

Unusual products from CO/ethene reactions catalysed by β -ketophosphine and related complexes of rhodium

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Received (in Cambridge, UK) 3rd October 2000, Accepted 20th November 2000

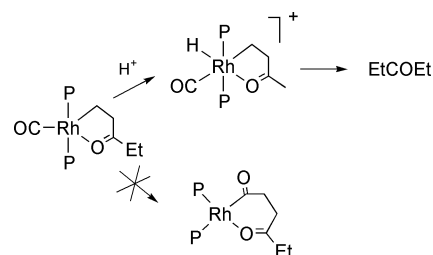
First published as an Advance Article on the web 15th December 2000

Using rhodium complexes of tertiary phosphines with carbonyl groups β to the P atom, ethene and CO react in methanol to give products involving increased chain growth (octane-3,6-dione, methyl 4-oxohexanoate) compared with PEt_3 complexes and unsaturated products (methyl propenoate, penten-3-one and 1-methoxypentan-3-one from addition of methanol to penten-3-one); mechanistic studies suggest that the ligand carbonyl group prevents coordination of the keto group in the growing chain.

Reactions between ethene and CO in methanol generally give perfectly alternating polyketones or methyl propanoate (MP), with the best catalysts being based on palladium complexes of mono- or ditertiary phosphines,^{1,2} although we have recently reported that highly electron rich rhodium phosphine complexes can give high selectivities to pentan-3-one (DEK), with the two extra H atoms required being derived from methanol, which forms methyl formate (MF).³ We presented evidence that the selectivity to pentan-3-one (DEK) arose because of binding of the keto-oxygen atom in the growing chain to the rhodium atom to give an η^2 -3-oxopentyl intermediate. Since this complex has 18e, it more readily protonates and reductively eliminates pentan-3-one than undergoing further insertion to give chain growth (Scheme 1).³

One of our interests is in the production of $\text{CO}/\text{C}_2\text{H}_4$ oligomers for use as low-volatility solvents containing relatively high oxygen content, so we were interested in the possibility of encouraging chain growth and hence of preventing the formation of the η^2 -3-oxopentyl intermediate. We, therefore, synthesised a range of phosphines which themselves contain carbonyl groups β to the P atom in the hope that these carbonyl groups might compete with coordination of the keto group in the growing chain and encourage chain growth.

The ligands shown in Table 1 were synthesised by the reaction of R_2PH (R = Et, Bu^t, Cy) with the appropriate bromo compound, $\text{R}'\text{COCH}_2\text{Br}$. (R' = Ph, Et, OEt), followed by



Scheme 1 Proposed role of an η^2 -3-oxopentyl intermediate in determining the selectivity of ethene carbonylation to pentan-3-one catalysed by Rh/PEt_3 complexes.³

removal of HBr with base (Scheme 2). Catalytic reactions were then carried out, synthesising the active catalyst *in situ* from the ligand and $[\text{Rh}(\text{acac})(\text{CO})_2]$ (Hacac = pentane-2,4-dione). The results of these reactions are shown in Table 1 and indicate that, apart from the complex derived from $\text{Bu}^t_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$, which does not give an active catalyst, catalysts based on these ligands show quite different selectivities compared with those involving PEt_3 . In particular, chain growth to octane-3,6-dione (OD) and methyl 4-oxohexanoate (M4OH) has become significant and the unsaturated products, penten-3-one (EVK) and methyl propenoate (MA) are observed. A further product, 1-methoxypentan-3-one (1M3P)[†] is a major product. We have shown in separate experiments that this is formed by addition of methanol to penten-3-one (EVK) in an uncatalysed reaction under the experimental conditions employed. The selectivity to medium chain products (≥ 7 chain atoms) can be as high as 57.6%,

