Supplementary Material (ESI) for Dalton Transactions

Bicyclic phosphines as ligands for cobalt-catalysed hydroformylation. Crystal structures of $[Co(Phoban[3.3.1]\text{-}Q)(CO)_3]_2$ (Q= C_2H_5, C_5H_{11}, $C_3H_6NMe_2$, C_6H_{11})

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Synopsis

A series of Phoban derivatives were evaluated as ligands in cobalt catalysed hydroformylation of linear internal decenes as substrate. The results for fully modified catalysis were very similar with linearities ranging from 85 - 90%, alcohol yields from 77 - 85%, hydrogenation from 9 – 15% and rates of 1.8 – 2.4 h^{-1}. In comparison PBu_3 gave 81% linear alcohols, 77% of alcohol yield and 17% of hydrogenation with a rate of 0.6 h^{-1}. Previous results from our group indicating very similar steric- and electronic properties for the Phoban family of ligands are confirmed by the similarities in the catalysis reported here.

Experimental

All reactions were performed using the following conditions: [Co] = 40 mmol dm^{-3}, T = 463 K, P = 80 bar, H_2:CO = 2:1, decene = 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.

The equilibrium between unmodified- and modified catalysis, as depicted below, was determined for selected ligands based on the results of the batch autoclave studies. The unmodified catalysis

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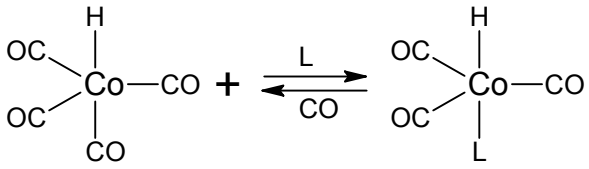
component is associated with high reaction rates, low hydrogenation and low linearities of the aldehyde products. In contrast modified catalysis is characterised by lower reaction rates, increased hydrogenation (also resulting in paraffins as side products) and high linearity of the alcohol products.



Scheme The ligand dependant equilibrium between the unmodified- and modified cobalt hydride species.

Values obtained for the reaction rate or alcohol linearity, as a function of ligand concentration, were fitted to the model given below:

Independant Variable: L_a	L_a = Ligand added initially
Dependant Variable: C	C = Catalytic parameter fitted, i.e. reaction rate or linearity
Parameters: C_M, C_U, K	C_M = Catalysis at fully modified conditions C_U = Catalysis at fully unmodified conditions K = Equilibrium constant
$K = M/(U*L_f)$	M = Concentration of modified catalyst U = Concentration of unmodified catalyst L_f = Concentration of free ligand at equilibrium
C = (Up*U + Mp*M)/(Co)	
M = Co - U	
$L_a = L_f + M$	
Co = 0.040	Co = Initial Co concentration
$M*M*K + M*(-K*Co - K*L_a - 1) + Co*K*L_a = 0$	

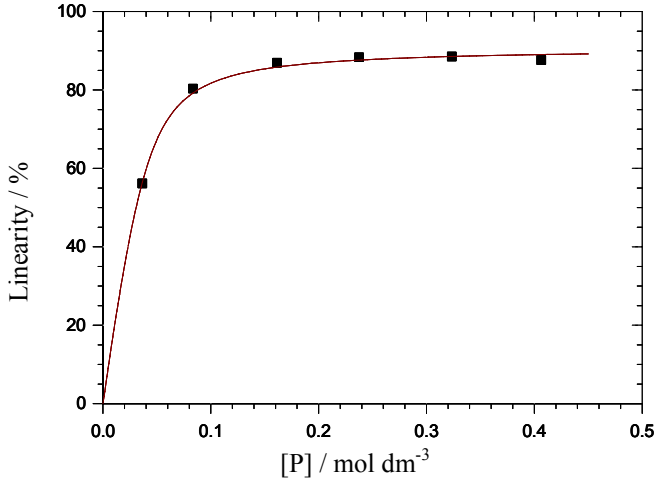
The most data points were available for the Phoban[4.2.1]-C_2 derivative. Using this data the best fit for linearity was obtained by fixing the linearity for fully unmodified catalysis at 0%. By fixing the value for K obtained in this way (142 mol^{-1} dm^3) and fitting the rate for fully unmodified catalysis resulted in a value of 27 h^{-1} being obtained. These values were then used where possible for all subsequent fits thus allowing for relative comparison between the different ligand derivatives on an equal basis. In some instances the amount of available experimental points did not allow for least squares fitting of the data and in those cases the parameters were manually adjusted and the simulated results were visually compared with the experimental values until the best agreement were obtained. Standard deviations are given for all fitted values but not for the simulated values.

Effect of ligand:metal ratio

Table S1: Phoban[4.2.1]-C_2.

