Direct formation of alcohols by hydrocarbonylation of alkenes under mild conditions using rhodium trialkylphosphine catalysts†

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The complex $[RhH(PEt_3)_3]$ catalysed the hydroformylation of hex-1-ene to heptanal and 2-methylhexanal in toluene, but heptanol and 2-methylhexanol were significant products in tetrahydrofuran especially over long reaction times (16 h). In protic solvents only alcohols were produced even after short reaction times. The reactions are very rapid and also occur readily with alkenes such as hex-2-ene, propene, ethene, styrene and 3,3-dimethylbutene. The highest rates observed are for ethene (54 000 turnovers h^{-1}) and the products in all cases are alcohols. Other phosphines containing primary alkyl groups also produced alcohols, but in contrast reactions in ethanol using rhodium complexes containing PPh_3, PPh_2Et, $PPhEt_2$ or PPr^i_3 produced significant amounts of aldehydes and/or acetals whilst $Me_2PCH_2CH_2PMe_2$ inhibited the reaction. The NMR studies showed that species present in equilibrium in ethanol solution are $[RhH(CO)(PEt_3)_3]$, $[RhH(CO)_2(PEt_3)_2]$, $[Rh_2(CO)_4(PEt_3)_4]$, $[Rh_2(CO)_2(PEt_3)_6]$ and PEt_3 but that $[RhH(CO)(PEt_3)_3]$ predominates under the catalytic conditions. Reactions carried out under D_2–CO in EtOH produced 90% $BuCHDCH_2CD_2OH/D$ and 10% $BuCHDCH_2CHDOH/D$ but hydrogenation of heptanal under the same conditions gave a mixture of $C_6H_{13}CHDOH/D$ (39%) and $C_6H_{13}CH_2OH/D$ (61%). These results are interpreted to indicate that the alcohols produced from hex-1-ene are primary reaction products and not produced *via* intermediate aldehydes. A new mechanism for this direct hydrocarbonylation is proposed in which the key acyl intermediate becomes protonated by the alcoholic solvent because of the high electron density it bears as a result of the presence of the electron-donating trialkylphosphines. Oxidative addition of H_2 followed by two H-atom transfers leads directly to the alcohol. High pressure NMR studies showed that $[Rh\{C(O\cdots HOEt)Et\}(CO)_2(PEt_3)_2]$ is present during catalytic hydrocarbonylation of ethene in ethanol. Two different cycles are proposed to explain the products obtained from the catalytic reaction of heptanal with D_2–CO. Again, protonation, this time of the metal, appears to be important.

The hydroformylation of alkenes is one of the major industrial processes currently carried out using homogeneous catalysts.[1,2] The products can be alcohols if cobalt-based catalysts promoted by trialkylphosphines are employed although forcing conditions of temperature (160–200 °C) and pressure (50–100 atm) are required.[2] Alternatively, aldehydes can be produced if the catalyst contains rhodium and the plant can be operated under much milder conditions (15–20 atm, 80–120 °C).[2,3] Using $[RhH(CO)(PPh_3)_3]$ and an excess of PPh_3, very high selectivities to the desirable linear aldehyde product can be obtained.[2,3]

Since the final products required from these types of reactions are often alcohols for use as plasticisers or in the synthesis of soaps and detergents, it would be desirable to have a catalytic system which produces alcohols directly under mild operating conditions. However, there is currently no commercial process of this kind. There have been sporadic reports of alcohols being produced under hydroformylation conditions using rhodium complexes. Perhaps the most comprehensive study has been reported in a series of patents to Lawrenson and co-workers,[4–9] in which it is shown that alcohols can be produced from hexene, CO and H_2 provided that the catalyst is promoted by a trialkylphosphine, rather than the more usual PPh_3. In all of the reactions the phosphine : rhodium ratio was always < 1.5 : 1 and it was elegantly demonstrated that aldehyde is the first product. This is subsequently hydrogenated to the alcohol. Alcohols have been produced as side products in reactions catalysed by $RhCl_3$ in the presence of PBu_3,[10] whilst trialkylphosphines also promote the formation of diols from pro-2-en-1-ol under hydroformylation conditions.[11,12]

Finally, amines[13–16] and other N-donors[17] can also promote the formation of alcohols under rhodium-catalysed hydroformylation conditions. Once again, sequential reactions involving the hydrogenation of intermediate alcohol have been implicated.

We have been carrying out extensive studies of the uses of rhodium complexes of trialkylphosphines in catalysis[18–25] and now report details of reactions of hex-1-ene under hydroformylation conditions. These reactions selectively produce alcohols and we present evidence that aldehydes are not intermediates in these reactions. Preliminary reports of some of these results have been communicated.[18–20]

Results

Effect of solvent on hydroformylation reactions

Hydroformylation of hex-1-ene in toluene under CO–H_2 (40 atm) and at 120 °C in the presence of $[RhH(PEt_3)_3]$[26] produces heptanal and 2-methylhexanal as the major products, although minor amounts of C_7 alcohols and isomerised hexenes are also produced (see Table 1). The amount of alcohols produced increases with time but even after 16 h they only account for *ca.* 4% of the hex-1-ene feed. By carrying out the reaction in tetrahydrofuran (thf) the selectivity changes so that after 2 h the major products are aldehydes whereas after 16 h they are mainly alcohols. In all of these reactions the linear : branched (n : i) ratio is of the order of 2–3 : 1. Changing to an alcoholic solvent has an even more dramatic effect in that aldehydes are

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† *Non-SI units employed:* atm = 101 325 Pa.

Table 1 Hydroformylation of alkenes catalysed by rhodium complexes[a]

Catalyst	10^3[Rh]/ mol dm^{-3}	Additive	10^3[Additive]/ mol dm^{-3}	Substrate	Solvent	p/atm	T/°C	t/h	Yield of C_7 aldehyde	n:i ratio	Yield of C_7 alcohol	n:i ratio
[RhH(PEt_3)$_3$]	8			Hex-1-ene	Toluene	40	120	2	92	2.1	4	(heptanol)
	8			Hex-1-ene	Toluene	40	120	16	92	2.2	1	(heptanol)
	7.6			Hex-1-ene	Toluene	80	120	16	75	1.4[b]	13	3.3
	8			Hex-1-ene	thf	40	120	2	101	2.4	0	—
	8			Hex-1-ene	thf	40	120	16	4	0.0	115	2.9
	8	H_2O	50%	Hex-1-ene	thf	40	120	2	46	1.1	50	7.5
	8	H_2O	50%	Hex-1-ene	thf	40	120	16	0	—	100	2.4
	8			Hex-1-ene	MeOH	30	120	16	0	—	105	2.4
	8			Hex-1-ene	EtOH	40	120	2	0	—	101	3.0
	8			Hex-1-ene	EtOH	30	120	16	0	—	102	2.3
	8			Hex-1-ene	Pr^{i}OH	30	120	16	0	—	99	2.4
	8			Hex-1-ene	Bu^{t}OH	40	120	16	0	—	105	2.4
	8			Hex-1-ene	Bu^{n}OH	30	120	16	0	—	102	2.2
	8			Hex-1-ene	Heptanol	40	120	2	0	—	100	2.0
	8			Hex-1-ene	Heptanol	40	120	16	0	—	100	1.8
	4			Hex-1-ene	EtOH	40	125	2.5	8	0.0	106	3.4
	2			Hex-1-ene	EtOH	40	125	2.5	26	0.6	86	5.2
	1			Hex-1-ene	EtOH	40	125	2.5	81	2.2	19	6.1
	1	PEt_3	10	Hex-1-ene	EtOH	40	125	2.5	24	1.1	33	6.3
	0.5			Hex-1-ene	EtOH	40	125	2.5	89	2.4	Trace	(heptanol)
	0.5	PEt_3	10	Hex-1-ene	EtOH	40	125	2.5	47	1.7	27	8.3
	0.4	PEt_3	4	Hex-1-ene	EtOH	40	125	16	3	0.0	100	2.9
	8	Hg	1 cm^3	Hex-1-ene	EtOH	40	116	2	2.9	0.1	99	2.8
	8	NEt_3	1 cm^3	Hex-1-ene	EtOH	40	125	3	2	1.0	87	2.4
	7	Proton sponge	1 g	Hex-1-ene	EtOH	40	125	2.5	4	0.6	78	2.9
[RhH(CO)(PPh_3)$_3$]	6			Hex-1-ene	EtOH	37	120	16	37	1.2[c]		
[Rh_2(O_2CMe)$_4$]	8			Hex-1-ene	EtOH	49	120	17	40	0.4[d]	10	0.2
	8	PMe_3	24	Hex-1-ene	EtOH	48	120	16	Trace		99	2.5
	8	PEt_3	24	Hex-1-ene	EtOH	59	80	16.5	Trace		103	2.4
	8	PBu_3	24	Hex-1-ene	EtOH	44	120	16	Trace		106	2.4
	8	PPr^i_3	24	Hex-1-ene	EtOH	52	120	16	79	1.1	19	2.3
	8	PEt_2Ph	24	Hex-1-ene	EtOH	45	120	16	3	0[e]	89	2.6
	8	$PEtPh_2$	24	Hex-1-ene	EtOH	45	120	16	66	1.1[e]	28	6.2
	8	$Me_2PCH_2CH_2PMe_2$	12	Hex-1-ene	EtOH	45	120	16	10	0.9[e]	17	0.5
[RhH(PEt_3)$_3$]	8			Hex-2-ene	EtOH	40	125	3	6[f]		36[g]	
	8	PEt_3	80	Hex-2-ene	EtOH	40	125	3	1[f]		7[g]	
	8			Hex-2-ene	EtOH	40	125	3	41[f]		6[g]	
	8	PEt_3	8	Hex-2-ene	EtOH	40	125	3	5[f]		2[g]	
	8			3,3-Dimethylbut-1-ene	EtOH	40	120	16			100	> 8
	8			Styrene	EtOH	40	120	16			100[h]	< 0.5
	8			Heptanal	EtOH	40	118	2			100	(heptanol)
	0.5			Heptanal	EtOH	40	125	2.5	88 (heptanal)		12	(heptanol)