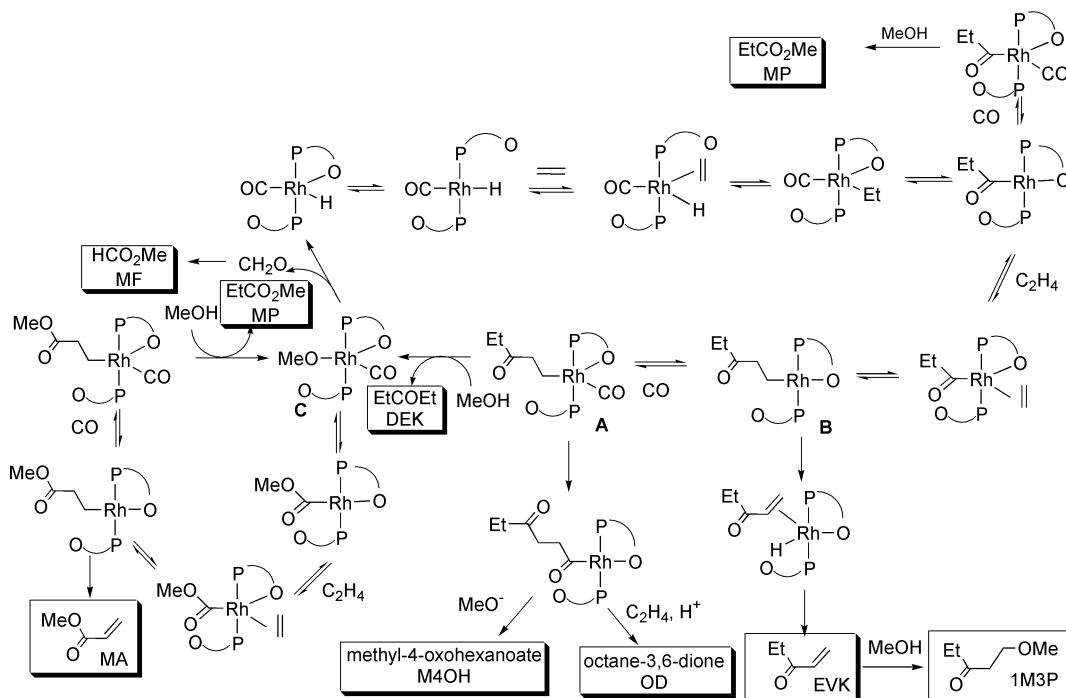


Scheme 2 Synthesis of β -ketophosphine ligands. R'' = H, R = Et, R' = Ph, OEt; Et; R'' = H, R = Bu^t, R' = Ph, OEt; R'' = H, R = Cy, R' = Ph; R'' = Me, R = Et, R' = Me. Reagent: i, NaOH.

Table 1 Products obtained from the carbonylation of ethene catalysed by rhodium complexes of β -ketophosphines and related ligands^a

Ligand	MA	MP	EVK	DEK	1M3P	M4OH	OD	Total turnover	MCP(%)
$\text{Et}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$	4.4	4.4	2.0	24.0	12.5	2.4	9.0	58.7	40.7
$\text{Et}_2\text{PCH}_2\text{C}(\text{O})\text{Et}$	6.7	7.8	3.1	23.4	12.0	2.6	7.1	62.7	34.6
$\text{Et}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$	12.2	6.8	3.7	38.2	14.3	5.8	9.7	90.7	32.9
$\text{Et}_2\text{PCH}(\text{Me})\text{C}(\text{O})\text{Me}$	7.2	6.9	1.4	39.7	6.7	2.5	3.1	67.5	18.2
$\text{Cy}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$	—	4.0	—	0.5	1.2	2.0	0.7	8.4	46.4
$\text{Bu}^t_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$	—	2.1	1.7	7.7	11.2	—	4.4	27.1	57.6
$\text{Bu}^t_2\text{PCH}_2\text{C}(\text{O})\text{Ph}$	—	—	—	—	—	—	—	0	—
$\text{Et}_2\text{PC}_2\text{H}_4\text{OMe}$	4.1	15.0	1.5	37.3	17.8	3.0	9.2	87.9	34.1
$\text{Et}_2\text{PC}_2\text{H}_4\text{NEt}_2$	—	26.9	trace	41.1	3.3	—	4.4	75.7	10.2
$\text{Me}_2\text{PCH}_2\text{P}(\text{O})\text{Me}_2$	—	10.7	0.9	3.5	3.7	—	2.9	21.7	30.4
$\text{Me}_2\text{PCH}_2\text{P}(\text{O})\text{Me}_2^b$	4.4	5.1	3.4	24.9	13.4	2.9	14.3	68.4	44.7

^a $[\text{Rh}(\text{acac})(\text{CO})_2]$ (0.1 mmol), phosphine (0.4 mmol), CO (35 bar), ethene (35 bar), methanol (10 cm³), 110 °C, 24 h. Amounts expressed as catalyst turnovers. ^b 2 equivalents of ligand used, *i.e.* (0.2 mmol). MA (methyl propenoate, methyl acrylate), MP (methyl propanoate), EVK (penten-3-one, ethyl vinyl ketone), DEK (pentan-3-one, diethyl ketone), 1M3P (1-methoxypentan-3-one), M4OH (methyl 4-oxohexanoate), OD (octane-3,6-dione), MCP (medium chain products, 7+ atoms in backbone).