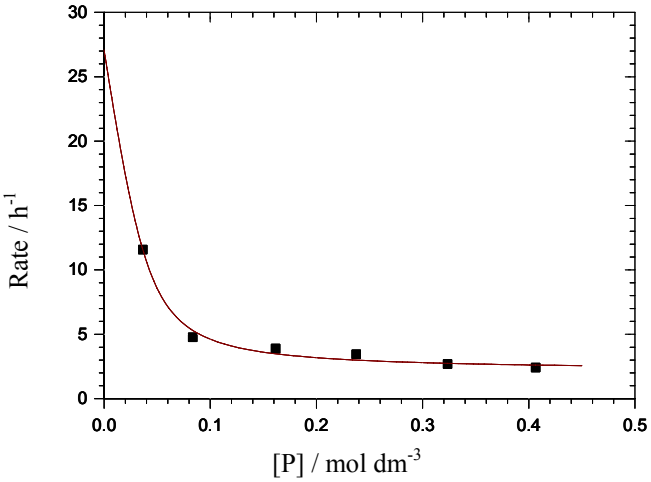
[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
37	0.93	11.5	56.0	8.3	74.4
84	2.08	4.7	80.2	9.2	81.6
162	4.02	3.8	86.8	10.0	82.1
238	5.92	3.4	88.2	10.6	83.3
324	8.05	2.6	88.4	10.5	82.4
407	10.13	2.4	87.5	9.9	85.0

Fix: $U_P = 0$



Parameter Name :	M_P	Parameter Name :	K
Estimate Value =	90.7292289	Estimate Value =	141.748391
Standard Deviation =	0.763421051	Standard Deviation =	14.8236422

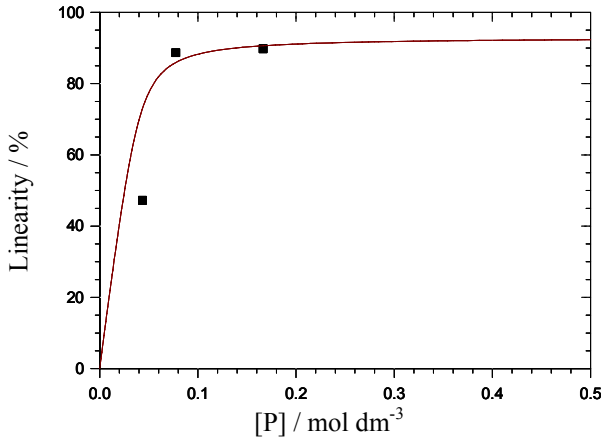
Fix: $K = 142$



Parameter Name :	M_P	Parameter Name :	U_P
Estimate Value =	2.13616891	Estimate Value =	27.0771057
Standard Deviation =	0.220951168	Standard Deviation =	1.22606759

Table S2: Phoban[3.3.1]-C_2.

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
44	1.10	6.8	47.1	11.8	75.4
78	1.94	2.3	88.5	11.7	77.4
167	4.15	2.4	89.6	12.0	77.7

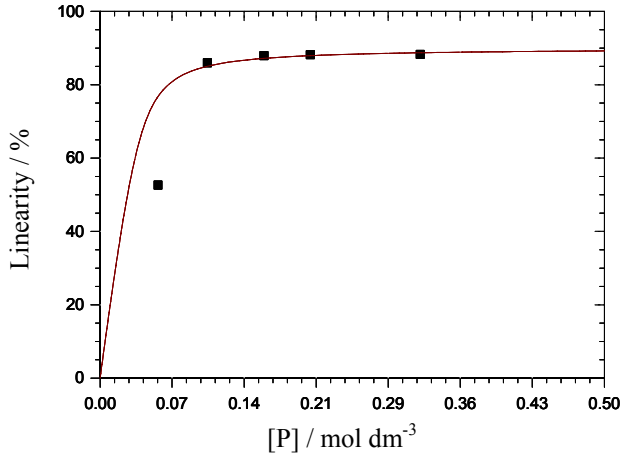


Parameters were adjusted and the simulation was visually evaluated to give the best fit.

$M_P = 93$ $U_P = 0$ $K = 300$

Table S3: Phoban-C_2 (mixture of isomers).

