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Selective formation of pentan-3-one from carbon monoxide and ethene in methanol

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In the presence of rhodium complexes of triethylphosphine, CO and ethene react in methanol to give pentan-3-one with selectivities up to 85%; model studies and deuterium labelling suggest that the mechanism involves hydroxycarbene and η²-3-oxopentyl derivatives.

In methanol, in the presence of a variety of complexes of palladium(II), CO and ethene react to give either perfectly alternating copolymers or methyl propanoate, which is formed being dependent upon the other ligands present in the complex.[1] Pentan-3-one is sometimes observed as a side-product, but high selectivities to this product, which is a useful solvent of relatively low volatility, are only obtained if water or hydrogen gas is also a component of the mixture.[2] Using triphenylphosphine complexes of rhodium, long chain polymers are not formed, but rather a mixture of oligoesters and oligoketones.[3] Hydrogen is again required, but this can be produced from added water *via* the water gas shift reaction; no reaction occurs in dry methanol in the absence of hydrogen.[3] We have previously shown that trialkylphosphine complexes of rhodium show high activity for the direct formation of alcohols[4,5] in hydrocarbonylation reactions of alkenes and that similar products are also formed in the absence of hydrogen, with the alcohol solvent acting as the source of hydrogen.[6] We now report that the same system can afford relatively high selectivity to pentan-3-one from CO and ethene in methanol.

Heating a solution of [RhH(PEt$_3$)$_4$] (**1**) (Strem) or [Rh(acac)(CO)$_2$][4] (**2**)/4PEt$_3$ (acacH = pentane-2,4-dione) in methanol under an atmosphere of CO and ethene at 110 °C produces pentan-3-one as the major product, with selectivities up to 85% (see Table 1). The other main products are methyl propanoate and methyl formate, whilst traces of products formed by further chain growth, octane-3,6-dione and methyl 4-oxohexanoate are also detected. Analysis of the gas phase at the end of the reaction shows that no ethane is produced. Increasing the temperature increases the rate but reduces the selectivity to pentan-3-one, whilst diluting the methanol with tetrahydrofuran or propan-2-one reduces the yield without greatly affecting the selectivity. In propan-2-one, 2,2-dimethoxypropane is also formed by a direct ketalisation reaction.

At first sight, this high selectivity towards the formation of pentan-3-one, without the formation of ethane is rather surprising, since the intermediates that would lead to these products are very similar. Ethane would be formed from an ethyl complex, whilst pentan-3-one would arise from a 3-oxopentyl intermediate. Both should have very similar environments at the metal (see Fig. 1). CO insertion would lead to propanoyl or 3-oxohexanoyl intermediates, whilst methanolysis would lead to ethane and pentan-3-one respectively. The observed products demonstrate that for the ethyl intermediate, CO insertion occurs exclusively, whilst for the 3-oxopentyl intermediate, methanolysis is much preferred. We have attempted to probe the origin of this unusual selectivity by studying a closely related model system and by deuterium labelling studies.

^{31}P NMR studies have shown that [RhH(PEt$_3$)$_4$] dissolves in methanol to give [RhH$_2$(PEt$_3$)$_4$]$^+$ and that this reacts with CO to give [RhH(CO)(PEt$_3$)$_3$] and then [Rh$_2$(CO)$_2$(PEt$_3$)$_6$].[4] This last product is also formed from [Rh(acac)(CO)$_2$] and excess PEt$_3$ in methanol at room temperature. Assuming that the active species in the catalytic reaction is [RhH(CO)(PEt$_3$)$_2$], we attempted to study the reactions of [RhMe(CO)(PEt$_3$)$_2$], a model of the necessary ethyl intermediate. We have already reported[4] that [RhMe(CO)(PEt$_3$)$_2$] reacts with CO in toluene to give [Rh(MeCO)(CO)$_2$(PEt$_3$)$_2$] and that on addition of methanol and passing argon, this complex is transformed into the hydroxycarbene complex, [Rh(=C(OH)Me)(CO)(PEt$_3$)$_2$]$^+$, characterised by the very low field chemical shift of the C atom of the hydroxycarbene (δ 301).† In methanol, ethene also converts [Rh(MeCO)(CO)$_2$(PEt$_3$)$_2$] into [Rh(=C(OH)Me)(CO)(PEt$_3$)$_2$]$^+$, although we have not found direct evidence for, the product of the reaction of this hydroxycarbene complex with ethene.