[a] EtOH, 4 cm^3; substrate, 1 cm^3; $CO:H_2$ = 1:1; isomerised hexenes < 2% are formed. [b] Some 2-ethylpentanal produced. [c] Diethyl acetals of C_7 aldehydes are also formed (50%, n:i = 3.9). [d] As in footnote *c*, 48%, n:i = 2.0. [e] Trace of acetals formed. [f] Mixture of 2-methylhexanol and 2-ethylpentanal. [g] Mixture of 2-methylhexanol and 2-ethylpentanol. [h] Of soluble product; some polystyrene is also formed.

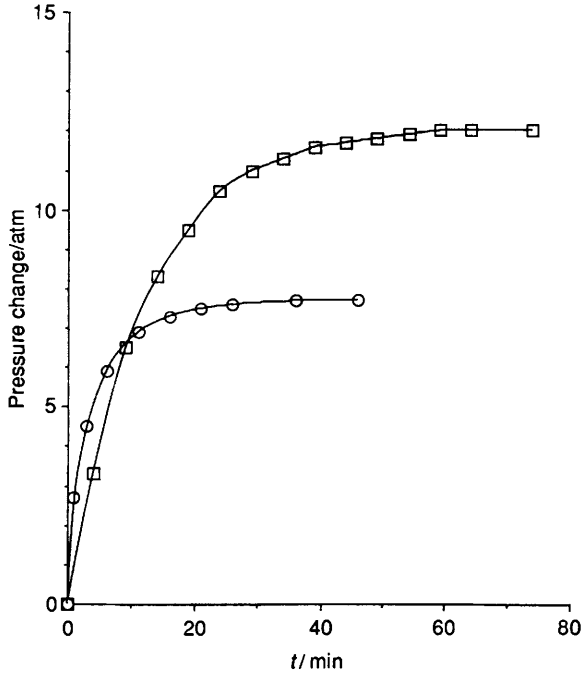

Fig. 1 Plot of uptake of CO–H_2 (1 : 1, 60 atm) from a ballast tank during hydrocarbonylation of hex-1-ene (3 cm^3) in ethanol (30 cm^3) catalysed by $[RhH(PEt_3)_3]$ (3.6 mmol dm^{-3}) at 120 °C in the absence (○) or presence (□) of PEt_3 (36 mmol dm^{-3})

no longer observed but alcohols are produced in high yield even after only 2 h of reaction.* Primary, secondary or tertiary alcohols all seem to be effective solvents for this reaction. The reaction in ethanol was shown to be homogeneous since it was hardly affected by the presence of liquid mercury in the autoclave[27] (see Table 1). The yield of alcohols is also increased if water is added to thf as the solvent. In this case after 2 h both aldehydes (46%) and alcohols (50%) are formed. Interestingly, in this case, the linear to branched ratio for the aldehydes is only 1 : 1 whilst for the alcohols it is 7.5 : 1. Finally, addition of NEt_3 or 'proton sponge' to the reaction in ethanol retards it somewhat and aldehydes become minor products.

These reactions clearly proceed at a reasonable rate but in order to obtain a better idea of the actual reaction rate we have carried out certain reactions in a system which allows catalyst or substrate injection once the system has equilibrated at the desired temperature and pressure. The rate of gas uptake was then monitored at constant pressure. Fig. 1 presents the results obtained with hex-1-ene in the presence or absence of an excess of PEt_3 and with a substrate:catalyst ratio of 200:1. The reaction is essentially complete within 20 min in the absence of an excess of PEt_3 and indeed is so fast that the initial stages could not be monitored by this method. This accounts for the fact that the overall gas uptake is apparently lower in the absence of PEt_3 than in its presence. In both cases, analysis of the products showed essentially complete conversion into C_7 alcohols. The initial rates of reaction correspond to 2300 catalyst turnovers h^{-1} in the absence of added phosphine and 700 turnovers h^{-1} in the presence of a ten-fold excess. The linear branched ratio is not, however, greatly affected by the presence of an excess of PEt_3 (see Table 2). Owing to the problems associated with monitoring the start of the reaction in the absence of an excess of PEt_3, the value of 2300 h^{-1} must be considered as a lower limit.

Similar reactions were carried out using ethene and propene (Fig. 2). In the case of ethene, the reaction, even in the presence of an excess of PEt_3 was so rapid that on adding the catalyst to the reagents there was an immediate rise in temperature to 160 °C because of the heat evolved during the exothermic reaction. The temperature was restabilised at 120 °C with cooling over the next 2 min. The pressure drop in the ballast vessel that occurred during this period corresponded to a rate (again a lower limit) of 54 000 catalyst turnovers h^{-1}. The only detectable product was propan-1-ol. For propene, the initial rate was slower (3500 h^{-1}). A slightly slower rate (3060 h^{-1}) was observed if the CO : H_2 ratio was 1 : 2 rather than the usual 1 : 1, although in both cases the major products were C_4 alcohols. This lower rate almost certainly arises from the lower rate of stirring used in this experiment, 400 rather than the usual 1000 r.p.m.

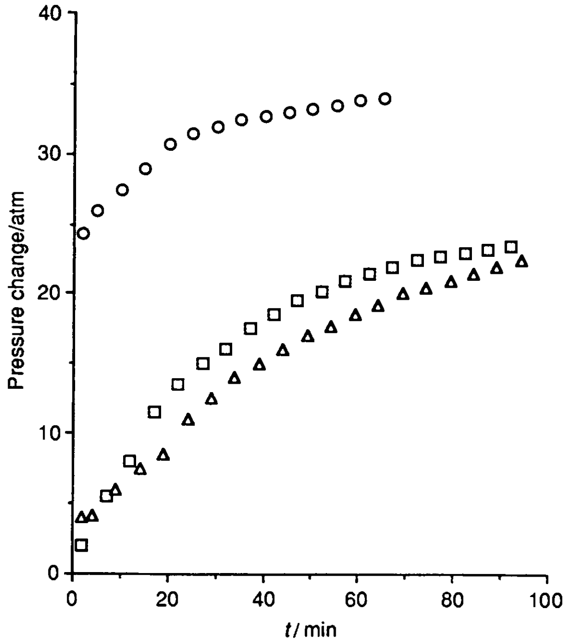

Fig. 2 Plot of uptake of CO–H_2 from a ballast tank during hydrocarbonylation in ethanol (30 cm^3) catalysed by $[RhH(PEt_3)_3]$ (2 mmol dm^{-3}) at 120 °C in the presence of PEt_3 (20 mmol dm^{-3}). ○ Ethene (9 g), CO–H_2 (1 : 2, 50 atm), stirring speed = 1000 revolutions min^{-1} (r.p.m.); □, propene (6.64 g), CO–H_2 (1 : 1, total p = 56.3 atm), stirring speed = 1000 r.p.m.; △, propene (6.5 g), CO–H_2 (1 : 2, total p = 82.4 atm), stirring speed = 400 r.p.m.

Table 2 Effect of added PEt_3 on the n : i ratio of the C_7 alcohols derived from hydrocarbonylation of hex-1-ene catalysed by $[RhH(PEt_3)_3]$[a]

$[PEt_3]$/mol dm^{-3}	n : i
0	2.7
0.04	2.6
0.08	2.7
0.12	2.7
0.16	2.8
1.20	2.9

[a] $[RhH(PEt_3)_3]$ (0.008 mol dm^{-3}); hex-1-ene (1 cm^3); EtOH (4 cm^3); CO–H_2 (1 : 1, 40 atm); 120 °C; 16 h; 100% conversion into C_7 alcohols is observed in all cases.

Batch autoclave reactions were carried out on other substrates (see Table 1) and in general the homologated alcohols were produced. Steric and electronic effects appear to be important in determining the regioselectivity of the reaction, with styrene giving largely 2-phenylpropan-1-ol and 3,3-dimethylbut-1-ene giving mainly 4,4-dimethylpentan-1-ol. These regioselectivities are usually observed in hydroformylation reactions using these substrates.[3,28,29] In the case of styrene, some polymerisation occurred as a side reaction.