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	%
58	1.45	9.7	52.5	10.5	78.8
107	2.65	2.8	85.9	11.1	85.4
163	4.05	2.5	87.8	11.3	83.7
209	5.20	2.6	88.1	11.7	82.3
318	7.92	2.4	88.1	11.7	85.1



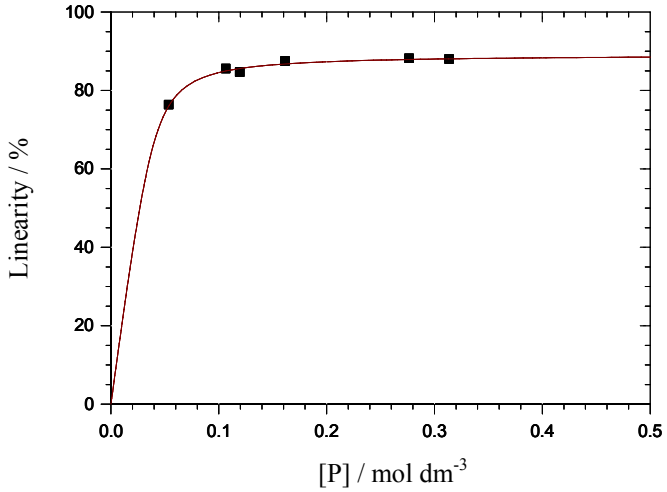
Parameters were adjusted and the simulation was visually evaluated to give the best fit.

$M_P = 90$; $U_P = 0$ $K = 250$

Table S4: Phoban-C_5 (mixture of isomers).

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
54	1.34	4.5	76.3	8.9	84.4
107	2.65	3.0	85.5	9.7	83.3
120	3.01	3.1	84.6	10.5	80.4
162	4.05	2.7	87.3	11.3	80.2
277	6.92	2.6	88.1	11.2	80.5
314	7.82	2.4	87.9	10.4	80.4

Fix: $U_P = 0$



Parameter Name :	M_P	Parameter Name :	*K*
Estimate Value =	89.1428397	Estimate Value =	297.563393
Standard Deviation =	0.438316694	Standard Deviation =	28.8218004

Table S5: Phoban-C_{10} (mixture of isomers).

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
184	4.60	2.3	87.7	11.6	86.8
324	8.05	2.2	87.8	10.5	85.3

Table S6: Phoban-C_{20} (mixture of isomers).

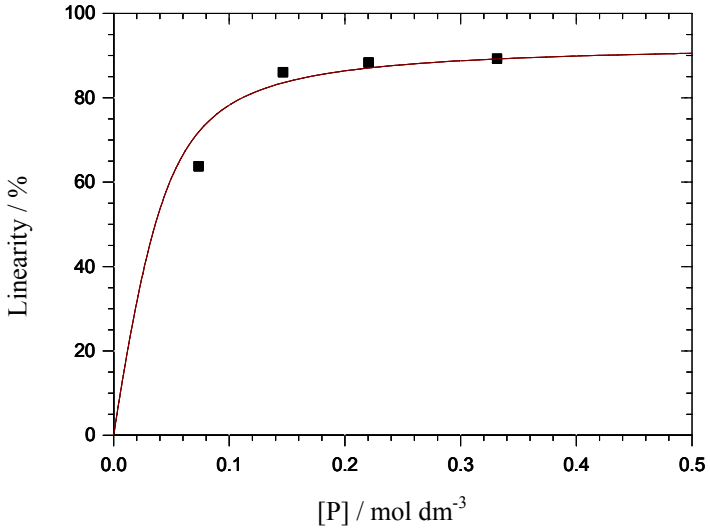
[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
324	8.05	2.2	87.8	10.5	85.3

Table S7: Phoban-C_3NMe_2 (mixture of isomers).

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
240	6.00	2.3	87.9	11.3	86.0
328	8.20	2.2	87.9	11.0	85.6

Table S8: Phoban-Cy (mixture of isomers).

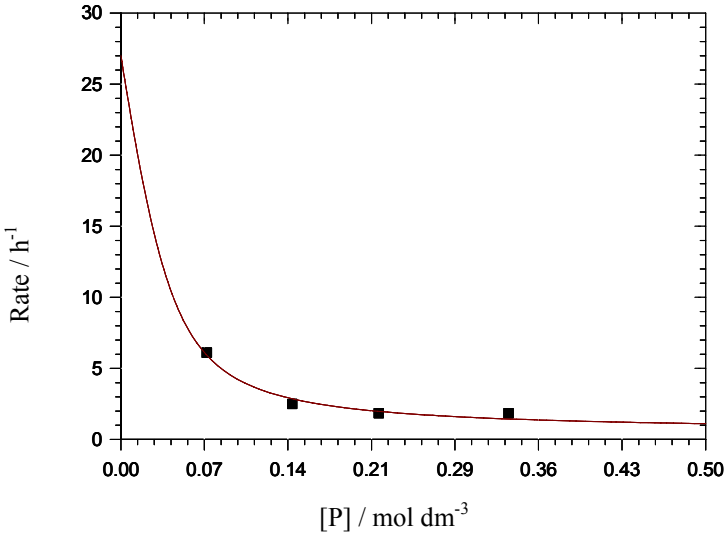
[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
74	1.84	6.1	63.6	10.2	79.3
147	3.68	2.5	85.9	13.5	76.9
221	5.53	1.8	88.2	14.6	76.4
332	8.30	1.8	89.1	14.6	76.1



Parameters were adjusted and the simulation was visually evaluated to give the best fit.

