, $J_{P\text{-}Rh}$ 204.8); δ_C (75.48 MHz; 258 K; $CDCl_3$; Me_4Si): 132.99 (br, C_o), 129.54

(br, C_p), 127.90 (br, C_m), 73.56 (CH_2O), 70.85 (CH_2CH_3), 28.82 (dd, J_{C-P} 13.6, CH_2P), 22.84 (CH_2), 14.72 (CH_2CH_3); MS (ESI+, MeOH) *m/z*: 647 (M^+).

Reaction of $[Rh\{Ph_2P(CH_2)_3OEt\}_2]PF_6$ (4) with piperidine. Formation of $[Rh\{Ph_2P(CH_2)_3OEt\}_2(piperidine)_2]$ (8). Piperidine (5.11 mg, 5.93 μL, 0.06 mmol) was added to a suspension of $[Rh\{Ph_2P(CH_2)_3OEt\}_2]PF_6$ (**4**) (17.1 mg, 0.02 mmol) in THF-d^8 (0.5 mL) to give an orange solution of complex **8**. The compound has a fluxional behaviour and was characterized at low temperature by spectroscopic means. Spectroscopic data: δ_H (300.13 MHz; 193 K; THF-d^8; Me_4Si): 7.89-7.16 (20H, m, 4 x Ph), 3.37 (4H, q, J_{H-H} = 6.9, 2 x CH_2CH_3), 3.34 (4H, br, 2 x CH_2O), 3.14 (2H, m, CH_2-pip), 2.91 (2H, t, 11.0, CH_2-pip), 2.84 (2H, m, CH_2-pip), 2.49 (2H, t, *J* 11.0, CH_2-pip), 2.04 (2H, m, CH_2-pip), 1.92 (4H, m, 2 x CH_2), 1.69 (2H, m, CH_2-pip), 1.50-1.32 (10H, m, 2 x CH_2-pip, CH_2-pip and 2 x CH_2), 1.16 (6H, t, *J* 7.0, 2 x CH_2CH_3), 0.42 (2H, m, CH_2-pip); δ_P (121.48 MHz; 193 K, THF-d^8; H_3PO_4): 38.29 (d, J_{P-Rh} 170.2); δ_C (75.48 MHz; 193 K, THF-d^8, Me_4Si): 136.52-129.00 (Ph), 70.62 (CH_2O), 66.04 (CH_2CH_3), 50.26 (CH_2-pip), 46.71 (CH_2-pip), 27.95 (CH_2-pip), 27.49 (CH_2P), 26.30 (CH_2-pip), 25.01 (CH_2-pip), 23.76 (CH_2), 15.13 (CH_2CH_3).

Heating of a solution of $[Rh\{Ph_2P(CH_2)_3OEt\}_2(piperidine)_2]$ (8). Formation of $[Rh\{Ph_2P(CH_2)_3OEt\}_2(NC_5H_{10})]$ (9). A solution of $[Rh\{Ph_2P(CH_2)_3OEt\}_2(piperidine)_2]$ (**8**) (0.02 mmol) in), generated in situ from **4**, in THF-d^8 (0.5 mL) was heated at 343 K for 2 hours to give a red solution containing $[Rh\{Ph_2P(CH_2)_3OEt\}_2(NC_5H_{10})]$ (**9**) and $[H_2NC_5H_{10}][PF_6]$.

Spectroscopic data: **$[Rh\{Ph_2P(CH_2)_3OEt\}_2(NC_5H_{10})]$ (9)**: δ_H (300.13 MHz; 298 K, THF-d^8; Me_4Si): δ 7.53-7.35 (20H, m, 4 x Ph), 3.87 (1H, br, CH_2-amide), 3,59 (2H, br, CH_2O), 3.42 (2H, q, *J* 7.2, CH_2CH_3), 3.36 (2H, q, *J* 7.0, CH_2CH_3), 3.25 (2H, br, CH_2O), 3.09 (1H, br, CH_2-amide), 3.01 (1H, br, CH_2-amide), 2.44 (1H, br, CH_2-amide), 2.43 (1H, br, CH_2-amide), 2.28 (1H, br, CH_2-amide), 1.98 (1H, br, CH_2-amide), 1.97 (1H, br, CH_2-amide), 1.81 (2H, br, CH_2P), 1.78

(2H, br, CH_2), 1.55 (1H, br, CH_2-amide), 1.40 (1H, br, CH_2-amide), 1.34 (2H, br, CH_2P), 1.27 (2H, br, CH_2), 1.12 (3H, t, *J* 7.0, CH_2CH_3), 1.10 (3H, t, *J* 7.5, CH_2CH_3); δ_P (121.48 MHz; 193 K, THF-d^8; H_3PO_4): 39.60 (dd, $J_{P\text{-}Rh}$ 165.0, $J_{P\text{-}P}$ 51.3), 36.31 (dd, $J_{P\text{-}Rh}$ 173.1, $J_{P\text{-}P}$ 51.3); δ_C (75.48 MHz; 193 K, THF-d^8, Me_4Si): 131.28-127.89 (Ph), 70.52 (d, $J_{C\text{-}P}$ 13.4, CH_2O), 70.38 (d, $J_{C\text{-}P}$ 13.6, CH_2O), 69.94 (d, CH_2CH_3), 65.61 (CH_2CH_3), 53.28 (CH_2-amide), 49.40 (CH_2-amide), 29.53 (d, $J_{C\text{-}P}$ 25.9, CH_2P), 29.40 (CH_2-amide), 27.42 (d, $J_{C\text{-}P}$ 20.9, CH_2P), 25.92 (CH_2-amide), 23.86 (CH_2-amide), 22.22 (d, $J_{C\text{-}P}$ 14.5, CH_2), 22.20 (d, $J_{C\text{-}P}$ 17.3, CH_2), 14.65 (CH_2CH_3), 14.59 (CH_2CH_3). $\mathbf{[H_2NC_5H_{10}]^+}$: δ_H (300.13 MHz; 298 K, THF-d^8; Me_4Si): 4.38 (2H, br, NH_2^+), 2.85 (4H, br, 2 x CH_2), 1.57 (4H, br, 3 x CH_2); δ_C (75.48 MHz; 193 K, THF-d^8, Me_4Si): 46.61, 26.11, 24.49 (CH_2).

S-2 General Procedure for Hydroamination Catalytic Experiments. The catalytic hydroamination reactions were carried out under an argon atmosphere in a thick glass reaction tube fitted with a greaseless high-vacuum stopcock. In a typical experiment, the reactor was charged with a solution of the catalyst (0.020 mmol) in THF (2 cm^3), 2 mg of molecular sieves in powder (4Å) and the reactants in the following order: piperidine (0.800 mmol, 79 μL), tetradecane as internal standard (0.350 mmol, 91 μL) and styrene (3.24 mmol, 371 μL). The mixture was stirred at room temperature until the catalyst was completely dissolved, and then placed in an thermostatized oil bath at the required temperature.

The yield and selectivity were determined by GC analysis under the following conditions: Initial T^a 50ºC for 4 min, ramp 15º/min, and final T^a 250º for 10 min.

Retention time, s	*Compound*
4.90	piperidine
7.16	ethylbenzene
7.94	styrene
14.62	tetradecane
15.42	1-phenylethylpiperidine
17.84	(*E*)-1-styrylpiperidine

(i) G. Giordano, R. H. Crabtree, *Inorg. Synth.* 1979, **19**, 218–219.

(ii) A. van der Ent, A. L. Onderdelinden, *Inorg. Synth.* 1973, **14**, 92–94.

(iii) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, L. A. Oro, *Synthesis* 2009, 1916–1922.