Scheme 3 Proposed mechanism of ethene carbonylation catalysed by Rh/ β -ketophosphine ($P(O)C$) complexes. The products shown in boxes have been observed (Table 1), but the assignments of the metal containing intermediates are tentative.

whereas with PEt_3 the selectivity to pentan-3-one (DEK) can be > 80% with only traces of medium chain products being formed. Similar results to those for the β -ketophosphines are obtained (Table 1) using other ligands with O γ to the P atom such as $Me_2PCH_2P(O)Me_2$, or $Et_2PCH_2CH_2OMe$, but not with N in this position; $Et_2PCH_2CH_2NEt_2$ behaves more like PEt_3 , although the rate is lower.

We have also carried out the reaction using $PhCOCH_2PEt_2$ in CD_3OD and find that the methyl groups of pentan-3-one (DEK) and of methyl propanoate (MP) contain 0 or 1 D atoms. \ddagger This contrasts with reactions involving PEt_3 , 3 where multiple deuteration of the methyl groups of pentan-3-one (DEK) is observed.

These results point to the conclusion that, in these systems, the carbonyl group in the growing chain does not coordinate, presumably because the coordination site is blocked by the carbonyl group β to the phosphine (Scheme 3). Intermediate **A** in Scheme 3 is an 18e complex, so may protonate and reductively eliminate pentan-3-one (DEK). Alternatively, CO may insert leading to chain growth. We have shown that multiple D incorporation into the methyl group of pentan-3-one (DEK) in the Rh/ PEt_3 catalysed reactions carried out in CD_3OD occurs *via* β -H abstraction in the η^2 -3-oxopentyl intermediate to give an enolate. A similar β -H abstraction in the η^1 -3-oxopentyl intermediate, **B** in Scheme 3, would lead to penten-3-one (EVK) bound only through the double bond and it appears that this decoordinates to give free penten-3-one (DEK), rather than undergoing reversible C-H bond breakage and multiple D incorporation.

The formation of methyl propanoate (MA) is also of considerable interest, not only because it indicates that acrylates can be products from CO/ C_2H_4 reactions under non-oxidative conditions, but also because it indicates that a carbomethoxy

mechanism 1 is operating in addition to the hydride mechanism which is responsible for the other products. This suggests that CO insertion into the Rh-OMe bond competes with β -H abstraction and CO can insert in the 18e complex (**C** in Scheme 3). Acrylates can be products of CO/alkene reactions in the presence of oxygen. 5,6

In conclusion, all of the products obtained from the reaction of CO with ethene in methanol in the presence of rhodium complexes containing phosphine ligands with a carbonyl β to the P atom can be explained as in Scheme 3 if one carbonyl group in the phosphine is coordinated to the rhodium.

We thank BP and the EPSRC for funding (R. A. M. R.) and Dr E. Ditzel and Mr P. Howard for helpful discussions.

Notes and references

\dagger Since this product has seven atoms in the chain and contains two O atoms (bp 62 °C at 24 Torr), 4 it may be a suitable component of a low volatility solvent mixture, so is included when calculating the percentage of medium-chain products produced in the reaction.

\ddagger The methylene groups contain from 0 to 2 D atoms on account of post-reaction exchange with the solvent. 3

- 1 E. Drent, J. A. M. van Broekhoven and P. H. M. Budzelaar, in *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, Weinheim, 1996, vol. 1, p. 333 and references therein.
- 2 E. Drent and P. H. M. Budzelaar, *J. Organomet. Chem.*, 2000, **593–594**, 211.
- 3 R. A. M. Robertson, A. D. Poole, M. Payne and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2000, 1817.
- 4 I. N. Nazarov and I. V. Torgov, *Chem. Abstr.*, 1948, **42**, 7736a.
- 5 D. M. Fenton and K. L. Olivier, *US Pat.*, 3 349 119, 1967.
- 6 W. Gaenzler and K. Kabs, *US Pat.*, 3 907 882, 1975.