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**Alcohols  
from  
Rhodium Catalysed  
Hydroformylation  
and  
Transfer Hydroformylation**

a thesis presented by

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to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews

October 1991



## DECLARATION

I, Joanna Katherine MacDougall, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed ..... Date 14th October 1991

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on 1st October 1988 and as a candidate for the degree of Ph.D. on 29th September 1989.

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To  
Iain,  
Arthur, Howard, Dugald and Ellen.

## ACKNOWLEDGEMENTS

I would like to thank Professor David J. Cole-Hamilton for giving me the opportunity to return to chemistry after my absence for raising my family. I am very grateful for his guidance, encouragement and enthusiasm during the course of my studies at St. Andrews. I would also like to thank my industrial supervisor, Dr. Michael J. Green, for his invaluable ideas and assistance.

I would also like to thank all those who have helped and encouraged me in relearning old techniques and acquiring new ones:- All the members of the DCH's group; in particular Peter Pogorzelec, Therese Arliguie and Imelda Utuk, who got me going.

The technical staff in the Chemistry Department; in particular Colin Smith (glassblowing), Melanja Smith (nmr), Colin Millar (GCMS), Sylvia Smith (micro analysis), Jim Rennie, Bobby Cathcart and Dave Clarke (workshop) and Jim Bews (computing).

Neil Cooley and Jill Laurie for their assistance with autoclave work, also Andy Lucy and Jane Boyle for help with high pressure nmr studies at B.P. Research Centre, Sunbury.

Special thanks go to my husband, Iain, for his faith in me, unstinting encouragement and support at home, to my children for their amused interest and to Dad for holding the fort while I was in the department.

I am indebted to B.P. Research Centre, Sunbury and the S.E.R.C. for a C.A.S.E. award.

## ABBREVIATIONS

acac	acetylacetonate.
$\text{BPh}_4^-$	tetraphenylborate.
CO	carbon monoxide.
dppp	1,3-bis(diphenylphosphine)propane.
DMF	dimethylformamide.
DMPE	bis(dimethylphosphino)ethane.
$\text{Et}_3\text{PO}$	triethylphosphine oxide.
GCMS.	gas chromatography - mass spectroscopy.
glc.	gas liquid chromatography.
$\text{H}_3\text{PO}_4$	phosphoric acid.
I.R.	infra-red.
n:i	normal to iso = straight to branched chain ratio.
nmr.	nuclear magnetic resonance.
OAc	ethanoate.
$\text{PCy}_3$	tricyclohexenylphosphine.
$\text{PEt}_3$	triethylphosphine.
$\text{PEtPh}_2$	ethyldiphenylphosphine.
$\text{PEt}_2\text{Ph}$	diethylphenylphosphine.
$\text{P}^i\text{Pr}_3$	triisopropylphosphine.
$\text{PMe}_3$	trimethylphosphine.
$\text{PMePh}_2$	methyldiphenylphosphine.
$\text{P}^n\text{Bu}_3$	tri-n-butylphosphine.
$\text{P}^n\text{Pr}_3$	tri-n-propylphosphine.
$\text{PPh}_3$	triphenylphosphine.
$\text{P}^t\text{Bu}_3$	tri-tertiary-butylphosphine.
thf	tetrahydrofuran.
thf-d8	perdeuterotetrahydrofuran.
TMS	tetramethylsilane.
WGSR	water gas shift reaction.

## ABSTRACT

One step hydroformylation of hex-1-ene using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, with  $\text{CO}/\text{H}_2$  in the gas phase is shown to give complete conversion to  $\text{C}_7$  alcohols, and transfer hydroformylation with  $\text{CO}$  and alcohols, as the hydrogen source, to give >60% conversion to  $\text{C}_7$  alcohols.

The effect on product distribution on hydroformylation of hex-1-ene using  $\text{Rh}_2(\text{OAc})_4$  with varying trisubstituted phosphine ligands in ethanol as solvent is studied. The effects of varying solvent, ratio of added  $\text{PEt}_3:\text{Rh}$ , reactant gas pressure, catalyst concentration and reaction temperature when using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor for the hydroformylation of hex-1-ene are investigated. The hydroformylation of other alkenes, and the hydrogenation of heptanal with this catalytic system are reported.

Studies of the transfer hydroformylation of hex-1-ene with an alcohol as the hydrogen source, and only  $\text{CO}$  in the gas phase, using  $\text{RhH}(\text{PEt}_3)_3$ , without and with free excess  $\text{PEt}_3$ , as catalyst precursor, including comparisons of differing alcohols as hydrogen source, show that primary alcohols are more effective hydrogen donors than propan-2-ol with this catalytic system. The effect of varying  $\text{CO}$  pressure, temperature, catalyst concentration and reaction time are studied. Transfer hydroformylation of other alkenes and transfer hydrogenation of heptanal are demonstrated.

Deuteration studies suggest that  $\text{C}_7$  aldehyde is not formed as a reaction intermediate in hydroformylation. Mechanisms are proposed for the hydrogenation of heptanal and one step hydroformylation/transfer hydroformylation of hex-1-ene to  $\text{C}_7$  alcohols, suggesting a rhodium-hydroxycarbene intermediate. Nmr studies of catalytic species and model studies of possible intermediates are included.

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Chapter 1. Literature survey of hydroformylation producing alcohols under mild conditions.

1.1 Introduction.

The hydroformylation reaction was discovered in 1938 when Roelen was investigating the source of oxygenated by-products from the Fischer-Tropsch synthesis<sup>1</sup>. The process is given the name hydroformylation as it involves the addition of one hydrogen and a formyl group to an alkene double bond. Thus an alkene, with CO and H<sub>2</sub>, yields aldehydes, which may be further hydrogenated to alcohols. This addition may take place to yield two possible products if the alkene is not symmetrical. Markownikoff addition to a terminal alkene leads to a branched (iso) product with a 2-methyl group, while anti-Markownikoff addition gives a straight chain (normal) product, as shown in figure 1.1.. The normal isomer is generally the desired product.

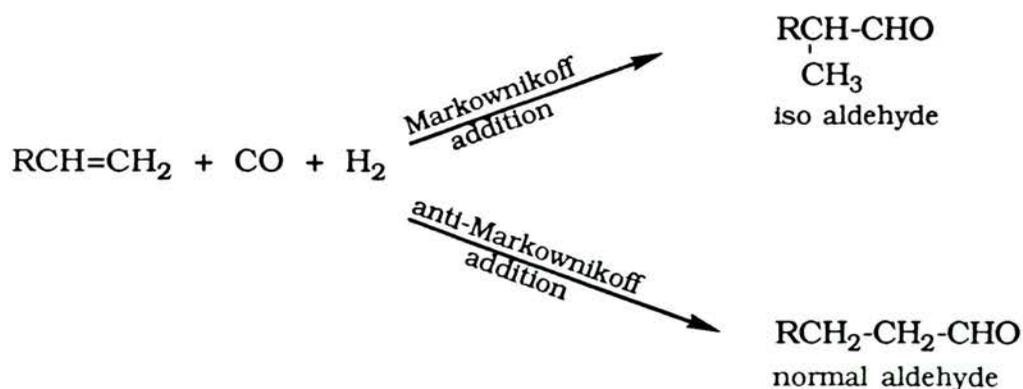


Figure 1.1.

Experiments showed that this reaction was homogeneously catalysed by cobalt carbonyl species. High pressures (250-350 atmos.) and temperatures in the range 140-180°C are required to hydroformylate alkenes to give aldehydes (80%) as the major product with some alcohol formation (10%). These catalytic systems give products with n:i (normal to iso) ratio of 3-4:1<sup>2</sup>. The addition of trisubstituted phosphine ligands improves the n:i ratio of products to

6-8:1, but although the reactant gas pressure may be lowered (50-100 atmos.), higher temperatures are required, in the range 160-200°C, and the product is hydrogenated to alcohol (80%) with some concurrent hydrogenation of substrate to alkane (15%)<sup>2</sup>.

Rhodium catalysts modified with trisubstituted phosphine ligands allow milder conditions (15-25 atmos. and 80-120°C) to be employed with far lower catalyst concentrations being required, due to the greater reactivity of rhodium compared with cobalt (rhodium is ~100 times more reactive than cobalt). These systems give aldehyde as product with n:i ratios in the range 10-14:1<sup>2</sup>. Commercially a system based on  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  is now used to produce butanal from propene. As rhodium catalysts decompose at the temperatures required for stripping long chain products from the catalytic solution cheaper cobalt systems are employed to produce longer chain alcohols.

Considering the milder conditions of temperature and pressure favoured by the rhodium systems in the production of aldehydes, it is of interest to review the direct production of alcohols under mild conditions, particularly those catalysed by rhodium based systems.

### 1.2. Rhodium based systems using CO/H<sub>2</sub> in the gas phase.

In 1965 Osborn, Wilkinson and Young<sup>3</sup> reported that hydroformylation of hex-1-ene with CO/H<sub>2</sub> (1:1) at 90 atmos. in benzene/ethanol (1:1) as solvent catalysed by 1,2,3-(PPh<sub>3</sub>)<sub>3</sub>RhCl<sub>3</sub> or 1,2,6-Py<sub>3</sub>RhCl<sub>3</sub> (or with Rh<sub>2</sub>Cl<sub>2</sub>(SnCl<sub>2</sub>,EtOH)<sub>4</sub> in ethanol) at 55°C yielded aldehydes (90%, n:i 3.5) as product, while at ~100°C alcohols were formed. These same catalytic precursors were also shown to hydrogenate heptanal at 110°C with H<sub>2</sub> at 50 atmos.. Comment was made that the product alcohol could also be used as solvent and then stripped off leaving the catalyst in situ. (This work was subsequently

patented<sup>4</sup>).

A U.S. patent was published the following year<sup>5</sup> claiming production of aldehydes, with lesser amounts of alcohols, on hydroformylation of terminal alkenes, using a rhodium-carbonyl-n-butylphosphine complex as catalyst. This catalyst was formed in situ by heating  $\text{RhCl}_3$  and  $\text{P}^n\text{Bu}_3$  (1:2) with a sixfold excess of sodium ethanoate, as stabiliser, in octane in the hydroformylation vessel at  $195^\circ\text{C}$  under  $\text{CO}/\text{H}_2$  (1:2.1) at 30 atmos. It was then used to hydroformylate pent-1-ene to  $\text{C}_6$  aldehydes (~60%) and  $\text{C}_6$  alcohols (~25%) in 12 hours. Hydroformylation of but-1-ene in n-hexane with a higher proportion of  $\text{P}^n\text{Bu}_3$  in the reaction mixture, such that the ratio of  $\text{Rh}:\text{P}^n\text{Bu}_3:\text{CH}_3\text{COONa}$  was 1:8:8, was reported to produce predominantly n-pentanal when  $\text{CO}/\text{H}_2$  (2.1:1) at  $195^\circ\text{C}$  was employed.

During the same period research at B.P. was showing similar rhodium systems to produce alcohols at much lower temperatures<sup>6</sup>. It was found that  $[\text{Rh}(\text{CO})(\text{RCOO})]_2$ , where  $\text{RCOO}$  = an organic carboxylate ligand, with added trialkylphosphine ligand would catalyse the hydroformylation of terminal alkenes to give aldehydes and/or alcohols. Reaction temperatures of  $<100^\circ\text{C}$  with  $\text{CO}/\text{H}_2$  (1:2) at  $<40$  atmos. were employed. By varying the phosphine and carboxylate ligands, and altering the solvent, the proportion of alcohol in the product could be increased. Table 1.1. shows that, of the trialkylphos-

Table 1.1. Effect of varying phosphine ligand in heptane as solvent.

Phosphine ligand (L)	time /hours	temp. / $^\circ\text{C}$	pressure /atmos.	% yield		
				hexane	aldehyde(n:i)	alcohol(n:i)
$\text{PEt}_3$	6	90	41-22	2	6 (0)	92 (2.4)
$\text{P}^n\text{Pr}_3$	5.5	95	40-22	2	3 (0)	95 (2.2)
$\text{P}^n\text{Bu}_3$	6	95	40-20	2	7 (0)	91 (2.5)

$[\text{Rh}(\text{L})_2(\text{CO})(\text{CH}_3\text{COO})]$ , 2.0 g in heptane,  $30\text{ cm}^3$ ; hex-1-ene,  $15\text{ cm}^3$ ;  $\text{CO}/\text{H}_2$ , (1:2).

Table 1.2. Effect of varying carboxylic acid ligand in octanol as solvent.

Carboxylate ligand	time /hours	Temp. /°C	% yield				
			hexane	aldehyde(n:i)		alcohol(n:i)	
(C <sub>2</sub> H <sub>5</sub> COO) <sup>-</sup>	2	88	1	41	(0.9)	51	(7.5)
	4	88	2	14	(0.1)	80	(3.4)
(C <sub>3</sub> H <sub>7</sub> COO) <sup>-</sup>	0.5	94	tr	73	(2.2)	20	(9.0)
	4	94	2	4	(0.0)	93	(2.9)
(C <sub>7</sub> H <sub>15</sub> COO) <sup>-</sup>	2	90	1	31	(0.3)	61	(4.1)
	4	90	2	16	(0.1)	79	(2.6)
(PhCH=CHCOO) <sup>-</sup>	1	88	3	75	(1.8)	17	(17.0)
	4	88	3	27	(0.3)	70	(4.4)
(HCOO) <sup>-</sup>	21.5	93	tr	86	(1.8)	nil	
(CF <sub>3</sub> COO) <sup>-*</sup>	4	80	2	97	(2.2)	2	(∞)

[Rh(P<sup>n</sup>Bu<sub>3</sub>)<sub>2</sub>(CO)(RCOO)], 2.0 g in octanol, 30 cm<sup>3</sup>; hex-1-ene, 15 cm<sup>3</sup>; CO/H<sub>2</sub> (1:2), 33 atmos.; tr, trace.

\* CO/H<sub>2</sub> (1:1), 33-20 atmos.

phine ligands listed, P<sup>n</sup>Pr<sub>3</sub> gave the highest yield of alcohol in the shortest time. Each of these basic phosphine ligands gave some hydrogenation of hex-1-ene to hexane and some unhydrogenated aldehyde remained at the end of the hydroformylation reaction when heptane was used as solvent.

Comparison was made of various carboxylate ligands, coordinated together with P<sup>n</sup>Bu<sub>3</sub> and CO on the rhodium centre. Octanol was employed as solvent, and as may be seen in table 1.2. there was good conversion to alcoholic products in reactions lasting 4 hours. Shorter reactions yielded aldehyde in greater proportion and indicate that the formation of alcohol was via an aldehydic intermediate, the straight chain aldehyde being hydrogenated faster than the branched form. The butanoate ligand appeared to give the best yield of alcohol in 4 hours, when used in conjunction with tri-n-butylphosphine, while

Table 1.3. Effect of varying solvent and phosphine ligand with Rh(L)<sub>2</sub>(CO)(PhCH=CHCOO) as catalyst.

solvent	ligand (L)	time /hours	Temp. /°C	P. /atmos.	% yield hexane	aldehyde(n:i)	alcohol(n:i)
heptane	PEt <sub>3</sub>	8	95	41-23	2	3 (0.0)	95 (4.4)
heptane	P <sup>n</sup> Bu <sub>3</sub>	9	86	33	2	47 (0.9)	51 (6.3)
octanol	P <sup>n</sup> Bu <sub>3</sub>	4	88	33	3	27 (0.3)	70 (2.4)

[Rh(L)<sub>2</sub>(CO)(PhCH:CHCOO)], 2.0 g in solvent, 30 cm<sup>3</sup>; hex-1-ene, 15 cm<sup>3</sup>; CO/H<sub>2</sub>, (1:2) at pressure P..

methanoate and trifluoroethanoate gave little or no product alcohol. The substitution of fluorine on the methyl group of the ethanoate anion causes electron withdrawal from the carboxylate group thus forming a less basic anion.

All the reactions listed in table 1.2. were run for shorter times than those shown in table 1.1., which were carried out in heptane as solvent. The use of an alcoholic solvent would appear to enhance production of C<sub>7</sub> alcohol from hex-1-ene. This was confirmed by the results for Rh(P<sup>n</sup>Bu<sub>3</sub>)<sub>2</sub>(CO)(PhCH=CHCOO), shown in table 1.3.. A far greater yield of C<sub>7</sub> alcohol was recorded, in a shorter reaction time, using octanol as solvent when compared with a reaction carried out in heptane, with the other conditions being unaltered.

Table 1.3. also shows that on changing from P<sup>n</sup>Bu<sub>3</sub>, as the added phosphine ligand, to PEt<sub>3</sub>, in heptane as solvent, with slightly altered reaction conditions, a yield of 95% C<sub>7</sub> alcohol was achieved, confirming the slightly better results found on changing from P<sup>n</sup>Bu<sub>3</sub> to PEt<sub>3</sub> with ethanoate as the carboxylate ligand.

This work by Johnson and Lawrenson showed that both an alcoholic solvent and rhodium coordinated to basic ligands (phosphines and/or carboxylate) were found to promote the formation

of alcoholic products on hydroformylation of terminal alkenes. It is worth noting that in all these reactions the maximum ratio of P:Rh was 2:1.

Lawrenson<sup>7</sup> went on to show that similar systems to those discussed above, in nonalcoholic solvent, at low catalyst concentration, would yield only aldehydes. For this to occur a ratio of catalyst to alkene of the order of 1:100,000 was required, while for alcohol production in earlier work, ratios of 1:360-3600 had been employed.

Similar systems formed from rhodium carbonyls with neutral phosphorus, nitrogen, arsenic, antimony or sulphur donor ligands, as modifier, were patented during the same period by Foster and Lawrenson<sup>8</sup>. The preferred type of modifier was a trialkylphosphine and reactions were carried out within a temperature range of 60-150°C with CO/H<sub>2</sub> (in the ratio range 4:1-1:4) at pressures of 0-50 atmos.. The solvents covered by this patent were aromatic and aliphatic hydrocarbons, aliphatic alcohols, disubstituted amines and carboxylic acids. The latter two examples could also provide coordinating species which had been suggested in the earlier patents published by Lawrenson. Two examples of hydroformylation of hex-1-ene at ~82°C were quoted in this patent. In the first example PPh<sub>3</sub> was used as modifier in heptane, with CO/H<sub>2</sub> (1:1) in the pressure range 41-14 atmos., when C<sub>7</sub> aldehydes (n:i 3.2) were produced in a 6 hour experiment. Contrasted with this was a reaction using P<sup>n</sup>Bu<sub>3</sub> as modifier in octan-1-ol, with CO/H<sub>2</sub> (1:2) in the pressure range 44-25 atmos.. This combination led to the production of C<sub>7</sub> alcohols (81%, n:i 2.5), with lesser amounts of C<sub>7</sub> aldehydes (19%, n:i=0.1) forming, in 12 hours. In these reactions the ratio of Rh:P was 1:1.68 for PPh<sub>3</sub> and 1:2.26 for P<sup>n</sup>Bu<sub>3</sub>.

Bidentate ligands, such as β-diketones, which can coordinate to rhodium through at least one oxygen atom were also shown to be

suitable ligands for catalysing the hydroformylation of alkenes to aldehydes and alcohols when used in conjunction with basic ligands such as trialkylamines, trialkylphosphines or heterocycles containing nitrogen<sup>9</sup>. Alcoholic solvents were again found to promote formation of alcohols, with monohydric alcohols containing 4-20 carbon atoms being preferred as lower alcohols tended to form acetals with the aldehydic intermediate. These reactions were also shown to proceed via an aldehyde, which was then hydrogenated to alcohol. Table 1.4. shows the effect of altering solvent, phosphine ligand and bidentate ligand. The more basic phosphine ligand, in an alcoholic solvent, gave almost complete conversion of hex-1-ene to C<sub>7</sub> alcohol under mild conditions of temperature and pressure in 11 hours, and trialkylphosphines were generally preferred over amines and nitrogen containing heterocycles. Selectivity was shown to be dependent on the ratio of catalyst to substrate with ratios of 1:100-5000 yielding alcohols. Aldehydes were produced with catalyst to substrate ratios of 1:50,000-500,000. The ratio of CO:H<sub>2</sub> in the reactant gas mixture also had some influence on the products, with aldehydes being favoured with CO/H<sub>2</sub> in the ratio 1:1, and alcohols when the ratio was 1:2, as

Table 1.4. Hydroformylation of hex-1-ene using catalysts of the type Rh(PR<sub>3</sub>)(CO)(acetylacetonate).

Ligand	solvent	temp. /°C	pressure /atmos.	time /hours	% yield hexane	aldehyde (n:i)	alcohol (n:i)
P <sup>n</sup> Bu <sub>3</sub>	n-heptane	85	41-21	1	2	74 (2.1)	4 (∞)
P <sup>n</sup> Bu <sub>3</sub>	n-octanol	72	41-21	11	1	nil	99 (2.4)
PPh <sub>3</sub>	n-heptane	85	41-21	4.5	2	97 (2.2)	nil
P <sup>n</sup> Bu <sub>3</sub> *	n-heptane	69-70	41-24	12	1	32 (0.1)	67 (0.8)

Rh(PR<sub>3</sub>)(CO)(acac):hex-1-ene ratio 1:360; acac, CH<sub>3</sub>COCHCOCH<sub>3</sub>; CO/H<sub>2</sub>, (1:2)

\* Rh(PR<sub>3</sub>)(CO)(3-Etacac):hex-1-ene ratio 1:400; 3-Etacac, CH<sub>3</sub>COC(CH<sub>2</sub>CH<sub>3</sub>)COCH<sub>3</sub>.

might be expected. The ratio of phosphine to rhodium was just 1:1 and increased isomerisation activity of these catalysts was noted.

A further patent was published by Lawrenson<sup>10</sup> concerning the improvement of n:i ratios of products, from 1.31 to 1.95, by rigorous removal of oxygen from the system catalysed by  $\text{Rh}(\text{P}^n\text{Bu})(\text{CO})(\text{acac})$ .

Lawrenson also used a system based on  $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\text{PR}_3)$ <sup>11</sup>, R = alkyl or cycloalkyl with < 10 carbon atoms. Aliphatic or aromatic hydrocarbon, or alcohol, was used as solvent for the hydroformylation of terminal alkenes with 2-20 carbon atoms in the temperature range 60-140°C and  $\text{CO}/\text{H}_2$  (1:1-4) at 0-102 atmos.. Propene was reported to be hydroformylated to butanols at 82-86°C at  $\text{CO}/\text{H}_2$  (1:1) pressure 88-64 atmos. (falling during the reaction) using n-heptane as solvent, although the main claims of this patent are for aldehyde production.

A system based on rhodium carbonyls modified with trialkyl- or triarylphosphine ligands was patented by Smith<sup>12</sup>, for the hydroformylation of 2-propen-1-ol to yield mainly diols as product.  $\text{Rh}_6(\text{CO})_{16}$  with  $\text{PBU}_3$  in benzene at 125°C, with  $\text{CO}/\text{H}_2$  at ~63 atmos., was reported to hydroformylate 2-propen-1-ol to 1,4-butanediol (41%) and 2-methyl-1,3-propanediol with hydrogenation of the 2-propen-1-ol to propan-1-ol (38%) and formation of 2-methylpropan-1-ol (6%) also occurring.

Hydroformylation systems based on rhodium-carbonyl-tertiary amine complex catalysts were studied and reported by Fell and Guerts<sup>13</sup> during the early 1970s. One step synthesis of alcohols was carried out at temperatures of <100°C and were expected to find wide application because of the mild reaction conditions. Jurewicz et al.<sup>14</sup> published information on systems modified by monomeric and polymeric amines, with dimethylbenzylamine used as an example. It was found that variation in basicity and concentration of the amine used affected the rate of hydrogenation of aldehyde formed during

hydroformylation. I.R. studies showed that anionic rhodium clusters were formed on addition of amine to the catalytic mixture.

Patents for systems based on rhodium, using amine promoters, were published in 1982 and 1984. These patents deal with adaptations to the system, the former<sup>15</sup> covering recycling of catalyst, and the latter<sup>16</sup> the dehydrogenation of alkane over a heterogeneous bimetallic catalyst prior to hydroformylation yielding almost exclusively alcoholic products. In both patents the hydroformylation was carried out using a catalyst formed in situ from a rhodium salt (eg nitrate, halide, ethanoate or carbonyl) with an amine promoter (eg trialkyl, triaryl, heterocyclic or cycloalkyl). The specific examples cited were of  $[\text{RhCl}(\text{CO})_2]_2$  with dimethyldodecylamine,  $\text{N}(\text{CH}_3)_2(\text{C}_{12}\text{H}_{25})$ , in the ratio 1:30-300, hydroformylating  $\text{C}_{11}$  alkenes (catalyst to alkene ratio 1:300-3000) to  $\text{C}_{12}$  alcohols in 3 hours using  $\text{CO}/\text{H}_2$  (1:1) at 150 atmos. and  $150^\circ\text{C}$ . These conditions are fairly forcing but the patents cover a pressure range of 10-300 atmos., some of which could be made up of inert gas such as nitrogen, helium or argon, and a temperature range of  $50\text{-}350^\circ\text{C}$ . Organophosphine modifiers were specifically excluded as they were thought to suppress selectivity to alcohol.

Imai also patented work on alcohol formation using  $[\text{RhCl}(\text{CO})_2]_2$  modified with nitriles<sup>17</sup>.  $\text{C}_{11}$  alkenes were hydroformylated to  $\text{C}_{12}$  aldehydes (80%) and  $\text{C}_{12}$  alcohols (20%) over  $[\text{RhCl}(\text{CO})_2]_2$ , but when the system was modified with succinonitrile the selectivity for  $\text{C}_{12}$  alcohols increased to 81%.

2-propen-1-ol may be directly hydroformylated to 1,4-butanediol using a rhodium system modified with a tri-n-alkylphosphine, when a carbonitrile is used as solvent, as patented by Drent<sup>18</sup> in 1985. Reactions covered by this patent favour ratios of Rh:substrate in the range 1:100-1000, and of Rh:P of at least 1:3, with 1:>5 being

preferred. The temperature range of 30-150°C and CO/H<sub>2</sub> within a pressure range of 20-70 atmos. are covered, with CO/H<sub>2</sub> ratios of 5:1 to 1:5, 1:2 being the most desirable for production of 1,4-butanediol. An example quoted used Rh(acac)(CO)<sub>2</sub> with P<sup>n</sup>Bu<sub>3</sub> as modifier in nonacarbonitrile as solvent. This catalytic mixture hydroformylated 2-propen-1-ol with CO/H<sub>2</sub> (1:2) at 60 atmos. at 95°C to 1,4-butanediol in 69% yield in 5 hours.

### 1.3. Ruthenium and platinum based systems using CO/H<sub>2</sub> in the gas phase.

Ugo et al. reported<sup>19</sup> partial hydrogenation of aldehydes formed on hydroformylation of oct-1-ene in toluene with [η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ru(CO)<sub>2</sub>]<sub>2</sub> at CO/H<sub>2</sub> (1:1) pressures of ~100 atmos and temperatures in the range 130-180°C, to give C<sub>9</sub> alcohols. Alcohol production was enhanced above 150°C. At this temperature the cyclopentadienyl ligand was lost from the ruthenium centre and Ru<sub>3</sub>(CO)<sub>12</sub> was shown to be the major species present.

Wilkinson's group reported on a similar system in 1976<sup>20</sup> where Ru<sub>3</sub>(CO)<sub>12</sub>, with various substituted phosphine and phosphite ligands, in benzene was shown to hydroformylate alkenes to aldehydes. CO/H<sub>2</sub> (1:1) at 100 atmos was used with the temperature at 120°C. The ligand P(OR)<sub>3</sub>, R = 2-naphthyl, was found to promote hydrogenation of product aldehyde to alcohol. Also studied by this group, and found to be more efficient hydroformylation catalysts were ruthenium/PPh<sub>3</sub> systems. Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> was found in catalyst solutions in benzene after hydroformylation with CO/H<sub>2</sub> (1:1) at 100 atmos. at 120°C. No reduction to alkane was observed but catalyst precursors RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> and RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> promoted further hydrogenation of product aldehydes to alcohols. The reactions were thought to be two step as Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> was shown to hydrogenate propanal to propan-1-ol

with 99% conversion with just H<sub>2</sub> in the gas phase at 50 atmos and 150°C. RuH<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was the ruthenium species recovered after this hydrogenation reaction.

Knifton's work on ruthenium carbonyl catalyst systems in quaternary phosphonium salts (eg. Bu<sub>4</sub>P<sup>+</sup> Br<sup>-</sup>) as dispersant was based on a trinuclear carbonyl, in the form [HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup>, with [Ru(CO)<sub>3</sub>Br]<sup>-</sup> also studied. The aim of this work<sup>21</sup> was to produce linear alcohols from internal alkenes, the high boiling melt providing a very polar solvent from which the products could be distilled, leaving undegraded catalyst in solution. Best conversions of octene mixtures to C<sub>9</sub> alcohols were achieved with RuO<sub>2</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, Ru(acac)<sub>3</sub> and RuO<sub>2</sub> with PBu<sub>3</sub> (Ru:P 1:2). Chelating ligands such as 2,2'-bipyridyl and tris(2-diphenylphosphinoethyl)phosphine were found to improve linearity of the product alcohols but at reduced yield, while PBu<sub>3</sub> at higher concentrations reduced activity until at Ru:P 1:5 gave almost zero conversion.. These reactions were carried out at with CO/H<sub>2</sub> (1:2) at 83 atmos at the relatively high temperature of 180°C.

Work published by Knifton in the following year<sup>22</sup> showed 60-80% conversions of oct-1-ene to C<sub>9</sub> alcohols under similar conditions of temperature and pressure. The presence of the quaternary phosphonium salt, the character of ruthenium source and the type of N-promoter were all found to be of importance in controlling product distribution, with bidentate heterocyclic nitrogen containing ligands such as 2,2'-bipyridyl and 2,2'-bipyrimidine together with RuO<sub>2</sub> or Ru<sub>3</sub>(CO)<sub>12</sub> as catalyst precursors dispersed in a Bu<sub>4</sub>P<sup>+</sup> Br<sup>-</sup> melt giving best conversion to C<sub>9</sub> alcohols. The relative positioning of nitrogens in bipyridyl was shown to affect the conversion and the linearity of the product, with highest conversion and greatest linearity being observed in the order 2,2'- > 2,3'- > 2,4'- bipyridyl. Bidentate phosphine ligands of the type Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> were less effective promoters with

maximum conversion to C<sub>9</sub> alcohols ~60% with n = 5. At temperatures above 160°C greater conversion to alcohol over aldehyde production was achieved but the substrate was also hydrogenated to alkane to a greater extent with decreasing linearity of products, implying more isomerisation of substrate. Lower ratios of CO/H<sub>2</sub> (eg ~1:3) and high ruthenium concentration also helped alcohol production. The reaction was again thought to be a two step process via aldehydic intermediates.

Recently a platinum complex has been shown to hydroformylate styrene to give phenylpropanals, with lesser amounts of phenylpropanols also being produced<sup>23</sup>. Reactions were carried out using Pt(C<sub>2</sub>H<sub>4</sub>)(PP), where PP = 1,2-bis[(diphenylphosphino)methyl]benzene or (+)-DIOP = (+)-1,4-bis(diphenylphosphino)-1,4-diethoxy-2,3-O-isopropyliden-D-threitol, modified with methylsulphonic acid, CH<sub>3</sub>SO<sub>3</sub>H, in toluene as solvent, with CO/H<sub>2</sub> (1:1) at 100 atmos. at 100°C. As shown in table 1.5., the hydroformylation to aldehydic products was fairly fast, while the production of alcohols was brought about by a far slower hydrogenation step of low efficiency, there being

Table 1.5. Hydroformylation of styrene using Pt(C<sub>2</sub>H<sub>4</sub>)(PP) with CH<sub>3</sub>SO<sub>3</sub>H as catalyst.

(PP)	time /hours	% styrene conversion	% yield products			
			ethylbenzene	aldehyde (n:i)	alcohol (n:i)	high boiling
1	24	99.8	4.4	64.0 (3.9)	12.0 (16.2)	19.4
(+)-DIOP	4	80.0	2.9	67.3 (7.5)	2.9 (27.5)	6.9
(+)-DIOP	24	91.4	3.7	52.7 (5.7)	11.6 (18.2)	23.4
(+)-DIOP	72	97.5	4.5	44.3 (5.0)	18.3 (17.2)	30.4

Styrene 16 mmol.; Pt:styrene = 1:320; Pt:CH<sub>3</sub>SO<sub>3</sub>H = 1.1; solvent, toluene (20 cm<sup>3</sup>); CO/H<sub>2</sub> (1:1), 100 atmos..

1 = 1,2-bis[(diphenylphosphino)methyl]benzene; (+)-DIOP = (+)-1,4-bis(diphenylphosphino)-1,4-diethoxy-2,3-O-isopropyliden-D-threitol.

considerable formation of high boiling condensation products.

#### 1.4. Systems using only CO in the gas phase.

Various groups have researched the use of rhodium water gas shift reaction (WGSR) catalysts as possible hydroformylation catalysts with water as the hydrogen source, when the reaction becomes known as hydrohydroxymethylation if alcohols are produced. Some of these systems which produce alcohols are discussed here.

Hydrohydroxymethylation was reported by Reppe<sup>24</sup> who used the inefficient system consisting of  $\text{Fe}(\text{CO})_5$  with base as catalyst. High temperature ( $\sim 170^\circ\text{C}$ ) and CO pressure (250-350 atmos.) were required for this reaction, as was shown in a patent, for the hydrohydroxymethylation of propene, in a solution containing trimethylamine and methanol with water, published by Reed and Lenel<sup>25</sup>. Kutepow and Kindler<sup>26</sup> reported the reaction occurring under milder conditions (CO at 15 atmos. and  $100^\circ\text{C}$ ) with N-butylpyrrolidine and water when propene was converted to  $\text{C}_4$  alcohols in 90% yield. The reaction was found to be catalysed by species of the type  $[\text{NR}_3\text{H}]^+ [\text{HFe}_3(\text{CO}_{11})]^-$ . Similar catalytic species were reported by Lapidus et al.<sup>27,28</sup> from their studies of the hydroformylation of propene to butanols at  $120^\circ\text{C}$  with CO in the pressure range 3.5-30 atmos.. Maximum yield of  $\text{C}_4$  alcohols (90%) was achieved with CO at 20 atmos. using DMF as solvent. A variety of solvents was studied with DMF aiding best conversion and highest n:i ratio of product alcohols.