Deuterium labelling studies obtained by carrying out the reaction in CD$_3$OD (Table 2) shed further light on the mech-

Table 1 Products (expressed as catalyst turnovers) after 24 h from the reaction of CO (35 bar) and ethene (35 bar) in methanol

Solvent	Ratio	Catalyst system[a]	*T*/°C	Pentan-3-one	Methyl propanoate	Octane-3,6-dione	Selectivity to pentan-3-one (%)
MeOH	—	**1**	110	168	34	tr	83
MeOH	—	**2**	110	164	56	7	72
MeOH/H$_2$O	4:1	**1**	110	106	19	tr	85
MeOH/propan-2-one	1:3	**1**	110	79	21	3	77
MeOH/propan-2-one	1:3	**2**	110	81	24	2	76
MeOH[b]	—	**1**	140	221	111	tr	66
MeOH[c]	—	**2**	110	25	10	—	71

[a] **1** [RhH(PEt$_3$)$_4$] (0.01 mol dm^{-3}) as catalyst precursor, **2** [Rh(acac)(CO)$_2$] (0.01 mmol)/PEt$_3$ (0.04 mmol) as catalyst precursor. Methyl formate (not quantified) is also a product in all cases. [b] 6 h reaction time. [c] CO was omitted from this reaction, but paraformaldehyde (2 g) was added instead.

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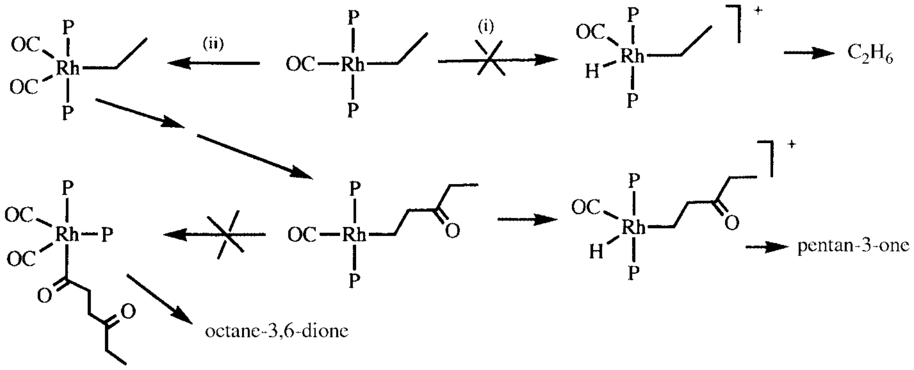

Fig. 1 Possible products of reactions of ethyl and 3-oxohexanoyl complexes of rhodium with (i) methanol or (ii) CO. The reactions marked with a cross are disfavoured. P = PEt_3.