The internal alkene, hex-2-ene, can also be hydroformylated

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* It should be noted that these reactions were carried out in batch autoclaves placed cold into a preheated oven. It takes > 2 h to reach the temperature of the oven.

in this system, although the reaction is slower than for hex-1-ene and both aldehydes and alcohols are formed, their relative ratio depending on the reaction conditions. The products were the expected regioisomers, 2-methylhexanol(al) and 2-ethylpentanol(al).

Effect of different phosphines

It was found that the catalyst could be synthesised *in situ* from $[Rh_2(O_2CMe)_4]$ and PEt_3, and that the products obtained from hex-1-ene in batch autoclave reactions were still C_7 alcohols provided that the reactions were carried out in alcoholic solution. Reactions were, therefore, carried out using a variety of different phosphines. The results obtained are collected in Table 1 and show that all tris(primaryalkyl)-phosphines studied give alcohols as the only detectable products. With no added phosphine or using PPh_3 {catalyst added as pre-prepared $[RhH(CO)(PPh_3)_3]$} the products were the expected aldehydes together with their diethyl acetals whilst PEt_2Ph and $PEtPh_2$ gave mixtures of alcohols and aldehydes. Using PPr^i_3 as the promoter, the products were mainly aldehydes with small amounts of alcohol and only trace acetals. Finally, the *cis*-bidentate phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) tends to inhibit the reaction markedly.

Other reaction parameters

For the hydrocarbonylation of hex-1-ene in ethanol catalysed by $[RhH(PEt_3)_3]$ at 115 °C for 3 h, both the yield and regioselectivity of the reaction are independent of pressure between 20 and 60 atm in the presence or absence of an excess of PEt_3. In all cases complete conversion into alcohols was observed and the linear : branched ratio was *ca.* 2.5 : 1. This was also the case (total pressure 15–45 atm) for $CO–H_2$ of 1 : 2 (the stoichiometry required for the reaction) except that the linear : branched ratio was somewhat higher (2.8 : 1). Changes in $CO–H_2$ ratio often affect the selectivity of hydroformylation reactions.[30]

The temperature dependence of the hydrocarbonylation reaction was investigated by carrying out the reaction of hex-1-ene in ethanol over a 5 h period in an oven set at the desired temperature. Owing to the slow heating of the autoclave these experiments only give a partial indication of the effect of temperature on the reaction. The results (Fig. 3) indicate that measurable reaction occurs at 50 °C in the absence of an excess of PEt_3 but not in its presence until ≈60 °C. The optimum temperature appears to be 80–140 °C (120–140 °C in the presence of an excess of PEt_3) but above 140 °C catalyst decomposition sets in. This is most obvious for the reaction carried out at 170 °C, where a black deposit was observed on the inside of the autoclave liner. All the reactions gave C_7 alcohols as the major products although traces of aldehydes were observed in the reactions carried out below 60 or above 140 °C.

Finally, a dramatic dependence of the nature of the products on the concentration of the catalyst was noted (Table 1). At lower concentrations aldehydes predominate (less so in the presence of an excess of PEt_3) and sequential reactions apparently lead to the alcoholic products.

Hydrogenation of heptanal

Under identical conditions to those used in the hydrocarbonylation of hex-1-ene, heptanal was used in place of hex-1-ene as the substrate. Complete conversion into heptanol occurred after 2 h at 118 °C.

Labelling studies

In order to test whether the hydrocarbonylation reactions gave alcohols as the primary products or whether a two-stage process *via* intermediate aldehyde was occurring, reactions were carried out in the presence of EtOD and/or D_2. The C_7 alcoholic products were fractionally distilled and analysed by $^{13}C-\{^1H\}$ and ^1H NMR spectroscopies. Details of the analytical method used for obtaining quantitative data on the product distributions have been published.[25]

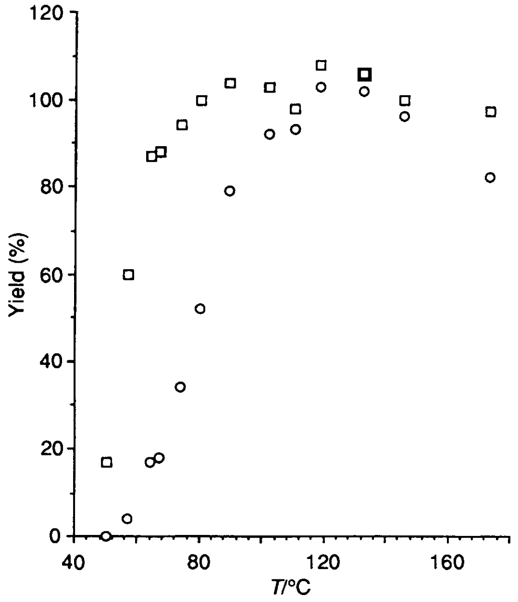

Fig. 3 Effect of temperature on the hydrocarbonylation of hex-1-ene (1 cm^3) in ethanol (4 cm^3) catalysed by $[RhH(PEt_3)_3]$ (8 mmol dm^{-3}) in the absence (□) or presence (○) of PEt_3 (80 mmol dm^{-3}). $CO–H_2$ (1 : 1, 40 atm), 5 h

Table 3 summarises the products formed in the various reactions. Reaction of hex-1-ene carried out in EtOH using $D_2–CO$ gave 90% $BuCHDCH_2CD_2OH/D$ and $BuCH(CH_2D)CD_2OH$ with 10% of the alcohols containing CHDOH/D, whilst the same reaction using heptanal gave a mixture of $C_6H_{13}CHDOH/D$ (39%) and $C_6H_{13}CH_2OH/D$ (61%). Using $D_2–CO$ in EtOD and heptanal as the substrate the only product was $C_6H_{13}CHDOH/D$.

Rhodium-containing species present in catalytic solutions

Proton and ^{31}P NMR parameters of $[RhH(PEt_3)_3]$ in $[^2H_8]$toluene were consistent with those already reported (see Table 4).[26] On addition of C_2D_5OH or in neat C_2D_5OH a slow reaction (at 25 °C) to give $[RhH(CO)(PEt_3)_3]$[30] occurred. Two unidentified intermediates containing hydrides were also detected. Gas–liquid chromatography (GLC) analysis of the gases above the solution indicated CH_4 and H_2 were also produced. A trace of a second species, identified as $[RhH_2(PEt_3)_4]^+$,[26,34] presumably with $C_2D_5O^-$ as the counter ion, was also detected in the early stages of the reaction. In C_2D_5OH in the presence of an excess of PEt_3 $[RhH_2(PEt_3)_4]^+$ was the major initial product formed, but this slowly transformed to $[RhH(CO)(PEt_3)_3]$.

Bubbling CO through a solution of $[RhH(PEt_3)_3]$ in $[^2H_8]$toluene for 5 min produced three species, identified from their spectroscopic properties as $[RhH(CO)(PEt_3)_3]$, $[RhH(CO)_2(PEt_3)_2]$ and $[Rh_2(CO)_4(PEt_3)_4]$. Similar species are produced on carbonylation of $[RhH(CO)(PPh_3)_3]$.[35]

The ^{31}P NMR spectra of $[Rh_2(CO)_4(PEt_3)_4]$ at various temperatures are shown in Fig. 4. This rather unusual behaviour indicates that all the phosphines exchange rapidly with one another, but not with free PEt_3 at room temperature. At −80 °C there are two distinct types of phosphine and the breadth of the signal probably hides a small P–P coupling. One doublet has J_{RhP} = 184 Hz whilst the other has J_{RhP} = 115 Hz. Two of the peaks overlap to form the most intense signal in the

Table 3 Products (heptanol) obtained from reactions of hex-1-ene or heptanal with D_2–CO and/or EtOD catalysed by $[RhH(PEt_3)_3]$[a]

Substrate	$[PEt_3]$/ mol dm^{-3}	D_2 (%)	Pressure/ atm	EtOD (%)	$C_6H_{13}CHDOH/D$	$C_6H_{13}CH_2OH/D$
Hex-1-ene[b]	0	100	23	0		
Heptanal	0	100	34	0	39	61
	0.08	100	28	0	53	47
	0	0	34	100	21	79
	0	100	34	100	100	

[a] $[RhH(PEt_3)_3]$ = 0.008 mol dm^{-3}, 120 °C, 2 h, 23–34 bar, CO : D_2 or H_2 = 1 : 1. Only the heptanol products are shown; similar results are obtained for 2-methylhexanol. [b] Products: 90% $BuCHDCH_2CD_2OH/D$, 10% $BuCHDCH_2CHDOH/D$.

spectral region near δ 5. Since the two coupling constants are so different, the separation of the two pairs of peaks undergoing coalescence is different and this accounts for the different coalescence temperatures (−70 °C for the further apart signals and −75 °C for the closer ones). The couplings are very similar to those for $[Rh_2(CO)_4\{Ph_2P(CH_2)_3PPh_2\}_2]$[36] which has crystallographically been shown to have the structure in Scheme 1 but with the PEt_3 groups replaced with the bidentate phosphine. We conclude that $[Rh_2(CO)_4(PEt_3)_4]$ has the structure shown.