Laine reported he had improved on the original  $\text{Fe}(\text{CO})_5$  based reaction by using a system catalysed by basic  $\text{Rh}_6(\text{CO})_{16}$ <sup>24</sup>, a WGSR catalyst. He found that pentene was converted to  $\text{C}_6$  alcohols via  $\text{C}_6$  aldehydes. With methanol as solvent mixed with KOH solution at pH  $\sim 13$  and CO at  $\sim 55$  atmos., pentene was converted to  $\text{C}_6$  alcohols (hexan-1-ol and 2-methylpentan-1-ol) in 60% yield at  $135\text{-}150^\circ\text{C}$ .

Isomerisation of the substrate, prior to CO insertion, was suggested by the low selectivity to straight chain alcohol, and also by the production of traces of (<1%) 2-ethylbutan-1-ol. Other non aldehydic products were methyl hexanoate and methyl 2-methylpentanoate (1-5%), with ester production increasing at lower pH, ~10. At this lower pH the rate of hydrogenation through to alcoholic product was reduced to 20% of that at pH 13. This same system at pH 13 was shown to hydrogenate aldehydes readily at 135°C with CO at 55 atmos. and H<sub>2</sub>O as the hydrogen source. Preferential hydrogenation of straight chain aldehydes was observed. I.R. analysis of catalytic solutions suggested [Rh<sub>12</sub>(CO)<sub>34</sub>]<sup>2-</sup> as the reactive hydrohydroxymethylation species, this same species having been identified as important in the production of ethylene glycol from CO/H<sub>2</sub><sup>24</sup>. [HRh<sub>6</sub>(CO)<sub>15</sub>]<sup>-</sup> was found to be present in solution during the hydrogenation reaction.

Rh<sub>6</sub>(CO)<sub>16</sub> has also been used by Kaneda et al.<sup>29</sup> under WGSR conditions, with amine modifiers, for the hydrohydroxymethylation of alkenes to give alcoholic products under mild conditions. Again an alcoholic solvent, in this case 2-ethoxyethanol, was used but the reaction temperature (80°C) was lower than in Laine's reactions, as was the CO pressure (5 atmos.). The most efficient amine for promotion of alcohol production was N,N,N',N',-tetramethyl-1,3-propanediamine at pH 10.2 giving 84% yield of alcohol (n:i 2.8) while at pH 9.0 the yield of alcohol dropped to 58% (n:i 4.8) with aldehyde yield at 26% (n:i 1.9). This again suggests preferential hydrogenation of normal aldehyde. In both cases 16% yields of isomerised alkene were recorded. Pyridine related additives promoted aldehyde production, without hydrogenation on to alcohol, and generally increased isomerisation of substrate. Alcohol production was generally favoured at high pH.

This same type of system was used by Kaneda et al.<sup>30</sup> in the

direct formation of 1,4-butanediol from 2-propen-1-ol. Over 60% yield of 1,4-butanediol was achieved at 60°C with CO at 20 atmos., with water as hydrogen source, N,N'-tetramethyl-1,3-propanediamine used as catalyst promoter and 2-ethoxyethanol again added to the system. By altering the amine promoter to 4-dimethylaminopyridine butyrolactone could be preferentially formed at lower CO pressures in the temperature range 50-80°C. Thus the nature of the amine modifier was shown to determine the selectivity of the reaction.

### 1.5. Conclusions.

It would appear that hydroformylation reactions yielding alcoholic products take place via the hydrogenation of an aldehydic intermediate. Systems based on ruthenium and platinum give poorer yields, and require more forcing conditions, than those using modified rhodium catalysts.

The most efficient rhodium systems reported are those patented by Lawrenson and coworkers, which use a combination of basic trialkylphosphine and monocarboxylate ligands, together with an alcoholic solvent. The required catalyst concentration is also relatively high, aldehydes being formed when the ratio of catalyst to substrate is less than 1:3000. The maximum ratio of Rh:P used by Lawrenson was 1:2.26.

## Chapter 2. Hydroformylation reactions with CO/H<sub>2</sub>.

### 2.1. Introduction.

The overall aim of this work was to see if alcohols could be used as sources of hydrogen in hydroformylation reactions. For this to be investigated it first had to be ascertained what effect, if any, using an alcoholic solvent would have on the products of hydroformylation reactions.

It was decided that a rhodium system should be investigated as, compared with other commercially used hydroformylation systems based on cobalt carbonyls, both unmodified and modified with substituted phosphine ligands, those systems based on rhodium generally require less forcing conditions of temperature and pressure<sup>31</sup>. Also rhodium systems with phosphine ligands are known to dehydrogenate aqueous and alcoholic substrates<sup>32</sup>. It was found that RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor, with CO would catalyse the hydroformylation of hex-1-ene when ethanol was used as hydrogen source, so most of this work has been based on this catalyst precursor, although hydroformylation with CO/H<sub>2</sub> using rhodium ethanoate, Rh<sub>2</sub>(OAc)<sub>4</sub>, alone and with a variety of substituted phosphine ligands was also investigated.

#### 2.1.1. Autoclave system used at St Andrews.

The experiments were carried out in a stainless steel autoclave with a glass liner, a diagram of which is shown in figure 2.1. The autoclave was closed while empty, with the top screwed down tightly onto the rubber seal. Prior to priming with the reactants the autoclave was purged with the reactant gases by connecting the autoclave to a high pressure cylinder at connection A. The pressure in the autoclave was then reduced to atmospheric and cap B removed to allow

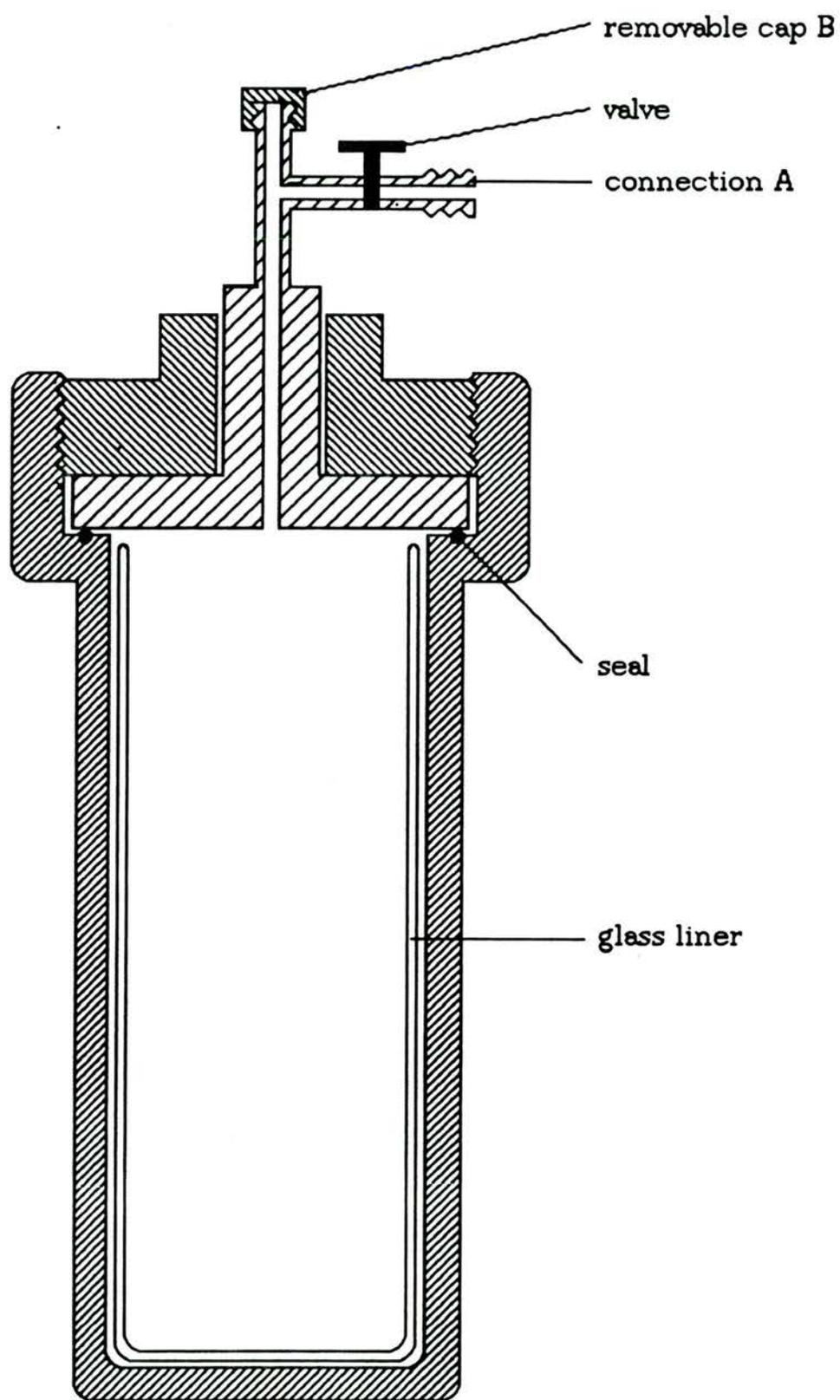


Figure 2.1.

injection of the substrate and catalyst solution under a light flow of the reactant gases. The removable cap B was then tightened and the autoclave pressurised as required for reaction. The autoclave was then fully sealed by closing the valve. It was next placed in a preheated oven where it remained for a timed period, after which it was removed and cooled to room temperature in a cold water bath. The pressure was then reduced to atmospheric by gently opening the valve and allowing the reaction gases to vent. The top was then unscrewed and the reaction mixture removed from the autoclave for analysis.

There were several problems with this system which should be noted. Firstly, because the autoclave was cold at the start of the reaction, there was a lot of uncertainty about the time taken to reach the recorded reaction temperature. A test run, with ethanol (5 cm<sup>3</sup>) in the glass liner and a thermocouple inserted via a sealed finger into a similar autoclave, showed that, in a fan-assisted oven it took 1.25 hours to reach the oven temperature of 125°C, from room temperature. In a non-fan-assisted oven the time taken more than doubled to over three hours (see appendix). Thus short reactions in a non-fan-assisted oven did not reach the recorded temperature.

Secondly the autoclave was not stirred and so the rate of diffusion of the reactant gases would determine the rate of reaction if this were slower than the rate determining step of the catalytic cycle. Both these problems were overcome in those reactions done in the more sophisticated rigs at B.P. Research Centre, Sunbury, where the catalyst solution could be heated, with stirring, under pressure and then the substrate introduced to the system, once the required conditions had stabilised. Stirring continued throughout the reaction, and the uptake of reactant gases could be monitored during the reaction.

There was also a problem with quantitative analysis stemming

from the autoclave. The solvent, particularly when a volatile one was used, tended to condense between the autoclave and the liner. On removal of the reaction mixture for analysis this condensate was added to the main bulk of the reaction mixture from the liner but inevitably small amounts were left in the autoclave thus effectively concentrating the products in the analysed solution, which in some cases led to an apparent conversion of over 100%. Also some volatile components may have been vented with the reactant gases and so slightly altered the concentrations recorded, leading to some inaccuracy in calculating percentage yields.

#### 2.2.1. Effect of varying solvent with $\text{RhH}(\text{PEt}_3)_3$ as catalyst precursor.

Most hydroformylation reactions are carried out in aprotic, nonpolar solvents. The effect of using an alcoholic solvent was investigated to see if it altered the distribution of products. Table 2.1. shows the products obtained when hex-1-ene was hydroformylated in a variety of solvents, using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, with  $\text{CO}/\text{H}_2$  (1:1) mixture at 30-40 atmos. and the oven temperature set at 115-122°C. The products were analysed using GCMS and quantified by glc.

It may be seen that in toluene, a nonpolar, aprotic solvent, the product was a mixture of heptanal and 2-methylhexanal, with an n:i ratio of ~2.2. A small amount of heptanal was hydrogenated through to heptanol but even in sixteen hours this was only a minimal percentage of the original hexene. In dry tetrahydrofuran, thf, which is significantly more polar than toluene, there was complete conversion of hex-1-ene in two hours to  $\text{C}_7$  aldehydes, n:i ratio of ~2.4. If the reaction mixture was heated for a total of sixteen hours there was almost complete hydrogenation of the initially formed  $\text{C}_7$  aldehyde to  $\text{C}_7$  alcohol, with only a small proportion of 2-methylhexanal remaining.

Table 2.1. Hydroformylation in varying solvents.

Solvent.	time /hours.	pressure CO/H <sub>2</sub> (1:1) /atmos.	C <sub>7</sub> aldehyde		C <sub>7</sub> alcohol	
			% yield	n:1	% yield	n:1
toluene	16	40	92	2.1	4	(heptanol)
	2	40	92	2.2	1	(heptanol)
thf	16	40	4	0.0	115	2.9
	2	40	101	2.4	-	-
thf/H <sub>2</sub> O	16	40	-	-	100	2.4
	2	40	46	1.1	50	7.5
t-butanol	16	40	-	-	105	2.4
i-propanol	16	30	-	-	99	2.4
methanol	16	30	-	-	105	2.4
ethanol	16	30	-	-	102	2.3
	2	40	-	-	101	3.0
n-butanol	16	30	-	-	102	2.2
n-heptanol	16	40	-	-	hexene all consumed	(1.8)
	2	40	tr	-	hexene all consumed	(2.0)

[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; hex-1-ene, 1 cm<sup>3</sup>; solvent, 4 cm<sup>3</sup>; temperature, 115-122°C; tr, trace.

When a 50:50 mixture of thf and distilled water was used as solvent there was faster formation of C<sub>7</sub> alcohol (50% in 2 hours) but the reaction was still obviously a two stage process with C<sub>7</sub> aldehyde being formed initially, this then being hydrogenated to C<sub>7</sub> alcohol in a second reaction, as may be seen from the products of the two hour reaction. The rate of hydrogenation of heptanal appeared to be greater than that of 2-methylhexanal. This was presumably because there was less steric crowding at the catalytic centre with the intermediate formed by coordination of straight chain aldehyde, thus allowing preferential hydrogenation of this species. By using a polar solvent the overall n:i ratio of the products (aldehyde and alcohol combined) was

improved marginally from 2.2 in toluene to 2.4-2.5 in thf and thf/water (This is only an increase from 68.8% to 71.4% of straight chain product and so is not significant.). It is worth noting that if the substrate and  $\text{RhH}(\text{PEt}_3)_3$  solution in thf were mixed and allowed to stand at room temperature isomerisation of hex-1-ene to hex-2-ene and hex-3-ene took place. Reactions carried out on solutions which had been mixed and allowed to stand overnight before pressurising with  $\text{CO}/\text{H}_2$  showed 2-ethylpentanal and a high proportion of 2-methylhexanal among the product aldehydes. Thus isomerisation took place readily in thf. The reactions in thf recorded in table 2.1. were, therefore, carried out on mixtures made up with hex-1-ene added to  $\text{RhH}(\text{PEt}_3)_3$  solution in the autoclave, followed by immediate pressurisation with  $\text{CO}/\text{H}_2$  and heating.

When an alcoholic solvent, which could act as a proton source, was employed there was complete conversion to  $\text{C}_7$  alcohol in sixteen hours which might have been predicted from the thf result, but it was also found that  $\text{C}_7$  alcohol was the only product in ethanol in a two hour experiment. Similarly in heptanol, all the hex-1-ene was consumed in two hours and there was evidence of only a trace of  $\text{C}_7$  aldehyde present. Thus it would appear that by using an alcohol as solvent there was fast hydroformylation, with hydrogenation, of hex-1-ene to  $\text{C}_7$  alcohol.

The n:i ratio of products did not improve significantly over ~2.5 in any of these solvents though the figure of 3.0 obtained in the 2 hour experiment in ethanol may have been due to slower conversion of isomerised hexene which was vented with the reaction gases and so not detectable. The n:i ratio figures listed for the reactions carried out in heptanol and shown in brackets were calculated from the concentration of 2-methylhexanol, assuming 100% conversion of the original hex-1-ene to  $\text{C}_7$  alcohol, and are therefore not as accurate as

those where the concentration of both products, heptanol and 2-methylhexanol, were known. There might be a reduction in the n:i ratio where longer chain, and therefore less polar, alcohols were used as solvent but this trend was not shown conclusively from these experiments.

It is very apparent that the choice of solvent in these hydroformylation experiments, using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, had a profound effect on the products formed. Only when an alcohol was used as solvent was hex-1-ene converted rapidly to C<sub>7</sub> alcohol. The overall n:i ratio of hydroformylation products did not alter significantly with change of solvent, among those studied here, provided isomerisation of hex-1-ene was not allowed to take place prior to pressurisation with CO/H<sub>2</sub> and heating.

#### 2.2.2. Effect of varying the ratio of hex-1-ene to ethanol with $\text{RhH}(\text{PEt}_3)_3$ as catalyst precursor.

In this series of reactions the ratio of hex-1-ene to ethanol was altered while the total volume (5 cm<sup>3</sup>) remained unaltered throughout. As two moles of hydrogen and one mole of carbon monoxide were required to hydroformylate/hydrogenate hex-1-ene to C<sub>7</sub> alcohol a ratio of CO/H<sub>2</sub> of (1:2) was employed. From table 2.2. it may be seen that C<sub>7</sub> alcohol was formed as product in all reactions where ethanol was present, but as the proportion of ethanol was decreased so the percentage of C<sub>7</sub> aldehyde formed in 3 hours increased. The proportion of branched chain aldehyde also increased, and 2-ethylpentanal was detected. The presence of 2-ethylpentanal indicated that the hex-1-ene was being isomerised to hex-2-ene (and possibly hex-3-ene) prior to hydroformylation. Analysis of the C<sub>7</sub> alcohol produced by GCMS and glc separated heptanol from 2-methylhexanol, but any 2-ethylpentanol present was eluted from the

Table 2.2. Varying ratio of solvent to substrate used.

Ratio hex-1-ene : ethanol	products		C7 alcohol		other
	C7 aldehyde % yield	n:i	% yield	n:i	
1 : 4			84	2.7	
2 : 3	tr		90	2.5	hexane
3 : 2	tr		78	2.4	hexane, esters
4 : 1	11*	0.0	65	2.8	hexane, esters
9 : 1	22*	0.2	43	3.5	hexane, esters
1 : 0	84*	1.5	2	(heptanol)	hexane

[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; total volume of solvent + substrate, 5 cm<sup>3</sup>; pressure, CO/H<sub>2</sub> (1:2), 60 atmos; temperature, 125°C; time, 3 hours.

\* 2-ethylpentanal also produced.

chromatographic column at the same rate as 2-methylhexanol and so could not be distinguished from it by this means. <sup>13</sup>C nmr of a mixture of 2-methylhexanol and 2-ethylpentanol showed the two different species (see section 2.8.5.) but the reaction mixture was not generally analysed for 2-ethylpentanol and only the ratio of heptanol to branched C7 alcohol was calculated in this instance to give an indication of n:i ratio, the heptanol being the desired product.

The esters formed in the reactions with a higher proportion of hex-1-ene in the initial reaction mixture were ethyl heptanoate, ethyl 2-methylhexanoate and heptyl heptanoate with its branched 2-methyl isomers. A total of less than 3% of the original hex-1-ene was converted to these esters. These are Reppe type products formed by nucleophilic attack on a rhodium-acyl species by an alcohol<sup>33</sup>. The percentage yield of hexane produced, as a side product due to hydrogenation of hexene, did not appear to increase as the proportion of hex-1-ene in the reaction mixture increased, although its concentration was not ascertained accurately.

Clearly the presence of an alcohol aids the formation of an

alcoholic product on hydroformylation of hex-1-ene with this catalytic system. It is possible that the alcohol produced further catalyses the hydrogenation of any aldehyde formed in a low concentration of solvent alcohol, ie is autocatalytic.

### 2.3.1. Hydroformylation using various ligands.

In commercial hydroformylation reactions based on rhodium  $\text{RhH(CO)(PPh}_3)_3$  has been used as the catalyst precursor<sup>2</sup>. A series of reactions was carried out in ethanol using a variety of ligands to see what effect this had on the products. Table 2.3.1. shows the results

Table 2.3.1. Hydroformylation using various ligands.

Catalyst precursor.	acetals		C7 aldehyde		C7 alcohol	
	% yield	n:1	% yield	n:1	% yield	n:1
$\text{RhH(CO)(PPh}_3)_3$ . <sup>a</sup>	main product		product		-	
$\text{Rh}_2(\text{OAc})_4$ .	48	2.0	40	0.4	10	0.2
$\text{Rh}_2(\text{OAc})_4 + \text{P}^i\text{Pr}_3$ . (1:6)	tr.		79	1.1	19	2.3
$\text{Rh}_2(\text{OAc})_4 + \text{PEtPh}_2$ . (1:6)	tr.		66	1.1	28	6.2
$\text{Rh}_2(\text{OAc})_4 + \text{DMPE}$ . (1:10)	tr.		10	0.9	17	0.5
$\text{Rh}_2(\text{OAc})_4 + \text{PEt}_2\text{Ph}$ . (1:6)	tr.		3	0.0	89	2.6
$\text{Rh}_2(\text{OAc})_4 + \text{PMe}_3$ . (1:6)	-		tr.		99	2.5
$\text{Rh}_2(\text{OAc})_4 + \text{PEt}_3$ . <sup>b</sup> (1:6)	-		tr.		103	2.4
$\text{Rh}_2(\text{OAc})_4 + \text{P}^n\text{Bu}_3$ . (1:6)	-		-		106	2.4
$\text{RhH(PEt}_3)_3$ . <sup>c</sup>	-		-		102	2.3

$[\text{Rh}_2(\text{OAc})_4]$ , 0.004 moles  $\text{dm}^{-3}$ ; hex-1-ene, 1  $\text{cm}^3$ ; ethanol, 4  $\text{cm}^3$ ; pressure  $\text{CO}/\text{H}_2$  (1:1), 37 - 52 atmos; temperature, 120-125°C; time 16 h.

<sup>a</sup>  $[\text{RhH(CO)(PPh}_3)_3]$ , 0.006 moles  $\text{dm}^{-3}$ ; hex-1-ene, 2  $\text{cm}^3$ ; ethanol, 10  $\text{cm}^3$ ; <sup>b</sup> 80°C;

<sup>c</sup>  $[\text{RhH(PEt}_3)_3]$ , 0.008 moles  $\text{dm}^{-3}$ ; DMPE, bis dimethylphosphinoethane.

obtained for reactions carried out with the pressure of CO/H<sub>2</sub> (1:1) at 37-52 atmos. and the oven temperature between 120-125°C for 16 hours.

RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> gave C<sub>7</sub> aldehyde as product and no C<sub>7</sub> alcohol. Most of the aldehyde formed had reacted with the solvent to form acetals, namely 1,1-diethoxyheptane and 1,1-diethoxy-2-methylhexane. Acetal formation from aldehyde and alcohol is generally acid catalysed but probably took place here at the metal centre. When Rh<sub>2</sub>(OAc)<sub>4</sub> was used as catalyst precursor the product was again mainly a combination of acetals and C<sub>7</sub> aldehyde, but 10% of the original hex-1-ene was converted to C<sub>7</sub> alcohol. The overall n:i ratio of products was 0.85 and the highest proportion of straight chain product was in the form of 1,1-diethoxyheptane. The addition of a tertiary phosphine ligand to the reaction mixture such that the ratio of Rh:PR<sub>3</sub> was at least 1:3 increased the proportion of C<sub>7</sub> alcohol produced. Substituted phosphine ligands may be categorised according to their basicity<sup>34</sup> with P<sup>i</sup>Pr<sub>3</sub> the most and PPh<sub>3</sub> the least basic of those listed:



An alternative means of categorising substituted phosphine ligands is by their calculated cone angle<sup>34</sup>, which gives a measure of the steric crowding at the metal centre.

P <sup>i</sup> Pr <sub>3</sub>	=160°.	P <sup>n</sup> Bu <sub>3</sub>	=132°.
PPh <sub>3</sub>	=145°.	PEt <sub>3</sub>	=132°.
PEtPh <sub>2</sub>	=140°.	PMe <sub>3</sub>	=118°.
PEt <sub>2</sub> Ph	=136°.	DMPE	=115°.

Bearing these two parameters in mind it would appear that the nature of the ligand coordinated to the catalyst has significant influence on the production of alcohols from hex-1-ene. It would seem that a basic ligand that is not greatly sterically crowded is a

prerequisite for alcohol production, with  $\text{PEt}_2\text{Ph}$  being the least basic ligand with the largest cone angle which gave good conversion to C7 alcohol in 16 hours. It is not clear if DMPE would produce a higher conversion to alcohol if it were used at a lower concentration. In the experiment recorded the ratio of Rh:P was 1:10 which may have been high enough to slow the reaction rate significantly (see section 2.3.2.). Alternatively, as DMPE is a chelating ligand, cis rather than trans phosphine ligand coordination on the rhodium centre, or the formation of dimers or higher units via the chelating ligand, may have altered the catalytic system significantly.

Those basic ligands, in the presence of which complete conversion of hex-1-ene to C7 alcohols was observed, did not give any significant variation of n:i ratio of products. By increasing the steric bulk of the ligands, which in other hydroformylation systems is found to improve the n:i ratio of products<sup>35</sup>, there was a decrease in both the overall proportion of straight chain product and the proportion of product formed as alcohol. Marko et al.<sup>36</sup> found that when a series of rhodium trisubstituted phosphine systems were used to catalyse the hydrogenation of acetone in benzene/methanol solution the combination of basicity and cone angle was important, with  $\text{PEt}_3$  giving most efficient hydrogenation, and bulkier basic ligands being less effective.

### 2.3.2. Effect of varying concentration of $\text{PEt}_3$ .

As it is known that increasing the ratio of  $\text{PPh}_3$  to rhodium in hydroformylation systems using  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  as catalyst precursor improves the n:i ratio of product by reducing isomerisation<sup>37</sup>, the effect of increasing the concentration of free  $\text{PEt}_3$  in this system based on  $\text{RhH}(\text{PEt}_3)_3$  was investigated. There was complete conversion to C7 alcohol in these 16 hour reactions and the n:i ratio of product

Table 2.3.2. Effect of varying concentration of  $\text{PEt}_3$ .

$[\text{PEt}_3]$ . /moles $\text{dm}^{-3}$	n:i ratio of C7 alcohol produced.
0.00	2.7
0.04	2.6
0.08	2.7
0.12	2.7
0.16	2.8
0.20	2.9

$[\text{RhH}(\text{PEt}_3)_3]$ , 0.008 moles  $\text{dm}^{-3}$ ; hex-1-ene, 1  $\text{cm}^3$ ; ethanol 4  $\text{cm}^3$ ; pressure,  $\text{CO}/\text{H}_2$  (1:1), 40 atmos; temperature, 120°C; time, 16 hours.

alcohols, at varying concentration of free  $\text{PEt}_3$ , are shown in table 2.3.2..

It may be seen that the n:i ratio of product C7 alcohol only increased slightly, from 2.6 to 2.9, (an increase from 72.2% to 74.5% of straight chain over branched chain alcohol) on the addition of a twenty five fold excess of free  $\text{PEt}_3$  compared with the concentration of  $\text{RhH}(\text{PEt}_3)_3$  in the catalytic system. In reactions carried out over a shorter time it was evident that addition of excess free  $\text{PEt}_3$  reduced

Table 2.3.3. Effect of varying reaction time with and without free  $\text{PEt}_3$ .

Time /hours.	approx temperature /°C	without free $\text{PEt}_3$ .		with free $\text{PEt}_3^{\text{a}}$ .	
		C7 alcohol % yield	n:i	C7 alcohol % yield	n:i
0.5	55	14	7.72	-	
0.75	70	52	4.53	~3	(heptanol)
1.0	80	64	4.57	19	4.92
1.5	95	100	2.77	64	3.59
2.0	105	101	3.00	84	3.00

$[\text{RhH}(\text{PEt}_3)_3]$ , 0.008 moles  $\text{dm}^{-3}$ ; hex-1-ene, 1  $\text{cm}^3$ ; ethanol 4  $\text{cm}^3$ ; pressure,  $\text{CO}/\text{H}_2$  (1:1), 40 atmos; temperature, 120°C.

<sup>a</sup>  $[\text{PEt}_3]$ , 0.08 moles  $\text{dm}^{-3}$ .

the reaction rate as is shown in table 2.3.3. Without excess free  $\text{PEt}_3$  there was complete conversion to C7 alcohol within 1.5 hours, while in the same time, in the presence of a tenfold excess of  $\text{PEt}_3$ , only 63.7% conversion to C7 alcohol had taken place. In all these reactions unreacted hexene remained unisomerised, but in the three reactions without free  $\text{PEt}_3$ , showing incomplete conversion to C7 alcohol, a trace of C7 aldehyde was evident. No aldehyde was detected in the incomplete reactions with free  $\text{PEt}_3$ . Some indication of the probable temperature within the autoclave is also indicated in table 2.3.3. and it would appear that the reaction mixture with a tenfold excess of  $\text{PEt}_3$  required to reach  $\sim 70^\circ\text{C}$  before the reaction would start (see section 2.6.).

Although in shorter reactions the n:i ratio of C7 alcohol produced was higher than in longer reactions it should be noted that the percentage yield was low. It appeared that production of heptanol proceeded faster than production of 2-methylhexanol, with the latter being formed in greater proportion later in the reaction.

Thus there was no significant improvement achieved in the n:i ratio of product C7 alcohol by increasing the concentration of free  $\text{PEt}_3$  and the rate of conversion of hex-1-ene to C7 alcohol was noticeably reduced. Further evidence of the change in rate was found in reactions carried out at B.P Research Centre, Sunbury and are discussed in section 2.7..

#### 2.4. Effect of varying pressure.

Most of the hydroformylation reactions in this project were carried out using a 1:1 mixture of carbon monoxide and hydrogen as a high pressure cylinder of these gases in this ratio was available. It is worth noting that the hydroformylation with hydrogenation of hex-1-ene to C7 alcohols required two moles of hydrogen and one of carbon

monoxide. Thus hex-1-ene ( $1 \text{ cm}^3$ ,  $8.0 \times 10^{-3}$  moles) required hydrogen ( $16.0 \times 10^{-3}$  moles) and carbon monoxide ( $8.0 \times 10^{-3}$  moles); a total of  $24.0 \times 10^{-3}$  moles. The deadspace in the autoclave, after priming with  $5 \text{ cm}^3$  of reaction mixture, was  $\sim 220 \text{ cm}^3$ . Assuming that the reactant gases behaved as ideal gases and by using the Gas Law:

$$P.V. = n.R.T. \quad \text{where:}$$

P. = pressure drop due to gas taken up (atmos),

V. = volume of gas in autoclave ( $\text{cm}^3$ ),

n. =  $24 \times 10^{-3}$  moles,

R. = gas constant,  $82.06 \text{ cm}^3 \text{ atmos K}^{-1} \text{ gmole}^{-1}$ ,

T. = 297 K, temperature at which autoclave was primed,

giving the expected pressure drop of  $P = 2.7$  atmos. (ie 0.9 atmos CO and 1.8 atmos  $\text{H}_2$ ) on complete conversion to  $\text{C}_7$  alcohols. When a 1:1 mixture of CO/ $\text{H}_2$  was used this ratio would alter during the course of the reaction such that on conversion of  $8 \times 10^{-3}$  moles of hex-1-ene the following changes would occur:

initial pressure. /atmos.	final pressure. /atmos.	final CO/ $\text{H}_2$ ratio. CO/ $\text{H}_2$ .
20	17.3	1.00 : 0.90
40	37.3	1.00 : 0.95
60	57.3	1.00 : 0.97
80	77.3	1.00 : 0.98

Thus the higher the initial pressure the smaller the change in the CO/ $\text{H}_2$  ratio of reactant gases during the reaction. With the change in CO/ $\text{H}_2$  ratio to 1.00:0.90 in the reactions primed at 20 atmos the hydrogen partial pressure would still be 8.2 atmos which should have been sufficient to prevent the catalytic species being removed from the reaction due to dimerisation (see section 5.3.1.) and the reaction

Table 2.4. Effect of varying pressure and ratio of CO/H<sub>2</sub>.

Temperature oven setting /°C	CO/H <sub>2</sub> partial pressure /atmos.	without free PEt <sub>3</sub> . n:i ratio C <sub>7</sub> alcohol	with free PEt <sub>3</sub> <sup>a</sup> . n:i ratio C <sub>7</sub> alcohol.
115 for 3 hours.			
	10:10	2.5	2.6
	20:20	2.5	2.4
	30:30	2.5	2.5
	40:40	2.5	2.5
125 for 2.5 hours.			
	5:10	2.8	
	10:20	2.8	
	15:30	2.8	

[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; hex-1-ene, 1 cm<sup>3</sup>; ethanol 4 cm<sup>3</sup>.

<sup>a</sup> [PEt<sub>3</sub>], 0.08 moles dm<sup>-3</sup>.

mixture should still have been active.

The effect of varying the pressure of the reactant gases, and of changing the ratio of CO/H<sub>2</sub> from 1:1 to 1:2, on the n:i ratio of product alcohols is shown in table 2.4.. Those reactions carried out over 3 hours gave complete conversion to C<sub>7</sub> alcohol while only a trace of aldehyde was detected in the reactions with the pressure set at 15 and 30 atmos in 2.5 hours, the remaining hex-1-ene being converted to C<sub>7</sub> alcohols. There was no significant change in the n:i ratio of product seen in the range of partial pressures of the reactant gases studied, but it may be seen that with the initial pressure of CO/H<sub>2</sub> (1:2) as low as 15 atmos the reaction still proceeded rapidly, without starvation of reactant gases.

### 2.5. Varying the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub>.

A series of reactions was carried out at varying concentration of catalyst precursor to see what effect this might have on the products.