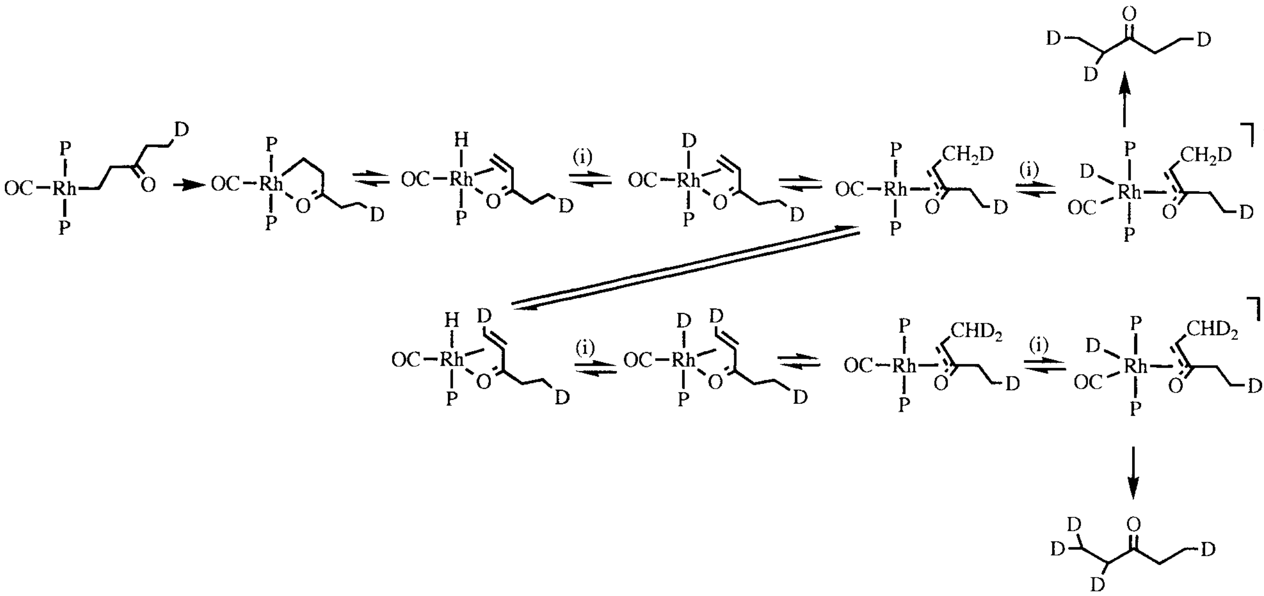

Fig. 2 Proposed mechanism for multiple incorporation of deuterium into the methyl group of pentan-3-one, during CO, C_2H_4 reactions in CD_3OD. (i) CD_3OD, P = PEt_3.

Table 2 Labelling pattern (% of each isotopomer) for ethyl groups of products obtained from ethene and CO in CD_3OD_2

Compound	CH_3CH_2	CH_3CHD	CH_3CD_2	CH_2DCH_2	CH_2DCHD	CH_2DCD_2	CHD_2CH_2	CHD_2CHD	CHD_2CD_2
Et_2CO	16.8	35.0	21.2	4.4	9.1	5.5	1.8	3.8	2.3
$EtCO_2Me$	39.0	23.4	15.6	11.0	6.6	4.4	0	0	0

anism of formation of the products. Control experiments show that exchange of D with the CH_2 (but none of the CH_3) H atoms in both methyl propanoate and pentan-3-one occurs under the reaction conditions. The CH_3 resonance of the pentan-3-one in the $^{13}C\{^1H,^2H\}$ NMR spectrum is remarkable since it shows α, β and δ shifts, so we can be sure that the two methylene groups are equally exchanged. The important result is that the CH_3 groups in pentan-3-one are d_0 (73%), d_1 (19%) and d_2 (8%) and that <1% of the pentan-3-one molecules have d_2 at each end. In contrast, none of the methyl propanoate molecules contains d_2 in the methyl group (d_0 (78%), d_1 (22%)).

The presence of a large amount of d_0 methyl groups in pentan-3-one and in methyl propanoate confirms that the hydride mechanism is operating since these isotopomers must form by β-H abstraction in Rh–CH_2CH_2D, initially formed by migration of Rh–D to coordinated ethene, to give RhH(CH_2-CHD). H migration onto the undeuteriated end of the coordinated CH_2=CHD or exchange with CH_2=CH_2 followed by H migration would then give the observed isotopomer. The latter clearly occurs since, for both pentan-3-one (17%) and for methyl propanoate (39%) a significant proportion of C_2H_5 is present. Multiple reversible insertions of this kind with H/D exchange with the solvent cannot, however, be responsible for the multiple deuteriation of the methyl groups in pentan-3-one, since this would also lead to multiple deuteriation in the methyl groups of methyl propanoate, which is not observed.

This multiple deuteriation must, therefore, arise *via* an enolate mechanism, as shown in Fig. 2 and provides evidence for a η^2-3-oxopentyl intermediate. Without the binding of the oxo group, penten-3-one would be released and should be observed as a product and/or react with methanol to produce 1-methoxypentan-3-one, since we have observed these products when we have deliberately hindered oxo binding in the 3-oxopentyl intermediate.[7] For the PEt_3 complexes, these products are not observed, confirming that η^2 binding of the oxopentyl intermediate occurs. Chelating oxoalkyl intermediates have been proposed before to explain the perfectly alternating nature of the polymers obtained from palladium catalysed copolymerisation of CO and ethene,[1] but they have seldom been directly observed for ethene.[8,9] Furthermore, a similar enolate mechanism has been shown by D labelling studies to operate in CO/C_2H_4 copolymerisation using Pd complexes[8] and in the hydrocarbonylation of ethene to pentan-3-one.[10]