$M_P = 93$; $U_P = 0$ $K = 80$

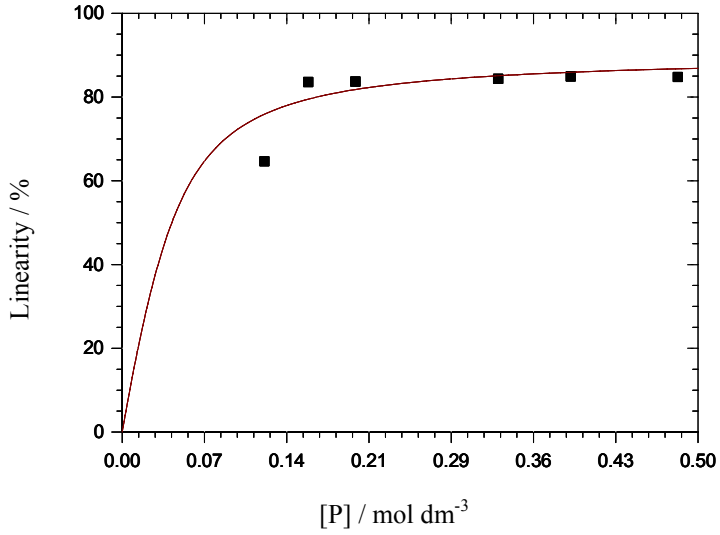
Fix: $U_P = 27$



Parameter Name :	M_P	Parameter Name :	K
Estimate Value =	0.507764245	Estimate Value =	93.5650982 (value reported)
Standard Deviation =	0.436596713	Standard Deviation =	16.3016039

Table S9: Phoban-Ph (mixture of isomers).

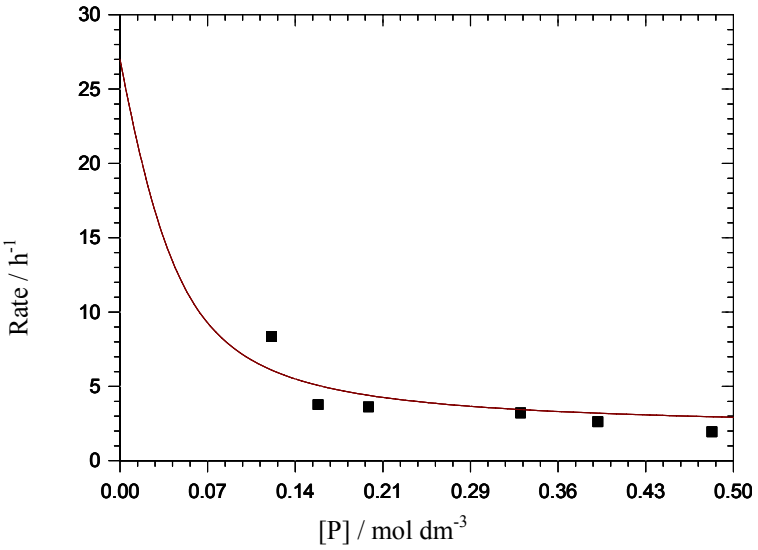
[L]	**L:M**	**k** (± 0.1)	**Linearity**	**Hydrogenation**	**Yield**
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
124	3.08	8.3	64.5	7.7	78.1
162	4.04	3.7	83.5	9.2	79.3
203	5.05	3.6	83.5	9.5	78.0
327	8.13	3.2	84.2	8.9	80.8
390	9.70	2.6	84.8	8.6	82.2
483	12.02	1.9	84.7	8.8	77.0



Parameters were adjusted and the simulation was visually evaluated to give the best fit.

$M_P = 90$; $U_P = 0$; $K = 60$

Fix: $U_P = 27$ and $M_P = 2$



Parameter Name : *K*
Estimate Value = 56.6989063 (value reported in paper)
Standard Deviation = 15.0031107

Table S10: PBu_3.

[L]	L:M	k (± 0.1)	Linearity	Hydrogenation	Yield
mmol dm^{-3}		**h^{-1}**	**%**	**%**	**%**
162	4.02	0.8	80.2	17.3	75.5
239	5.92	0.7	80.4	17.0	75.9
325	8.05	0.6	80.7	16.6	76.8

K estimated at > 150 mol^{-1} dm^3 assuming at least 98% modified catalysis at [L] = 162 mM.