**Table 2.5. Varying the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub>.**

Time /hours.	[RhH(PEt <sub>3</sub> ) <sub>3</sub> ]. /moles dm <sup>-3</sup> .	[PEt <sub>3</sub> ]. /moles dm <sup>-3</sup> .	C7 aldehyde		C7 alcohol		overall
			% yield	n:i.	% yield	n:i.	n:i.
<b>2.5</b>							
	0.008	0.00	-		115	2.8	2.8
	0.004	0.00	8	0.0	106	3.4	2.8
	0.002	0.00	26	0.6	86	5.2	2.7
	0.001	0.00	81	2.2	19	6.1	2.5
	0.001	0.01	24	1.1	33	6.3	2.6
	0.0005	0.00	89	2.4	tr	(heptanol)	2.4
	0.0005	0.01	47	1.7	27	8.3	2.6
<b>16.0</b>							
	0.0004	0.00	48	0.9	3	(heptanol)	(0.9)
	0.0004	0.004	3	0.0	100	2.9	2.7

hex-1-ene, 1 cm<sup>3</sup>; ethanol, 4 cm<sup>3</sup>; temperature, 125°C; pressure CO/H<sub>2</sub> (1:1), 40 atmos.

With no excess PEt<sub>3</sub> present in the reaction mixture, which was heated to 125°C for 3 hours, as the catalyst concentration decreased so a greater proportion of C<sub>7</sub> aldehyde was found in the product, until with the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> at 0.0005 moles dm<sup>-3</sup> almost all the product was in the form of C<sub>7</sub> aldehyde, with ~11% of the original hexene remaining. At this same catalyst concentration, but with a twentyfold excess of PEt<sub>3</sub> present, there was again unreacted hexene remaining, as would be expected, but 36% of hydroformylated material had been further hydrogenated to C<sub>7</sub> alcohol. When a mixture with low concentration of catalyst precursor (0.0004 moles dm<sup>-3</sup>) was allowed to react for 16 hours there was a distinct difference between the products of a reaction without excess PEt<sub>3</sub> compared with a reaction with a tenfold excess of PEt<sub>3</sub>. The presence of free PEt<sub>3</sub> allowed almost complete conversion of products to C<sub>7</sub> alcohol, while in the absence of free PEt<sub>3</sub> only a trace of heptanol formed, the remainder being C<sub>7</sub> aldehyde or its condensation products.

The concentration of catalyst precursor thus had a significant influence on the products formed, controlling whether they were simply hydroformylation products (aldehydes) or further hydrogenated to alcohols. Also of importance was the presence of excess free  $\text{PEt}_3$  which contributed to the promotion of alcohol formation. Alcohol formation therefore required either high concentration of  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, or in longer reactions the presence of an excess of  $\text{PEt}_3$ . It is possible that two competing systems were present here, firstly one at low concentration of  $\text{RhH}(\text{PEt}_3)_3$ , with no free  $\text{PEt}_3$ , which produced aldehyde, and a second system which predominated at higher concentration of catalyst precursor (with excess  $\text{PEt}_3$  present), which gave a one stage reaction producing alcohol, and also hydrogenated any aldehyde produced by the first system. The overall n:i ratio of alcohol + aldehyde produced remained in the range 2.4-2.8 and seemed to be the same whichever of these catalytic species predominated.

#### 2.6. Varying reaction temperature.

As mentioned earlier the exact reaction temperature was not accurately known, due to the uncertain time required to heat a cold autoclave to the temperature of the preheated oven into which it had been placed. This series of reactions was carried out with the autoclave placed in the preheated oven and left for a 5 hour period prior to cooling, venting and analysis. This time span should have allowed all reactions to reach the recorded temperature and thus give some idea of the range of temperatures over which this system would catalyse the hydroformylation, with hydrogenation, of hex-1-ene. Table 2.6. shows the results obtained, which are also shown in graph form in figure 2.2..

It was apparent that some hydroformylation with hydrogenation

Table 2.6. Effect of varying reaction temperature.

Oven temperature setting. /°C.	without free PEt <sub>3</sub> .		with free PEt <sub>3</sub> <sup>a</sup> .	
	C7 alcohol % yield	n:1	C7 alcohol % yield	n:1
50	17	4.2	-	
57	60	3.2	4	4.5
64	87	2.9	17	3.3
67	88	2.8	18	3.1
74	94	2.7	34	2.9
80	100	2.7	52	2.9
89	104	2.6	79	2.7
102	103	2.5	92	2.5
110	98	2.5	93	2.5
118	108	2.5	103	2.5
132	106	2.5	102	2.5
145	100	2.5	96	2.6
173 <sup>b</sup>	97	2.6	82	2.6

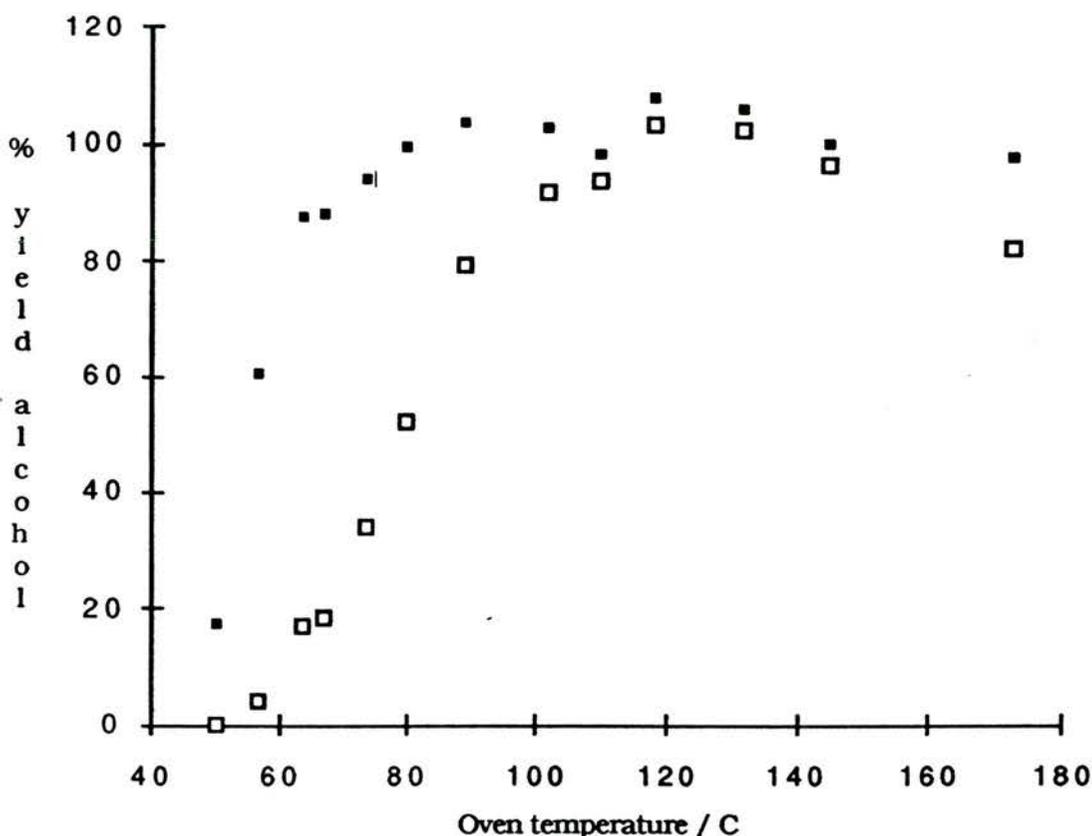
[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; hex-1-ene, 1 cm<sup>3</sup>; ethanol 4 cm<sup>3</sup>; time, 5 hours; pressure CO/H<sub>2</sub> (1:1), 40 atmos.

<sup>a</sup> [PEt<sub>3</sub>], 0.08 moles dm<sup>-3</sup>; <sup>b</sup> 4 hours, catalyst decomposition evident.

took place at 50°C in the absence of excess phosphine but the presence of a tenfold excess of PEt<sub>3</sub> caused a higher temperature to be required for the reaction to take place. A trace of C7 aldehyde was detected by GCMS in those reactions without free PEt<sub>3</sub> carried out below 60°C. In all reactions where unreacted hexene remained it appeared to be unisomerised. There was evidence of catalyst decomposition, blackening of the autoclave liner, when the oven temperature was set at 173°C, particularly in the absence of free PEt<sub>3</sub>, but no blackening of the autoclave liner was apparent at 145°C. At both these temperatures a trace of hexane and a trace of C7 aldehyde were also detected, possibly indicating a breakdown of the catalytic species above ~145°C.

It appears that in the absence of free PEt<sub>3</sub> this system was active

Effect of varying reaction temperature.



$[\text{RhH}(\text{PET}_3)_3]$ ,  $0.008 \text{ moles dm}^{-3}$ ; hex-1-ene,  $1 \text{ cm}^3$ ; ethanol  $4 \text{ cm}^3$ ; time, 5 hours; pressure  $\text{CO}/\text{H}_2$  (1:1), 40 atmos.

■ without added  $\text{PET}_3$ ; □  $[\text{PET}_3]$ ,  $0.08 \text{ moles dm}^{-3}$ .

Figure 2.2.

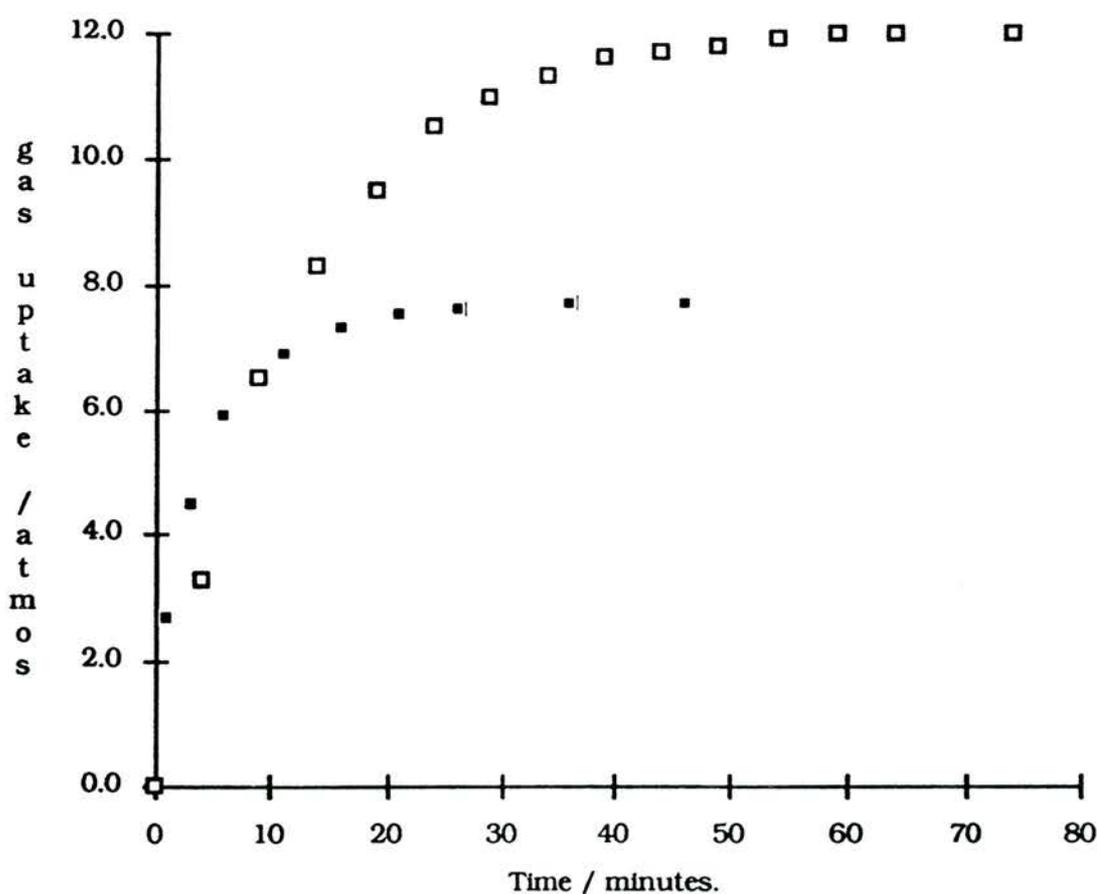
in the temperature range  $60\text{-}145^\circ\text{C}$ , while in the presence of a tenfold excess of  $\text{PET}_3$  the lower end of the active temperature range was raised to  $\sim 80^\circ\text{C}$ .

It was apparent in these reactions, and many others, that the n:l ratio of products decreased as the conversion increased. The rate of formation of heptanol was therefore faster than the formation of 2-methylhexanol, but it was not clear why more 2-methylhexanol should form later in the reaction, if the unreacted hexene remained unisomerised, as it appeared to do.

2.7. Hydroformylation of hex-1-ene carried out using a rig at B.P. Research Centre, Sunbury.

For these two reactions using hex-1-ene as substrate the autoclave was primed with a solution of  $\text{RhH}(\text{PEt}_3)_3$  in ethanol ( $0.004 \text{ moles dm}^{-3}$ ,  $30 \text{ cm}^3$ ), both without and with excess free  $\text{PEt}_3$  ( $0.04 \text{ moles dm}^{-3}$ ), and heated with stirring to  $120^\circ\text{C}$  with  $\text{CO}/\text{H}_2$  (1:2) at  $\sim 40$  atmos prior to injection of hex-1-ene ( $3 \text{ cm}^3$ ). The pressure in the reaction vessel was at this point raised to  $\sim 60$  atmos and held here

Rate of hydroformylation, with hydrogenation, of hex-1-ene in ethanol using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor.



$[\text{RhH}(\text{PEt}_3)_3]$ ,  $0.0036 \text{ moles dm}^{-3}$ ; hex-1-ene,  $3 \text{ cm}^3$ ; ethanol,  $30 \text{ cm}^3$ ; pressure  $\text{CO}/\text{H}_2$  (1:2), 60 atmos; temperature,  $120^\circ\text{C}$ .

■ no added  $[\text{PEt}_3]$ .; All hex-1-ene consumed giving 97% conversion to  $\text{C}_7$  alcohols,  $n:i=2.62$ .

□  $[\text{PEt}_3]$  added,  $0.036 \text{ moles dm}^{-3}$ ; All hex-1-ene consumed giving 99% conversion to  $\text{C}_7$  alcohol,  $n:i=2.53$ .

Figure 2.3.

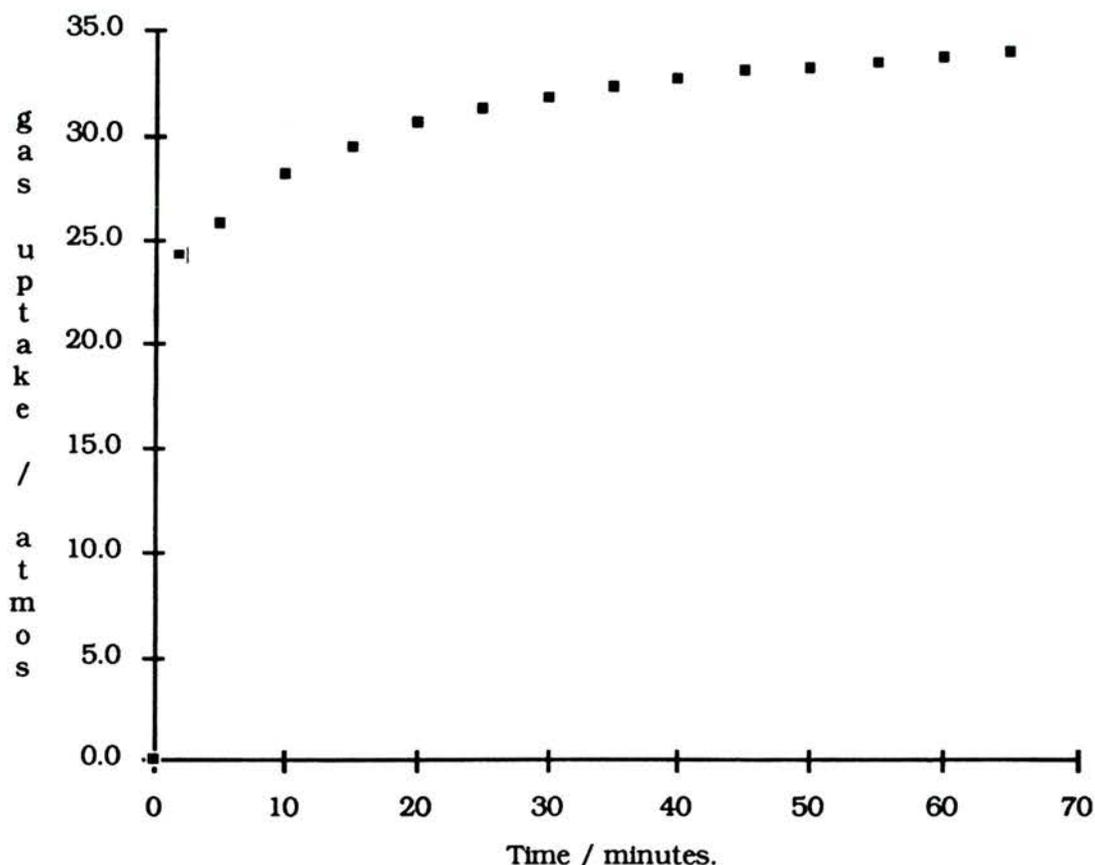
throughout the reaction, with the stirring rate set at ~1000 rpm.. The pressure in the ballast vessel (130 cm<sup>3</sup>) was monitored and this allowed a plot of gas uptake against time, as shown in figure 2.3., to be drawn. Comparison of the initial rates of reaction of the systems, without excess PEt<sub>3</sub> and with a tenfold excess of free PEt<sub>3</sub>, showed that addition of free PEt<sub>3</sub> slowed the rate. Both reactions should have required the same volume of CO/H<sub>2</sub> (1:2) to go to completion. The apparent smaller uptake of reactant gases in the reaction without excess free PEt<sub>3</sub> may have been due to the start of the reaction, which was very rapid, being missed and the initial fall in pressure in the ballast vessel not being noted. The initial gradient for the reaction without excess free PEt<sub>3</sub> indicated a turnover rate for the catalyst of 38.5 turnovers minute<sup>-1</sup> (≅2300 catalyst turnovers hour<sup>-1</sup>) while in the reaction with a tenfold excess of free PEt<sub>3</sub> the initial turnover rate was 11.9 turnovers minute<sup>-1</sup> (≅700 catalyst turnovers hour<sup>-1</sup>).

## 2.8. Substrates other than hex-1-ene.

### 2.8.1. Ethene.

As ethene is a gas at room temperature it would not have been practical to carry out hydroformylation reactions on this substrate in the autoclave system used at St Andrews but an experiment to hydroformylate ethene in ethanol with CO/H<sub>2</sub> (1:2) was carried out in the rig at B.P. Research Centre Sunbury with conversion of ethene to propan-1-ol. In this experiment the autoclave was primed with ethanol (27 cm<sup>3</sup>) and PEt<sub>3</sub> (88.5 μl.) and then pressurised with ethene (9-10 g) and heated under an atmosphere of nitrogen to 120°C. As the pressure in the autoclave at this stage was ~32 atmos. when the reactant gases were used to inject the catalyst solution, RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.02 moles dm<sup>-3</sup>, 3 cm<sup>3</sup>), into the autoclave the pressure was set at 80 atmos, to give a pressure of CO/H<sub>2</sub> (1:2) of ~50 atmos for the

Rate of hydroformylation, with hydrogenation, of ethene in ethanol using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor.



$[\text{RhH}(\text{PEt}_3)_3]$ ,  $\sim 0.002$  moles  $\text{dm}^{-3}$ ;  $[\text{PEt}_3]$  added,  $\sim 0.02$  moles  $\text{dm}^{-3}$ ; ethene, 9-10 g; ethanol, 30  $\text{cm}^3$ ; pressure  $\text{CO}/\text{H}_2$  (1:2),  $\sim 50$  atmos; temperature,  $120^\circ\text{C}$ .

Figure 2.4.

reaction. This reaction was stirred at  $\sim 1000$  rpm. throughout. On addition of the catalyst solution to the reaction mixture there was a rapid rise in temperature to  $>160^\circ\text{C}$  before it could be cooled to the required region of  $120^\circ\text{C}$ , within 2 minutes. There was a rapid uptake of reactant gases, monitored as pressure drop in the (larger) ballast vessel ( $450$   $\text{cm}^3$ ), and shown in Figure 2.4.. A pressure drop of 24.3 atmos. was registered in the first 2 minutes, which gives a catalyst turnover rate of  $\sim 900$   $\text{minute}^{-1}$  ( $\cong 54000$   $\text{turnovers hour}^{-1}$ ).

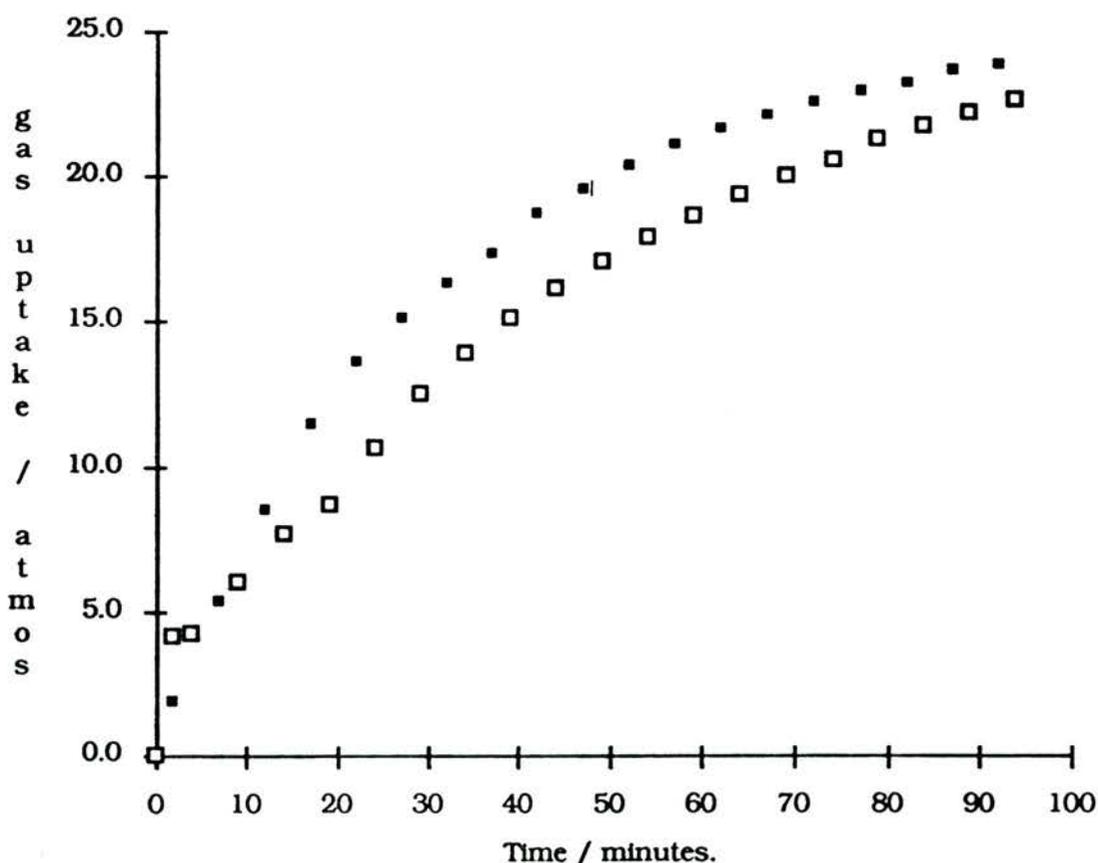
Analysis of the products showed that most of the ethene had been converted to propan-1-ol as the only product. As ethene only contains two carbon atoms, linked by a double bond, the product is the

same whichever carbon is hydroformylated and no branched chain product can form.

### 2.8.2. Propene.

Two hydroformylation reactions were carried out on propene, one with CO/H<sub>2</sub> in the ratio (1:1) and the other with CO/H<sub>2</sub> in the ratio (1:2) ie in the proportion which would be taken up on conversion of propene to butanol and 2-methylpropanol. In both reactions the autoclave was primed with ethanol (27 cm<sup>3</sup>) and PEt<sub>3</sub> (88.5 μl) under

#### Rate of hydroformylation, with hydrogenation, of propene in ethanol using RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor.



RhH(PEt<sub>3</sub>)<sub>3</sub>, ~0.002 moles dm<sup>-3</sup>; [PEt<sub>3</sub>] added, ~0.02 moles dm<sup>-3</sup>; ethanol, 30 cm<sup>3</sup>; temperature, 120°C.

■ propene, 6.64 g; pressure CO/H<sub>2</sub> (1:1) + C<sub>3</sub>H<sub>6</sub>, 52.5-56.3 atmos; stirrer speed ~1000 rpm..

□ propene, 6.50 g; pressure CO/H<sub>2</sub> (1:2) + C<sub>3</sub>H<sub>6</sub>, 77.6-82.8 atmos; stirrer speed ~400 rpm..

Figure 2.5.

nitrogen and then propene (~6.5 g) was condensed into the autoclave. On heating to 120°C the pressure in the autoclave rose to ~15 atmos.. The solution of RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.02 moles dm<sup>-3</sup>, 3 cm<sup>3</sup>), was injected into the preheated autoclave by the reactant gas mixture at the pressure at which the reaction was to take place. In both reactions the partial pressure of CO was kept at ~20 atmos and the pressure drop in the (larger) ballast vessel (450 cm<sup>3</sup>) monitored. As well as the difference in reactant gas ratio there was also a difference in rate of stirring of the two reactions, the 1:1 mixture being stirred at ~1000 rpm. while the 1:2 reaction mixture being stirred at a slower rate of ~400 rpm.. This difference in rate of stirring is the probable reason for the slower reaction rate shown by the 1:2 reaction mixture, see figure 2.5., the limiting factor here being the rate of diffusion of the reactant gases into solution as stirring was not fast enough to keep the solution saturated with propene, CO and H<sub>2</sub>. Calculated catalyst turnover rates were 58.3 turnovers minutes<sup>-1</sup> (≅3500 turnovers hour<sup>-1</sup>) for CO/H<sub>2</sub> 1:1 mixture in the first 7 minutes. For CO/H<sub>2</sub> 1:2 the rate was 157 turnovers minutes<sup>-1</sup> (≅9400 turnovers hour<sup>-1</sup>) in the first 2 minutes, falling to 51 turnovers minutes<sup>-1</sup> (≅3060 turnovers hour<sup>-1</sup>) overall for the first 9 minutes. Thus there was an initial rapid exothermic reaction, followed by a fall off in the rate as the availability of substrate decreased.

Analysis of the products of each reaction showed that C<sub>4</sub> alcohol had been produced as the sole product of the reaction with CO/H<sub>2</sub> (1:2) mixture while with CO/H<sub>2</sub> (1:1) mixture in the gas phase a small proportion of the product formed as C<sub>4</sub> aldehyde, with the major part as C<sub>4</sub> alcohol. The overall n:i ratio of products in both reactions was ~1.9.

Comparison of these rates with those for ethene and hex-1-ene could not be made directly due to the differing concentrations of

catalyst and substrate (not known accurately for ethene or propene) in the different reactions. Also as hex-1-ene is a liquid, and therefore fully dissolved in the solvent, and propene and ethene are gases and therefore not fully dissolved the systems were not directly comparable. The general trend observed, however, was that the rate of hydroformylation, with hydrogenation, decreased with increasing chain length of substrate, as might be expected. This was probably due to steric factors and the reduced probability of the correct positioning of the double bond in relation to the rhodium centre with increasing chain length.

### 2.8.3. 3,3-dimethylbut-1-ene.

A hydroformylation reaction with 3,3-dimethylbut-1-ene (1 cm<sup>3</sup>) as substrate and RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, with CO/H<sub>2</sub> (1:1) at 40 atmos. and the oven set at 120°C for 16 hours gave complete reaction of the 3,3-dimethylbut-1-ene to give only C<sub>7</sub> alcohols, 4,4-dimethylpentan-1-ol being the major product with only a small proportion of the Markownikoff addition product, 3,3,2-trimethylbutan-1-ol. The n:i ratio of these product alcohols was not measured.

### 3.8.4 Styrene.

When styrene (1 cm<sup>3</sup>) was hydroformylated with CO/H<sub>2</sub> (1:1) at 40 atmos., using RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, with the oven set at 120°C for 16 hours it was converted to alcoholic product with the major proportion being the branched chain product, 2-phenylpropan-1-ol, and the minor product being the straight chain, anti-Markownikoff addition product, 3-phenylpropan-1-ol. Some polymerisation also took place. The high proportion of Markownikoff addition product will probably have been

due to the electronic interaction of the benzene ring dictating the stability of the catalytic intermediate and overriding steric hindrance, due to congestion at the metal centre with the branched intermediate. This is also found using the  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  system to hydroformylate styrene in benzene, which gives the Markownikoff addition product, 2-phenylpropanal, in greater yield than 3-phenylpropanal<sup>38,39</sup>.

### 2.8.5. Hex-2-ene.

A series of four reactions was carried out on hex-2-ene to compare the products and rate of reaction with hex-1-ene. With  $\text{RhH}(\text{PEt}_3)_3$  in ethanol ( $0.008 \text{ moles dm}^{-3}$ ,  $4 \text{ cm}^3$ ), both with and without free  $\text{PEt}_3$  ( $0.08 \text{ moles dm}^{-3}$ ) as catalyst precursor, with  $\text{CO}/\text{H}_2$  (1:1) at 40 atmos. and heating to  $125^\circ\text{C}$  for 3 hours hex-2-ene ( $1 \text{ cm}^3$ ) was hydroformylated, with hydrogenation, to  $\text{C}_7$  alcohol with some product as  $\text{C}_7$  aldehyde, see table 2.7.. As, on analysis, 2-methylhexanol and 2-ethylpentanol were eluted from the glc and GCMS columns at the same time these means could not be used to analyse the products. Instead they were separated from the solvent ethanol and catalyst by fractional distillation and studied by  $^{13}\text{C}$  nmr.

Table 2.7. Hydroformylation of hex-2-ene.

$[\text{RhH}(\text{PEt}_3)_3]$ . /moles $\text{dm}^{-3}$ .	$[\text{PEt}_3]$ . /moles $\text{dm}^{-3}$ .	$\text{C}_7$ aldehyde % yield.	$\text{C}_7$ alcohol % yield.
0.008	0.00	6	36
0.008	0.08	1	7
0.0008	0.000	41	6
0.0008	0.008	5	2

hex-2-ene,  $1 \text{ cm}^3$ ; ethanol,  $4 \text{ cm}^3$ ; temperature,  $125^\circ\text{C}$ ; pressure  $\text{CO}/\text{H}_2$  (1:1), 40 atmos; time, 3 hours.

**Table 2.8. Assignment of  $^{13}\text{C}$  nmr peaks for C7 alcohols and aldehydes.**

2-methyl hexanal.		2-methyl hexanol.		2-ethyl pentanal.		2-ethyl pentanol.	
3 CH <sub>3</sub>   1 2 4 5 6 7	O=CH-CH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> .	3 CH <sub>3</sub>   1 2 4 5 6 7	HO-CH <sub>2</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> .	3 CH <sub>2</sub> -CH <sub>3</sub>   4 1 2 5 6 7	O=CH-CH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> .	3 CH <sub>2</sub> -CH <sub>3</sub>   4 1 2 5 6 7	HO-CH <sub>2</sub> -CH-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> .
	1/ppm		2/ppm		3/ppm		4/ppm
2-methylhexanol - calculated values.	69.9	2-methylhexanol - calculated values.	34.9	2-ethylpentanal - calculated values.	16.1	2-ethylpentanol - calculated values.	32.9
2-methylhexanol - supplied sample.	68.20	2-methylhexanol - supplied sample.	35.81	2-ethylpentanal - supplied sample.	16.67	2-ethylpentanol - supplied sample.	33.01
2-ethylpentanol - calculated values.	67.4	2-ethylpentanol - calculated values.	40.3	2-ethylpentanal - calculated values.	22.6	2-ethylpentanol - calculated values.	11.5
impurity in 2-methylhexanol sample.	65.09	impurity in 2-methylhexanol sample.	41.83	2-ethylpentanal - calculated values.	23.41	2-ethylpentanol - calculated values.	11.09
2-methylhexanal - calculated value.	-	2-methylhexanal - calculated value.	49.3	2-ethylpentanal - calculated value.	12.3	2-ethylpentanol - calculated value.	30.5
2-ethylpentanal - calculated value.	-	2-ethylpentanal - calculated value.	51.0	2-ethylpentanal - calculated value.	20.0	2-ethylpentanol - calculated value.	11.3

**Table 2.9. Products of hydroformylation of hex-2-ene catalysed by [RhH(PEt<sub>3</sub>)<sub>3</sub>].**

with catalyst concentration 0.008 molar giving:		with catalyst concentration 0.0008 molar giving:	
2-methylhexanol.	68.10	2-methylhexanol.	68.26
2-ethylpentanol.	64.99	2-ethylpentanol.	65.15
2-methylhexanal.	205.95	2-methylhexanal.	205.62
2-ethylpentanal.	206.24	2-ethylpentanal.	205.9
	1/ppm		1/ppm
	2/ppm		2/ppm
	3/ppm		3/ppm
	4/ppm		4/ppm
	5/ppm		5/ppm
	6/ppm		6/ppm
	7/ppm		7/ppm

The peak assignments were made using a formula published by Williams and Fleming<sup>40</sup>, see table 2.8., and comparison of the products was made with purchased 2-methylhexanol. This commercial 2-methylhexanol was found to contain an impurity, the spectrum of which exactly matched that of the second product from the hydroformylation, with hydrogenation, reaction above, and fitted well with the calculated spectrum for 2-ethylpentanol. The spectrum of the C<sub>7</sub> fraction of the reaction mixture, shown in table 2.9. confirmed the production of 2-methylhexanol and 2-ethylpentanol from hex-2-ene. There was no evidence of heptanol formation, so isomerisation causing the double bond to migrate to the terminal position in hexene did not appear to have taken place.

Hydroformylation of hex-2-ene by this system was appreciably slower than hydroformylation of hex-1-ene, probably due to the reduced accessibility of the internal double bond compared with a terminal double bond. Also there was an appreciably higher proportion of C<sub>7</sub> aldehyde formed than with the terminal alkene possibly because the catalytic intermediate was more crowded and access for hydrogenation reactants was consequently more restricted.

