Supplementary Data

High chemo and regioselective formation of alcohols from the hydrocarbonylation of alkenes using cooperative ligand effects

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Effect of CO partial pressure on the chemoselectivity to alcohols

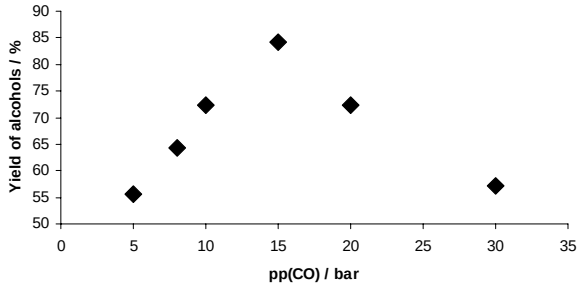

Fig. S1 Effect of CO partial pressure on the selectivity to alcoholic produts (1,4-butanediol and 2-methylpropanol) from the hydrocarbonylation of allyl alcohol in ethanol (4 cm^3) using [Rh(acac)$(CO)_2$], (8 mmol dm^{-3}), **1** (16 mmol dm^{-3}) and PEt_3 (16 mmol dm^{-3} (Rh/allyl alcohol = 1/185, 120°C, 40 bar, pp_{H_2} = 20 bar, (the remaining pressure was made up using argon), 3 h)

Full list of catalytic reaction products

Table S1: Product profile for hydrocarbonylation of allyl alcohol with diphosphine/PEt_3/Rh systems in ethanol.[a]

		allyl alcohol-based selectivity (mol %)														
		1-propanal	1-propanol	2-methyl-propanal	methacrolein	2-methyl-propannol	2, 3- dihydrofuran	2-ethoxyfuran	crotonaldehyde	2-methyl-pentnal	2-methyl-1,3-propanediol	1, 4- butanediol	γ-butyrolactone			
	[PEt_3] (mM)													C=O[b] (l/b)	C-OH[c] (l/b)	C_3[d]
XANTPHOS	0	9	1	2	13	0	10	54	11	0	0	0	0	89(5.1)	0	11
	0.5	8	0	0	14	1	6	62	6	1	0	0	0	89(5.1)	1 (b)	10
	4	6	1	2	11	2	7	52	5	1	0	10	2	89(5.2)	2 (0.2)	9
	10	0	4	3	0	9	3	12	0	3	2	56	5	18(4.9)	72 (5.3)	10
	16	1	3	2	0	11	3	6	1	3	1	59	6	12(4.9)	78 (5.2)	10
	24	1	5	2	0	18	0	12	0	3	1	49	7	13(4.8)	75 (2.9)	12
	32	0	4	3	0	21	0	14	1	4	2	40	9	16(4.7)	72 (2.4)	12
DIOP	0	2	0	2	11	2	15	63	4	0	0	1	0	96(6.3)	3 (0.5)	2
	4	1	0	5	6	2	13	56	2	0	0	15	0	81(6.3)	17 (6.5)	2
	10	1	0	3	0	9	7	11	0	0	1	61	7	20(6.3)	78 (6.5)	1
	16	1	1	2	0	10	5	8	0	0	1	67	5	15(6.3)	83 (6.5)	2
	24	0	1	2	0	15	3	8	3	0	1	61	5	17(6.2)	82 (4.3)	2
	32	1	1	3	0	17	0	12	5	0	2	52	8	19(6.2)	79 (3.7)	2
CBM-DXP	0	3	0	1	5	0	27	57	7	0	0	0	0	97(13.2)	0	3
	4	2	1	5	1	1	31	45	3	1	0	8	1	85(13.1)	10 (14.3)	5
	10	1	1	2	0	4	13	11	2	1	1	58	6	28(13.1)	68 (14.3)	4
	16	0	2	1	0	5	7	12	1	1	0	66	5	20(13.1)	76 (14.3)	4
	24	0	0	1	0	7	7	15	2	2	1	58	6	24(13.0)	72 (10.3)	4
	32	0	2	2	0	7	5	17	3	1	1	56	6	26(12.9)	70 (9.2)	4
BISBI	0	9	1	1	14	0	13	49	5	4	0	0	0	82 (4.5)	0	18
	4	7	2	2	13	0	10	52	4	4	0	3	0	80 (4.5)	3 (4.7)	17
	10	4	4	4	1	10	4	15	0	4	1	49	0	24 (4.5)	60 (4.6)	16
	16	4	6	3	0	11	5	9	0	4	1	49	5	17 (4.5)	65 (4.5)	18
	24	4	7	3	1	20	3	13	1	3	2	38	3	20 (4.4)	63 (4.4)	17
	32	6	5	4	0	23	3	15	2	3	1	31	4	23 (4.4)	60 (4.4)	17

[a]Conditions: 4 mL ethanol, 8 mM [Rh], diphosphine/Rh = 2, Rh/allyl alcohol = 1/185, 120°C, 40 bar CO/H_2 = 1, 4 hours. [b]Hydroxyaldehyde derivatives. [c]Diol derivatives.[d]Products of isomerisation and hydrogenation