Passing CO through a solution of $[RhH(PEt_3)_3]$ in $C_6D_5CD_3$ containing ethanol produces the same species as described above, although with slight solvent shifts, together with a new species, **A**. Similar products were obtained in neat C_2D_5OD, but addition of an excess of PEt_3 to this solution led to **A** being the major rhodium-containing species observed. The NMR and IR data for this species are collected in Table 4 and we tentatively assign it as being $[Rh_2(CO)_2(PEt_3)_6]$ with the structure shown in Scheme 1. The related $[Rh_2(CO)_2(PBu_3)_6]$ has been isolated and characterised.[37] The IR data ($\nu_{C\equiv O}$ 1959 cm^{-1}) are similar to those for **A**.

Passing CO through a solution in $[^2H_8]$toluene containing $[RhH(CO)(PEt_3)_3]$, $RhH(CO)_2(PEt_3)_2]$ and $[Rh_2(CO)_4(PEt_3)_4]$ produced an increase in the amount of PEt_3 and $[Rh_2(CO)_4(PEt_3)_4]$ which gradually precipitated as a yellow solid but redissolved on passing H_2. All the free PEt_3 was taken up at this stage and the major solution species was $[RhH(CO)(PEt_3)_3]$. These changes were reversed on passing CO again.

Passing H_2 through an ethanolic solution that largely contained species **A** produced $[RhH(CO)(PEt_3)_3]$ exclusively, but this was converted into a mixture of $[RhH(CO)(PEt_3)_3]$, $[RhH(CO)_2(PEt_3)_2]$, $[Rh_2(CO)_4(PEt_3)_4]$, species **A** and PEt_3 on bubbling CO.

On heating a solution containing all of the species discussed above to 100 °C in a mixture of $C_6D_5CD_3$ and ethanol, in the presence of CO and H_2, all of the major species underwent exchange (see Fig. 5).

Phosphorus-31 NMR studies of a reaction solution recovered from a catalytic reaction involving hex-1-ene and CO–H_2 in ethanol showed the presence of **A** as the predominant species, whilst *in situ* high-pressure NMR studies carried out on a catalytic solution with ethene as the substrate cooled to −60 °C after partial reaction at 100 °C showed the presence of **A** and a new species **B** with the NMR parameters shown in Table 4.

Models of possible reaction intermediates

Reaction of $[RhCl(CO)(PEt_3)_2]$[31] with LiMe produces $[RhMe(CO)(PEt_3)_2]$ which has been fully characterised and is analogous to $[RhMe(CO)(PMe_3)_2]$.[38] Reaction of $[RhMe(CO)(PEt_3)_2]$ with CO in $[^2H_8]$toluene, $[^2H_8]$thf or CD_2Cl_2 produces a fluxional species with the NMR parameters shown in Table 4. These parameters are very similar to those reported for $[Rh(COC_8H_{17})(CO)_2(PPh_3)_2]$[39] so we assign it to $[Rh(COMe)(CO)_2(PEt_3)_2]$ with the structure shown in Scheme 2. Addition of ethanol to the solution of $[Rh(COMe)(CO)_2(PEt_3)_2]$ causes changes in certain of the NMR parameters, the most significant of these being a shift of the resonance from the acyl C atom to higher frequency. This shift increases with increasing amounts of ethanol and is *ca.* 10 ppm in pure ethanol. Using the more acidic CF_3CH_2OH the increased shift is greater (see Fig. 6) and in neat CD_3OD, a slightly stronger alcohol than EtOD, which also has a higher concentration of OD, the shift is 16 ppm, rather higher than in neat EtOD. The ^{31}P NMR parameters for this species are almost identical to those of **B** observed under catalytic conditions with ethene as the substrate (see Table 4).

Bubbling argon through the solution of $[Rh(COMe)(CO)_2(PEt_3)_2]$ in CD_3OD causes more major changes in the spectrum with the resonance from the acyl C atom appearing at δ 304. The ratio of CO:acyl is changed from 2:1 for $[Rh(COMe)(CO)_2(PEt_3)_2]$ to 1:1 for the new species **C**.

The complex $[RhMe(CO)(PEt_3)_2]$ also reacts with an excess of PEt_3 (2 molar equivalents) to give $[RhMe(CO)(PEt_3)_3]$ with all the phosphines equivalent and exchange occurs at room temperature between the two species and the excess of PEt_3.

Discussion

Trialkylphosphines clearly promote the production of alcohols from alkenes under hydroformylation conditions. Superficially, these results are similar to those of Lawrenson,[4–9] the main difference being that we always use >2 PEt_3 per Rh whilst he always used <1.5. Solution NMR studies show that in our system there are always two or more PEt_3 molecules coordinated to the Rh atom. The major difference in reaction chemistry is that Lawrenson's system gives aldehydes as the primary products whereas we present evidence that the primary products are the alcohols observed.

The major evidence for this comes from the labelling study. Thus, reaction of heptanal with D_2–CO in EtOH introduces both H and D onto the alcoholic C atom. Thus, if the formation of heptanol from hex-1-ene and D_2–CO in EtOH were occurring sequentially *via* heptanal, a major proportion (*ca.* 60%) of the product should contain only one H atom (this would be equivalent to $C_6H_{13}CH_2OH/D$ from heptanal) on the alcoholic C atom. Since only 10% of the products has the CHDOH/D group,* free heptanal can only be a minor intermediate and heptanol is a primary reaction product when reactions are carried out in alcoholic solvents. This is not always the case, however, since sequential reactions clearly occur in thf or when very low catalyst concentrations are used in ethanol as the solvent.

It is possible that heptanal forms but is hydrogenated before leaving the metal. However, the intermediate containing

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* The minor products may arise from a different pathway in which aldehydes are formed as intermediates, or may come from exchange of Rh–D with EtOH in one of the proposed cationic hydrido intermediates of Scheme 3.

Table 4 The NMR ([$^2H_8$]toluene) and IR (Nujol mull) parameters for rhodium complexes

		^{31}P (δ, J_{PRh}, J_{PP}/Hz)	^1H (δ)				^{13}C (δ)					IR
Complex	T/°C	δ	Me[a]	CH_2Me	CH$_2$CH_3	Rh–H[a]	CO[b]	COMe[b]	Me[b]	CH$_2$Me	CH$_2$CH$_3$	ν(C≡O)/cm^{-1}
$[RhH(PEt_3)_3]$	25	26.1 (br)				−8.4 (br m)						
	−40	26.6 (dd, 153, 28)				−8.1 (br d, —, ≈106)						
		23.2 (dt, 138, 28)										
Lit.[26]	25	26.6 (br)										
	−40	28.8 (m, 137, 28.5)				−7.9 (m, 18, —)						
		25.4 (m, 152, —)										
$[RhH_2(PEt_3)_4]^+$ [c]	−40	19.5 (dt, 101, 21)				−12.2 (br d, —, ≈126)						
		4.3 (dt, 89, 21)										
Lit. (BPh_4 salt)[d,32]						−11.7 (dd, 11, 124.5, 16.0)						
$[RhH(CO)(PEt_3)_3]$[c,e]	25	26.2 (d, 147, —)				−11.1 (br q)	212 (d,[f] 62, —)					1964
	−40	26.9 (d, 147, —)				−11.1 (dq, 4, 17)						
Lit.[f,g,30]						−11.3 (dq, 4, 17)						1952
$[RhH(CO)_2(PEt_3)_2]$	25	25.1 (d, 130, —)				−10.1 (br)						
	−40	23.5 (br)				−9.6 (br t, —, 30)						
c	25	24.5 (d, 127, —)				−10.2 (br)						
	−40	23.1 (br)				−9.8 (br)						
$[Rh_2(CO)_4(PEt_3)_4]$	25	4.4 (d, 158, —)					227.8 (br m)					1957, 1939,
c	25	4.2 (d, 158, —)					229.5 (br m)					1742, 1721
	−40	4.6 (d, 158, —)										
$[Rh_2(CO)_2(PEt_3)_6]$[c] A	25	16.8 (d, 96, —)										
	40	18.7 (d, 93, —)					197.6 (br d, 62, —)					
h	25	17.5 (d, 96, —)										
	−60	20.5 (d, 92, —)					200.2 (br d, 53, —)					1962[h]
$[RhCl(CO)(PEt_3)_2]$[f]	25	24.6 (d, 119, —)		1.9 (m)	1.3 (m)		197.7 (br d, 63, —)					
d	25	25.1 (d, 116, —)										1958
Lit.[i,31,33]	25	23.7 (116, —)										1953
$[RhMe(CO)(PEt_3)_2]$	25	26.6 (d, 140, —)	−0.35 (dt, 1.6, 8.2)	1.6 (m)	1.0 (m)		192.8 (dt, 57, 14)		−4.2 (dt, 20, 13)	18.1 (t)	8.9 (s)	1938
c	25	26.3 (d, 140, —)	−0.5 (dt, 1.6, 8.2)									
$[RhMe(CO)(PEt_3)_3]$	−70	11.0 (d, 144, —)	−0.2 (br)									
$[Rh(COMe)(CO)_2(PEt_3)_2]$	25	14.3 (br d)	2.7 (br)									
	−60	17.8 (dd, 71, 36)	2.9	1.4 (m)	1.1 (m)		200.1 (br)		53.0 (br)			2006, 1997
		12.1 (dd, 140, 36)			0.9 (m)		200.5 (dt, 75, 21)	238 (ddd, 78, 21, 9)	53.8 (dd, 32.7, 4)			
c	25	14.3 (br d)	2.5 (br)				199.9 (dt, 73, 21)	247 (ddd, 81, 21, 9)	53.4 (d, 30.2, —)			
	−60	18.0 (dd, 72, 36)	2.7									
		10.3 (dd, 137, 36)										
j	−60							257 (ddd, 80, 21, 9)	53.7 (dd, 28, 5)	21.6 (d)[l]	8.7 (s)	
k	−60						200.8 (dt, 73, 20.5)	253 (ddd, 84, 22, 17)		18.0 (d)[m]	7.8 (s)	
$[Rh\{=C(OH)Me\}(CO)(PEt_3)_2]^+$ [j]	−20	17.2 (dd, 68.5, 36)					200.2 (br, 42, —)	301.2 (br, 32, —)	45.5 (br)	19.1 (s)	8.9 (s)	1956
$[Rh(COEt)(CO)_2(PEt_3)_2]$[n] B	−60	10.2 (dd, 135, 36)										