Table 2.7. also shows the products of hydroformylation reactions carried out on hex-2-ene (1 cm<sup>3</sup>) at lower catalyst concentration, with RhH(PET<sub>3</sub>)<sub>3</sub> in ethanol (0.0008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>), both without and with free PET<sub>3</sub> (0.008 moles dm<sup>-3</sup>), with CO/H<sub>2</sub> (1:1) at 40 atmos. and heating to 125°C for 3 hours. Slightly more hex-2-ene reacted in the experiment without excess PET<sub>3</sub> present than had reacted at higher catalyst concentration, with 41% being hydroformylated to C<sub>7</sub> aldehyde and 6% being further hydrogenated to C<sub>7</sub> alcohol. With a tenfold excess of free PET<sub>3</sub> present the reaction was much slower and only 6.5% of the original hex-2-ene reacted but twice as much of the hydroformylated material was further hydrogenated to C<sub>7</sub> alcohol as

had been in the absence of free  $\text{PEt}_3$  at this catalyst concentration. The products were again analysed, after fractional distillation, by  $^{13}\text{C}$  nmr as, although 2-methylhexanal and 2-ethylpentanal were separated in the chromatographic column of the GCMS, there was no recorded mass spectrum for 2-ethylpentanal. Its  $^{13}\text{C}$  nmr spectrum on comparison with a calculated spectrum (again using the formula published by Williams and Fleming<sup>40</sup> as above) confirmed the presence of 2-ethylpentanal in the reaction mixture (see table 2.8.).

These reactions on hex-2-ene indicate that this catalytic system will hydroformylate internal alkenes as well as terminal alkenes but that the reaction is significantly slower, no doubt partly due to the greater crowding at the catalytic centre on coordination of the internal double bond. The system at low catalyst concentration is reasonably efficient at hydroformylating this internal alkene there being  $\sim 300$  catalyst turnovers  $\text{hour}^{-1}$  for the reaction listed without free  $\text{PEt}_3$ . The further hydrogenation to C<sub>7</sub> alcohol was far less efficient than where the reaction was carried out on a terminal alkene.

#### 2.8.5. Acetylene.

A 3 hour hydroformylation on acetylene ( $\sim 4$  atmos.) using  $\text{RhH}(\text{PEt}_3)_3$  in ethanol ( $0.001$  moles  $\text{dm}^{-3}$ ,  $4$   $\text{cm}^3$ ) with  $\text{CO}/\text{H}_2$  (1:1) at  $\sim 40$  atmos. and heating to  $125^\circ\text{C}$  showed no products on analysis by GCMS, but as the solution was dark brown it may have contained polymeric material. On reacting acetylene ( $\sim 4$  atmos.) with  $\text{RhH}(\text{PEt}_3)_3$  in butan-1-ol ( $0.01$  moles  $\text{dm}^{-3}$ ,  $4$   $\text{cm}^3$ ) as catalyst precursor, with  $\text{CO}/\text{H}_2$  (1:1) at  $\sim 40$  atmos. and heating to  $125^\circ\text{C}$  for 20 hours a dark brown polymer (insoluble in petrol but soluble in butan-1-ol and thf), formed, which  $^{13}\text{C}$  nmr analysis showed to contain unsaturated bonds, (peaks at  $151.3$  ppm. and  $116.3$  ppm.). GCMS analysis also indicated the formation of cyclopentanone and pentan-3-

one, among other unidentified products. The hoped for butanediol which could be expected to form by hydroformylation, with hydrogenation, at each of the acetylenic carbon atoms was not detected.

#### 2.8.6. Heptanal.

Heptanal (1 cm<sup>3</sup>) was reacted with CO/H<sub>2</sub> (1:1) at 40 atmos, with RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, with the oven set at 118°C for 2 hours, and showed complete hydrogenation to heptanol. Deuteration studies of the hydrogenation of heptanal showed that the solvent ethanol was involved in this reaction with ethanol-OH being largely converted to ethanol-OD when the reaction was carried out under CO/D<sub>2</sub>, see sections 4.2.2. - 4.2.4..

A similar reaction carried out with a more dilute solution of RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.0005 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, with heptanal (1 cm<sup>3</sup>) as substrate and CO/H<sub>2</sub> (1:1) at 40 atmos. and the oven set at 125°C for 2.5 hours showed only ~12% conversion to heptanol and the formation of some 1,1-diethoxyheptane.

This catalytic system will readily hydrogenate the aldehydic C=O bond of heptanal, provided there is a high enough concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor, in an alcoholic solvent.

#### 2.9. Test for homogeneity.

As metallic rhodium, which could have been formed by decomposition of the homogeneous catalytic species, might have been responsible for heterogeneous hydrogenation of intermediate aldehyde to alcohol, a reaction was carried out to test for homogeneity of the complete reaction. This test for homogeneity was not carried out

exactly as suggested by Anton and Crabtree<sup>41</sup> as it was the possible second, hydrogenation reaction step that was being investigated. There is little doubt that the possible first step, namely hydroformylation of hexene to C<sub>7</sub> aldehyde, was homogeneous but colloidal rhodium could be formed during this step which would then go on to heterogeneously hydrogenate intermediate aldehyde to alcohol and therefore removing metallic rhodium before starting the reaction would not prevent its formation during the reaction. Similarly incapacitating the homogeneous catalytic species with cyclooctatetrene would prevent the hydroformylation occurring. For this reason it was decided to carry out a reaction in an unlined autoclave, set in a stirred preheated oil bath, with mercury (~1 cm<sup>3</sup>) added to the hydroformylation reaction mixture of hex-1-ene (1 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, and CO/H<sub>2</sub> (1:1) at 40 atmos and the oil bath heated to 110-116°C for 2 hours. The system was stirred with a magnetic stirrer bar and any colloidal rhodium formed should have amalgamated with the mercury and so not been available to catalyse the hydrogenation of intermediate aldehyde. On analysis the product was found to be 99% C<sub>7</sub> alcohol (n:i 2.78) and 2.9% C<sub>7</sub> aldehyde (n:i 0.08), a similar product distribution to that in reactions without an excess of free PEt<sub>3</sub> and without mercury present, which would appear to indicate that no heterogeneous catalysis by colloidal rhodium was causing the hydrogenation of intermediate C<sub>7</sub> aldehyde to C<sub>7</sub> alcohol.

#### 2.10. Reactions with either NEt<sub>3</sub> or proton sponge present.

It was felt that the hydroformylation/hydrogenation was taking place as a single stage process, in the most part, when a high concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> (>0.006 moles dm<sup>-3</sup>) was used as catalyst precursor in an alcoholic solvent. A proposed intermediate formed by

the protonation of a rhodium-acyl intermediate would give a hydroxy-alkyl-carbene ligand attached to the rhodium centre which would then proceed to yield an alcoholic product without an aldehyde being reductively eliminated from the metal centre later to be re-coordinated and hydrogenated. This is discussed in chapter 4.

If protonation of an acyl intermediate were taking place, the removal of this proton source by the addition of triethylamine might reduce the proportion of C<sub>7</sub> alcohol produced. A reaction was carried out on hex-1-ene (1 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.008 moles dm<sup>-3</sup>, 3 cm<sup>3</sup>) as catalyst precursor, and CO/H<sub>2</sub> (1:1) at 40 atmos with NEt<sub>3</sub> (1 cm<sup>3</sup>) added to the reaction mixture which was heated to 125°C for 3 hours. The products were analysed to show 87% C<sub>7</sub> alcohol (n:i 2.4) and 2% C<sub>7</sub> aldehyde (n:i 1.0). This was only a slight reduction in rate and conversion to C<sub>7</sub> alcohol. It is possible that the system was being altered by the presence of NEt<sub>3</sub> which is capable of coordinating with rhodium in place of, or as well as, PEt<sub>3</sub>, and has been used as a ligand in hydroformylation reactions which yield alcoholic products<sup>12-16</sup>.

A further reaction for comparison was carried out on hex-1-ene (1 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (~0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) as catalyst precursor, and CO/H<sub>2</sub> (1:1) at 40 atmos with proton sponge, 1,8-bis(dimethylamino)naphthalene, (1 g, ~1 cm<sup>3</sup>) added to the reaction mixture which was heated to 125°C for 2.5 hours. A concurrent reaction was run with the same reaction conditions but without proton sponge, and the products of both reactions compared as shown in table 2.10. The effect of adding proton sponge was apparently to reduce the rate of reaction and slightly increase the proportion of aldehyde produced. No unreacted hexene was detected. The percentage of product in the form of C<sub>7</sub> aldehyde was 5%, the remainder being C<sub>7</sub> alcohol. Thus there was a slight reduction in the

Table 2.10. Effect of adding proton sponge to reaction mixture.

	C7 aldehyde		C7 alcohol	
	% yield	n:1	% yield	n:1
without proton sponge.	<1	0.0	95	2.5
with proton sponge <sup>a</sup> .	4	0.6	78	2.9

[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; hex-1-ene, 1 cm<sup>3</sup>; ethanol 4 cm<sup>3</sup>; pressure CO/H<sub>2</sub> (1:1), 40 atmos; temperature 125°C; time, 2.5 hours.

<sup>a</sup> [RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.0067 moles dm<sup>-3</sup>; proton sponge, 1 g (~1 cm<sup>3</sup>); overall volume ~6 cm<sup>3</sup>.

conversion to C7 alcohol but not enough to show that protonation of a catalytic intermediate was being prevented by the proton sponge. It is possible, as ethanol was used as the solvent and so in excess over the proton sponge added, that there was still adequate ethanol available to protonate, or to hydrogen bond to, the catalytic intermediate even in the presence of the proton sponge.

These two experiments, therefore, do not either confirm or deny the possibility of the proposed protonated intermediate. As earlier experiments have shown it is possible that two catalytic routes were running concurrently, the first a one stage cycle forming only C7 alcohol, and the second a two stage cycle which initially produced aldehyde that was then hydrogenated in a second stage to C7 alcohol.

### 2.11. Conclusions.

Hydroformylation using rhodium based catalysts usually give aldehydic products. Here hydroformylation with RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor, at high concentration, with CO/H<sub>2</sub> (1:1) mixture in alcoholic solvents takes place rapidly, and under mild conditions, with concurrent hydrogenation, to give alcoholic products. Aldehydes may be produced rapidly with RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor, at low concentration, unless excess PET<sub>3</sub> is present when the rate is reduced

and further hydrogenation of initially produced aldehyde will take place to produce alcohol.

Deuteration studies on the hydroformylation/hydrogenation of hex-1-ene at high concentration of  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, when compared with products of deuteration of heptanal with the same catalytic system, seem to indicate that a one stage process is occurring to give  $\text{C}_7$  alcohol from hex-1-ene (see chapter 4.). Heterogeneous hydrogenation does not appear to be taking place.

At intermediate concentration of catalyst precursor the two catalytic systems will be running concurrently. Which system predominates will be dictated by the concentration of  $\text{RhH}(\text{PEt}_3)_3$  and the presence or absence of free  $\text{PEt}_3$ .

The n:i ratio of products could not be improved by altering the concentration of free  $\text{PEt}_3$ , or by varying the  $\text{CO}/\text{H}_2$  partial pressures.

The formation of alcoholic product was determined by the presence in adequate supply of basic substituted phosphine ligands of not too great bulk (cone angle) on the rhodium catalyst, and the presence of an alcoholic solvent.

## Chapter 3. Hydroformylation with CO in the gas phase and alcohols as sources of hydrogen.

### 3.1. Introduction.

Hydroformylation reactions with CO/H<sub>2</sub> as reactant gas feedstock require to be carried out at higher pressures than would be necessary if only CO were used in the gas phase, and a liquid compound containing hydrogen were used as the source of hydrogen. Such potential hydrogen sources might take the form of primary or secondary alcohols which should dehydrogenate fairly readily to give aldehydes or ketones respectively. Use of alcohols as hydrogen sources, as well as requiring lower reaction pressures and therefore more easily maintained plant, would increase ease of transport and handling. Another advantage of alcoholic feedstock is that it may be regenerated from biomass and so limited fossil fuel reserves would be released from syngas production for more specialised use.

For these reasons it was of interest to investigate the use of alcohols as sources of hydrogen in hydroformylation reactions. Both rhodium and ruthenium based systems, with tertiary phosphine ligands, have been shown to be active dehydrogenation catalysts<sup>32,42</sup>.

#### 3.1.1. Transfer hydrogenation.

Various transition metal species have been shown to be active transfer hydrogenation catalysts with alcohols frequently used as the hydrogen source<sup>43</sup>.

Generally alkene double bonds are hydrogenated, as for example in the work of Bennett and Welling<sup>44</sup>, who showed that the vinyl bond of (2-vinylphenyl)diphenylphosphine,  $o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ , SP, was hydrogenated to  $o\text{-CH}_3\text{CH}_2\text{C}_6\text{H}_4\text{PPh}_2$ , when the five coordinate rhodium species  $\text{RhCl}(\text{SP})_2$  was dissolved in a methanolic solution of

sodium carbonate,  $\text{Na}_2\text{CO}_3$ . SP is a bidentate ligand coordinating to rhodium via the phosphorus atom and the vinyl double bond. The product following transfer hydrogenation from methanol was the square planar complex  $\text{RhCl}(\text{CO})(o\text{-CH}_3\text{CH}_2\text{C}_6\text{H}_4\text{-PPh}_2)_2$ , with the phosphine ligand now only monodentate. Methanol was shown to be the source of both hydrogen and CO, with formaldehyde proposed as an intermediate ligand on the rhodium. This stoichiometric reaction shows the potential for transfer hydrogenation and decarbonylation of methanol by a rhodium species.

Ugo et al.<sup>45</sup> showed that several rhodium hydrido carbonyl triphosphine species would act as hydrogen transfer catalysts for the hydrogenation of oct-1-ene to octane at  $130^\circ\text{C}$  under an atmosphere of nitrogen, with a solution of potassium benzoate in benzyl alcohol acting as the hydrogen source. The most efficient catalyst of the type  $\text{RhH}(\text{CO})(\text{L})_3$ , where  $\text{L} = \text{PEt}_3$ ,  $\text{P}^n\text{Bu}_3$ ,  $\text{PEt}_2\text{Ph}$  and  $\text{PMePh}_2$ , was found to be  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  which gave 50% conversion of benzoate to benzoate and 35% conversion of oct-1-ene to octane. Isomerisation of unreduced octene was seen to occur and, interestingly, it was also observed that these systems were deactivated in a carbon monoxide atmosphere.

Transfer hydrogenation of the carbonyl group in cyclohexanone to give cyclohexanol as product was reported by Spogliarich et al.<sup>46</sup> using a variety of cationic rhodium-diene complexes with substituted phosphine ligands as catalyst precursors, and propan-2-ol with aqueous KOH as hydrogen source. The diene ligands chosen were cyclooctadiene and norbornadiene, both with bis(diphenylphosphino)ethane giving >84% hydrogenation of cyclohexanone when refluxed with aqueous KOH solution ( $\text{Rh}:\text{KOH} = 1:10$ ) in propan-2-ol under argon. A 30 minute activation period was required followed by injection of substrate and a 15 minute reaction time with

catalyst:substrate = 1:1900. The presence of KOH was required for transfer hydrogenation to take place, with increasing conversion found at higher concentrations of base. Bidentate phosphine ligands were found to increase the catalytic activity over monodentate ligands. This was thought to be due to the restricted geometry imposed by the chelating ligand preventing a trans-dihydride intermediate from forming. A ratio of bidentate ligand:Rh of 1-2:1 gave best results; at higher concentrations catalytic activity decreased rapidly.  $\text{RhCl}(\text{PPh}_3)_3$  was similarly shown to catalyse this reaction giving 59% hydrogenation of cyclohexanone in 15 minutes.

Vol'pin et al.<sup>47</sup> studied the use of a variety of rhodium, ruthenium and iridium complexes with  $\text{PPh}_3$  as hydrogen transfer catalysts, using either methanoic acid,  $\text{HCOOH}$ , lithium methanoate,  $\text{HCOOLi}$ , or  $\text{HCOOH}$  with  $\text{HCOOLi}$  as hydrogen source, for the reduction of oct-1-ene to octane, with DMF as solvent in reactions lasting 3 hours. Wilkinson's catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ , gave 100% conversion at 40 and 60°C with  $\text{HCOOH} + \text{HCOOLi}$  as hydrogen source (also giving complete hydrogenation of oct-4-ene at 60°C), while a temperature of 100°C was required by  $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$ , to give 65% conversion, and by  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , to give 60% hydrogenation of oct-1-ene to octane. In all these examples the ratio of substrate: $\text{HCOOH}$ : $\text{HCOOLi} \cdot \text{H}_2\text{O}$ :catalyst was 30:100:30:1. With just  $\text{HCOOLi}$  as hydrogen source (ratio of substrate: $\text{HCOOLi} \cdot \text{H}_2\text{O}$ :catalyst = 30:60:1) the best conversion (50%) was achieved with  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  at 100°C, yields generally being <50% with this hydrogen source. Using just  $\text{HCOOH}$  as hydrogen source (ratio of substrate: $\text{HCOOH}$ :catalyst = 30:100:1) yields were again generally <50%, complete conversion only being shown with  $\text{IrBr}(\text{CO})(\text{PPh}_3)_2$  as catalyst, at 100°C.

Ruthenium based catalysts for transfer hydrogenation generally require higher temperatures than those discussed above for rhodium.

For example Sasson and Blum<sup>48</sup> showed that a system based on  $\text{RuCl}_2(\text{PPh}_3)_3$  would hydrogenate the alkene bond in 1-phenylbut-1-en-3-one to 1-phenylbutan-3-one (~94% yield) with benzyl alcohol as the hydrogen source in a 4 hour reaction at ~200°C without a solvent. Of the  $\alpha,\beta$ -unsaturated carbonyl compounds studied, ketones gave the best results, as there was partial self-condensation of the aldehydes, and the esters underwent transesterification with the donor alcohol lowering yields when these materials were used as substrate. Saturated ketones were not reduced under these conditions, while hydrogenation of alkenes took place more slowly with isomerisation also occurring.

Speier and Marko<sup>49</sup> carried out mechanistic studies on a similar system for the transfer hydrogenation of the alkene bond of an  $\alpha,\beta$ -unsaturated carbonyl compound, benzylideneacetone, with  $\text{RuCl}_2(\text{PPh}_3)_3$  as catalyst precursor and benzyl alcohol, diphenyl carbinol, methylphenyl carbinol and benzion as hydrogen sources. Dibenzylether was used as solvent and reactions were carried out at 170-190°C.  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  was shown to form in the reaction mixture on dehydrogenation and decarbonylation of the solvent alcohol at elevated temperature. This species was then believed to rapidly form  $[\text{Ru}(\text{CO})(\text{PPh}_3)_3]$  which, on dissociation of a  $\text{PPh}_3$  ligand, would then coordinate olefin and add alcohol oxidatively to give  $\text{RuH}(\text{OR})(\text{alkene})(\text{CO})(\text{PPh}_3)_2$ . This would then be followed by hydrogen abstraction to form  $\text{RuH}_2(\text{alkene})(\text{CO})(\text{PPh}_3)_2$ , with elimination of aldehyde, allowing reductive elimination of hydrogenated product to follow. The rate determining step was considered to be the oxidative addition of the O-H bond of the donor alcohol to the ruthenium centre, this requiring more drastic conditions than similar addition of H-H.

The use of base with a secondary alcohol as hydrogen source has

recently been reported to allow transfer hydrogenation of ketones to alcohols to take place at lower temperatures. Chowdhury and Backvall<sup>50</sup> have used refluxing propan-2-ol as the hydrogen source in transfer hydrogenation of cyclohexanone to cyclohexanol (89% in 1 hour) using  $\text{RuCl}_2(\text{PPh}_3)_3$ , with NaOH as catalyst. No hydrogenation took place at this temperature (82°C) in the absence of NaOH. The presence of NaOH was thought to effect the attack of isopropoxide ion on the ruthenium complex to give an anionic species, followed by  $\beta$ -abstraction of hydrogen to eliminating propanone from an anionic ruthenium hydride species. Protonation of this anionic species would give a ruthenium dihydride, which in turn could reduce the cyclohexanone to cyclohexanol.

### 3.1.2. Hydrogen transfer reactions also involving CO.

Both ruthenium and rhodium systems were shown by Isnard et al.<sup>51</sup> to catalyse the formation of pentan-3-one, DEK, from ethene and CO with propan-2-ol as hydrogen source. The reaction was carried out at 160°C with  $\text{C}_2\text{H}_4:\text{CO}$  (1:2) at 15 atmos. in propan-2-ol for 24 hours. With  $\text{RuCl}_3$  as catalyst, 37 mmol DEK/mmol catalyst were produced in the absence of an amine promoter, while with triethylamine present the production dropped to 7 mmol DEK/mmol catalyst. In comparison it was found that with the same conditions and  $\text{Rh}_6(\text{CO})_{16}$  as catalyst, 29 mmol DEK/mmol catalyst were produced in the absence of an amine promoter, while with triethylamine present the production rose to 50 mmol DEK/mmol catalyst. The reaction was not very efficient and as well as the expected products, DEK and propanone, the latter from dehydrogenation of propan-2-ol, other by-products were formed, including 2-methylethyl propionate and ethane.

Rhodium hydrides, with various basic trisubstituted phosphine

ligands including  $\text{PtBu}_3$ ,  $\text{P}^i\text{Pr}_3$ ,  $\text{PEt}_3$  and  $\text{PCy}_3$ , are reported<sup>52</sup> to catalyse the hydrogenation of carbonyl and nitro compounds with  $\text{H}_2\text{O}/\text{CO}$ . These compounds are also reported to hydroformylate alkenes with methanal,  $\text{HCHO}$ , as the source of hydrogen and  $\text{CO}$ .

A recent paper by Jenner et al.<sup>53</sup> discusses the use of aqueous methyl methanoate as a source of  $\text{CO}/\text{H}_2$  in a system catalysed by  $\text{Ru}_3(\text{CO})_{12}$  with tricyclohexylphosphine at  $180^\circ\text{C}$ . Comment is made that this system will hydroformylate hex-1-ene to give 51%  $\text{C}_7$  alcohols and 24% hexane with methyl methanoate as the source of both hydrogen and  $\text{CO}$ , but this reaction has not yet been published in full.

A system based on  $\text{RhH}(\text{PEt}_3)_3$  was found to act as a catalyst precursor for the hydroformylation of hex-1-ene in the presence of  $\text{CO}$  with ethanol acting as both hydrogen source and solvent. This rhodium based system was therefore investigated further and the results are recorded below.

### 3.2. Comparison of differing alcohols as hydrogen source.

A series of reactions was carried out on hex-1-ene ( $1 \text{ cm}^3$ ) using  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor in an alcoholic solvent ( $0.008 \text{ moles dm}^{-3}$ ,  $4 \text{ cm}^3$ ) with  $\text{CO}$  (30 atmos) in the gas phase and the oven set at  $\sim 144^\circ\text{C}$  for 16 hours. The results are shown in table 3.1.

It may be seen that in all the reactions listed the major product was  $\text{C}_7$  alcohol, as had been the case in hydroformylation with  $\text{CO}/\text{H}_2$  (see chapter 2.), rather than  $\text{C}_7$  aldehyde, but esters had also formed. These were a mixture of Reppe product esters<sup>33</sup>, for example with ethanol as solvent/hydrogen source ethyl heptanoate, ethyl 2-methylhexanoate and heptyl heptanoate formed, as well as the not so readily expected ethyl ethanoate, heptyl ethanoate and 2-methylhexyl ethanoate. The Reppe products were probably formed by nucleophilic

Table 3.1. Alcohols as sources of hydrogen.

Solvent/ hydrogen source	C <sub>7</sub> alcohol		other products <sup>a</sup>
	% yield	n:i	
methanol <sup>b</sup>	66	1.4	MH. M2MH. HH. MM.
methanol <sup>c</sup>	74	1.4	MH. M2MH. HH. MM
ethanol <sup>b</sup>	45	1.7	EE. EH. E2MH. ethanal.
ethanol <sup>c</sup>	66	1.7	EE. EH. HE. E2MH. 2MHE. HH. ethanal.
butan-1-ol <sup>b</sup>	32	2.0	BB. BH. B2MH. butanal.
butan-1-ol <sup>c</sup>	50	2.9	BB. BH. B2MH. HH. butanal.
propan-2-ol <sup>b</sup>	8	4.6	iPrH. HH. C <sub>7</sub> aldehyde, 6.5%, n:i = 1.5
propan-2-ol <sup>c</sup>	12	4.1	iPrH. HH. C <sub>7</sub> aldehyde, 7.5%, n:i = 1.5
propan-2-ol <sup>bde</sup>	5	7.2	iPrH. HH. propanone.
propan-2-ol <sup>cd</sup>	8	4.0	iPrH. HH. propanone.

[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.008 moles dm<sup>-3</sup>; hex-1-ene, 1 cm<sup>3</sup>; alcohol, 4 cm<sup>3</sup>; CO pressure, 30 atmos; temperature, 142-145°C; time, 16 hours.

<sup>a</sup> MH. methyl heptanoate; M2MH. methyl 2-methylhexanoate; HH. heptyl heptanoate; MM methyl methanoate; EE. ethyl ethanoate; EH. ethyl heptanoate; E2MH. ethyl 2-methylhexanoate; HE. heptyl ethanoate; 2MHE. 2-methylhexyl ethanoate; BB. butyl butanoate; BH. butyl heptanoate; B2MH. butyl 2-methylhexanoate; iPrH. isopropyl heptanoate.

<sup>b</sup> no PEt<sub>3</sub> added.

<sup>c</sup> [PEt<sub>3</sub>], 0.08 moles dm<sup>-3</sup>.

<sup>d</sup> 64 hours.

<sup>e</sup> some evidence of catalytic decomposition.

attack of ethanol on an intermediate rhodium-acyl species (or in the case of heptyl heptanoate, nucleophilic attack of product heptanol on the same rhodium-acyl species, once the concentration of heptanol produced was sufficient to allow this) while the ethanoate esters were similarly formed by nucleophilic attack of ethanol, and C<sub>7</sub> alcoholic products, on a Rh-CO-CH<sub>3</sub> intermediate, itself formed when ethanal added oxidatively to the rhodium centre across the aldehydic C-H bond, as shown in figure 3.1. and discussed in chapter 4. (ie. Reppe type products, formed later in the catalytic cycle).

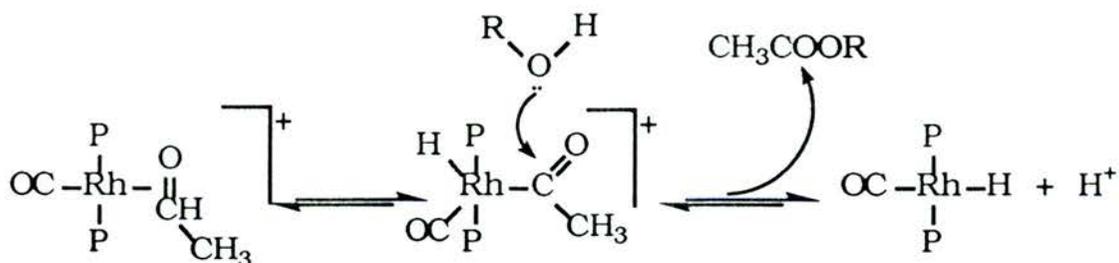


Figure 3.1.

Thus all the ethanoate esters were solvent dehydrogenation products. Similarly solvent dehydrogenation accounted for the formation of methanoates from methanol and butanoates from butanol. The formation of aldehyde was expected on dehydrogenation of the primary alcoholic solvent and seen in the case of ethanal and butanal, from ethanol and butanol respectively. The volatility of methanal is such that it will have been vented with the reactant gases at the end of the reaction, and so was not detected in methanol reaction mixtures. When propan-2-ol was used as solvent the expected dehydrogenation product, propanone, was detected by GCMS in the reaction mixture of the experiments lasting 64 hours. These samples had to be run under different conditions, from those usually employed for GCMS of products from these reactions, for the propanone to be separated from isomerised hexenes and propan-2-ol. It is probable that if similar analysis conditions had been used for the samples from the 16 hour experiments propanone would again have been detected.

It is apparent from table 3.1. that methanol was a more efficient source of hydrogen with this catalytic system than ethanol, which in turn was more efficient than butan-1-ol. All three primary alcohols studied were better sources of hydrogen for hydroformylation reactions than the only secondary alcohol looked at, namely propan-2-ol. The fact that by extending the reaction time in propan-2-ol the yield of C<sub>7</sub> alcohol was not increased was probably due to isomerisation of the unreacted hexene making the double bond of the alkene sterically less obtainable. The comparatively poor performance

of propan-2-ol, which might be expected to be more readily dehydrogenated than a primary alcohol,<sup>54</sup> was probably due to steric factors. The active site on the catalyst would be required to allow the hydrogen donating solvent to approach and if that donor were too bulky it would not be able to align itself correctly for dehydrogenation to take place. The observation that of the primary alcohols, the most active was methanol, also the least bulky, and that activity dropped off as the alcoholic bulk increased would seem to confirm the importance of steric factors in this dehydrogenation process.

The addition of a tenfold excess of  $\text{PEt}_3$  to the reaction mixture in all cases improved the yield of  $\text{C}_7$  alcohol but also increased the variety and quantity of esters produced. Without free  $\text{PEt}_3$ , esters solely from the solvent, ie methyl methanoate, ethyl ethanoate and butyl butanoate, were detectable, together with heptyl heptanoate in reactions with over 60% yield of  $\text{C}_7$  alcohol. In the presence of free  $\text{PEt}_3$ , oxidative addition of ethanal, produced by dehydrogenation of the solvent, led to the formation of a rhodium-acyl species as shown in scheme 3.1.. This was then subject to nucleophilic attack by the product  $\text{C}_7$  alcohols producing ethanoate esters, which were detected in ethanol. This type of ester also probably formed in methanol, but was not detected by GCMS as the mass spectrum of a methanoate is very similar to the spectrum of the alcohol forming the methanoate ester. Thus as the spectra of heptanol and heptyl methanoate are very similar in appearance and both materials would also be eluted together from the GCMS column they would not be distinguishable.

All reactions carried out without excess  $\text{PEt}_3$  present showed extensive isomerisation of the unreacted hexene, while little isomerisation took place when  $\text{PEt}_3$  was present. Thus the catalytic species formed in the presence of excess  $\text{PEt}_3$  reduced the rate of isomerisation. The increased yield in the presence of excess  $\text{PEt}_3$

could either have been brought about by a faster reaction rate, or by a seemingly larger source of feed in the form of hex-1-ene.

The n:i ratio of C<sub>7</sub> alcohol produced was seen to decrease with increased conversion. This was also found to be the case in hydroformylation reactions with CO/H<sub>2</sub>, but at 142-145°C the ratio was lower than that observed with an elemental hydrogen source. This low n:i ratio with methanol or ethanol as the hydrogen source could have been due to more isomerisation, as shown in figure 3.2., taking place at the higher temperature, and becoming evident because of the slower hydrogenation step with an alcohol as the hydrogen source.

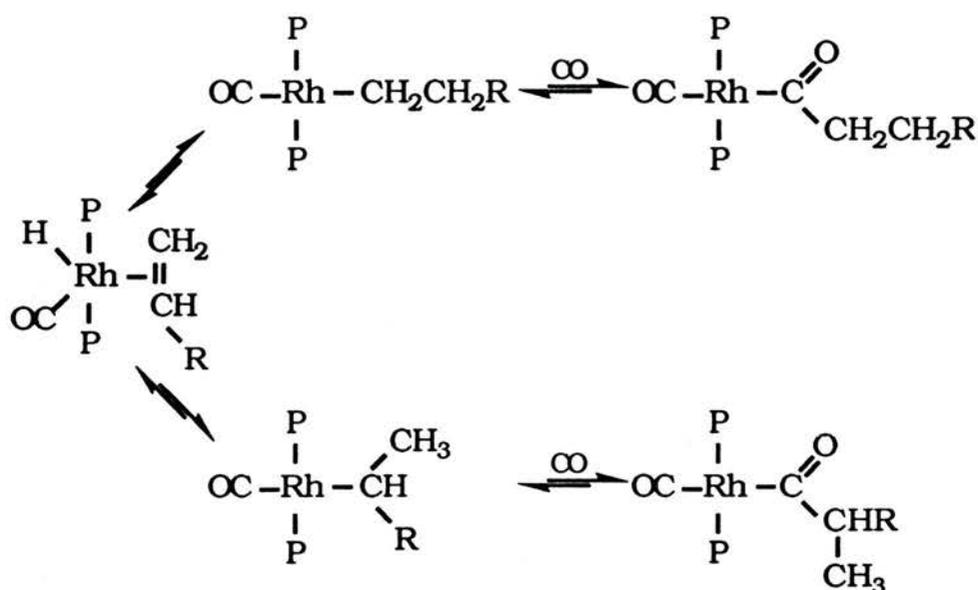


Figure 3.2.

### 3.3. Attempted use of RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> and Rh<sub>2</sub>(OAc)<sub>4</sub> with PEt<sub>3</sub> as catalyst precursor.

One other catalyst system based on rhodium was tested to see if it would act as a catalyst for hydroformylation reactions using ethanol as the hydrogen source. RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> in ethanol (0.0006 moles dm<sup>-3</sup>, 8 cm<sup>3</sup>) gave no product when hex-1-ene (2 cm<sup>3</sup>) was reacted with CO at 40 atmos and the oven set at 120°C for 16 hours, but the hexene had isomerised. A reaction with higher concentration of

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$  in ethanol ( $0.0069 \text{ moles dm}^{-3}$ ,  $4 \text{ cm}^3$ ) on hex-1-ene ( $1 \text{ cm}^3$ ) with CO at 30 atmos and the oven set at  $101^\circ\text{C}$  for 17 hours, gave a possible trace of 1,1-diethoxyheptane but no significant hydroformylation product and unreacted hexene was again isomerised.