Experimental

Materials. Chemicals were purchased from Lancaster Synthesis, Sigma-Aldrich and Strem. All operations were performed under N_2 (passed through column of dichromate adsorbed on silica) in a glove box or using standard Schlenk and catheter tubing techniques. All glassware was flame-dried under vacuum. Toluene, hexane and THF were distilled from sodium benzophenone ketyl, absolute ethanol was distilled from magnesium ethoxide, methanol was distilled from calcium methoxide, acetone, *tert*-butanol and *tert*-amyl alcohol were distilled from calcium hydride, all under N_2 onto activated Linde 4 Å molecular sieves. All solvents were degassed prior to use by freeze – pump – thaw cycles. XANTPHOS,[S1] DIOP[S2] and BISBI[S3] were prepared according to the literature procedures; CBM-DXP was provided by LyondellBasell.

Analytical techniques. NMR spectra were recorded on Bruker Avance 300 and Bruker Avance II 400 spectrometers with tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P) as external references. Gas chromatography was performed on a Hewlett-Packard 6890 chromatograph fitted with a 30 m BP10™ column (carrier gas 3.2 psi He, flame-ionisation detector).

Catalysis. *General procedure. Syn*gas was purchased from BOC (**Caution!** Carbon monoxide is extremely poisonous and accidents may be lethal. A sensitive personal detector was carried and all experiments were performed in a well-ventilated fume-hood fitted with a detector, maintaining the concentration of carbon monoxide below the mac value at all times). Hydrocarbonylation reactions were carried out on the CATS rig with stirrer speed set at 800 rpm. In a typical experiment, a solution of the diphosphine (0.08 mmol) and triethylphosphine (0.00-0.16 mmol) in ethanol (3 mL) was added to [Rh(acac)$(CO)_2$] (10.4 mg, 0.04 mmol). The resulting solution was sonicated over 10 minutes and transferred into the autoclave under CO/H_2 = 1; any residues were transferred with a further aliquot of ethanol (1 mL). The solution was incubated for 20 minutes at 120°C and 30 bar CO/H_2 =1. After alkene (1 mL) (for allyl alcohol, 14.70 mmol, azeotropically dried with toluene and distilled) was injected, the pressure was adjusted to 40 bar, and the reaction was run to completion. The autoclave was then cooled and depressurised. 50 μL diglyme was added as internal standard to a 1 mL aliquot of the product solution, and the sample was analysed by GC. The experiments were performed at least in duplicate.

Addition of base N, *N*-dimethylbenzylamine (5.94 μL, 0.04 mmol) was added to a pre-catalyst solution of [Rh(acac)$(CO)_2$] (10.4 mg, 0.04 mmol), diphosphine (0.08 mmol) and triethylphosphine (11.6 μL, 0.08 mmol) in ethanol (4 mL). Conversion was calculated from the pressure change in a ballast vessel

from which gas was fed into the autoclave to keep the internal pressure at the desired level, using $\Delta P = \Delta c \cdot R \cdot T$. Experiments at variable carbon monoxide partial pressures were performed in a Hastelloy autoclave. The autoclave was primed with a solution of [Rh(acac)$(CO)_2$] (10.4 mg, 0.04 mmol), XANTPHOS (46.4 mg, 0.08 mmol), triethylphosphine (11.6 μL, 0.08 mmol) and allyl alcohol (1 mL, 14.70 mmol) in ethanol (4 mL) under carbon monoxide, then pressurised to the required partial pressure of CO. After 20 bar H_2 was introduced, the total pressure was adjusted with argon to 40 bar, and the autoclave heated to 120°C. After 4 hours the autoclave was cooled, depressurised and the contents analysed by GC.

Deuterium labelling. Carbon monoxide was purchased from BOC and D_2 was purchased from Cambridge Isotope Laboratories. Labelling reactions were performed in a Hastelloy autoclave. In a typical experiment a solution of [Rh(acac)$(CO)_2$] (10.4 mg, 0.04 mmol), XANTPHOS (46.4 mg, 0.08 mmol) and triethylphosphine (11.6 μL, 0.08 mmol) in ethanol (4 mL) was sonicated over 10 minutes and transferred into the autoclave under carbon monoxide, together with substrate (1 mL). The autoclave was pressurised with D_2 (20 bar) and carbon monoxide (20 bar), and then heated to 120°C. After 3 hours the autoclave was cooled and depressurised. The product mixture was fractionally distilled off the catalyst. The C_7-fraction was analysed qualitatively by $^{13}C\{^1H\}$ NMR spectroscopy and quantitatively by $^{13}C\{^1H, ^2H\}$ NMR spectroscopy and the solvent fraction was analysed by ^1H NMR spectroscopy.

S1 Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081.

S2 Townsend, J. M.; Blount, J. F.; Sun, R. C.; Zawoiski, S.; Valentine, J. D. *J. Org. Chem.* **1980**, *45*, 2995.

S3 Devon, T. J.; Phillips, G. W.; Puckette, T. A.; Stavinoha, J. L.; Vanderbilt, J. J. *US Pat.* 4.694.109.