[a] J_{HRh}, J_{PH}/Hz. [b] J_{RhC}, J_{PC}/Hz. [c] Solvent contains ethanol. [d] In [$^2H_8$]thf. [e] ν(Rh-H) 1884 cm^{-1}. [f] In C_6D_6. [g] ν(Rh-H) 1880 cm^{-1}. [h] In C_2D_5OD. [i] In CD_2Cl_2. [j] Solvent contains CF_3CH_2OH. [k] In CD_3OD. [l] J_{PC} 22.1 Hz. [m] J_{PC} 16.5 Hz. [n] In EtOH.

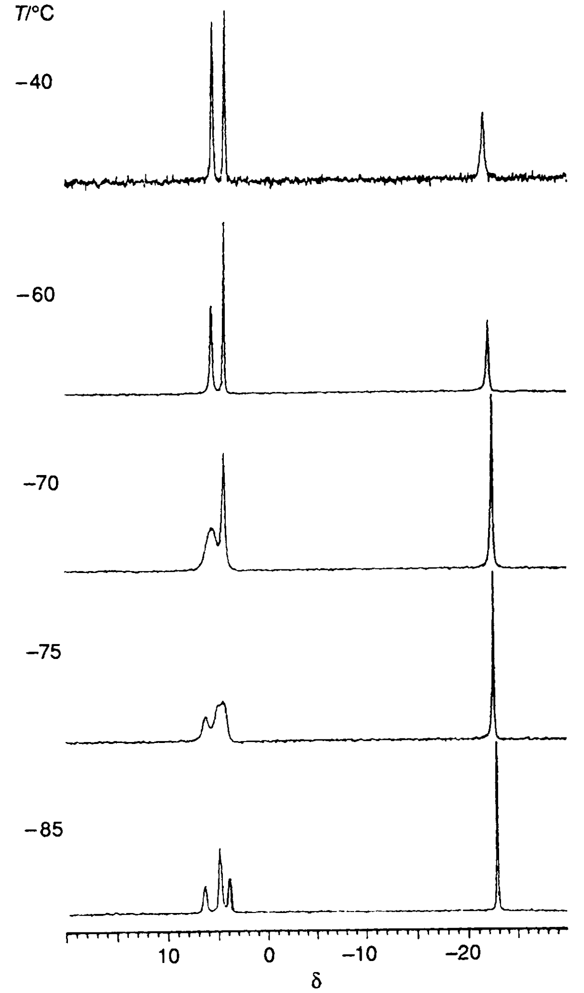
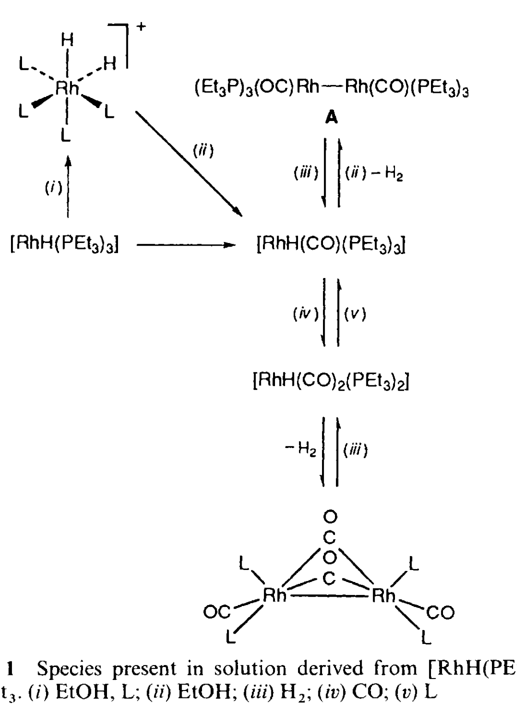


Fig. 4 The ^{31}P NMR spectra of $[Rh_2(CO)_4(PEt_3)_4]$ at various temperatures. The signal at δ -22.8 is from free PEt_3



Scheme 1 Species present in solution derived from $[RhH(PEt_3)_3]$. L = PEt_3. (*i*) EtOH, L; (*ii*) EtOH; (*iii*) H_2; (*iv*) CO; (*v*) L

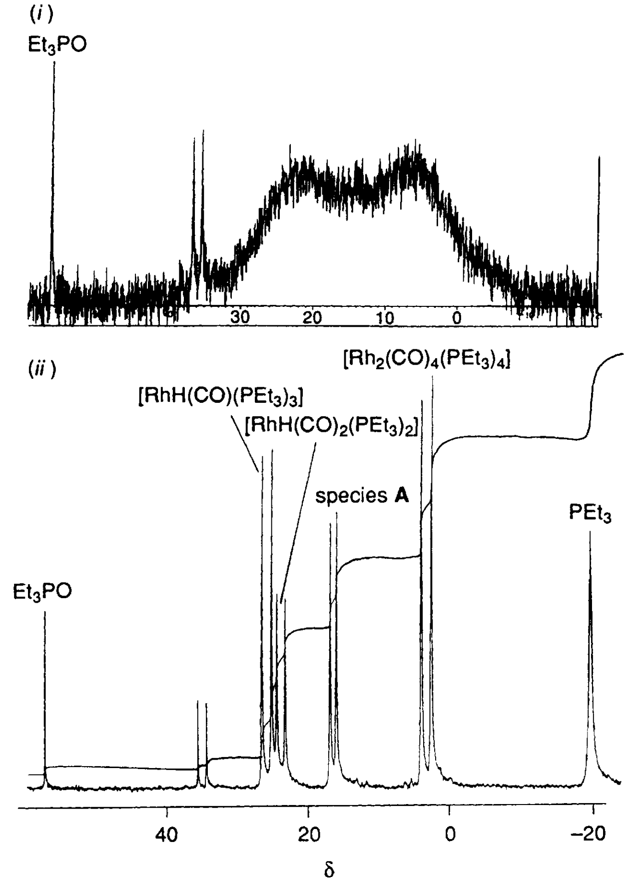


Fig. 5 The ^{31}P NMR spectra of a solution prepared from $[RhH(PEt_3)_3]$ in ethanol under CO–H_2 (1 : 1, 40 atm): (*i*) 100; (*ii*) 25 °C