An attempt was made to prepare  $\text{RhH}(\text{PEt}_3)_3$  in situ using  $\text{Rh}_2(\text{OAc})_4$  with  $\text{PEt}_3$  as catalyst precursor, as had been used in some hydroformylation reactions with CO/ $\text{H}_2$ . When  $\text{Rh}_2(\text{OAc})_4$  ( $0.004 \text{ moles dm}^{-3}$ ) with  $\text{PEt}_3$  ( $0.024 \text{ moles dm}^{-3}$ ) in ethanol ( $4 \text{ cm}^3$ ) was used in a reaction with CO at 40 atmos and the oven set at  $120^\circ\text{C}$  for 17 hours there was only 10% conversion to C<sub>7</sub> aldehyde (n:i 2.7) with no C<sub>7</sub> alcohol produced, and most of the remaining hexene was isomerised. It was felt that an induction period might be needed for the formation of the required catalyst and so a second experiment was carried out with the same reaction conditions but prior to adding the substrate the catalytic mixture was allowed to stand for 2 hours under CO/ $\text{H}_2$  (28 atmos) at ambient temperature. Again after allowing the reaction to take place for 16 hours, only 10% conversion to C<sub>7</sub> aldehyde (n:i 2.4) occurred, with no C<sub>7</sub> alcohol being produced. Isomerisation of the hexene had again taken place.

A further pair of reactions were carried out at lower pressure of CO with this system. In both cases the autoclave was primed with  $\text{Rh}_2(\text{OAc})_4$  ( $0.004 \text{ moles dm}^{-3}$ ) and  $\text{PEt}_3$  ( $0.024 \text{ moles dm}^{-3}$ ) in ethanol ( $4 \text{ cm}^3$ ) and pressurised with CO/ $\text{H}_2$  (1:1) to 40 atmos.. The first mixture was allowed to stand at room temperature for 2.5 hours while in the same time the second solution was heated to  $125^\circ\text{C}$  for 2 hours and then cooled in a water bath. The CO/ $\text{H}_2$  was then vented from the autoclaves prior to injection of hex-1-ene ( $1 \text{ cm}^3$ ) and pressurisation with CO to 20 atmos.. The autoclaves were then heated in an oven set at  $125^\circ\text{C}$  for 16 hours after which they were cooled, vented and their contents analysed by GCMS and glc. There had been similar

conversion in both cases to yield 60% C<sub>7</sub> aldehyde (n:i 1.3) and 15% C<sub>7</sub> alcohol (n:i 6.9) with 4% ethyl heptanoate, 1% ethyl 2-methylheptanoate. Some 1,1-diethoxyheptane and 1,1-diethoxy-2-methylhexane also formed. There was also some indication of a small amount of aldol condensation products. The unreacted hexene was isomerised to hex-2-ene and hex-3-ene. The sole dehydrogenation product from ethanol detected was a trace of ethanal, the major part having been vented with the reactant gas, but no ethanoate products were observed.

It therefore appears that the catalytic system generated from rhodium ethanoate and triethylphosphine in ethanol with CO was not the same as that produced by RhH(PEt<sub>3</sub>)<sub>3</sub>. Provided the pressure of CO was low enough hex-1-ene was hydroformylated to C<sub>7</sub> aldehydes in good yield with some hydrogenation on to C<sub>7</sub> alcohols. This hydrogenation was probably not direct but involved preformed C<sub>7</sub> aldehydes given the proportion of aldehyde present and the formation of acetals. A higher concentration of added PEt<sub>3</sub> in the reaction mixture might possibly have altered the product distribution in favour of C<sub>7</sub> alcohols.

#### 3.4. Varying the pressure of CO.

A series of reactions was carried out at varying pressure of CO. The results, in table 3.2., show that using RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol as catalyst precursor, with the oven set at 120°C the conversion of hex-1-ene to C<sub>7</sub> alcohol was dependent on the pressure of CO. Maximum conversion took place when the pressure was ~20 atmos. The drop in conversion above this pressure was probably due to the formation of either an inactive dimer, which formed in the absence of H<sub>2</sub> with excess CO present, or a less active hydroformylation catalyst forming on coordination of a higher proportion of CO. Similar equilibria have

Table 3.2. Varying pressure of CO.

Temp. /°C	solvent	CO pressure /atmos.	without $\text{PEt}_3$ .				with $\text{PEt}_3^{\text{a}}$ .			
			C <sub>7</sub> alcohol % yield	n:i	C <sub>7</sub> aldehyde % yield	n:i	C <sub>7</sub> alcohol % yield	n:i	C <sub>7</sub> aldehyde % yield	n:i
120	ethanol	40	44	2.6	5	0.6	49	2.4	4	0.6
		30	44	2.5	5	0.6	62	2.4	5	0.6
		25	46	2.5	5	0.5	73	2.3	2	0.6
		20	55	2.0	3	nk	80	2.2	2	0.6
		15	52	2.4	3	0.5	75	2.1	2	0.5
		10	34	4.1	3	0.4	60	2.6	3	0.4
145	methanol	40	52	1.4	13	0.4	66	1.7	-	-
		30	66	1.4	-	-	73	2.0	-	-
		20	69	1.8	tr	-	85	1.4	-	-

[RhH( $\text{PEt}_3$ )<sub>3</sub>], 0.008 moles  $\text{dm}^{-3}$ ; hex-1-ene, 1  $\text{cm}^3$ ; alcohol, 4  $\text{cm}^3$ ; time, 16 hours.

<sup>a</sup> [ $\text{PEt}_3$ ], 0.08 moles  $\text{dm}^{-3}$ ; tr, trace; nk, not known.

been observed with  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  and  $\text{CO}^{55}$  (see sections 5.3.1.-5.3.3.). A small proportion of product was detected in the form of C<sub>7</sub> aldehyde, slightly less at lower CO pressure than when the pressure was at or above 25 atmos. Also detected were esters, as described in section 3.2.. These were mainly in the form of ethyl heptanoate, which accounted for ~6% of the original hex-1-ene in reactions without free  $\text{PEt}_3$  while with a tenfold excess of  $\text{PEt}_3$  ~10% conversion to ethyl heptanoate had taken place, although traces of heptyl ethanoate, heptyl heptanoate and the equivalent branched chain esters were also detected.

As before in all reactions without excess  $\text{PEt}_3$  present the unreacted hex-1-ene was almost completely isomerised to hex-2-ene

and hex-3-ene, while in the presence of excess  $\text{PEt}_3$  unreacted hexene remained unisomerised and this could have accounted for the observed increased yield of  $\text{C}_7$  alcohol in the presence of excess  $\text{PEt}_3$ .

The reactions carried out in methanol at  $145^\circ\text{C}$  also seem to show the same trend, although none were attempted with the CO pressure below 20 atmos. There was less  $\text{C}_7$  aldehyde produced, except in the case of the reaction with CO pressure at 40 atmos without free  $\text{PEt}_3$ . There was no apparent reason for the higher proportion of aldehyde being produced in this reaction although there may have been some deterioration of the catalyst at this temperature in the absence of excess  $\text{PEt}_3$  (see section 3.6.).

### 3.5. Varying concentration of $\text{RhH}(\text{PEt}_3)_3$ .

It had been found that, when low concentrations of  $\text{RhH}(\text{PEt}_3)_3$  had been used as catalyst precursor for hydroformylation reactions with  $\text{CO}/\text{H}_2$ , the major product was  $\text{C}_7$  aldehyde (see section 2.5.). Table 3.3. shows the results of a series of reactions carried out on hex-1-ene at varying concentration of  $\text{RhH}(\text{PEt}_3)_3$ , with the oven set at  $125^\circ\text{C}$  for 16 hours, to see if similar results would be obtained using only CO in the gas phase and ethanol as the hydrogen source.

Considering first those reactions listed in table 3.3. without added  $\text{PEt}_3$ , at concentrations of  $\text{RhH}(\text{PEt}_3)_3$  below  $0.002 \text{ moles dm}^{-3}$  there was less than 5% conversion to  $\text{C}_7$  aldehyde, with no  $\text{C}_7$  alcohol being formed. With the concentration of  $\text{RhH}(\text{PEt}_3)_3$  between  $0.004$  and  $0.006 \text{ moles dm}^{-3}$  there was ~34% conversion overall with the proportion of  $\text{C}_7$  alcohol formed increasing at higher concentration of catalyst precursor. As the catalyst concentration increased from  $0.008 \text{ moles dm}^{-3}$  to  $0.010 \text{ moles dm}^{-3}$  the conversion to  $\text{C}_7$  alcohol also increased significantly, from 47% to 80%, with little or no  $\text{C}_7$  aldehyde being detected in the reaction mixture.

Table 3.3. Varying concentration of RhH(PEt<sub>3</sub>)<sub>3</sub>.

[RhH(PEt <sub>3</sub> ) <sub>3</sub> ] /moles dm <sup>-3</sup>	Without PEt <sub>3</sub> added.				With PEt <sub>3</sub> added.				
	C <sub>7</sub> aldehyde % yield	n:i	C <sub>7</sub> alcohol % yield	n:i	[PEt <sub>3</sub> ] /moles dm <sup>-3</sup>	C <sub>7</sub> aldehyde % yield	n:i	C <sub>7</sub> alcohol % yield	n:i
0.0008	3	3.8	-	-	0.008	9	2.5	3	25.0
0.0016	4	2.3	-	-	0.016	9	1.0	12	12.7
0.002	4	0.9	8	5.6	0.02	6	2.0	8	15.3
0.004	10	0.7	24	6.8	0.04	3	0.6	50	3.2
0.006	5	0.4	29	4.2	0.06	1	0.7	56	3.5
0.008	3	0.3	47	3.3	0.08	2	0.6	65	3.2
0.010	-	-	80	2.1	0.10	1	0.7	80	2.5

hex-1-ene, 1 cm<sup>3</sup>; ethanol, 4 cm<sup>3</sup>; pressure CO, 20 atmos; temperature, 125°C; time, 16 hours.

With a tenfold excess of PEt<sub>3</sub> present, comparing reactions with the same concentration of RhH(PEt<sub>3</sub>)<sub>3</sub>, there was slightly higher conversion to both C<sub>7</sub> aldehyde and C<sub>7</sub> alcohol at concentrations below 0.002 moles dm<sup>-3</sup> than had been the case in reactions without free PEt<sub>3</sub>, but the yield was still low. There appears to have been similar conversion both with and without PEt<sub>3</sub> when the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> was 0.002 moles dm<sup>-3</sup>, though the overall n:i ratio of products was far higher in the reaction with excess PEt<sub>3</sub>. With the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> at 0.004 moles dm<sup>-3</sup> there was a large increase in conversion to C<sub>7</sub> alcohol, with only a small proportion of C<sub>7</sub> aldehyde being produced. The maximum yield of C<sub>7</sub> alcohol was 80% with the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> at 0.010 moles dm<sup>-3</sup>, as in the reaction without excess PEt<sub>3</sub> at this catalyst concentration.

The limiting factor in both these systems, with and without excess PEt<sub>3</sub>, would appear to have been the ability of the catalytic species to dehydrogenate ethanol, thus allowing the hydroformylation

to proceed. The yield of C<sub>7</sub> aldehyde was not above 10% in any of these reactions, whereas, with molecular hydrogen present, at low catalyst concentration (RhH(PEt<sub>3</sub>)<sub>3</sub> at ~0.001 moles dm<sup>-3</sup>), rapid production of C<sub>7</sub> aldehyde took place in a short reaction time (see section 2.5.). At high catalyst concentration (RhH(PEt<sub>3</sub>)<sub>3</sub> at >0.006 moles dm<sup>-3</sup>) the C<sub>7</sub> product was alcoholic in form with up to 80% yield. Results would suggest that at a concentration of 0.004 moles dm<sup>-3</sup> with a tenfold excess of PEt<sub>3</sub> the catalyst concentration was such that the equilibrium allowed sufficient active species to form to allow dehydrogenation of ethanol to take place fairly readily, enabling 50% of the substrate, hexene, to be converted to C<sub>7</sub> alcohol. The turnover rate was >6 turnovers hour<sup>-1</sup> for the production of C<sub>7</sub> alcohol under these conditions.

It seems surprising that a short chain alcohol, such as ethanol, should dehydrogenate to give a mixture of ethanal and ethyl ethanoate and allow hex-1-ene to hydroformylate yielding a mixture of C<sub>7</sub> alcohols. This process was aided by the presence of excess PEt<sub>3</sub> which, being a relatively basic tertiary phosphine species and a poor π-acceptor, would produce a high electron density at the catalytic metal centre if multiple coordination took place. It is felt that this is a key to understanding this reaction, as the electron density could then be transmitted through a rhodium-acyl intermediate which could then either hydrogen bond with, or be protonated by, the alcoholic solvent. It is possible that a cationic hydroxycarbene-rhodium intermediate could form, as shown in figure 3.3., which would then proceed to give

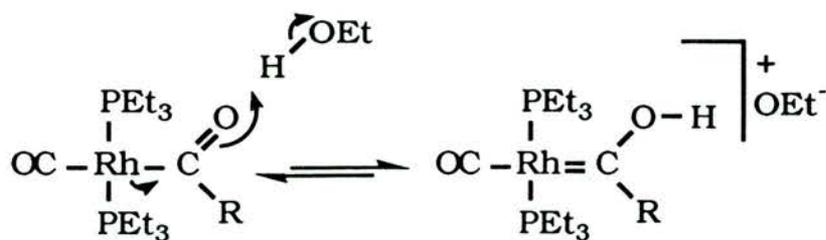


Figure 3.3.

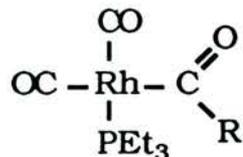
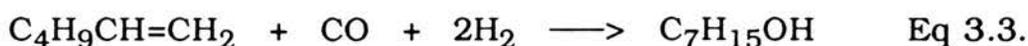
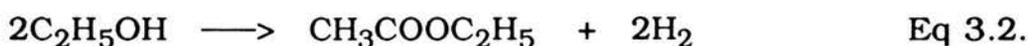
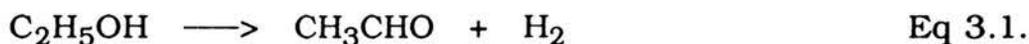


Figure 3.4.

an alcoholic product without an aldehydic species leaving the metal centre (see section 4.3.4.).

Thus at low concentration of  $\text{RhH}(\text{PET}_3)_3$  with CO at 20 atmos the equilibrium was such that the major species formed, possibly that shown in figure 3.4., could not dehydrogenate ethanol, and little hydroformylation took place as there was no significant source of hydrogen. At higher concentration of  $\text{RhH}(\text{PET}_3)_3$  or with excess  $\text{PET}_3$  present the equilibrium shifted to form a species richer in  $\text{PET}_3$  which could dehydrogenate ethanol and also allowed hydroformylation, with concurrent hydrogenation, giving C<sub>7</sub> alcohols to take place.

Also measured in this series of reactions was the concentration of ethyl ethanoate produced. This allowed calculation of the proportion of C<sub>7</sub> alcohol, that could be accounted for, gaining hydrogen from this source, rather than from dehydrogenation of ethanol to give ethanal as shown in equation 3.1..



Equations 3.2. and 3.3. show that two molecules of ethanol are required to form one molecule of ethyl ethanoate, releasing two molecules of hydrogen in the process. The conversion of hex-1-ene to C<sub>7</sub> alcohol also requires two molecules of hydrogen, so each mole of ethyl ethanoate accounts for one mole of C<sub>7</sub> alcohol. Table 3.4. shows the percentage of C<sub>7</sub> alcohol produced which gained its hydrogen from the production of ethyl ethanoate. At concentrations of catalyst precursor between 0.006 and 0.010 moles dm<sup>-3</sup>, in the absence of free  $\text{PET}_3$ , between 33% and 55% of the C<sub>7</sub> alcohol produced gained its required hydrogen from ethyl ethanoate production. At concentrations of catalyst precursor between 0.004 and 0.010 moles

Table 3.4. Percentage of C<sub>7</sub> alcohol accounted for by hydrogen from ethyl ethanoate production.

RhH(PET <sub>3</sub> ) <sub>3</sub> /moles dm <sup>-3</sup>	[PET <sub>3</sub> ] /moles dm <sup>-3</sup>	yield C <sub>7</sub> alcohol /moles dm <sup>-3</sup>	yield ethyl ethanoate /moles dm <sup>-3</sup>	% C <sub>7</sub> alcohol from ethyl ethanoate
0.006	0.00	0.23	0.10	43
0.008	0.00	0.40	0.22	55
0.010	0.00	0.64	0.21	33
0.004	0.04	0.40	0.10	25
0.006	0.06	0.45	0.32	71
0.008	0.08	0.52	0.35	67
0.010	0.10	0.64	0.31	48

hex-1-ene, 1 cm<sup>3</sup> (0.80 moles dm<sup>-3</sup>); ethanol, 4 cm<sup>3</sup>; pressure CO, 20 atmos; temperature, 125°C; time, 16 hours.

dm<sup>-3</sup>, when a tenfold excess of PET<sub>3</sub> was present in the reaction mixture, ethyl ethanoate accounted for between 25% and 71% of hydrogen required for the C<sub>7</sub> alcohol produced. This would appear to indicate that the catalytic route leading to C<sub>7</sub> alcohol using hydrogen from ethyl ethanoate production tended to be favoured in the presence of excess PET<sub>3</sub> and at catalyst concentration between 0.006 and 0.008 moles dm<sup>-3</sup>. Several reactions carried out with catalyst concentration at 0.008 moles dm<sup>-3</sup>, both with and without a tenfold excess of PET<sub>3</sub>, showed a wide range in the percentage of C<sub>7</sub> alcohol produced which gained its hydrogen from ethyl ethanoate. Some error in the calculated percentage was inevitable as the volatility of ethyl ethanoate is such that some of that produced will have been vented with the reactant gases leading to low measured concentration of this by-product. It is also possible that some other factor, as yet unaccounted for, also determined which route was the more favoured

under the conditions prevailing at the time. Traces of ethanal, which was the expected product of dehydrogenation of ethanol, were detected by GCMS in all these reaction mixtures but no attempt was made to ascertain how much had been produced as almost all was vented with the reactant gases.

Another by-product found in reactions with over ~50% conversion to C<sub>7</sub> alcohols was butan-1-ol, produced by the Guerbet reaction<sup>56</sup>. Ugo et al found that a system based on Rh(CO)<sub>2</sub>Cl<sub>2</sub> + 8 PEt<sub>3</sub> in butan-1-ol, in the presence of butoxide ion, caused dimerisation of the solvent, via butanal and H<sub>2</sub> production, to give 2-ethylhexanol and water. RhH(CO)(PEt<sub>3</sub>)<sub>3</sub> was proposed as the active catalyst for this reaction. This species was known to be present in the reactions in ethanol discussed above, and the presence of ethoxide counter ions is proposed in the reaction mechanism (see chapter 4.), so production of butan-1-ol from ethanol might therefore be expected by the Guerbet reaction. As butanol was only found in reactions with over 50% conversion to C<sub>7</sub> alcohols it appeared that the Guerbet reaction only took place once hydroformylation to C<sub>7</sub> alcohols was nearing equilibrium conditions, when the concentration of ethanal (and ethoxide ion) had been able to build up.

### 3.6. Varying reaction temperature.

As mentioned in chapter 2. the temperature of the reactants in the autoclave was not known accurately but as most of these reactions, using alcohols as sources of hydrogen, were carried out over periods of 16 hours the temperature within the autoclave should have reached that of the oven, as recorded for the reaction, in under a quarter of the overall reaction time. This group of reactions was carried out to give some indication of the temperature range over which hex-1-ene would react with CO and ethanol to give C<sub>7</sub> alcohols as products, the results

Table 3.5. Varying reaction temperature.

Oven temperature. /°C	Without $\text{PEt}_3$ .				With $[\text{PEt}_3]$ (0.008 moles $\text{dm}^{-3}$ ).			
	C <sub>7</sub> aldehyde		C <sub>7</sub> alcohol		C <sub>7</sub> aldehyde		C <sub>7</sub> alcohol	
	% yield	n:i	% yield	n:i	% yield	n:i	% yield	n:i
85	2	2.6	2	16.0	1	0.8	3	4.8
96	2	1.3	14	11.6	1	1.0	7	3.8
102	4	1.2	14	13.4	2	0.6	15	4.8
102	4	0.8	21	7.4	2	0.5	17	4.8
113	5	0.7	27	6.9	3	0.5	45	3.3
121	4	0.3	43	2.8	3	0.6	63	2.6
129	3	nk	40	2.1	0		65	2.1
139	6	0.5	48	2.0	2	0.3	65	1.9
145	<sup>a</sup> 5	0.5	22	2.8	3	0.8	51	2.4
162					<sup>a</sup> 6	0.6	35	2.8
171	<sup>a</sup> 3	0.8	11	3.3	<sup>a</sup> 5	nk	10	4.9

$[\text{RhH}(\text{PEt}_3)_3]$ , 0.008 moles  $\text{dm}^{-3}$ ; hex-1-ene, 1  $\text{cm}^3$ ; ethanol, 4  $\text{cm}^3$ ; pressure CO, 20 atmos; time, 16 hours.; nk, not known.

<sup>a</sup> some evidence of catalyst decomposition

being shown in table 3.5.. The two systems, with and without free  $\text{PEt}_3$ , both required a temperature of  $\sim 100^\circ\text{C}$  before more than 10% conversion to C<sub>7</sub> alcohols would take place, with conversion occurring a little more readily in the absence of free  $\text{PEt}_3$  at this temperature. (Using molecular hydrogen alcohols were produced at  $50^\circ\text{C}$  in the absence of free  $\text{PEt}_3$  and at  $64^\circ\text{C}$  in the presence of free  $\text{PEt}_3$ ). This indicated that the dehydrogenation of ethanol, by this rhodium system, required a higher temperature for activation than oxidative addition of molecular hydrogen to the catalytic centre. Above  $110^\circ\text{C}$  there was greater conversion in the presence of free  $\text{PEt}_3$  than in its absence, with the greatest yield being achieved at  $129\text{-}139^\circ\text{C}$ . At, and above,  $145^\circ\text{C}$  there were indications of catalyst decomposition

(blackening of the autoclave liner), particularly in the absence of free  $\text{PEt}_3$ , and there was a slight increase in the proportion of  $\text{C}_7$  aldehyde in the product. Thus hydroformylation using ethanol as the source of hydrogen, with  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, took place in a narrower temperature range than hydroformylation using molecular hydrogen. This was due to the higher temperature requirement for dehydrogenation of ethanol to take place, and the reduced stability of the catalytic species in the absence of molecular hydrogen at elevated temperature. The presence of free  $\text{PEt}_3$  did help to improve high temperature stability slightly.

As found in hydroformylation reactions with incomplete conversion there was a reduction in n:i ratio of products as conversion increased. Also noted was the n:i ratio of the small proportion of  $\text{C}_7$  aldehyde produced. This was largely branched chain product and could be accounted for in one of two ways. Firstly hydrogenation of aldehyde, which might be formed as a reaction intermediate, was faster for heptanal than for 2-methylhexanal. Alternatively the acyl intermediate, formed by Markownikoff addition of hex-1-ene and shown in figure 3.5., was more readily reductively eliminated from the metal centre as aldehyde than the anti-Markownikoff intermediate as shown in figure 3.6.. This would come about because the protonation of the acyl species, formed by the Markownikoff addition intermediate was more sterically hindered than protonation of the anti-Markownikoff addition intermediate. Thus formation of the proposed cationic hydroxycarbene-rhodium intermediate (which would then

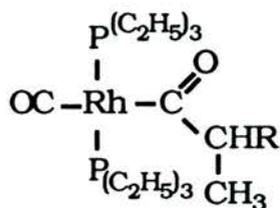


Figure 3.5.

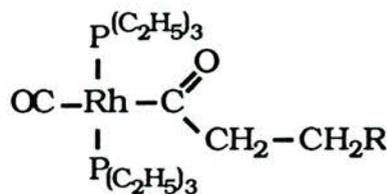


Figure 3.6.

react further to form the alcoholic product directly) was less likely and production of branched chain aldehyde was increased over that of straight chain aldehyde (see section 4.3.4.). As the major proportion of product was in the form of alcohol it is probable that both branched and straight chain intermediates preferentially formed C<sub>7</sub> alcohol directly but the probability of 2-methylhexanal, rather than heptanal, being reductively eliminated was greater.

Isomerisation of hexene was found to have taken place preferentially in the absence of free PEt<sub>3</sub> though it was observed, both with and without PEt<sub>3</sub>, at 149°C and above, at which temperature catalyst decomposition was also evident. At 85°C the hexene remained unisomerised in both systems. Thus, unlike a solution of hex-1-ene in thf under an atmosphere of nitrogen, when isomerisation took place gradually at room temperature, it did not occur as readily in ethanol under CO at 20 atmos.

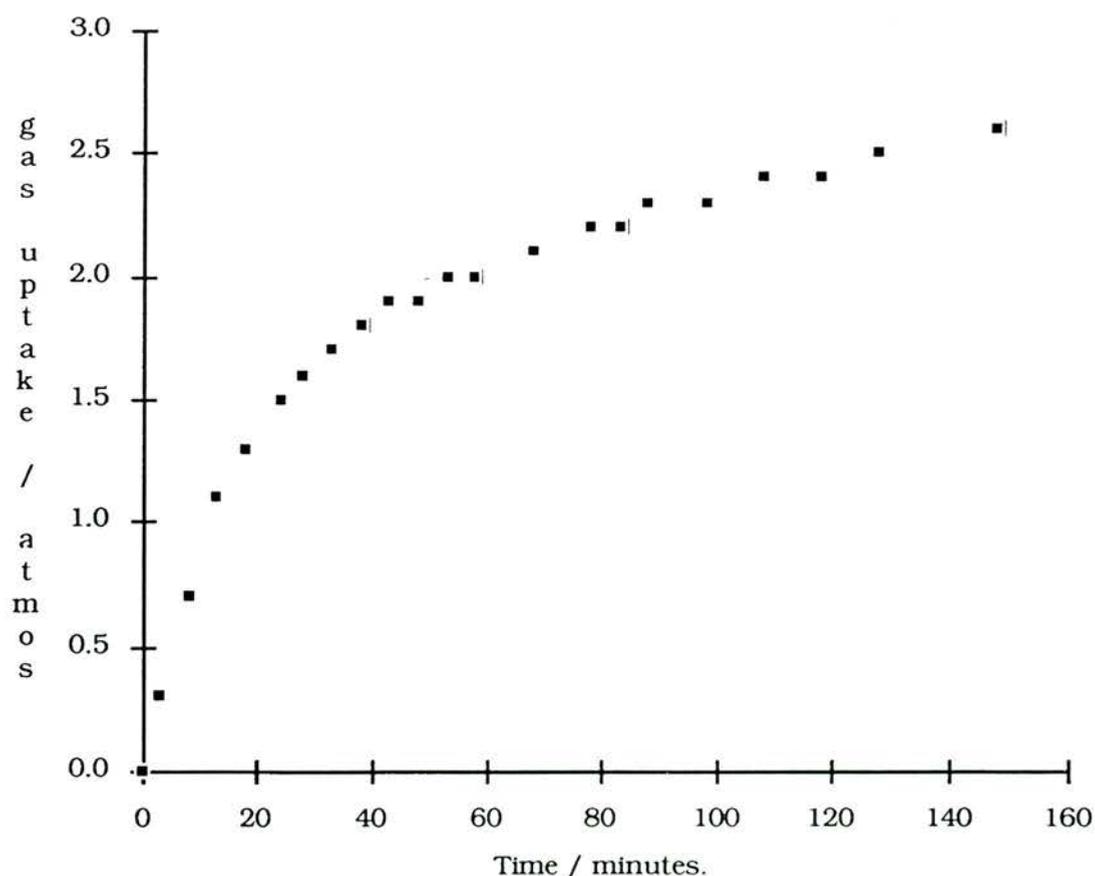
### 3.7. Reaction of hex-1-ene in ethanol with CO using RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor on the rig at B.P. Research Centre, Sunbury.

A reaction was carried out on hex-1-ene in ethanol with CO using RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor on the rig at B.P. Research Centre, Sunbury to be able to determine the rate of the reaction more accurately. The autoclave was primed with RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.004 moles dm<sup>-3</sup>, 30 cm<sup>3</sup>) with PEt<sub>3</sub> (177 μl, 0.04 moles dm<sup>-3</sup>). It was then heated to 120°C under nitrogen at 2 atmos before being pressurised with CO to ~16 atmos. CO at 22 atmos was then used to inject hex-1-ene (3 cm<sup>3</sup>) into the autoclave after which the pressure in the autoclave was held at 23-25 atmos. The stirrer speed was set at 1000 rpm and this speed was held for the first 80 minutes, after which it was lowered to 400 rpm. The progress of the reaction was monitored by logging the fall in pressure of the ballast vessel (130

cm<sup>3</sup>) from which CO was taken. Using this information a plot was drawn of gas uptake against time, as shown in figure 3.7..

Analysis of the products, after the 6 hour reaction, showed that there had been 49% conversion to C<sub>7</sub> alcohols (n:i 5.6), 4% to C<sub>7</sub> aldehydes (n:i 0.5) and 3% to ethyl heptanoate, with traces of ethyl 2-methylhexanoate and heptyl ethanoate also being detected. 36% of the hexene remained unreacted, though largely isomerised, with ethanal and ethyl ethanoate also being detected, as was a trace of butanol. The butanol will have been formed as a Guerbet product from ethanol and had been observed in small amount in other reactions (see

Rate of reaction of hex-1-ene in ethanol with CO using RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor



[RhH(PEt<sub>3</sub>)<sub>3</sub>], 0.0036 moles dm<sup>-3</sup>; [PEt<sub>3</sub>], 0.036 moles dm<sup>-3</sup>; hex-1-ene, 3 cm<sup>3</sup>; ethanol, 30 cm<sup>3</sup>; pressure CO, ~20 atmos; temperature, 120 °C.

Figure 3.7.

section 3.5.), particularly those carried out at high catalyst concentration or over a long reaction time.

Figure 3.7. shows an initial relatively rapid rate of reaction with  $7 \times 10^{-3}$  moles of CO being consumed in the first 20 minutes of the reaction. This is equivalent to 170 turnovers hour<sup>-1</sup>. After an hour the rate fell off to 10% of this value and enough CO had been taken up to account for 20% of the original hexene. The pressure dropped 4.3 atmos in 6 hours but the fall in pressure after 2.5 hours was not plotted as accurate readings were not taken and the ambient temperature was falling, thus altering the pressure in the ballast vessel without consumption of CO. In fact this total fall in pressure would not have accounted for a conversion of more than 46% of the hexene injected into the reaction vessel, while the total recorded conversion was 56%. It therefore seems likely that the exact start of the reaction was missed and gas uptake took place at or near the initial rate for slightly longer than noted.

### 3.8. Varying reaction time.

A series of reactions were carried out on hex-1-ene in ethanol with  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor, both without and with free  $\text{PEt}_3$ , with CO at 20 atmos and the oven set at 125°C over varying reaction times. The results are shown in table 3.6.. As was noted in section 2.1.1., the internal temperature of the autoclave did not reach that of the non-fan-assisted oven for >3 hours. As all the reactions listed in table 3.6. were carried out in such an oven there was an initial heating time before the recorded reaction temperature was reached which could have affected the product distribution, particularly in the shorter reactions listed.

It would appear that in the reactions without free  $\text{PEt}_3$  that C7 aldehyde formed initially, the conversion to C7 aldehyde remaining at

Table 3.6. Varying reaction time.

Time. /hours	Without $\text{PEt}_3$ .				With $[\text{PEt}_3]$ ( $0.008 \text{ moles dm}^{-3}$ ).			
	C7 aldehyde		C7 alcohol		C7 aldehyde		C7 alcohol	
	% yield	n:1	% yield	n:1	% yield	n:1	% yield	n:1
2	12	2.0	4	10.3	4	0.9	9	5.2
4	3	1.0	23	5.0	12	1.2	14	6.6
6	11	0.9	36	4.9	6	0.9	46	3.7
8	10	0.8	45	4.5	6	0.6	56	3.3
16	3	0.3	47	3.3	2	0.6	65	3.2
64 *					5	0.5	62	1.8

$[\text{RhH}(\text{PEt}_3)_3]$ ,  $0.008 \text{ moles dm}^{-3}$ ; hex-1-ene,  $1 \text{ cm}^3$ ; ethanol,  $4 \text{ cm}^3$ ; pressure CO, 20 atmos; oven temperature,  $125^\circ\text{C}$ .

\*  $139^\circ\text{C}$ .

~10% while the conversion to C7 alcohol increased with time as the temperature of the reaction mixture rose to  $125^\circ\text{C}$ . (There was also 9% conversion to ethyl heptanoate and 4% to ethyl 2-methylhexanoate in the 4 hour reaction which could have contributed to the apparently low yield of C7 aldehyde in comparison to reactions lasting 2, 6 and 8 hours). Little hydroformylation took place after 8 hours while most of the C7 aldehyde which still remained was hydrogenated to C7 alcohol.

With excess  $\text{PEt}_3$  present there was slower initial hydroformylation but a higher proportion of C7 alcohol produced from the onset of the reaction (except in the 4 hour reaction) and a higher yield overall after 6 hours. This would seem to confirm the observation made in section 3.6. that the system with free  $\text{PEt}_3$  present required a higher temperature for hydroformylation to take place, but when it did occur the main reaction proceeded to yield C7 alcohol as product. The results of the 4 hour experiments seem slightly anomalous and could have been due to irregular oven heating, as the oven temperature only averaged  $119^\circ\text{C}$  at the end of this

reaction.