The formation of the η^2-3-oxopentyl complex then explains

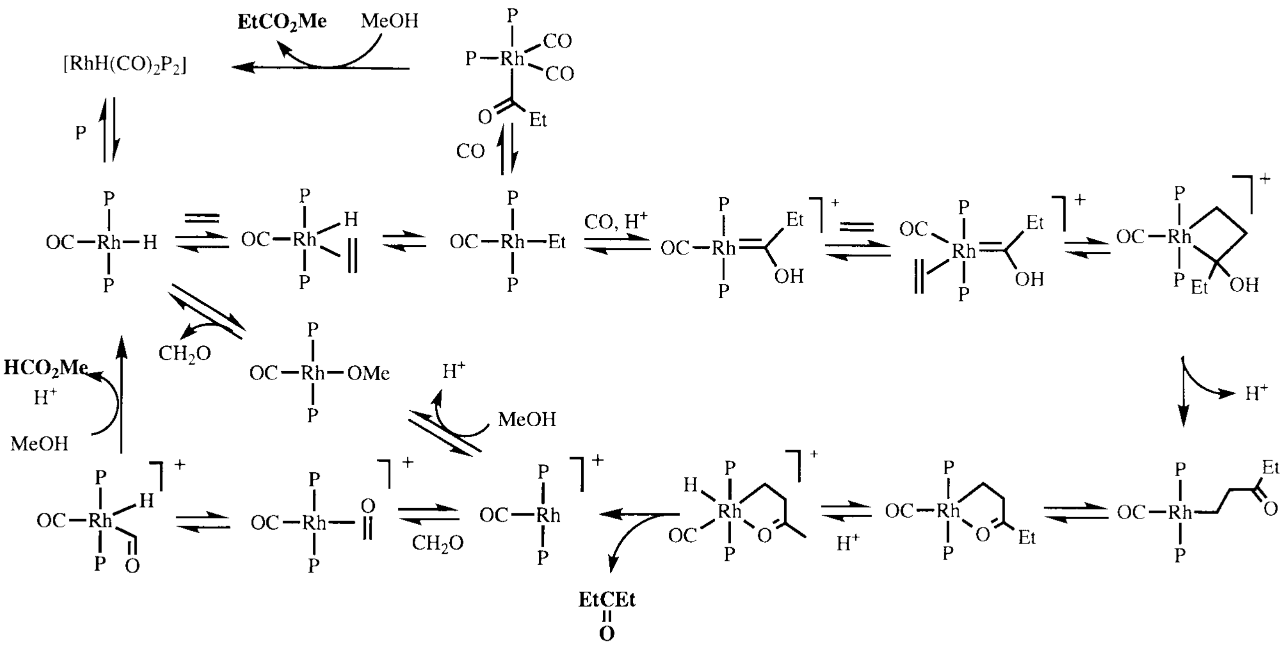

Fig. 3 Proposed mechanism for the formation of pentan-3-one, methyl propanoate and methyl formate (all shown in bold) from CO and ethene in methanol catalysed by rhodium triethylphosphine complexes. An alternative is that pentan-3-one is released by protonation of the enolate, as shown in Fig. 2. P = PEt_3.

the selectivity shown in Fig. 1. Since this complex has 18 e, it will need to decomplex a ligand to allow CO coordination and chain growth. Protonation on the other hand does not require the creation of a vacant site and produces pentan-3-one. The alternative of direct CO insertion would require an unfavourable ring expansion from a 5- to a 6-membered ring. The analogous ethyl complex has only 16 e so that CO coordination and chain growth are both facile.

Methanol is the source of the two H atoms that are required for the formation of pentan-3-one and the product derived from it is methyl formate. A reaction carried out in $^{13}CH_3OH$ produced $(C_2H_5)_2CO$, $C_2H_5CO_2{}^{13}CH_3$ and $H^{13}CO_2{}^{13}CH_3$. This last product shows that in the presence of CO, the formaldehyde formed by dehydrogenation of methanol provides one extra proton and the metal formyl complex undergoes nucleophilic attack by methanol rather than α-hydride abstraction. Paraformaldehyde can also be used as a source of CO if it is used to replace CO in the catalytic system (Table 1). It has been reported that formaldehyde can be used as a source of CO and H_2 with a related catalytic system.[11]

We conclude that rhodium trialkylphosphine complexes show good selectivity for the formation of pentan-3-one from CO and ethene, with the extra H atoms being derived from methanol. The mechanism of formation of this product, methyl propanoate and methyl formate is shown in Fig. 3.

Acknowledgements

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Notes and references

† In ref. 4, a typographical error gives the wrong ^{31}P NMR data for $[Rh(=C(OH)Me)(CO)(PEt_3)_2]^+$, which had not been measured at that time. The spectrum consists of a doublet at δ 19.0, J_{PRh} = 147 Hz.

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