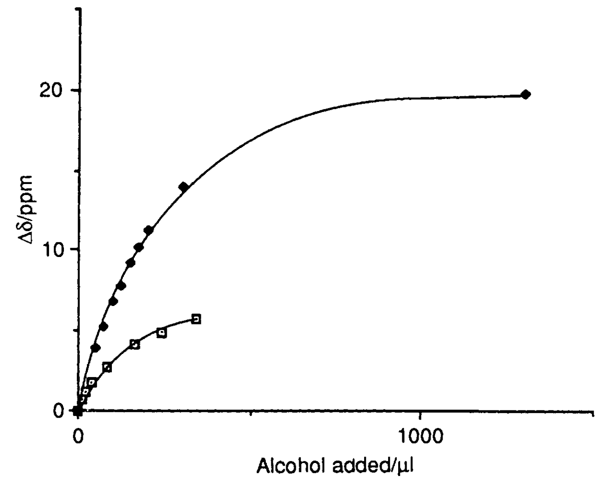
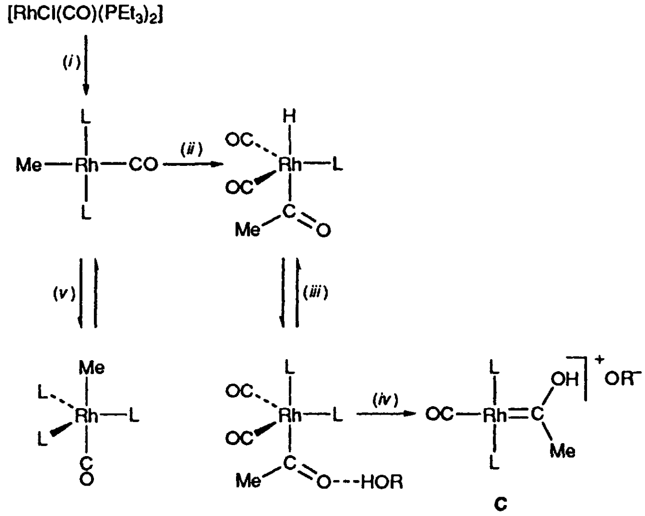


Fig. 6 Effect of added ethanol (□) or trifluoroethanol (◆) on the chemical shift of the resonance from the acyl C atom of $[Rh(COMe)(CO)_2(PEt_3)_2]$. The shifts are to higher frequency

heptanal (obtained by oxidative addition of D_2 to **D** in Scheme 3 followed by reductive elimination) would be equivalent to **H** in Scheme 4. Since the labelling study specifically excludes a common heptanal-containing intermediate on the pathways from hex-1-ene or from heptanal such a mechanism is also excluded. For heptanol to be a primary product it appears that tris(primary alkyl)phosphines must be used and a proton source (alcohols or water) must be present. The presence of a proton acceptor (NEt_3 or proton sponge) reduces the tendency to form alcohols, but only slightly.

A mechanism consistent with our observations is shown in Scheme 3. Solution studies of the rhodium complexes suggest that $[RhH(CO)(PEt_3)_3]$ is the major species present in solution under catalytic conditions, provided that the hydrogen concentration in solution is high enough. The equilibria shown in Scheme 1 are occurring, and $[Rh_2(CO)_2(PEt_3)_6]$ is present



Scheme 2 Models of certain proposed catalytic intermediates. L = PEt_3. (*i*) LiMe; (*ii*) CO; (*iii*) ROH; (*iv*) bubble argon; (*v*) L

under conditions of hydrogen depletion (unlikely to be a problem during the catalytic reaction). The first part of Scheme 3 exactly mimics the processes that are believed to occur during hydroformylation using *e.g.* $[RhH(CO)(PPh_3)_3]$.[1–3] In these reactions oxidative addition of H_2 occurs to a species analagous to **D** and reductive elimination of aldehyde product leads to regeneration of $[RhH(CO)(PPh_3)_2]$. If aldehyde is not to be a major product during this reaction this recycling of the catalyst must be frustrated. We propose that this occurs by protonation of the acyl C atom in species **D** to give the hydroxycarbene complex, **E**. This protonation will be favoured by the electron-donating trialkylphosphines which will increase the electron density on the rhodium and thence on the acyl O atom. It will also only occur if a proton source (alcohol or water) is present. Oxidative addition of H_2 to the hydroxycarbene complex will be followed by migration of H to give a hydroxylalkyl, **F**, and reductive elimination to give heptanol as the primary product and $[Rh(CO)(PEt_3)_2]^+$. Recycling of the catalyst involves oxidative addition of H_2 followed by deprotonation. These steps are shown using D_2 in Scheme 3, since they confirm that the labelling of the observed heptanol product is what would be expected.

The model studies also support this proposed mechanism. Thus, compound **B**, observed during high-pressure NMR studies of a solution cooled during a catalytic hydrocarbonylation of ethene, has ^{31}P NMR parameters very similar to those obtained for $[Rh(COMe)(CO)_2(PEt_3)_2]$ in ethanol.† The shift to high frequency of the resonance from the acyl C atom on addition of ethanol is consistent with the C atom becoming more carbene like, but it is clear that it does not actually become a carbene, *i.e.* full protonation of the acyl C atom does not occur since hydroxycarbenes generally resonate near δ 300.[42,43] Rather, the shift is more likely to arise from hydrogen bonding to the acyl O atom of the solvent. This conclusion is also supported by the observation that solutions of $[Rh(COMe)(CO)_2(PEt_3)_2]$ in ethanol are non-conducting. We feel that the results are best interpreted by the equilibrium (*iii*) shown in Scheme 2.

Further support for this suggestion comes from calculations of the equilibrium constant for these equilibria using EtOH and CF_3CH_2OH. In both cases, values of *ca.* 3 $dm^3\ mol^{-1}$ are observed. If full protonation were occurring, the value for CF_3CH_2OH would be expected to be higher than that for EtOH. Hydrogen bonding, on the other hand, requires the breakage of one hydrogen bonded structure and the formation of another. The strength of the hydrogen bond between the complex and CF_3CH_2OH would be compensated for by having to break stronger hydrogen bonds between CF_3CH_2OH molecules than between EtOH molecules and hence rather similar equilibrium constants might be expected. The larger shift observed in neat CF_3CH_2OH compared with that observed in neat EtOH can be rationalised because the hydrogen bond to the acyl will be stronger for the stronger acid (CF_3CH_2OH) and the product will be further along the path to full protonation (*i.e.* the rhodium–acyl interaction will be more carbene like).

However, $[Rh(COMe)(CO)_2(PEt_3)_2]$ is not the catalytic intermediate that we propose will protonate in the catalytic cycle, in that the proposed intermediate is the square-planar $[Rh(COR')(CO)(PEt_3)_2]$ **D**, with one less CO group. Removal of the electron-withdrawing CO group will render the O atom of the acyl group even more electronegative and even more susceptible to protonation. Fortunately, we have been able to generate the analogue of this intermediate, $[Rh(COMe)(CO)(PEt_3)_2]$ **C**, as $[Rh\{=C(OD)Me\}(CO)(PEt_3)_2]^+$, by passing argon through a solution of $[Rh(COMe)(CO)_2(PEt_3)_2]$ in CD_3OD. In this case the acyl C atom resonance is at δ 304, exactly the region expected for a hydroxycarbene ligand,[42,43] so we feel confident that full protonation does occur for the four-co-ordinate catalytic intermediate to give $[Rh\{=C(OH)R\}(CO)(PEt_3)_2]^+$. Protonation of acyl[42,43] and formyl species[44] is well known, but usually stronger acids than alcohols are required. Where ^{13}C NMR data are available, it seems that a shift of *ca.* 30–50 ppm downfield is to be expected.[42,43] Our observed shift of *ca.* 70 ppm (with the loss of one ligand) is therefore entirely consistent with full protonation.

Assuming that the mechanism of Scheme 3 is correct for the catalytic hydrocarbonylation of hex-1-ene, and assuming that the protonation of the acyl group is responsible for the rapid formation of alcohols as primary products, it is surprising that alcohols are not produced when the even more electron-donating phosphine PPr^i_3 is employed. We can only speculate as to why this might be but it could either be related to the larger steric bulk of this phosphine or protonation occurs on the metal either as well as or instead of on the acyl O atom and that direct reductive elimination of aldehyde occurs.

Finally, it is pertinent to attempt to rationalise the products obtained from hydrogenation of heptanal catalysed by $[RhH(PEt_3)_3]$ in the presence of D_2 and/or EtOD. The products indicate that 39% of the heptanal arises from addition of D_2 across the C=O but that 61% of the product incorporates H from the OH group of the solvent onto the aldehydic C atom.

In the hydrogenation of aldehydes, migration of H can occur from the metal onto either the O or the C atom of the aldehyde to give a hydroxylalkyl or an alkoxide intermediate.[45] Since the oxophilicity of rhodium is quite low, it is likely that the hydroxylalkyl intermediate will be formed. This is also consistent with the observed products since formation of the alkoxide will only incorporate H_2/D_2 from the gas phase onto the aldehydic C atom.