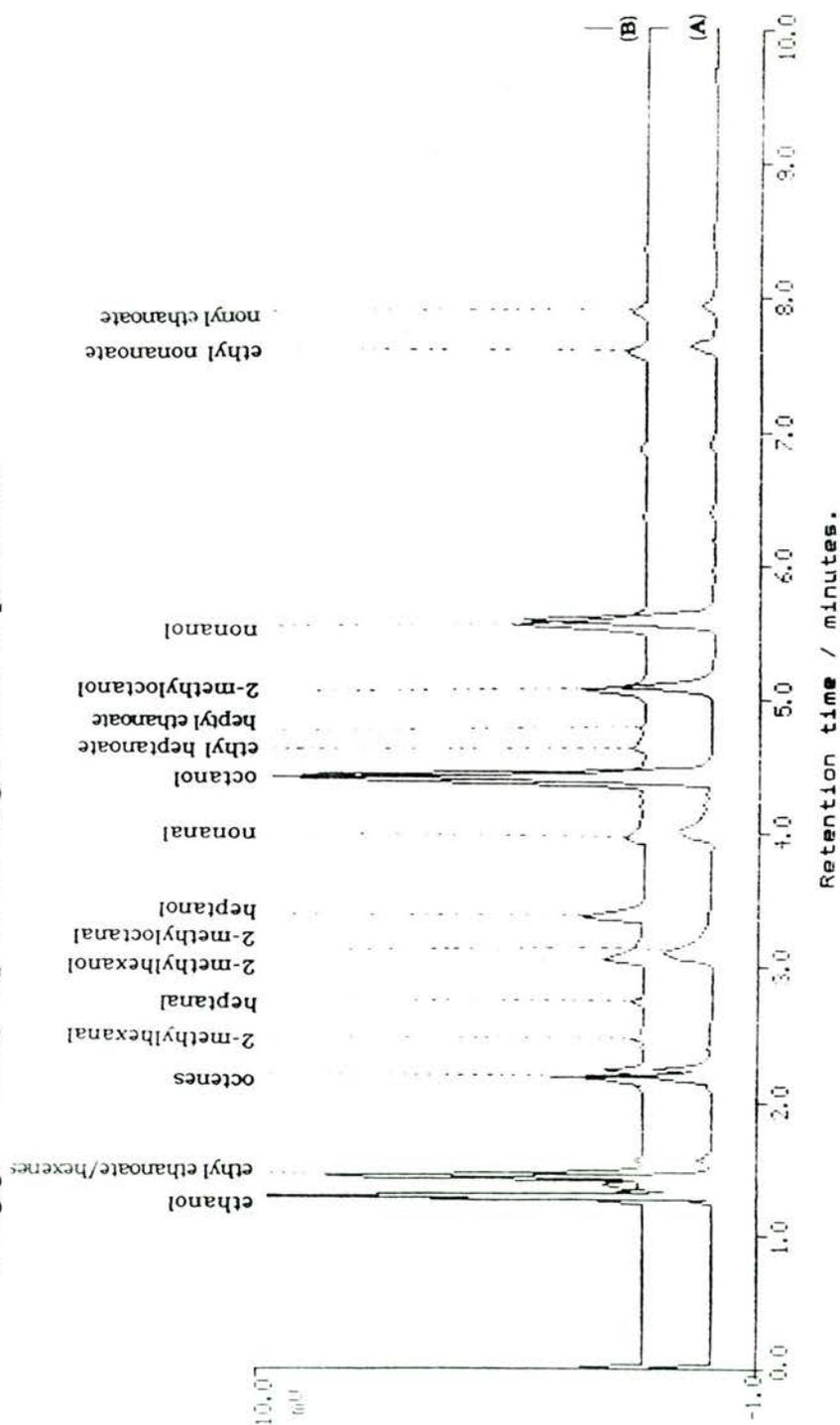
It was noted that complete conversion of hex-1-ene to C<sub>7</sub> alcohols did not take place, with a reaction which was heated to 139°C for 64 hours giving an overall yield of 67%. Some previous reactions gave a higher yield, of up to 80% C<sub>7</sub> alcohols in ethanol, and it was possible that either an equilibrium had been reached or that the catalyst was becoming poisoned as the reaction proceeded.

### 3.9. Reaction to test for catalyst poisoning.

Two identical reactions to hydroformylate oct-1-ene (1 cm<sup>3</sup>) in ethanol (4 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) and PEt<sub>3</sub> (0.08 moles dm<sup>-3</sup>) as catalyst precursor and CO at 20 atmos were carried out with the oven set at 125°C for 16 hours. Each autoclave was then cooled and vented. One sample (A) was used as a standard for comparison while the other (B) was repressurised with CO at 20 atmos after the addition of hex-1-ene (1 cm<sup>3</sup>) and then reheated to 125°C for a further 8 hours. Figure 3.8. shows the glc. trace of the products of both reactions. In both, oct-1-ene had been hydroformylated to the expected nonanol and 2-methyloctanol as major products, with some nonanal and 2-methyloctanal also being detected. The expected esters, ethyl nonanoate and nonyl ethanoate were also observed, as was some isomerisation of the unreacted octene. Sample (B) clearly showed that the hexene, which was added after the initial 16 hour reaction period, had also undergone hydroformylation with hydrogenation to give heptanol and 2-methylhexanol (combined yield 37%, n:i 1.23), with lesser yields of heptanal and 2-methylhexanal (combined yield 6%, n:i 1.17). Some ethyl heptanoate and heptyl ethanoate were also detectable.

This showed conclusively that the catalytic system had not been poisoned in the first 16 hour reaction but could still actively

Reaction of oct-1-ene in ethanol with CO for 16 hours followed by the addition of hex-1-ene for a further 8 hours, with  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor; glc trace of products.



(A)  $[\text{RhH}(\text{PEt}_3)_3]$ ,  $0.008 \text{ moles dm}^{-3}$ ;  $[\text{PEt}_3]$ ,  $0.08 \text{ moles dm}^{-3}$ ; oct-1-ene,  $1 \text{ cm}^3$ ; ethanol,  $4 \text{ cm}^3$ ; pressure CO, 20 atmos; oven temperature,  $125^\circ\text{C}$ ; time 16 hours.  
 (B) initial  $[\text{RhH}(\text{PEt}_3)_3]$ ,  $0.008 \text{ moles dm}^{-3}$ ; initial  $[\text{PEt}_3]$ ,  $0.08 \text{ moles dm}^{-3}$ ; oct-1-ene,  $1 \text{ cm}^3$ ; ethanol,  $4 \text{ cm}^3$ ; hex-1-ene added after 16 hours,  $1 \text{ cm}^3$ ; pressure CO, 20 atmos; oven temperature,  $125^\circ\text{C}$ ; time 16 hours + 8 hours.

Figure 3.8.

hydroformylate/hydrogenate hexene on fresh addition of substrate to the reaction mixture, although the n:i ratio of products was lower than in other reactions. Some oxidation of the catalyst may have occurred while the addition of hexene was taking place and thus altered the concentration of free  $\text{PEt}_3$  in solution; see next section. Venting the autoclave will have removed the accumulation of ethanal and some of the ethyl ethanoate, formed by dehydrogenation of ethanol in the first stage of this double reaction, thus destabilising the previous equilibrium by more than just the addition of hexene and allowing hydroformylation/hydrogenation to continue.

### 3.10. Catalyst sensitivity to air.

A sample of catalyst which had been dissolved in ethanol and had become partially oxidised on contact with air, was divided and used in two reactions, one without an addition of excess  $\text{PEt}_3$  and the other with a tenfold excess of  $\text{PEt}_3$  added, to see if it would still hydroformylate hex-1-ene in ethanol with only CO in the gas phase. In both reactions hex-1-ene ( $1 \text{ cm}^3$ ) and the partially oxidised  $\text{RhH}(\text{PEt}_3)_3$  ( $0.008 \text{ moles dm}^{-3}$ ) in ethanol ( $4 \text{ cm}^3$ ) as catalyst precursor pressurised with CO (30 atmos) were heated to  $140^\circ\text{C}$  for 17 hours, with  $\text{PEt}_3$  ( $0.08 \text{ moles dm}^{-3}$ ) added to only one of the reaction mixtures. The products of the reactions were analysed. While that without any addition of  $\text{PEt}_3$  showed no products other than isomerised hexene, the reaction with free  $\text{PEt}_3$  showed conversion to  $\text{C}_7$  alcohols in 64% yield (n:i 1.5; a decrease on that usually observed). This is in line with Lawrenson's finding<sup>10</sup> that stringent exclusion of molecular oxygen from the hydroformylation system catalysed by  $\text{Rh}(\text{P}^n\text{Bu}_3)(\text{CO})(\text{acac})$  improved the n:i ratio of product from 1.31 to 1.95).

This is further indication of the importance of  $\text{PEt}_3$  to this

catalytic system in ethanol and shows that the catalyst may be regenerated if partially oxidised on contact with air. The lability of the  $\text{PEt}_3$  ligands is such that uncoordinated  $\text{PEt}_3$  will mop up any molecular oxygen in the system, forming triethylphosphine oxide, which is only poorly coordinating to rhodium<sup>57</sup>. This would leave the rhodium centre depleted in this ligand,  $\text{PEt}_3$ , and solvent ethanol would be the only other species available for coordination. Addition of further free  $\text{PEt}_3$  allowed regeneration of the original system.

### 3.11. Reactions with other substrates.

#### 3.11.1. Ethene.

A reaction was carried out on ethene on the rig at B.P. Research Centre, Sunbury. The autoclave was primed with  $\text{RhH}(\text{PEt}_3)_3$  in ethanol ( $0.002 \text{ moles dm}^{-3}$ ,  $30 \text{ cm}^3$ ) with  $\text{PEt}_3$  ( $88.5 \mu\text{l}$ ,  $0.02 \text{ moles dm}^{-3}$ ). It was then heated to  $120^\circ\text{C}$  under nitrogen at 2 atmos before the introduction of CO/ethene (1:1) at  $\sim 42$  atmos. There was an initial rise in temperature, due to dissolution of CO and ethene in the catalyst solution, and a fall in the pressure of the ballast vessel ( $320 \text{ cm}^3$ ) from 166.0 to 157.8 atmos. due to pressurisation of the reaction vessel, but once the temperature was returned from  $\sim 124^\circ\text{C}$  to  $120^\circ\text{C}$ , by applying cooling, there was no further fall in the pressure of the CO/ $\text{C}_2\text{H}_4$  mixture in the ballast vessel while it was monitored for 1.5 hours. The mixture was stirred at  $\sim 1000$  rpm throughout. After cooling under pressure the reactant gases were vented and the liquid contents of the autoclave analysed by glc. A trace of propanal was observed but no significant reaction had taken place.

#### 3.11.2. Propene.

A reaction, similar to that attempted on ethene, was carried out on propene on the same rig at B.P.. The autoclave was primed with

ethanol (27 cm<sup>3</sup>) and PEt<sub>3</sub> (88.5 μl). Propene (5.9 g) was then condensed in, and the autoclave was sealed before allowing the mixture to stabilise at room temperature. The contents of the autoclave were then heated to 110°C under an atmosphere of CO at 20 atmos. when the catalyst precursor solution of RhH(PEt<sub>3</sub>)<sub>3</sub> in ethanol (0.02 moles dm<sup>-3</sup>, 3 cm<sup>3</sup>) was then injected into the autoclave with a positive pressure of CO at ~37 atmos.. The pressure in the (smaller) ballast vessel (130 cm<sup>3</sup>) was monitored for 2 hours as the reaction mixture was stirred at ~1000 rpm but no apparent gas uptake was observed. The autoclave was allowed to cool as before and analysis of the liquid products by GCMS showed trace amounts of butanal and 2-methylpropanal and ethanal produced on dehydrogenation of ethanol.

In both this reaction on propene and the one on ethene the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> in the initial solution was fairly low and may have been insufficient to allow dehydrogenation of ethanol to take place efficiently. (In the hex-1-ene reaction carried out on this rig, discussed in section 2.7., the concentration of RhH(PEt<sub>3</sub>)<sub>3</sub> was ~0.004 moles dm<sup>-3</sup>, ie twice that used for ethene and propene). It seems probable that hydroformylation using CO with ethanol as the hydrogen source would take place at higher concentrations of RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor particularly as traces of aldehydic product were observed in these reactions.

### 3.11.3. Styrene.

A reaction carried out on styrene (1 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) and CO at 40 atmos at 120°C for 16 hours showed production of 3- and 2-phenylpropanols as the major products, with lesser yields of 3- and 2-phenylpropanals, as well as ethyl esters of both normal and iso phenylpropionates and 3- and 2- phenylpropyl ethanoate esters. Some

polymerisation had also taken place.. All these products, apart from those of the polymerisation, were analogues of products formed in similar reactions with hex-1-ene.

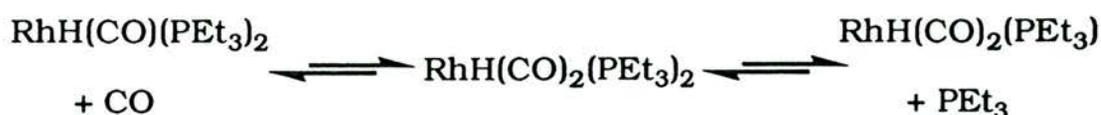
It is of interest to note that, although quantitative analysis was not carried out on this reaction mixture, the Markownikoff addition products (2-phenylpropanol etc) were formed in lower yield than the anti-Markownikoff addition products. This n:i distribution appeared similar to that found with hex-1-ene hydroformylation, both with CO/H<sub>2</sub> and CO with ethanol as the hydrogen source, but was the reverse of that found when styrene was hydroformylated with CO/H<sub>2</sub> using this catalytic system. Brown and Kent<sup>58</sup> found a similar result when using a system based on RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>, where nmr studies of a solution of the rhodium-acyl species formed as an intermediate in the hydroformylation of styrene showed the branched, Markownikoff addition species forming in high yields initially, but isomerisation to give greater yields of the normal, anti-Markownikoff addition species taking place on standing for 2 hours at 25°C. They concluded that in hydroformylation reactions at ambient temperature this isomerisation had little effect on the n:i ratio of products as hydroformylation took place rapidly, but that at higher temperatures it did become important, as 3-phenylpropanal became the major product at elevated temperature. In the system with RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor when hydroformylation was carried out in ethanol with CO/H<sub>2</sub> in the gas phase (section 2.8.3.), the rate of reaction was such that this isomerisation was again unimportant, but with ethanol as the source of hydrogen the rate at which hydrogen was extracted from ethanol was slow enough for this isomerisation to become apparent and influence the n:i ratio of products.

#### 3.11.4. Hex-2-ene.

Two reactions were carried out on hex-2-ene (1 cm<sup>3</sup>) with RhH(PEt<sub>3</sub>)<sub>3</sub> as catalyst precursor in ethanol (0.008 moles dm<sup>-3</sup>, 4 cm<sup>3</sup>) and CO at 20 atmos with the oven set at 125°C for 16 hours, to see if this system would hydroformylate an internal double bond both in the absence of free PEt<sub>3</sub>, and in its presence. The percentage yield of C<sub>7</sub> alcohols and C<sub>7</sub> aldehydes was measured but the ratio of Markownikoff addition product to anti-Markownikoff addition product was not ascertained.

In the absence of PEt<sub>3</sub> there was 47% conversion to C<sub>7</sub> alcohols and 5% conversion to C<sub>7</sub> aldehydes. Ethanal and ethyl ethanoate were also detected as expected and trace amounts ethyl 2-methylhexanoate and 2-methylhexyl ethanoate were also observed. In the presence of free PEt<sub>3</sub> there was 27% conversion to C<sub>7</sub> alcohols and 2% conversion to C<sub>7</sub> aldehydes. A trace of ethyl 2-methylhexanoate was also detected. In neither reaction was heptanol or heptanal detected so isomerisation to give hex-1-ene did not take place.

Thus, in the absence of free PEt<sub>3</sub>, RhH(PEt<sub>3</sub>)<sub>3</sub> was seen to hydroformylate/hydrogenate hex-2-ene to C<sub>7</sub> alcohols giving only slightly lower conversion in 16 hours at 125°C than was found with hex-1-ene. In the presence of a tenfold excess of PEt<sub>3</sub> the conversion was far lower than for hex-1-ene, probably due to steric factors inhibiting the reaction. The presence of free PEt<sub>3</sub> would favour the formation of a rhodium species with a higher proportion of PEt<sub>3</sub> coordinated to the metal centre than when no free PEt<sub>3</sub> were available, as suggested in equation 3.4., leading to greater steric



Eq 3.4.

crowding at the metal centre which would limit the access of the internal alkene, thus reducing the probability of coordination of the alkene double bond and reducing the reaction rate.

#### 3.11.5. Heptanal.

The rate of hydrogenation of heptanal (1 cm<sup>3</sup>) using ethanol (4 cm<sup>3</sup>) as the source of hydrogen and RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) with added PEt<sub>3</sub> (0.08 moles dm<sup>-3</sup>) and CO at 20 atmos as catalyst precursor in a reaction heated to 125°C for 6 hours was compared with the rate of hydroformylation/hydrogenation of hex-1-ene under the same conditions. It was hoped that this would give some indication as to whether or not C<sub>7</sub> aldehydes were formed as intermediates in the hex-1-ene reaction. While there was 14% conversion to C<sub>7</sub> alcohols from hex-1-ene (with 5% C<sub>7</sub> aldehyde and 1% ethyl heptanoate production), in the heptanal reaction only 7% conversion to C<sub>7</sub> alcohols had taken place and the condensation product 2-pentyl-2-nonenal was also detected. (A second pair of reactions, carried out under the same conditions as those listed above, confirmed these results with hex-1-ene giving 26% conversion to C<sub>7</sub> alcohols (with 6% C<sub>7</sub> aldehyde and 2% ethyl heptanoate) while heptanal yielded 8% C<sub>7</sub> alcohols). This demonstrated that the rate of hydroformylation/hydrogenation of hex-1-ene to C<sub>7</sub> alcohols was faster than the rate of hydrogenation of heptanal by the same system. Thus if C<sub>7</sub> aldehydes had been formed as intermediates their concentration would have built up during the reaction and not remained as low as that observed in reactions under similar reaction conditions discussed above.

Another difference noticed in the products of the heptanal hydrogenation reaction compared with the hex-1-ene hydroformylation/ hydrogenation reaction was in the dehydrogenation

products from ethanol. While both ethanal and ethyl ethanoate were seen in the hex-1-ene reactions only ethanal was formed when this system was used to hydrogenate heptanal.

Thus this system based on  $\text{RhH}(\text{PEt}_3)_3$  with CO as catalyst precursor, using ethanol as the hydrogen source will hydrogenate heptanal slowly but not in very high yield. As ethanal is produced on dehydrogenation of ethanol the combined concentration of aldehydes in solution will remain fairly steady with depletion only being effected by aldol condensation reactions.

### 3.12. Conclusions.

This catalytic system based on  $\text{RhH}(\text{PEt}_3)_3$  has been demonstrated to hydroformylate hex-1-ene with only CO in the gas phase and a primary alcohol as the source of hydrogen. Surprisingly  $\text{C}_7$  alcohols are formed as the major product with limited production of  $\text{C}_7$  aldehydes and Reppe product esters.

It is probable that the production of  $\text{C}_7$  alcohols is a single reaction process, without aldehydes being formed as intermediates. It is proposed that this occurs due to the formation of a rhodium-acyl catalytic intermediate, shown in figure 3.9., which is rich in the basic  $\text{PEt}_3$  ligand. The high electron density on the rhodium, transmitted to the acyl oxygen, promotes protonation by (or hydrogen bonding to) the solvent alcohol, as shown in figure 3.10.. The formation of this intermediate prevents the elimination of aldehyde, and reduces the production of esters (which might be expected to form on

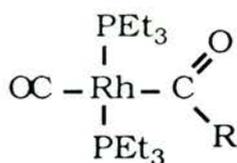


Fig 3.9.

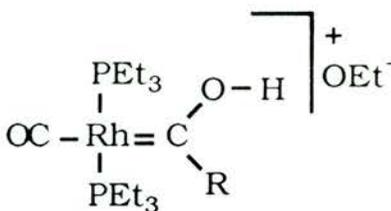


Fig 3.10.

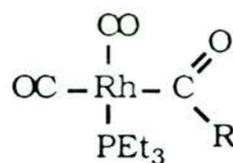


Fig 3.11.

nucleophilic attack by the solvent alcohol on a rhodium-acyl intermediate) and promotes the direct formation of C<sub>7</sub> alcoholic product. The small proportion of aldehyde detected in these reaction mixtures could be produced by a rhodium species, as shown in figure 3.11., which is more prevalent at low concentrations of RhH(PEt<sub>3</sub>)<sub>3</sub>, in the absence of free PEt<sub>3</sub> and at higher pressures of CO, in which one of the PEt<sub>3</sub> ligands is replaced by CO coordinated to the rhodium centre. If so produced, some C<sub>7</sub> aldehyde will have been hydrogenated to C<sub>7</sub> alcohol by the rhodium species richer in PEt<sub>3</sub> which has been shown to hydrogenate heptanal.

## Chapter 4. Deuteration and Mechanistic Studies.

### 4.1. Introduction.

It has been suggested that hydroformylation reactions using rhodium, modified with tris primary alkyl phosphine ligands, as catalyst precursor, that give alcohols as products take place as two stage reactions<sup>7</sup>. The initial product is an aldehyde of chain length one carbon more than that of the substrate alkene. Thus hex-1-ene would be hydroformylated to heptanal and 2-methylhexanal which would leave the catalytic metal centre and then undergo a separate hydrogenation reaction. If this were the case the products of hydroformylation, (followed by immediate hydrogenation), of hex-1-ene and the product of hydrogenation of heptanal would be the same, although no 2-methylhexanol would be produced in the latter reaction. To see if there was any difference in the mechanism of C<sub>7</sub> alcohol formation from hex-1-ene on the one hand and heptanal on the other, a series of reactions was carried out using combinations of either CO/D<sub>2</sub> or CO/H<sub>2</sub> (1:1) mixtures in the gas phase and ethanol-OD or ethanol-OH as the solvent. After fractional distillation, the deuterated products of these reactions were studied using <sup>13</sup>C nmr and the proportion of deuterium and its position within the alcohol compared for each substrate.

It should be noted that as the reactions were carried out in ethanol as solvent, the presence or absence of deuterium in the hydroxyl position of the product was impossible to determine as there is exchange of hydrogen and deuterium in this position between solvent and product and the equilibrium set up prevents one from determining the initial form of the product alcohol.

Table 4.1. shows the assignments of <sup>13</sup>C chemical shifts of heptanol and 2-methylhexanol. These were made by comparison with

values calculated using a formula published by Williams and Fleming<sup>40</sup>.

When a hydrogen is replaced by deuterium there are three effects observed. Firstly the signal is split into a triplet by coupling to the  $I=1$  deuterium nucleus. The coupling constant was found to be in the range 19 - 26 Hz. depending on the environment of the carbon affected. Secondly there is an  $\alpha$ -shift, upfield in the order of 0.37 ppm. per deuterium. Finally there is a  $\beta$ -shift of 0.05 - 0.12 ppm., also upfield, and again depending on the environment of the carbon to which the deuterium is bonded. These values fit with those observed by Doddrell and Burfitt<sup>59</sup> Table 4.1. also shows the effect of replacing the hydroxyl hydrogen on  $C_1$  with deuterium (by exchange with  $D_2O$ ). The  $C_1$  signal was  $\beta$ -shifted by 0.27 ppm. upfield in this sample. From comparison of the products of hydroformylation of hex-1-ene with  $H_2$  in ethanol-OH and those of hydrogenation of heptanal with  $D_2$  in ethanol-OD, it would appear that the value can exceed 0.3 ppm. where all the hydroxyl hydrogens are replaced with deuterium. The two peaks, due to non  $\beta$ -shifted and  $\beta$ -shifted carbon  $C_1$  signals, which would be expected in a solution containing heptanol-OH and heptanol-OD are not seen because of the rapid hydroxyl H/D exchange, but instead a single averaged signal occurs.

#### 4.2. Reactions involving gaseous $H_2$ or $D_2$ and $RhH(PEt_3)_3$ (0.008 moles $dm^{-3}$ ) as catalyst precursor.

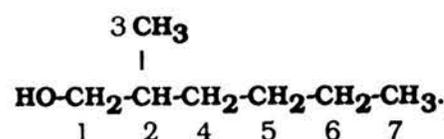
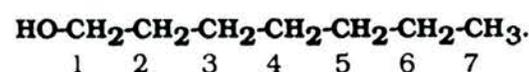
##### 4.2.1. Hex-1-ene with $CO/D_2$ in ethanol-OH.

Hex-1-ene in ethanol was reacted with  $CO/D_2$  (~1:1) at 23 atmos., with the oven set at 118°C, for 2 hours, using  $RhH(PEt_3)_3$  (0.008 moles  $dm^{-3}$ ) as catalyst precursor. The products were fractionally distilled off the catalyst and then the solvent and the  $C_7$  alcohol fractions were studied by  $^{13}C$  nmr. The solvent fraction only

Table 4.1. Assignment of  $^{13}\text{C}$  nmr peaks for C7 alcohols.

**Heptanol.**

**2-methyl hexanol.**



	1/ppm	2/ppm	3/ppm	4/ppm	5/ppm	6/ppm	7/ppm
heptanol - calculated values.	63.0	33.2	26.3	29.7	32.5	23.1	14.0
heptanol - supplied sample.	62.72	32.81	25.88	29.27	31.97	22.72	14.11
heptanol-OD - exchange with $\text{D}_2\text{O}$ .	62.45	32.74	25.94	29.34	32.03	22.77	14.14
2-methylhexanol - calculated values.	69.9	34.9	16.1	32.9	29.7	23.4	14.0
2-methylhexanol - supplied sample.	68.20	35.81	16.67	33.01	29.33	23.08	14.12

Table 4.2. Reactions catalysed by  $[\text{RhH}(\text{PEt}_3)_3]$  at high concentration ( $\sim 0.008$  moles  $\text{dm}^{-3}$ ).

	1/ppm	$J_{\text{C-D}}/\text{Hz}$	2/ppm	$J_{\text{C-D}}/\text{Hz}$	3/ppm	$J_{\text{C-D}}/\text{Hz}$	4/ppm	5/ppm	6/ppm	7/ppm
<u>Hex-1-ene + CO/D<sub>2</sub> in ethanol giving:</u>										
H/DO-CD <sub>2</sub> -CH <sub>2</sub> -CHD-C <sub>4</sub> H <sub>9</sub> .	61.84	m. 21.6	(32.62) 32.52		(25.90) 25.51	t. 19.1	(29.34) 29.24	32.01	22.77	14.13
H/DO-CD <sub>2</sub> -CH(CH <sub>2</sub> D)-C <sub>4</sub> H <sub>9</sub> .	67.25	m. 21.3	(35.66) 35.57		16.38	t. 19.1	33.05	29.41	23.15	14.13
<u>Heptanal + (CO)/D<sub>2</sub> in ethanol-OH giving:</u>										
H/DO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> .	62.39		32.82		26.02		29.41	32.11	22.83	14.14
H/DO-CHD-CH <sub>2</sub> -CH <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> .	62.02	t. 21.4	32.71							
<u>Heptanal + (CO)/H<sub>2</sub> in ethanol-OD giving</u>										
H/DO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> .	62.62		32.78		25.91		29.31	32.01	22.75	14.12
H/DO-CHD-CH <sub>2</sub> -CH <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> .	62.25	t. ~21.7	32.67							
<u>Heptanal + (CO)/D<sub>2</sub> in ethanol-OD giving:</u>										
DO-CHD-CH <sub>2</sub> -CH <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> .	62.03	t. ~21.5	32.69		25.99		29.40	32.09	22.81	14.15
<u>Heptanal (+ CO) + ethanol-OD giving:</u>										
heptanol.	62.76		32.76		25.79		29.15	31.90	22.66	14.09
	62.70		32.66		25.69					
	62.65		32.35	t. ~19.3	25.59					
	62.33	t. ~21.6	32.25	t. ~19.4						
	62.28	t. ~21.6								
<u>Hex-1-ene + CO + ethanol-OD giving:</u>										
heptanol.	62.60		32.79		25.93		29.31	32.03	22.77	14.14
	62.55		32.69		25.83		29.22			
	62.50		32.59		25.73					
	62.23	t. 21.4	32.49		25.54	t. 19.2				
	62.18	t. 21.6	32.39	t. 19.3	25.44	t. 19.7				
	62.13	t. 21.8	32.28	t. 19.8						
2-methylhexanol.	68.03		35.81		16.71		33.09	29.39	23.15	14.14
	67.97		35.72		16.59		32.98			
	67.64	t. 21.4	35.63							
	67.57	t. 21.5								

showed deuterium in the hydroxyl position (20% from the  $^1\text{H}$  nmr integration) while the  $\text{C}_7$  alcohol fraction (see figure 4.1.) showed incorporation of two deuterium atoms into the  $\text{C}_1$  position and one in the  $\text{C}_3$  position of both  $\text{C}_7$  alcohols produced. The  $\text{C}_1$  signal was thus a quintet for both heptanol ( $J_{\text{C-D}} = 21.6$  Hz.) and 2-methylhexanol ( $J_{\text{C-D}} = 21.3$  Hz.). It may be seen from table 4.2. that the  $\alpha$ -shift of the  $\text{C}_1$  signal was  $\sim 0.40$  ppm. per deuterium, allowing for some  $\beta$ -shift in the signal from the partial deuteration of the hydroxyl position. Similarly the  $\text{C}_3$  signal was a triplet ( $J_{\text{C-D}} = 19.1$  Hz.) due to a single deuterium on this carbon atom, with an  $\alpha$ -shift of 0.39 ppm. for heptanol and  $\sim 0.29$  ppm. for 2-methylhexanol. The  $\text{C}_2$  signal for both heptanol and 2-methylhexanol showed a  $\beta$ -shift of  $\sim 0.30$  ppm. due to three deuterium atoms on carbons adjacent to the  $\text{C}_2$  position (0.10 ppm. per deuterium). In the case of heptanol there was also a  $\beta$ -shift of 0.10 ppm. in the  $\text{C}_4$  signal brought about by the single deuterium on the  $\text{C}_3$  carbon.

Careful study of the spectrum of the  $\text{C}_7$  alcohol fraction showed, from the presence of a smaller peak  $\sim 0.10$  ppm. downfield of the main  $\text{C}_2$  signal, that 10% of the heptanol and 11% of the 2-methylhexanol was only dideuterated. Similarly the  $\text{C}_4$  signal of heptanol showed 7% of the  $\text{C}_3$  carbon to be undeuterated. This indicated that a small percentage of the product had incorporated hydrogen rather than deuterium into one of the addition sites. In the case of heptanol this appeared to be preferentially into the  $\text{C}_3$  position. It was not possible to tell from comparison of peak intensities of  $\beta$ -shifted and non  $\beta$ -shifted signals which position, the  $\text{C}_1$  or  $\text{C}_3$ , in 2-methylhexanol was preferentially taking up hydrogen as the only site with which these two carbons are bonded is the  $\text{C}_2$  carbon atom. The quintet of the  $\text{C}_1$  signal of 2-methylhexanol was not completely symmetrical, so this may indicate preferential hydrogen incorporation into this position as the

Hex-1-ene with CO/D<sub>2</sub> in ethanol-OH.

<sup>13</sup>C{<sup>1</sup>H} nmr of products.

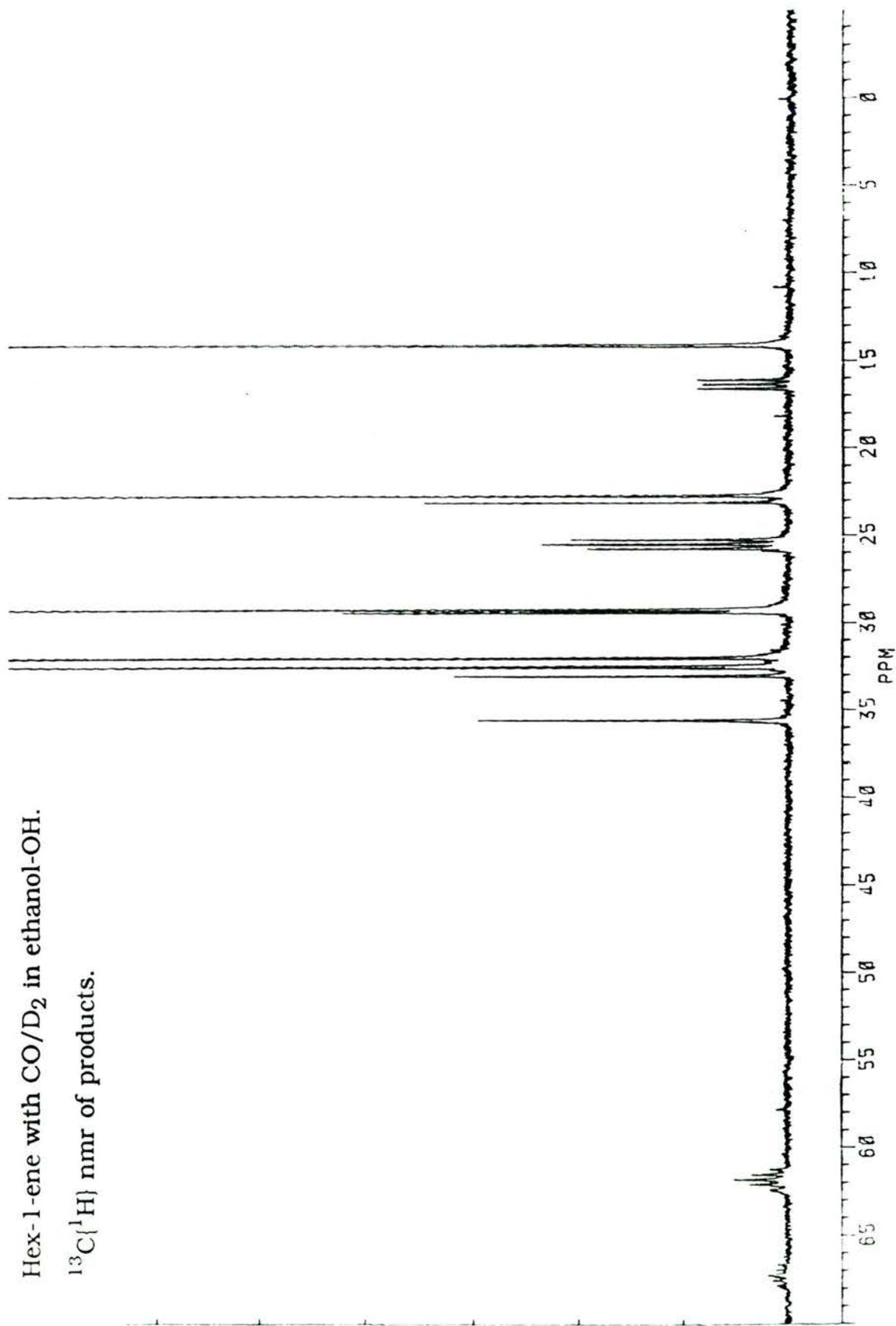


Figure 4.1.

triplet of the C<sub>3</sub> signal was not distorted. This hydrogen insertion could come about from hydrogen impurity in the D<sub>2</sub> (sold as 100.00%) or from hydrogen impurity in the carbon monoxide. It had previously been found that a cylinder of carbon monoxide of the type used for these experiments contained traces of hydrogen. The other source of hydrogen would be by exchange of hydrogen and deuterium with hydroxyl hydrogen of ethanol. Whatever the source of hydrogen, exchange was not occurring to a significant extent (see below). The solvent ethanol showed 20% conversion to ethanol-OD. This was compared with ~5% exchange of hydroxyl-H with D<sub>2</sub> in a blank comparison when ethanol was heated with RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) in the absence of hex-1-ene but with CO/D<sub>2</sub> (~3:2) at 21 atmos., with the oven set at 118°C, for 2 hours.

