

Electronic Supplementary Information to:

Evaluation of ligand effects in the modified cobalt hydroformylation of 1-octene. Crystal structures of $[\text{Co}(\text{L})(\text{CO})_3]_2$ (L= PA-C₅, PCy₃ and PCyp₃)

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Synopsis

A series of phosphine ligands with different electronic and steric properties were evaluated at fully modified conditions in cobalt catalysed hydroformylation of 1-octene. The Phoban and Lim ligand systems are superior both in terms of the highest reactivity and lowest alkene losses through hydrogenation. The observed catalytic behaviour provides evidence that is contrary to the dissociative substitution of CO by an alkene as the rate limiting step and indicate that the rate limiting step may have moved within the catalytic cycle and may now be situated at the carbonylation step where the chemoselectivity is also determined.

Keywords: Hydroformylation, Catalysis, Cobalt, Phosphine ligands, Crystallography

Experimental

All reactions were performed using the following conditions: $[\text{Co}] = 13 \text{ mmol dm}^{-3}$, $T = 453 \text{ K}$ (180°C), $P = 60 \text{ bar}$, $\text{H}_2:\text{CO} = 2:1$, 1-octene = 75% m/m with the ligand and toluene as adjustable parameters to obtain the final reaction volume.

Data treatment

The pressure drop in this ballast vessel was converted to grams of syngas consumed, also correcting for deviations from ideal gas behaviour. The grams of syngas consumed as a function of time displayed well behaved first order behaviour and was subsequently fitted to the usual first order equation using a least squares minimization protocol with the rate constant and the initial- and final gram of syngas consumed as adjustable parameters.

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Effect of ligand:metal ratio

Table S1: Rate and product distribution as a function of ligand concentration.

Ligand	[Ligand]/ mmol dm ⁻³	$k_{\text{obs}}(\pm 0.01)/$ h ⁻¹	Conv./ %	Lin./ %	OH Yield/ %	Hydrog./ %	¹ J _{Se-p/} Hz	Tolman/ °
VCH- ^t Bu	106	0.25	92.1	88.2	79.5	12.8		~168 ¹
"	132	0.25	92.5	88.6	80.2	12.9	672, 687	
PCy ₃	79	0.14	91.7	83.5	68	21.9		175 ²
"	132	0.15	91.4	84.7	69.5	22.5	676	
VCH-C ₅	53	0.16	89.9	86.8	80.2	14.2		est 163 ³
"	132	0.15	84.9	87.4	77.1	13.3	678	
P ⁿ Bu ₃	132	0.16	87.5	84.8	79.0	14.9	683	132 ⁴
Lim-C ₅	145	0.41	97.8	83.2	86.8	9.0	684, 686	163 ⁵
"	158	0.37	93.4	83.0	84.3	8.2		
Phoban-C ₅	54	0.43	95.7	90.4	82.9	9.9		163 ⁶
"	107	0.38	95.5	90.8	83.4	10.0	686, 709	
PCyp ₃	158	0.11	81.5	84.7	56.2	40.5		169 ²
"	171	0.10	81.2	84.8	56.1	40.2	687	
Lim-Cyp	132	0.42	93.4	75.7	84.9	9.3	687, 690	172 ⁷
"	145	0.40	94.9	77.4	82.8	11.1		
P ^t Bu ₃	132	0.26	97.8	73.2	82.8	11.9	688	164 ⁸
"	145	0.25	90.1	73.3	60	13.4		
P(<i>p</i> -MeOPh) ₃	106	0.15	13.9	78.6	46.8	11.5		145 ⁴
"	132	0.13	13.8	77.8	41.4	12.4	708	
PPH ₃	105	0.10	88.0	68.3	72.0	11.0		145 ⁴
"	132	0.08	90.3	69.8	79.0	12.4	732	
PA-C ₅	158	0.20	96.9	73.2	68.4	24.2	752	170 ²
"	145	0.2	86.8	72.2	65.6	23.2		

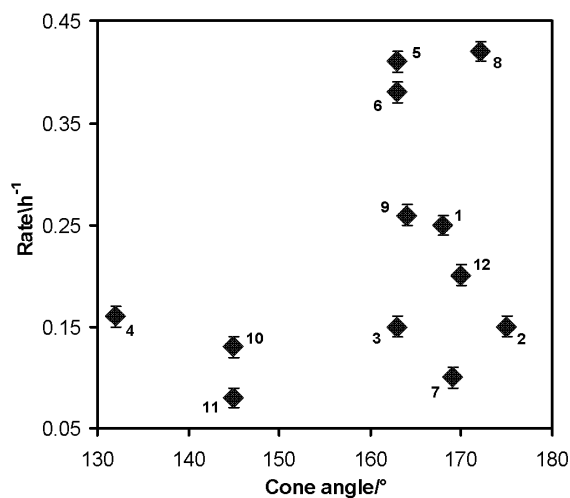


Figure S1: The effect of cone angle on the observed reaction rate during modified cobalt hydroformylation of 1-octene, the numbers refer to the entries in Table 5 in the manuscript.

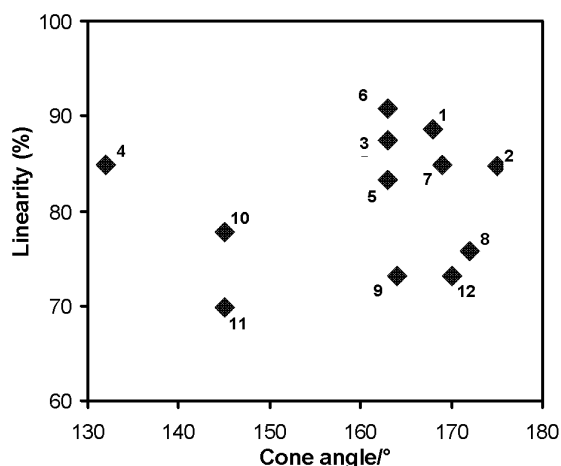


Figure S2: The effect of cone angle on the % product linearity for 1-octene hydroformylation using a fully modified cobalt catalyst system, the numbers refer to the entries in Table 5 in the manuscript.

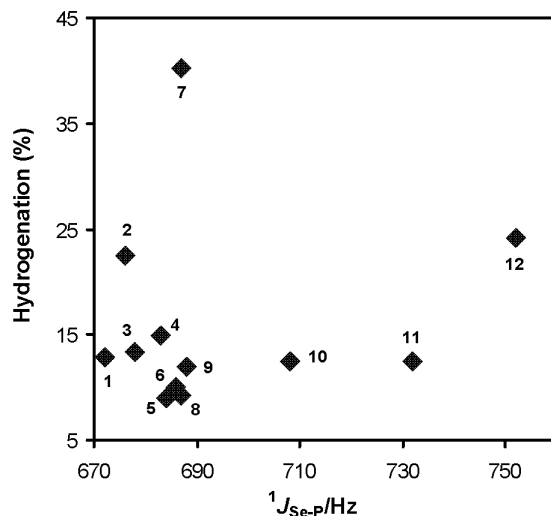


Figure S3: The effect of $^1J_{Se-P}$ coupling constant on the % hydrogenation during modified cobalt hydroformylation of 1-octene, the numbers refer to the entries in Table 5 in the manuscript.

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2 This work.

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