The upper cycle in Scheme 4 shows the formation of products by the mechanism expected for hydrogenation of an aldehyde *via* an hydroxylalkyl intermediate. However, intermediate **G** is the deprotonated form of **F** in Scheme 3. Since protonation equilibria are almost always rapidly established and since we have no evidence that **F** deprotonates to **G**, it is reasonable to assume that intermediate **G** should protonate, as shown in the cycle at the bottom of Scheme 4. The subsequent reactions are then as already suggested in the hydrocarbonylation reactions. The labelling will, however, be different because the metal-bound proton (that which ends up on the alcoholic C atom) is

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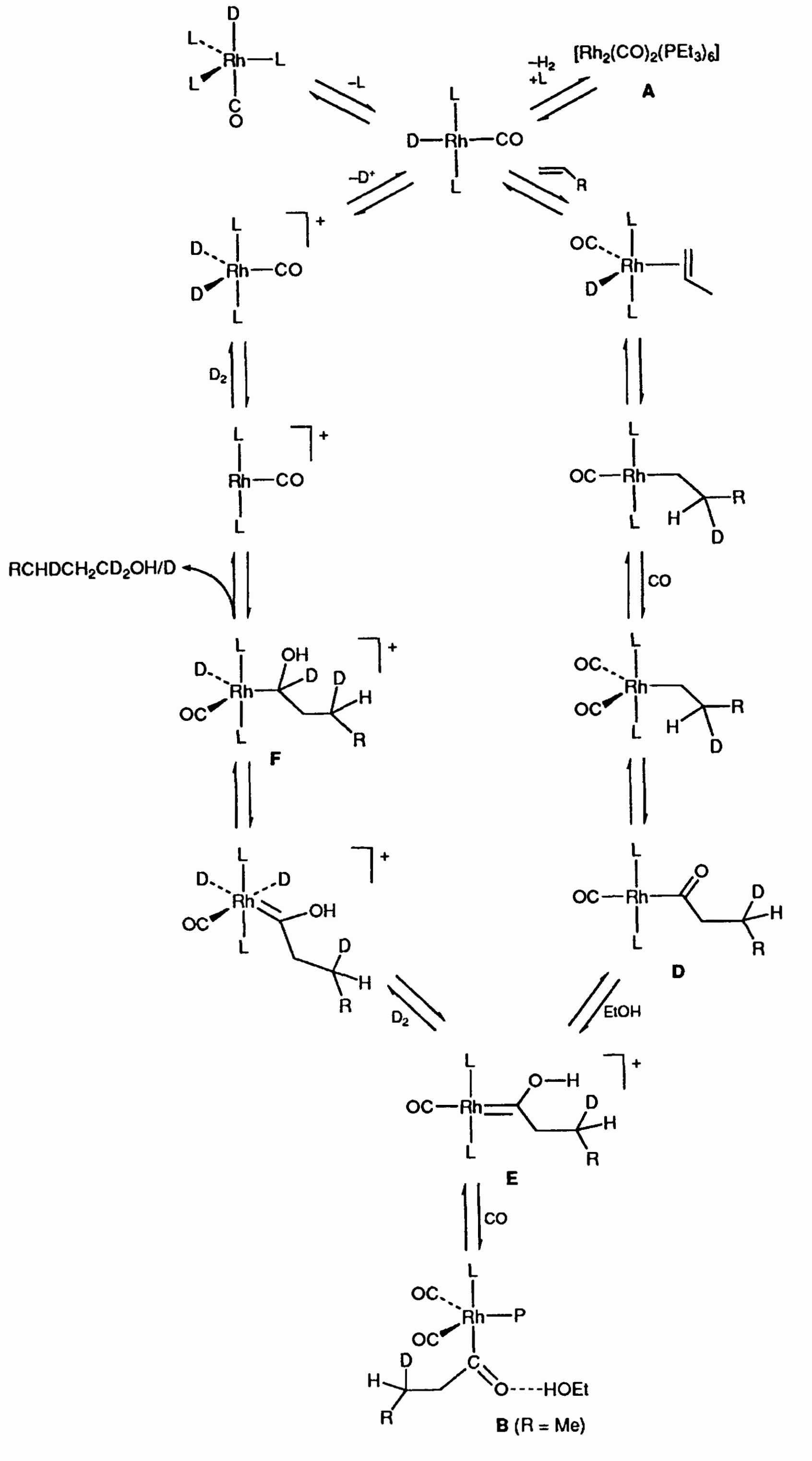
† Species **B** is presumably $[Rh\{C(O\cdots HOEt)Et\}(CO)_2(PEt_3)_2]$, a resting state of the catalyst during the cycle and related to $[Rh\{C(O)C_8H_{17}\}(CO)_2(PPh_3)_2]$ which is present as a resting state of the catalyst during the hydroformylation of octene catalysed by $[RhH(CO)(PPh_3)_3]$.[39–41]



Scheme 3 Proposed mechanism for the hydrocarbonylation of alkenes catalysed by $[RhD(CO)(PEt_3)_3]$ using D_2–CO in EtOH. L = PEt_3

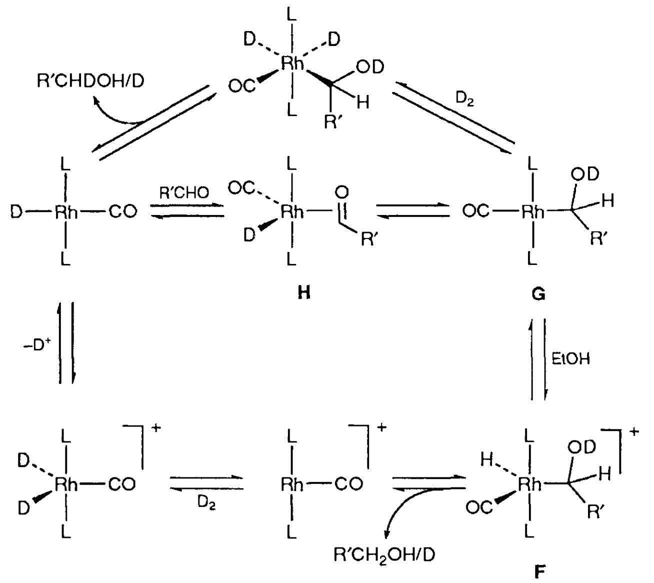
derived from the gas phase in the hydrocarbonylation of hex-1-ene but from the OH/D group of the solvent ethanol in the hydrogenation of heptanal.

It would appear, since products from both of the cycles in Scheme 4 are observed, that oxidative addition of D_2 to **G** competes with its protonation.

It should also be noted that when aldehydes are formed as intermediates and the alcohols are then derived from them, there is evidence that hydrogenation of heptanal is significantly faster than that of 2-methylhexanal since at partial conversion the aldehydes have a lower linear:branched ratio than usual, whilst the alcohols are heavily enriched in the linear product (see *e.g.* results obtained using $PEtPh_2$ in Table 1). We also find that in the direct formation of alcohols low conversions (obtained *e.g.* at low *T* for short times) give much better linear: branched ratios (up to 8:1 at 14% conversion).

Conclusion

We conclude that trialkylphosphine complexes of rhodium can catalyse the direct production of alcohols from alkenes under hydroformylation conditions, provided the reactions are carried out in protic solvents. Mechanistic studies confirm that aldehydes are not intermediates in these reactions and suggest a



Scheme 4 Proposed mechanism for the hydrogenation of heptanal catalysed by $[RhD(CO)(PEt_3)_3]$ using D_2–CO in EtOH. L = PEt_3, R' = C_6H_{13}

different mechanistic pathway from that normally observed in hydroformylation reactions. In the key intermediate the high electron density on the acyl oxygen atom allows it to be protonated to a hydroxycarbene to which two sequential hydrogen-transfer reactions occur generating the product alcohol. These catalysts are also effective for the hydrogenation of aldehydes.

Experimental

Microanalyses were by the University of St. Andrews Materials Analysis Service. The NMR spectra were recorded on Brüker Associates AM300 or JEOL GSS 270 spectrometers with, for ^{31}P and ^{13}C, proton-noise decoupling and IR spectra on a Perkin-Elmer PE 1720 spectrometer as Nujol mulls between KBr plates. Melting points were measured in sealed capillaries under argon and are uncorrected.

All solvents were dried by distillation from sodium diphenylketyl [thf, diethyl ether, toluene, light petroleum (b.p. 40–60 °C)], CaH_2 (CH_2Cl_2) or magnesium alkoxide (alcohols) and degassed before use. All manipulations were carried out using standard Schlenk-line and catheter-tubing techniques under argon. The compounds PEt_3, PPr^i_3 and PPh_3 were reagent grade and used as received; $[RhH(PEt_3)_n]$ (n = 3 or 4),[26] $[Rh_2(O_2CMe)_4]$[46] and $[RhCl(CO)(PEt_3)_2]$[31] were prepared by standard literature methods.

Preparation of carbonylmethylbis(triethylphosphine)rhodium(I)

The complex $[RhCl(CO)(PEt_3)_2]$ (1.08 g) was dissolved in diethyl ether (5 cm^3) and treated with methyllithium (2 cm^3, 1.4 mol dm^{-3} in diethyl ether). After stirring for 5 min at room temperature the yellow solution was filtered to remove precipitated LiCl and evaporated to dryness. Light petroleum (5 cm^3) was added, the solution was filtered, evaporated to 2 cm^3 and cooled to −30 °C. The yellow product was collected and dried *in vacuo*. M.p. 28–31 °C (Found: C, 42.7; H, 9.4. $C_{14}H_{33}OP_2Rh$ requires C, 43.9; H, 8.6%).