#### 4.2.2. Heptanal with (CO)/D<sub>2</sub> in ethanol-OH.

Comparison of the products of the reaction of hex-1-ene with CO/D<sub>2</sub> in ethanol was made with those of the deuteration of heptanal in ethanol using CO/D<sub>2</sub> (1:1) at 34 atmos., with the oven set at 125°C, for 3 hours, using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) as catalyst precursor. Here two products were observed on analysis using <sup>13</sup>C nmr (see figure 4.2. and table 4.2.). As the C<sub>3</sub> carbon was already bonded to two hydrogens in heptanal it was only possible for deuterium to be incorporated into the C<sub>1</sub> position. It was found that only 42% (calculated on the intensities of the β-shifted and non β-shifted C<sub>2</sub> signals) of the product was monodeuterated in this position, the remainder incorporating hydrogen. Integration of the <sup>1</sup>H spectrum of the C<sub>7</sub> fraction gave the following results:

Area for H bonded to C <sub>7</sub> position	= 33.5 ie. 11.2 per H.
Area for H bonded C <sub>3</sub> + C <sub>4</sub> + C <sub>5</sub> + C <sub>6</sub> positions	= 89.6 ie. 11.2 per H.
Area for H bonded to C <sub>1</sub> position	= 17 ie. 11.2 + 6.8.

Heptanal with (CO)/D<sub>2</sub> in ethanol-OH.  
<sup>13</sup>C{<sup>1</sup>H} nmr of products.

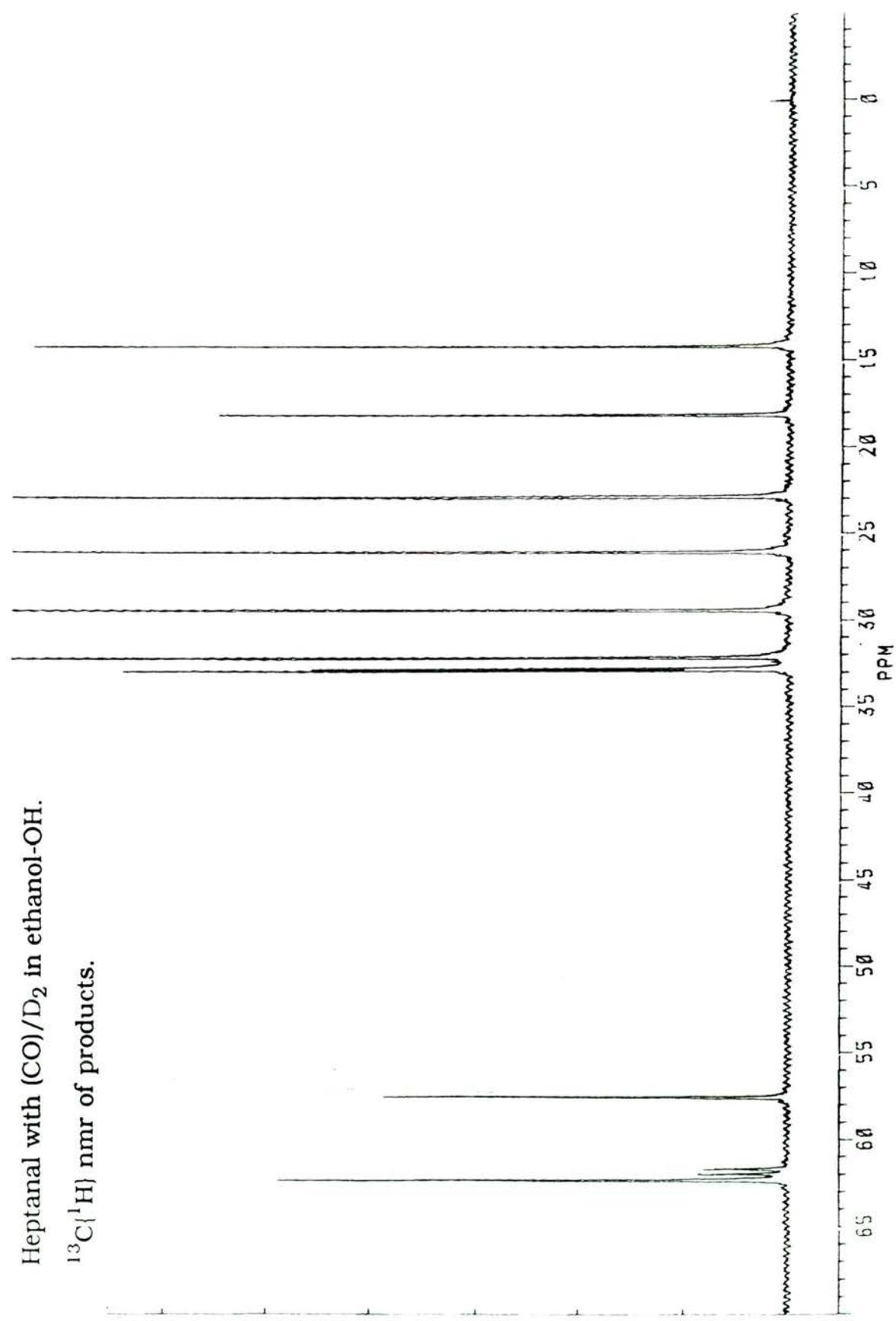


Figure 4.2.

This value of 6.8 gives a figure of 61% hydrogen incorporation in the C<sub>1</sub> position and only 39% deuterium (which corresponded well with the value obtained from β-shift intensities above). The coupling ( $J_{C-D} = 21.4$  Hz.), α-shift of 0.37 ppm. and β-shift of 0.11 ppm. all corresponded with those previously seen for deuteration in this site.

A similar reaction with CO/D<sub>2</sub> (1:1) at 28 atmos., with the oven set at 125°C for 3 hours, but with excess PEt<sub>3</sub> (0.08 moles dm<sup>-3</sup>) added gave 53% deuterium in the C<sub>1</sub> position, from <sup>13</sup>C β-shift intensities, and 55% from <sup>1</sup>H integration. The coupling to deuterium, α and β-shifts were the same as those observed for the reaction without excess PEt<sub>3</sub>. This indicated that excess phosphine slightly increases deuterium incorporation onto the carbonyl carbon atom.

In both these reactions the ethanol fraction showed extensive exchange of deuterium into the hydroxyl site:

~85% ethanol-OD without excess triethylphosphine and

~81% ethanol-OD with excess triethylphosphine

which was a much greater proportion than that observed in the reaction with hex-1-ene.

Both the formation of nondeuterated heptanol from heptanal and CO/D<sub>2</sub> and the exchange to form such a large proportion of ethanol-OD indicated that the hydroformylation/hydrogenation of hex-1-ene did not go via the aldehyde as an intermediate.

#### 4.2.3. Heptanal with (CO)/H<sub>2</sub> in ethanol-OD.

Confirmation of the participation of ethanol in the hydrogenation of heptanal using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) as catalyst precursor was seen on analysis of the products of the reaction of heptanal in ethanol-OD with CO/H<sub>2</sub> (1:1) at 34 atmos., with the oven set at 125°C,

Heptanal with (CO)/H<sub>2</sub> in ethanol-OD.

<sup>13</sup>C{<sup>1</sup>H} nmr of products.

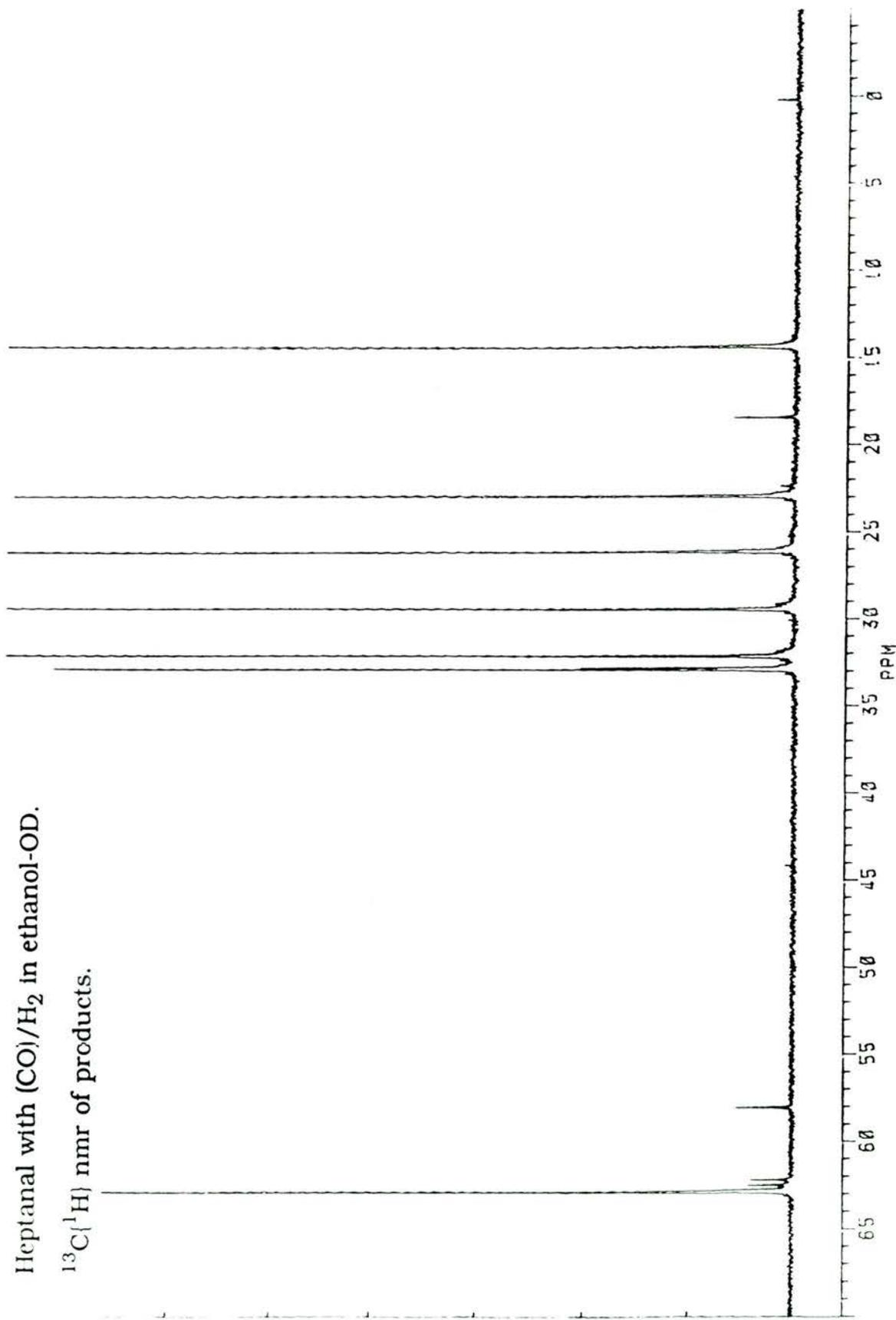


Figure 4.3.

for 3 hours as before. As figure 4.3. shows, this time deuterium from the ethanol was incorporated into the C<sub>1</sub> position with 21% of the C<sub>1</sub> position sites being monodeuterated, as shown by <sup>13</sup>C nmr β-shift intensities, the remainder being hydrogenated. Coupling to deuterium ( $J_{C-D} = 21.7$  Hz.), α-shift (0.37 ppm.) and β-shift (0.11 ppm.) corresponded with those previously observed for deuterium bonded to carbon in this environment (see table 4.2.). The percentage of deuterated product was not calculated from the <sup>1</sup>H spectrum in this case. The <sup>1</sup>H nmr spectrum of the solvent showed that ~70% of the deuterium in the hydroxyl position had been replaced by hydrogen.

The ethanol therefore was again seen to take part in the hydrogenation of heptanal in this catalytic system, but the evidence above did not tell us whether only hydroxyl hydrogen was involved, or if the hydrogen bonded to carbon in ethanol was also taking part. There was, however, no indication of deuterium incorporation at sites other than on the hydroxyl oxygen of ethanol, from the <sup>13</sup>C nmr of the solvent fraction.

#### 4.2.4. Heptanal with (CO)/D<sub>2</sub> in ethanol-OD.

The deuteration of heptanal was carried out using ethanol-OD and CO/D<sub>2</sub> (1:1) at 34 atmos. with the same reaction conditions as in previous experiments. As may be seen from figure 4.4. and table 4.2. analysis of the products showed that there was 100% monodeuteration in the C<sub>1</sub> position ( $J_{C-D} = 21.5$  Hz.) of the product heptanol. This result confirmed that only the hydroxyl hydrogen of the solvent ethanol was involved in the reaction.

#### 4.2.5. Proposed reaction mechanism for hydrogenation of heptanal to heptanol using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) as catalyst precursor.

The generally accepted route for the formation of alcohol from

Heptanal with (CO)/D<sub>2</sub> in ethanol-OD.

<sup>13</sup>C{<sup>1</sup>H} nmr of products.

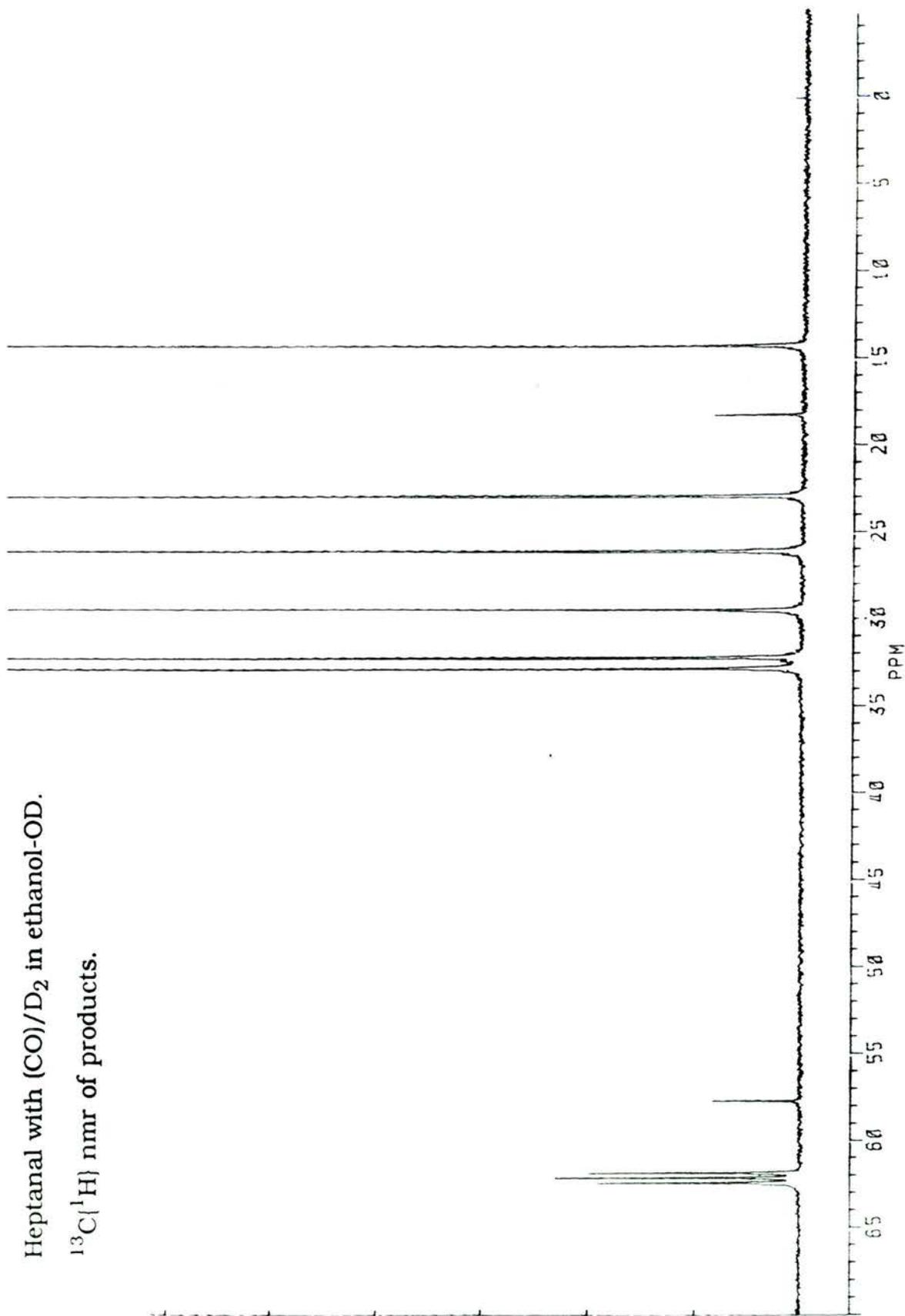
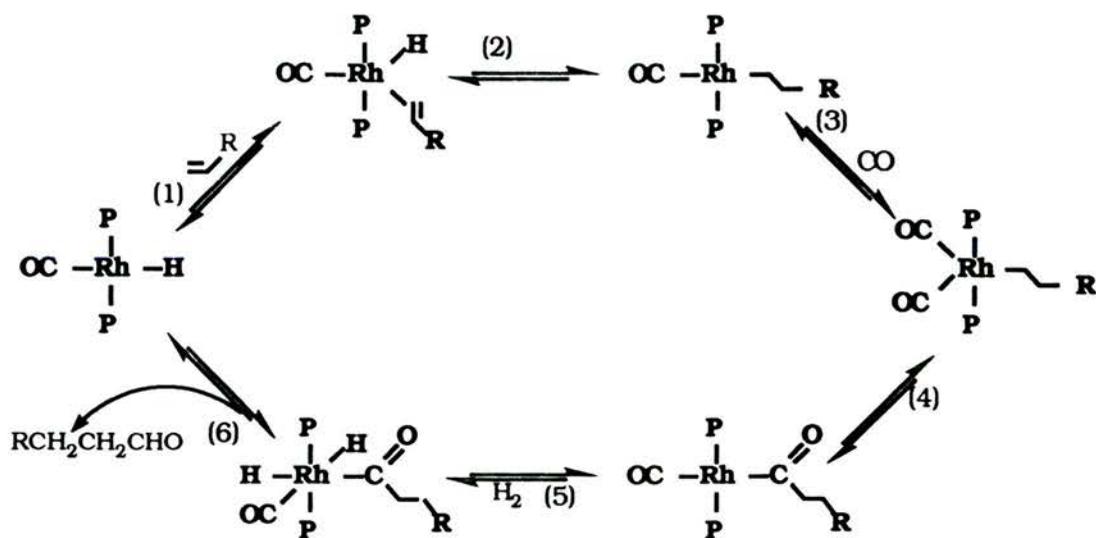


Figure 4.4.



Scheme 4.1.

an alkene via an aldehydic intermediate is shown in schemes 4.1. and 4.2. Firstly the alkene is hydroformylated to aldehyde in six steps (scheme 4.1.) :

(1). The alkene is coordinated to the metal centre.

(2). Hydrogen migrates from the metal centre and inserts into the double bond of the alkene to give an alkyl ligand. This may happen in such a way as to give a normal alkyl ligand, as shown (anti-Markownikoff addition) or to give a branched alkyl ligand (Markownikoff addition).

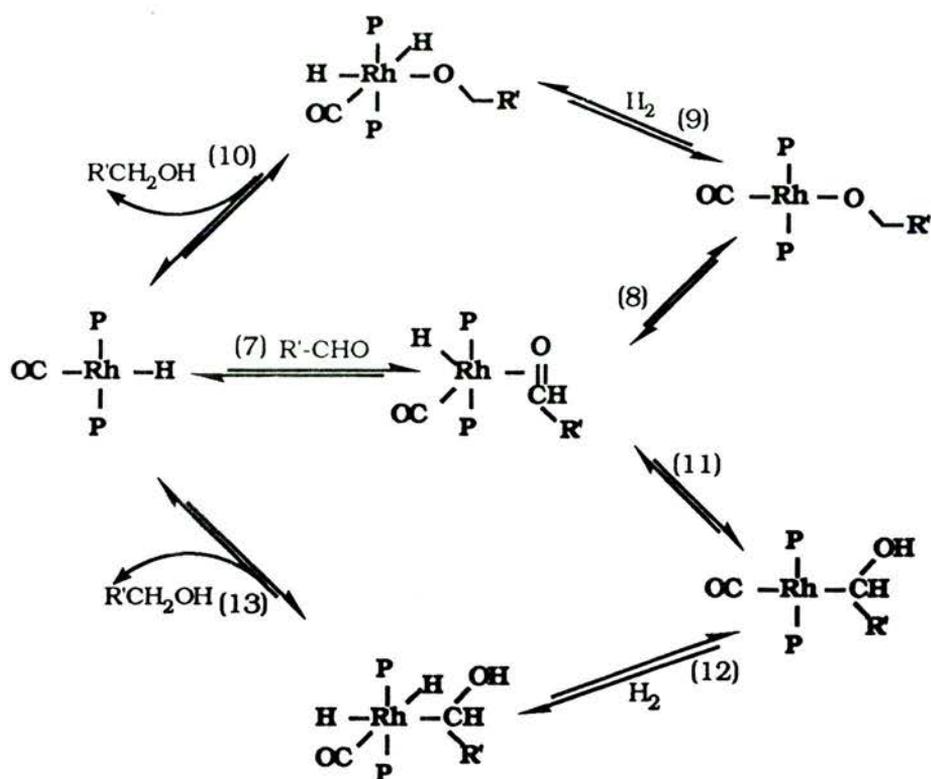
(3). Coordination of carbon monoxide.

(4). Migration and insertion of CO ligand into metal alkyl bond to give an acyl ligand.

(5). Oxidative addition of molecular hydrogen to the metal centre, followed by:

(6). reductive elimination of aldehyde with the metal species returning to that which coordinated alkene in step (1) thus allowing the hydroformylation cycle to continue.

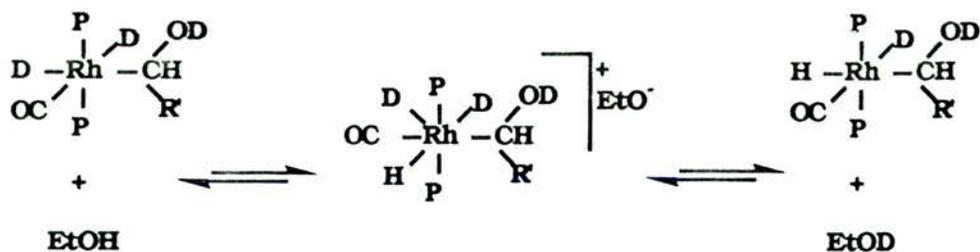
As is shown in scheme 4.2. the aldehyde can now coordinate with the rhodium centre, step (7), and undergo hydrogenation. The insertion of the aldehyde into the Rh-H bond can take place in two



Scheme 4.2.

possible ways. The hydrogen may either bond with the carbon to give an alkoxy ligand, as shown in step (8), or it may bond with the oxygen forming a hydroxy-alkyl ligand as shown in step (11). Either step will be followed by oxidative addition of molecular hydrogen, step (9) or (12), and then reductive elimination of heptanol, (10) or (13). It is generally accepted that the usual route<sup>60</sup> is the upper one shown in scheme 4.2., via the alkoxy ligand, but if the phosphine ligands are electron donating and thus the electron density on the rhodium centre is high the rhodium will not be so oxophilic and the lower route, via the hydroxy-alkyl ligand, could become more favoured.

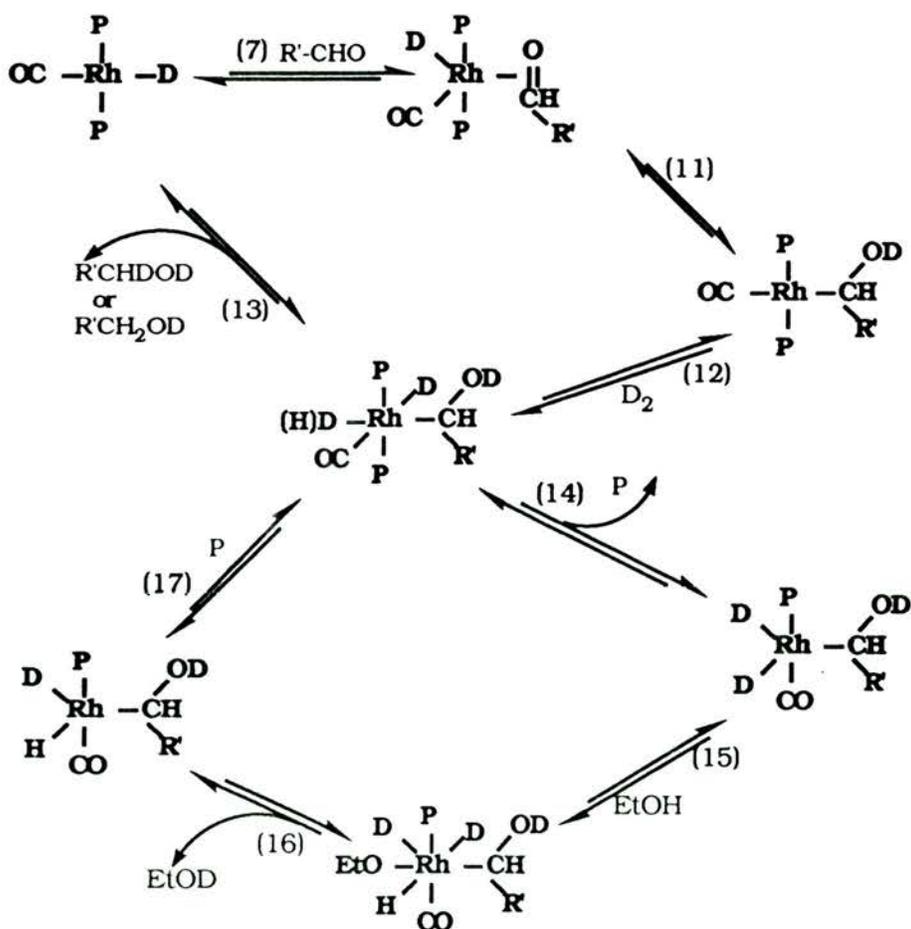
Neither of these routes as shown would involve hydrogen incorporation from the solvent as was found in the hydrogenation of heptanal nor would it allow for the formation of products other than  $C_6H_{13}CHDOD$  in hydrogenation using  $D_2$ . It is possible that there was protonation of the rhodium centre by ethanol-OH leading to exchange as shown in scheme 4.3..



Scheme 4.3.

This would not account for the slight reduction in EtOH : EtOD exchange, nor the increased incorporation of deuterium into the product heptanol, seen with the presence of excess phosphine.

The mechanism shown in scheme 4.4. is therefore now proposed to account for the exchange. This initially follows steps (7), (11) and (12) as shown in the hydroxy-alkyl route for the hydrogenation of heptanal in scheme 4.2. If before reductive elimination of heptanol, step (13), can take place one of the



Scheme 4.4.

phosphine ligands were to leave the metal centre, as shown in step (14), and this were followed by oxidative addition of ethanol-OH, step (15), it would give the seven coordinate, 18 electron species shown

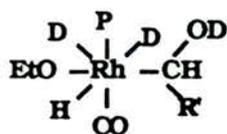


Figure 4.5.

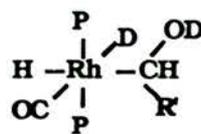


Figure 4.6.

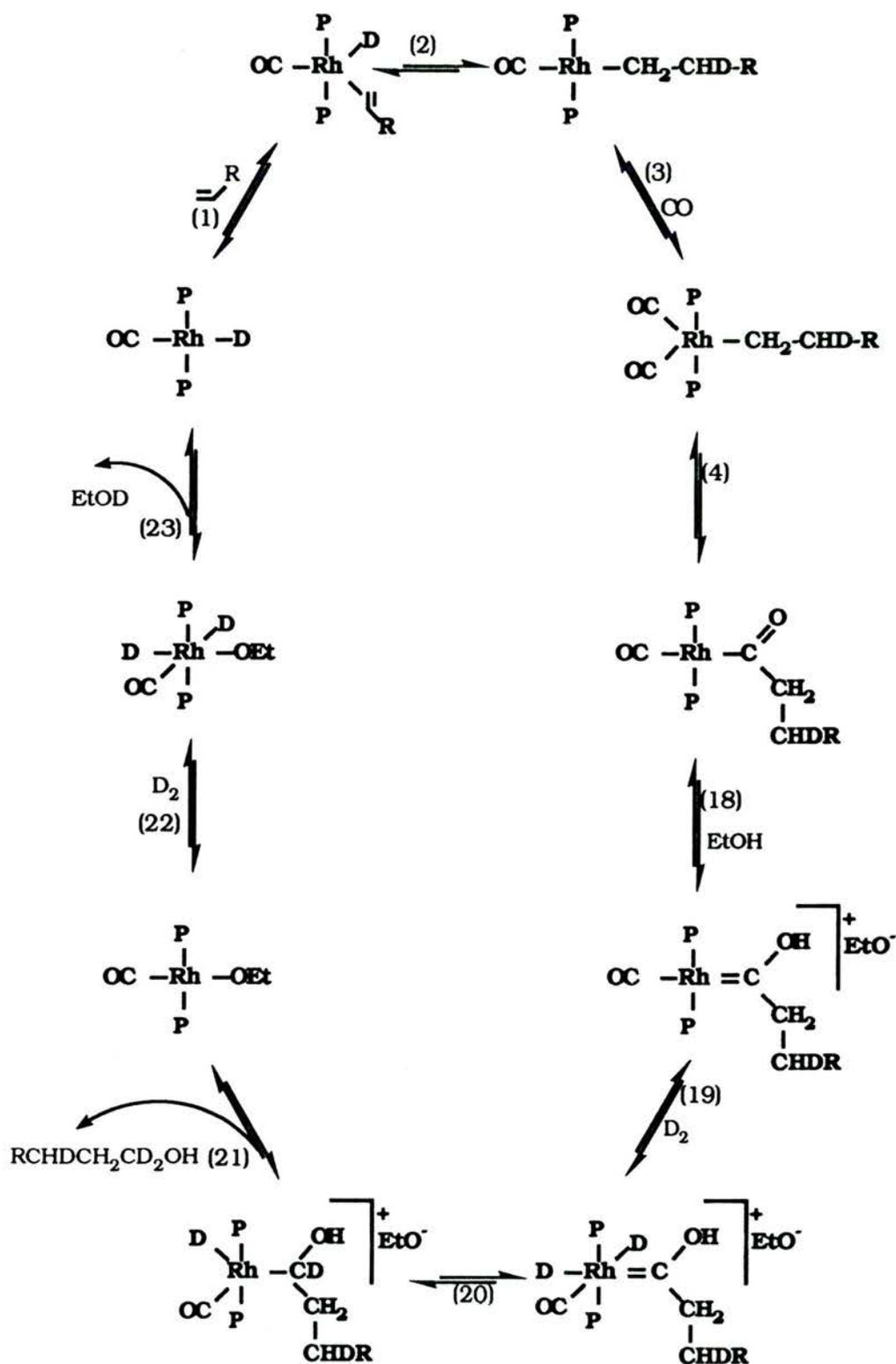
in figure 4.5.. Exchange could now take place and the ethanol be reductively eliminated from the metal centre as ethanol-OD, step (16), leaving hydrogen on the rhodium. This could then re-coordinate a phosphine ligand, step (17), to give the partially deuterated species shown in figure 4.6.. This species could now eliminate HD and then add  $D_2$ , step (12), followed by further exchange with ethanol-OH, steps (14) to (17), thus increasing the concentration of ethanol-OD in solution as was observed, or it could reductively eliminate either nondeuterated or monodeuterated heptanol as shown in step (13). It would therefore be assumed that the exchange step (12) and exchange of ethanol-OH with ethanol-OD are faster than reductive elimination of  $C_7$  alcohol in step (13).

Thus the mechanism shown in scheme 4.4. would account for the production of both monodeuterated and nondeuterated heptanol and also the EtOH : EtOD exchange. It would also explain the effect of adding excess phosphine, as step (14) would be less favourable in the presence of excess free phosphine and a greater proportion of monodeuterated product, as seen, would form. The route via the alkoxy ligand shown in steps (7), (8), (9) and (10) cannot be discounted as it would yield monodeuterated product and it probably accounts for some of the heptanol deuterated on carbon  $C_1$ .

4.2.6. Proposed reaction mechanism for hydroformylation of hex-1-ene to C<sub>7</sub> alcohols using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) as catalyst precursor.

When hex-1-ene was hydroformylated with CO/D<sub>2</sub> using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) as catalyst precursor, the product alcohols were found to be almost completely C<sub>4</sub>H<sub>9</sub>CHDCH<sub>2</sub>CD<sub>2</sub>OH/D and C<sub>4</sub>H<sub>9</sub>CH(CH<sub>2</sub>D)CD<sub>2</sub>OH/D. It would therefore appear that an intermediate aldehyde did not leave the metal centre prior to reduction to the alcoholic product. Referring to scheme 4.1. it would appear that in the presence of an alcohol the acyl species formed in step (4) did not undergo oxidative addition of hydrogen in step (5) but reacted with the solvent in some way which gave direct formation of an alcohol as product. A possible mechanism for this reaction is proposed in scheme 4.5..