Reaction of $[RhMe(CO)(PEt_3)_2]$ with CO

The complex $[RhMe(CO)(PEt_3)_2]$ (0.02 g) was dissolved in $[^2H_8]$toluene, $[^2H_8]$thf or CD_2Cl_2 (0.5 cm^3) in an NMR tube. Carbon monoxide was bubbled through the solution for 2–5 min. Proton, ^{31}P and ^{13}C NMR data indicated that the only compound formed was $[Rh(COMe)(CO)_2(PEt_3)_2]$. This compound was too unstable to isolate.

Reaction of $[Rh(COMe)(CO)_2(PEt_3)_2]$ with proton donors

Solutions of $[Rh(COMe)(CO)_2(PEt_3)_2]$ from $[RhMe(CO)(PEt_3)_2]$ (0.15 g for EtOH, 0.10 g for CF_3CH_2OH) in $[^2H_8]$thf (0.5 cm^3), prepared as described above, were treated with aliquots of the appropriate proton donor (EtOH or CF_3CH_2OH). The ^{13}C NMR spectrum was recorded after each addition. Equilibrium constants for hydrogen bonding of the proton donor to the acyl oxygen atom of the rhodium complex were calculated by assuming that in neat EtOH or CF_3CH_2OH all of the complex was hydrogen bonded and hence that the observed chemical shift of the acyl C atom represented that of the hydrogen-bonded complex. The relative amounts of hydrogen-bonded and of free complex could then be calculated at any point during the addition of the proton donor from the observed chemical shift of the acyl C atom. Knowing also the concentration of the proton donor and the initial concentration of the acyl complex, it was straightforward to calculate the equilibrium constant for the hydrogen-bonding reaction.

Action of argon on $[Rh(MeCO\cdots DOCD_3)(CO)_2(PMe_3)_2]$

The complex $[RhMe(CO)(PEt_3)_2]$ (0.5 g) was dissolved in CD_3OD (1 cm^3) and placed in an NMR tube. Carbon monoxide was bubbled through the solution for 2 min. Carbon-13 NMR studies at −50 °C confirmed that $[Rh(MeCO\cdots DOCD_3)(CO)_2(PEt_3)_2]$ was the only species present. Argon was passed through the solution for 2 min causing a yellowing of the solution. Carbon-13 NMR studies at −30 °C showed that all of the $[Rh(MeCO\cdots DOCD_3)(CO)_2(PEt_3)_2]$ had disappeared and a new complex identified as $[Rh\{{=}C(OH)Me\}(CO)(PEt_3)_2]^+$ (broad resonance at δ 304) had formed. This species proved to be thermally very sensitive, turning dark brown on standing even at −30 °C for a few hours.

In situ NMR studies of catalytic system

The complex $[RhH(PEt_3)_3]$ (0.1 g) was dissolved in the appropriate solvent ($[^2H_8]$toluene, C_2D_5OH or $[^2H_8]$toluene containing C_2D_5OH). The ^{31}P and ^1H NMR spectra were recorded immediately and after standing for varying lengths of time up to 14 d. In some cases CO was bubbled through the solution for 2 min and the spectra remeasured. Sometimes H_2 was bubbled through these solutions and then CO with the spectra being recorded after each reaction with gas.

High-pressure NMR studies

The complex $[RhH(PEt_3)_3]$ (0.2 g) was dissolved in ethanol in a 5 mm sapphire NMR tube fitted with a pressure head. The tube was pressurised with a mixture of CO, H_2 and C_2H_4 (40 bar). After heating briefly to 100 °C the tube was cooled to −60 °C and the ^{31}P NMR spectrum was recorded.

Catalytic experiments

Catalyst preparation. An accurately weighed amount of $[RhH(PEt_3)_4]$ was pumped *in vacuo* at 65–70 °C for 0.5 h to give the dichroic (red-green) oil $[RhH(PEt_3)_3]$. This was dissolved in the appropriate solvent to make a stock solution of concentration 0.01 mol dm^{-3}. For reactions using $[Rh_2(O_2CMe)_4]$, the complex and appropriate phosphine were dissolved in the appropriate solvent to give a solution 0.01 mol dm^{-3} in rhodium.

Autoclave reactions. Steel autoclaves of internal capacity 225 cm^3 fitted with a head such that the autoclave could also be used like a Schlenk tube were employed. A glass liner was inserted into the autoclave. The autoclave was closed apart from the valve to the pressurising gas cylinder. It was flushed by pressurising to 20 atm with CO–H_2 and venting. This process was repeated three times. The cap was then removed from the autoclave and CO–H_2 allowed to pass gently through the open top. The catalyst solution (4 cm^3, 1.0 mol dm^{-3}), an excess of PEt_3 (59 μl if required) and the substrate were injected into the open port and the cap replaced. The autoclave was pressurised to the required pressure, sealed and placed in an oven set to the required operating temperature for the appropriate reaction time. Studies using a thermocouple inserted into the autoclave have shown that the temperature rises slowly, only reaching 120 °C in >2 h. At the end of the reaction the autoclave was removed from the oven and placed in a cold water-bath for 20 min. Once the autoclave was cool the gases were slowly vented and the solutions poured out from inside and outside the autoclave liner. They were analysed separately.

The products were analysed by GLC as follows. An aliquot of the solution (100 μl) was diluted with ethanol (80 μl) containing octanol (20 μl) as an internal standard. A sample (0.1 μl) was then injected into a gas chromatograph (Phillips PU4500) fitted with a capillary column (stationary phase = methylsiloxane) with nitrogen as the carrier gas and a flame ionisation detector. The temperature was held at 75 °C for 1 min then raised at 16 °C min^{-1} to 130 °C where it was held for 2–6 min until all products had eluted. The chromatograph was calibrated using standard solutions of the analyte with octanol (10% by volume) as an internal standard. Some yields apparently exceeded 100%; in these cases, small amounts of solvent were found outside the liner of the autoclave.

Quantitative analysis for unreacted or isomerised hexenes was carried out similarly but using a sample size of 0.5 μl, a glass column packed with SP2340 as the stationary phase and a temperature programme 100 °C for 2 min, 16 °C min^{-1} to 130 °C, held for 2 min.

Methane and H_2 were analysed on a Philips Scientific 204 gas chromatograph using a glass column packed with molecular sieves (5 Å) at 80 °C, N_2 as the carrier gas and a thermal conductivity detector.

Labelling studies. Autoclaves were prepared as described above except that for reactions with D_2 the autoclave was first flushed with pure CO. After addition of the catalyst solution and reagents the autoclave was closed and pressurised with D_2 (17 atm) followed by CO to a total pressure of 34 atm. At the end of the reaction the products were fractionally distilled through a small Vigreux column in air. The fraction containing the C_7 alcohols was collected and analysed by $^{13}C-\{^1H\}$ and ^1H NMR spectroscopy. Analysis of the solvent ethanol showed that there was no incorporation of D into the ethyl group but that the OH/D group was *ca* 20% D. In a blank experiment in which $[RhH(PEt_3)_3]$ was heated in ethanol under D_2–CO in the absence of hex-1-ene D was incorporated into the ethanol OH group but only to the extent of 5%. In the reaction of heptanal with CO–D_2 the recovered ethanol was 85% EtOD.

Kinetic studies. An autoclave was attached to a ballast tank (130 cm^3) with a valve between them capable of maintaining a predetermined constant pressure within the autoclave. The autoclave was charged with a solution of $[RhH(PEt_3)_3]$ (0.004 mol) in ethanol (30 cm^3). Free PEt_3 (0.04 mol) was added if required and the autoclave was pressurised to 40 atm with CO–H_2 (1 : 1). It was then heated to 120 °C with stirring using an internal paddle stirrer (1000 r.p.m.). Once the temperature had stabilised, hex-1-ene (3 cm^3) was injected into the reaction and the pressure raised to 60 atm, at which it was held throughout the reaction. The pressure in the ballast vessel (held at 20 °C) was monitored and could be used to calculate the gas uptake within the autoclave.

For ethene or propene, the reactor was charged with ethanol and PEt_3 if required. It was then pressurised with ethene (9–10 g) or propene (6.5 g) was condensed into it. The autoclave was then heated to 120 °C at which time the pressure was 32 (ethene) or 15 atm (propene). The complex $[RhH(PEt_3)_3]$ in ethanol (3 cm^3, 0.02 mol dm^{-3}) was injected into the autoclave using CO–H_2 and the pressure set at 80 atm (≈ 50 atm, CO : H_2 = 1 : 2) for ethene, 55 atm (propene, CO : H_2 = 1 : 1) or 75 atm (propene, CO : H_2 = 1 : 2). In all cases the reactions were stirred at 1000 r.p.m. except for the propene reaction with CO : H_2 = 1 : 2 when the stirring rate was 400 r.p.m. A larger ballast vessel (450 cm^3) was used for all these reactions.

For the reaction with ethene there was a rapid rise in temperature (to >160 °C) on addition of the catalyst but forced cooling returned the temperature to 120 °C within 2 min of the addition.

After all of the reactions the autoclaves were opened and the products analysed by GLC as described above.

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