As it was found that trialkylphosphines, and primary alkyl phosphines in particular, were a required ligand for alcohol formation it was felt that the electron donating capacity of these ligands was crucial to the products formed. Trialkylphosphines are known to give a higher electron density on the metal centre than their triaryl equivalents<sup>34</sup> and this in turn would increase the electron density through the acyl carbon to the acyl oxygen. In an alcoholic solvent the δ<sup>-</sup> charge on the acyl oxygen could lead to strong hydrogen bonding with the hydroxyl hydrogen of the solvent alcohol, or even protonation by the solvent. This in turn would lead to the formation of a hydroxy-carbene ligand bound to rhodium in a cationic species as is shown in step (18) of scheme 4.5. Now oxidative addition of molecular deuterium could take place, step (19), followed by migration of deuterium onto the carbene carbon to give a hydroxy-alkyl ligand on the cationic rhodium species, step (20). Reductive elimination of heptanol with concurrent coordination of the alkoxy anion, step (21),



Scheme 4.5.

would give the product observed and after oxidative addition of molecular deuterium to the metal centre lead to reductive elimination of ethanol-OD, steps (22) and (23), and return the rhodium to the starting catalytic form.

Note that if the ethoxide ion were to deprotonate the species

formed in step (20) it would leave an uncharged rhodium species with a hydroxy-alkyl ligand, as was proposed might be formed in step (11) of scheme 4.4., for the deuteration of heptanal. It was then proposed that in subsequent steps exchange took place between ethanol-OH and ethanol-OD. As this exchange was not observed to any great extent in the deuteroformylation of hex-1-ene it seems unlikely that deprotonation occurred here, but rather that elimination of heptanol was the most likely next occurrence.

#### 4.3. Reactions involving CO with ethanol as the hydrogen source and $\text{RhH}(\text{PEt}_3)_3$ (0.008 moles $\text{dm}^{-3}$ ) as catalyst precursor.

If only CO was employed in the gas phase and ethanol was used as the source of hydrogen in hydroformylation reactions the major products were still found to be C<sub>7</sub> alcohols but, as was stated in chapter 3., esters were also formed. The deuteration products formed when ethanol-OD was used in place of ethanol-OH were studied using <sup>13</sup>C nmr as above, both for the reduction of heptanal to heptanol, and the reaction of hex-1-ene to give C<sub>7</sub> alcohols.

##### 4.3.1. Heptanal (with CO) in ethanol-OD.

Heptanal in ethanol-OD, and  $\text{RhH}(\text{PEt}_3)_3$  (0.008 moles  $\text{dm}^{-3}$ ) with  $\text{PEt}_3$  (0.08 moles  $\text{dm}^{-3}$ ) as catalyst precursor, was sealed in an autoclave with CO at 20 atmos and heated with the oven set at 125°C, for 16 hours. The solvent and products were fractionally distilled from the catalyst and the C<sub>7</sub> alcohol fraction studied by <sup>13</sup>C nmr (see figure 4.7.). Although heptanol was the only C<sub>7</sub> alcohol formed this showed a somewhat more complicated spectrum than expected with deuterium incorporated into the C<sub>1</sub> position as expected but also into the C<sub>2</sub> position. As may be seen in table 4.2. the C<sub>1</sub> carbon showed a nondeuterated signal which was split into three peaks in ratio of

Heptanal (with CO) in ethanol-OD.

$^{13}\text{C}\{^1\text{H}\}$  nmr of products.

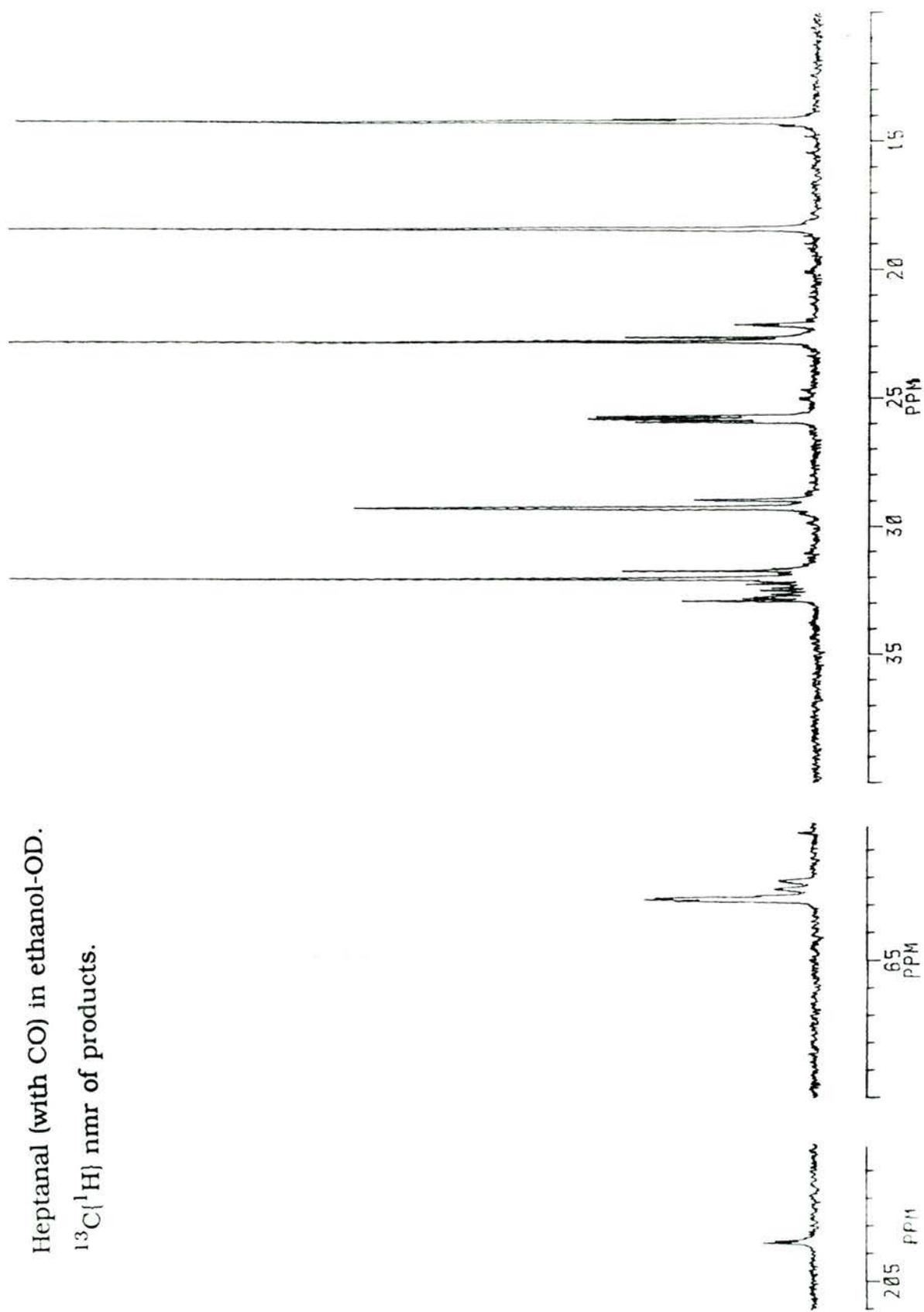
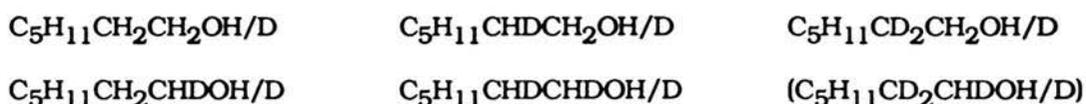


Figure 4.7.

intensities 1.00 : 1.19 : 1.10 due to the  $\beta$ -shift of zero, one and two deuterium atoms on the C<sub>2</sub> carbon, and also a triplet due to a deuterium in the C<sub>1</sub> position. This triplet ( $J_{C-D} = 21.6$  Hz. and  $\alpha$ -shift 0.37 ppm.) was further split into two by  $\beta$ -shifts ( $\sim 0.05$  ppm. per deuterium) due to one and two deuteriums on the C<sub>2</sub> carbon. The C<sub>3</sub> carbon signal was also split into three, ( $\beta$ -shift 0.10 ppm.), in the ratio 1.00 : 1.34 : 1.32, confirming there was a combination of zero, one and two deuterium atoms on carbon C<sub>2</sub>. The greater proportion of deuteration at carbon C<sub>2</sub> compared with nondeuteration, as shown by the  $\beta$ -shifted signals for carbon C<sub>3</sub> compared with carbon C<sub>1</sub>, would appear to indicate that there was preferential deuteration at carbon C<sub>1</sub> when carbon C<sub>2</sub> was already deuterated.

The signal for the C<sub>2</sub> carbon similarly showed a singlet, and a triplet ( $J_{C-D} = \sim 19.3$  Hz. and  $\alpha$ -shift 0.41 ppm.), due to some deuterium in the C<sub>2</sub> position, both signals being split into two ( $\beta$ -shift 0.10 ppm.) in the ratio 1.0 : 0.5, due to zero and one deuterium atoms on the C<sub>1</sub> carbon.

There was therefore evidence for five of the six possible species:

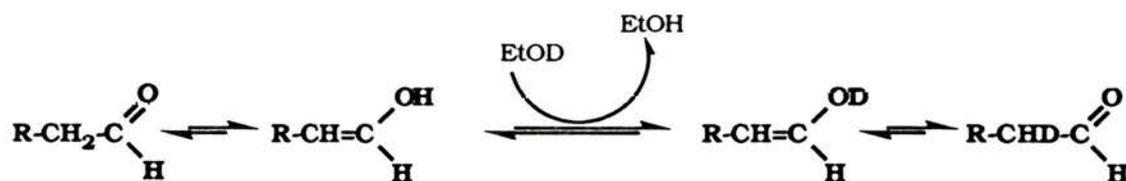


the major proportion being mono- or dideuterated on the C<sub>2</sub> carbon, and having hydrogen in the C<sub>1</sub> substitution position. The sixth possible species shown in brackets, with three deuterium atoms, may have been present in small amount but not detected as it would give rise to a triplet resonance from carbon C<sub>1</sub> and a quintet resonance from carbon C<sub>2</sub> both of too low an intensity to be resolved.

The presence of deuterium on the C<sub>2</sub> carbon was thought to come about by  $\beta$ -exchange. It was noted that the spectrum also showed the presence of unreduced heptanal which had likewise

undergone deuterium exchange in the C<sub>2</sub> position with 56% of the C<sub>2</sub> position being deuterated, as calculated from the non-β-shifted and β-shifted C<sub>3</sub> signal intensities.

A blank experiment where heptanal in ethanol-OD with PEt<sub>3</sub> (0.08 moles dm<sup>-3</sup>) under CO at 20 atmos was heated to 125°C for 16 hours showed similar deuterium incorporation at the C<sub>2</sub> position of heptanal. Non-, mono- and dideuteration at carbon C<sub>2</sub> was observed in the ratio of 1.00 : 3.33 : 4.00. This indicated that PEt<sub>3</sub> is a strong enough base to catalyse keto-enol tautomerism of heptanal as shown in scheme 4.6., the alkenol form exchanging its hydroxyl hydrogen for deuterium with the solvent ethanol-OD and returning to the aldehydic form with incorporation of deuterium onto carbon C<sub>2</sub>. Thus keto-enol tautomerism of substrate heptanal prior to hydrogenation accounted for the incorporation of deuterium at carbon C<sub>2</sub> in the product heptanol.



Scheme 4.6.

The mass spectrum of the ethanal, detectable in the reaction mixture, showed the usual molecular ion peak of 44 amu. and lower intensity peaks of 45 and 46 amu. which were not present in reaction mixtures where ethanol-OH was employed as solvent. These were assumed to be from mono- and dideuterated ethanal respectively, indicating that the ethanal produced by dehydrogenation of ethanol also incorporated deuterium, assumed to be in the C<sub>2</sub> position, due to keto-enol tautomerism and exchange with ethanol-OD.

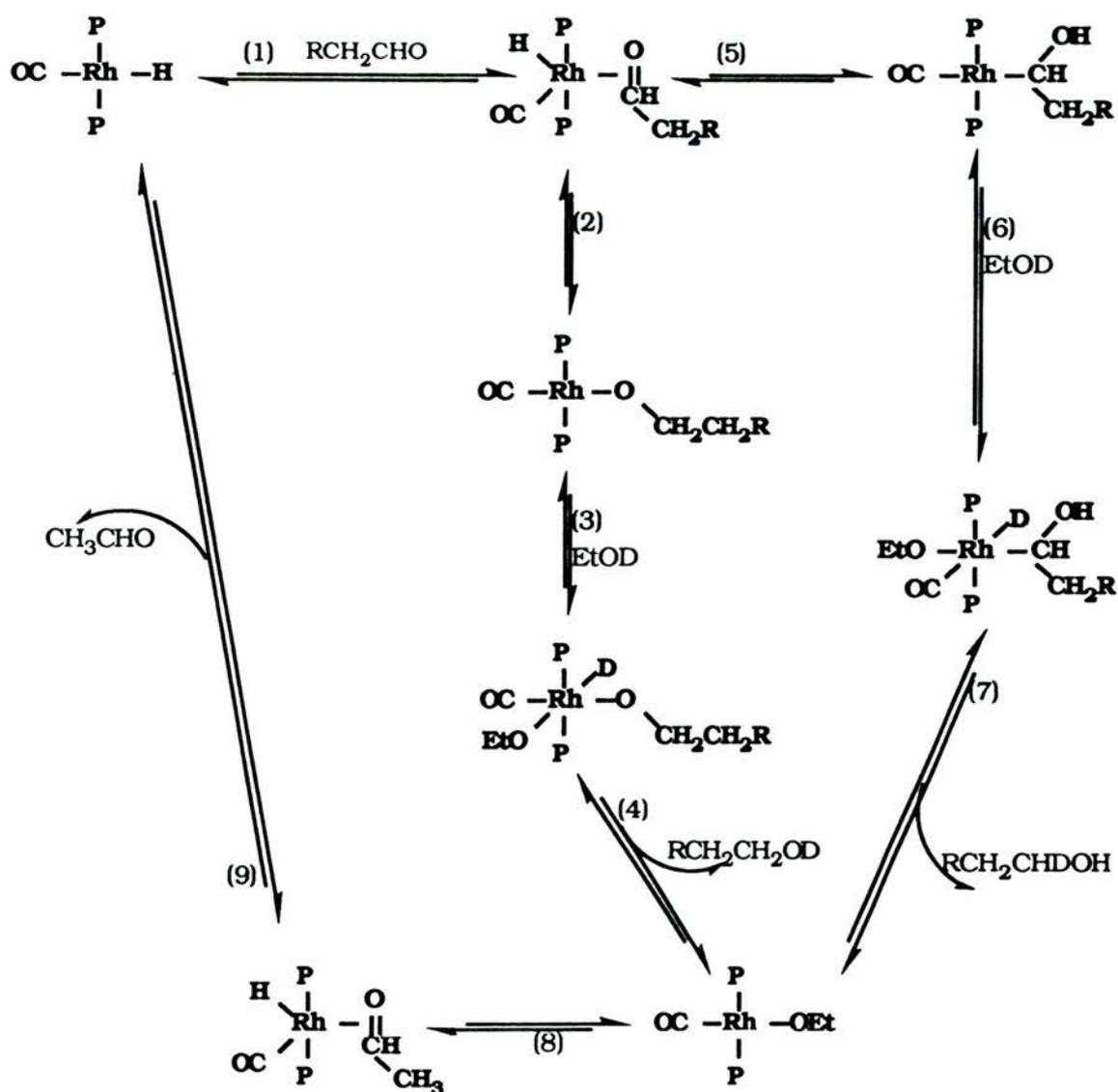
4.3.2. Proposed mechanism for the reduction of heptanal to heptanol with ethanol-OD, using  $\text{RhH}(\text{PEt}_3)_3$  (0.008 moles  $\text{dm}^{-3}$ ),  $\text{PEt}_3$  (0.08 moles  $\text{dm}^{-3}$ ) and CO (20 atmos.) as catalyst precursor.

The proposed mechanism for the reduction of heptanal to heptanol with ethanol-OD is shown in scheme 4.7.. Initial coordination of heptanal, step (1), would be followed by insertion of heptanal into the Rh-H bond. This could occur to give either an alkoxy ligand, as shown in step (2), or a hydroxy-alkyl ligand, as shown in step (5), leading to two competing routes for heptanol formation. Oxidative addition of ethanol-OD to either of these species (steps (3) or (6)) would now be required for the reaction to continue, as ethanol-OD is the only readily available source of hydrogen/deuterium present in the reaction mixture. This is likely to be a relatively slow step.

The alkoxide formed in step (2) would form an eighteen electron species, on oxidative addition of ethanol-OD, step (3), which would have two alkoxy ligands. This could reductively eliminate either heptanol-OD (with hydrogen bonded to carbon  $\text{C}_1$ ), step (4), or ethanol-OD in the reverse of step (3). (Step (4) might be slightly favoured here as it would relieve the crowding at the rhodium centre better due to loss of a longer chain ligand).

Similarly the hydroxy-alkyl species formed in step (5), on oxidative addition of ethanol-OD (step (6)), would go on to reductively eliminate heptanol with deuterium in the  $\text{C}_1$  position as shown in step (7).

Both step (4) and step (7) would yield a sixteen electron rhodium species with an ethoxide ligand. It is proposed that the rhodium would now abstract a  $\beta$ -hydrogen from this ligand (step (8)) and then eliminate the ethanal so formed (step (9)) thus returning to the starting catalytic species with a hydride ligand. These two competing routes, with that via steps (2), (3) and (4) probably being



twice as fast as that via steps (5), (6) and (7), would account for both the hydrogen and deuterium incorporation on carbon C<sub>1</sub> of the product heptanol in the observed proportion of 2:1, while the presence of deuterium in the C<sub>2</sub> position was accounted for by keto-enol tautomerism and hydrogen/deuterium exchange with the solvent ethanol-OD.

GCMS also showed a small proportion (1% by glc analysis) of ethyl heptanoate in the reaction mixture, together with the aldol condensation product, namely 2-pentyl-2-nonenal, and the acetal 1,1-diethoxyheptane which is generally formed by acid catalysed reaction

of ethanol with heptanal. The most likely source of the ethyl heptanoate would be from oxidative addition of the C-H bond of heptanal to the rhodium centre to give an acyl ligand which would then be subject to ethoxide attack and elimination as ethyl heptanoate. As so little ethyl heptanoate was formed it is unlikely that much heptanal reacted with the catalytic centre in this way.

#### 4.3.3. Hex-1-ene with CO in ethanol-OD.

Hex-1-ene in ethanol was reacted with CO at 20 atmos. in ethanol-OD, with the oven set at 125°C, for 16 hours, using RhH(PET<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) with PET<sub>3</sub> (0.08 moles dm<sup>-3</sup>) as catalyst precursor. The solvent and products were fractionally distilled from the catalyst and the C<sub>7</sub> alcohol fraction studied by <sup>13</sup>C nmr. The spectrum is shown in figure 4.8. with the data listed in table 4.2., from which it may be seen that the C<sub>7</sub> alcohol fraction yielded product with deuterium incorporated into the C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> positions. As with the reduction of heptanal using ethanol-OD as "hydrogen" source there was β-exchange of deuterium into the C<sub>2</sub> position as well as some incorporation of deuterium into the C<sub>1</sub> and C<sub>3</sub> positions, as might have been expected.

The spectrum of heptanol showed a C<sub>1</sub> carbon signal which was divided into a singlet and a triplet ( $J_{C-D} = 21.6$  Hz. and  $\alpha$ -shift 0.37 ppm.). The C<sub>3</sub> carbon similarly gave a singlet and a triplet ( $J_{C-D} = 19.5$  Hz. and  $\alpha$ -shift 0.39 ppm.) due to partial monodeuteration and partial hydrogenation at these sites. Both signals were further split by β-shift effects due to varying deuterium exchange at carbon C<sub>2</sub> (see below).

The complicated signal for the C<sub>2</sub> carbon on analysis showed a singlet and a triplet ( $J_{C-D} = \sim 19.5$  Hz. and  $\alpha$ -shift 0.40 ppm.). The singlet was divided into four peaks (β-shift 0.10 ppm.), due to zero,

Hex-1-ene with CO in ethanol-OD.

$^{13}\text{C}\{^1\text{H}\}$  nmr of products.

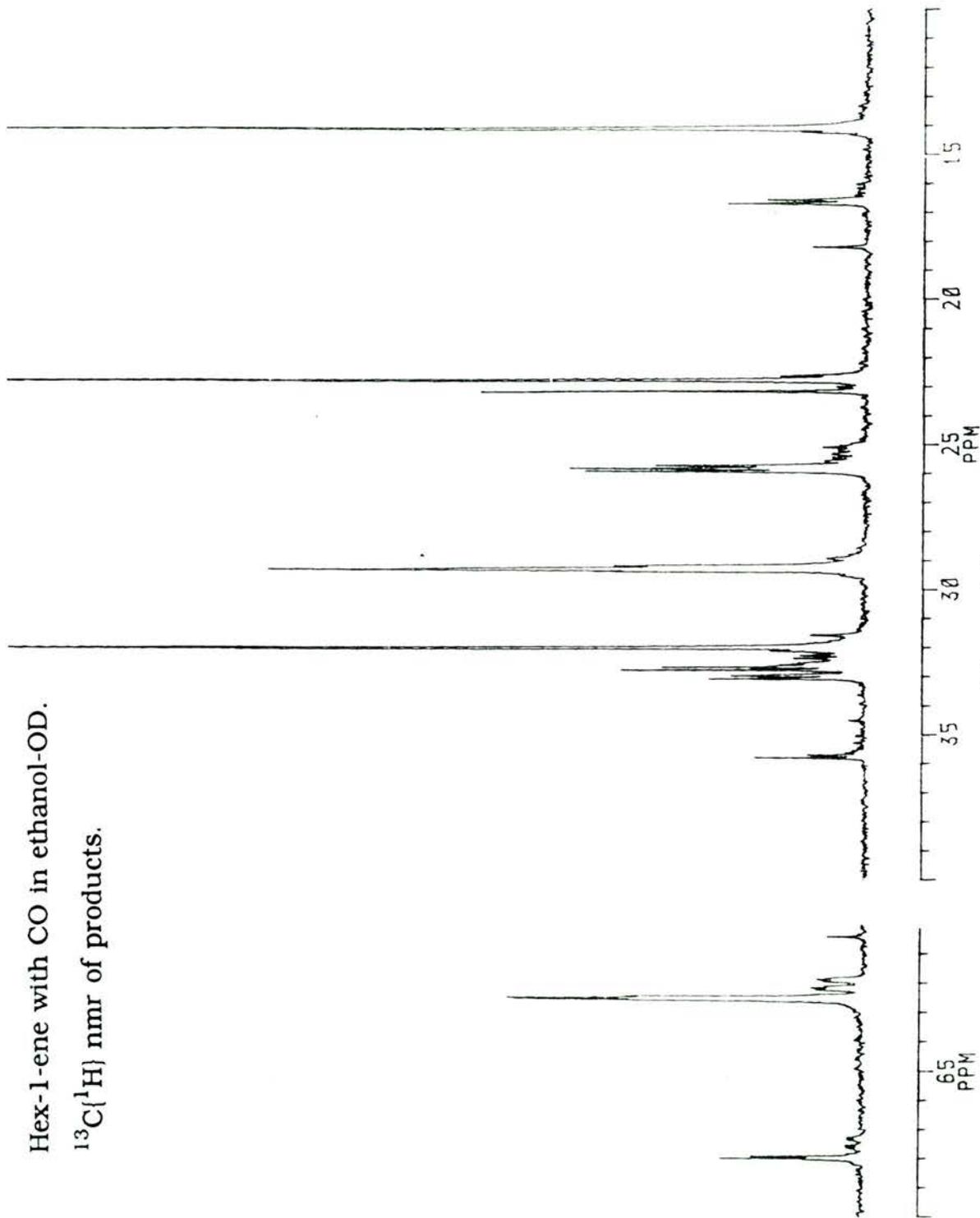


Figure 4.8.

one two and three deuterium atoms on the adjacent C<sub>1</sub> and C<sub>3</sub> carbons, of relative intensities 1.00 : 0.80 : 0.34 : 0.17. The triplet was resolvable into two signals ( $\beta$ -shift 0.11 ppm.) of almost equal intensity due to the presence of zero and one deuterium atoms on the adjacent carbons. The quintet due to three deuterium atoms on carbon C<sub>2</sub>, predicted from C<sub>1</sub> and C<sub>3</sub>  $\beta$ -shifted signals, was too weak to be resolvable.

The C<sub>4</sub> signal showed that the ratio of non to mono deuteration of carbon C<sub>3</sub> was 1.00 : 0.40. The C<sub>1</sub> and C<sub>3</sub> signals gave the following intensities from the  $\beta$ -shifts (0.05 ppm. and 0.10 ppm. per deuterium respectively):

C<sub>3</sub> singlet - non : mono : di deuteration at C<sub>2</sub> = 1.00 : 1.04 : 0.73.

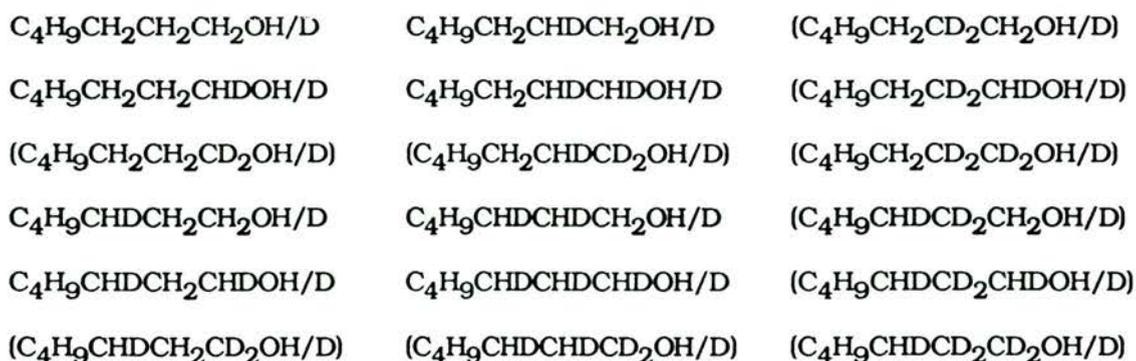
C<sub>3</sub> triplet - non : mono deuteration at C<sub>2</sub> = 1.00 : 0.84.

C<sub>1</sub> singlet - non : mono : di deuteration at C<sub>2</sub> = 1.00 : 1.03 : 0.69.

C<sub>1</sub> triplet - non : mono : di deuteration at C<sub>2</sub>  $\approx$  1.00 : 1.11 : 0.90.

i.e. slightly more product formed, overall, that was monodeuterated in the C<sub>2</sub> position than was nondeuterated, while least product was dideuterated in the C<sub>2</sub> position. So hydrogen was incorporated preferentially into the C<sub>3</sub> position, and into at least one of the substitution positions on carbon C<sub>1</sub>.

There were eighteen possible combinations of deuterated heptanol product which are shown below:



Of these, the ones with more than one deuterium incorporated on a

single carbon atom, shown in brackets, were not detectable directly except in the case of  $C_4H_9CHDCH_2CD_2OH/D$ ,  $C_4H_9CH_2CD_2CHDOH/D$  and  $C_4H_9CH_2CD_2CH_2OH/D$ . The remaining forms were possibly present but only in very small proportions. The majority of the product species were hydrogenated at carbon  $C_3$ , monodeuterated at carbon  $C_2$  and either non or monodeuterated at carbon  $C_1$ .

Markownikoff addition to hex-1-ene gave branched chain product in the form of 2-methylhexanol, with again deuterium incorporated into the  $C_1$ ,  $C_2$  and  $C_3$  positions (see table 4.2.). The  $C_1$  carbon gave a signal which was a singlet and a triplet ( $J_{C-D} = 21.5$  Hz. and  $\alpha$ -shift 0.40 ppm.) and the  $C_3$  carbon gave a singlet and a triplet the latter being of too low an intensity to resolve fully.

As the  $C_2$  carbon had only one hydrogen bound to it which could exchange with deuterium, it gave rise to signals at  $C_1$ ,  $C_3$  and  $C_4$  which were split into two peaks (with  $\beta$ -shifts of  $\sim 0.06$  ppm., 0.12 ppm. and 0.11 ppm. respectively) due to non- and monodeuteration at the  $C_2$  carbon. The extent of deuteration at the  $C_2$  carbon was indicated by  $\beta$ -shift intensities on adjacent carbons as follows:

$C_4$  singlet - non : mono deuteration at  $C_2$  = 1.00 : 0.85.

$C_3$  singlet - non : mono deuteration at  $C_2$  = 1.00 : 0.71.

$C_3$  triplet - unresolved.

$C_1$  singlet - non : mono deuteration at  $C_2$  = 1.00 : 0.79.

$C_1$  triplet - non : mono deuteration at  $C_2$  = 1.00 : 1.08.

The  $C_4$  signal indicated that overall 46% of 2-methylhexanol was deuterated on the  $C_2$  carbon.

The  $C_2$  carbon signal was split into three peaks ( $\beta$ -shift 0.09 ppm. per deuterium) with the ratio of their intensities 1.00 : 0.53 : 0.17. i.e. 59% of the product 2-methylhexanol was not deuterated at either the  $C_1$  or  $C_3$  position and only 31% was monodeuterated at one of these two sites. So as with the anti-Markownikoff addition product

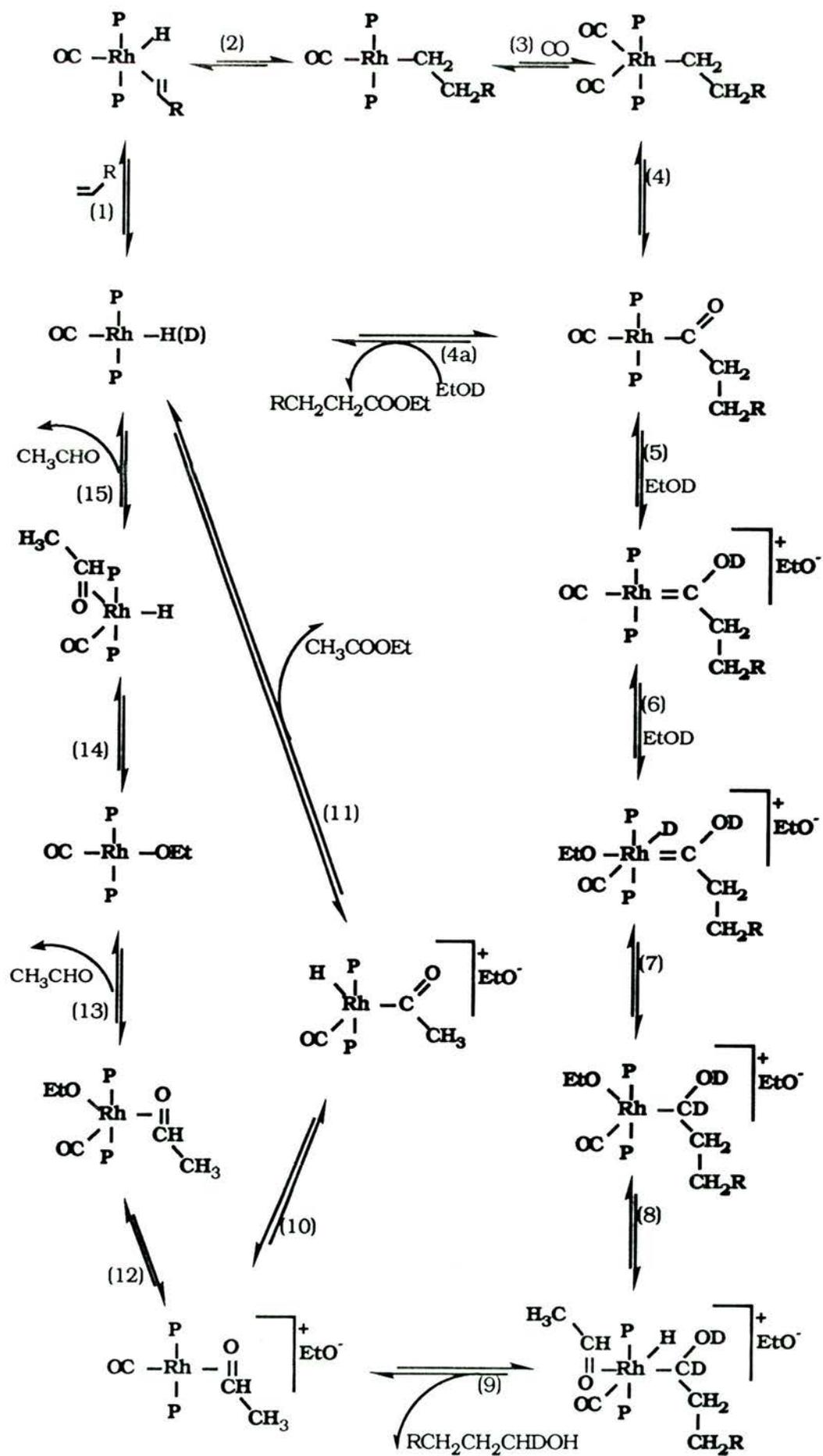
there was a tendency for hydrogen to be preferentially incorporated at C<sub>1</sub> and C<sub>3</sub> positions.

4.3.4. Proposed mechanism for the reaction of hex-1-ene with CO and ethanol-OD using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.008 moles dm<sup>-3</sup>) and PEt<sub>3</sub> (0.08 moles dm<sup>-3</sup>) as catalyst precursor.

The rate of hydroformylation with hydrogenation of hex-1-ene using ethanol as the hydrogen source was found to be greater than the rate of hydrogenation of heptanal under the same conditions (see section 3.11.5.). As the concentration of heptanal did not build up appreciably in the hex-1-ene reaction it may be assumed that aldehyde was not formed as an intermediate in this reaction. Another observed difference in the products of these two reactions was the production of ethyl ethanoate from the dehydrogenated ethanol in the hexene reaction but not in the case of heptanal.

Scheme 4.8. shows the mechanism proposed to account for the observed products. The first five steps are those proposed for the deuteroformylation of hex-1-ene to heptanol and 2-methylhexanol, in ethanol, using the same catalytic system, as shown previously:

- (1). Coordination of hexene.
- (2). Insertion of hexene into the Rh-H bond to give an alkyl ligand. This could occur by Markownikoff addition to give a branched chain alkyl ligand, which would lead on to produce 2-methylhexanol, or by anti-Markownikoff addition to yield the normal alkyl ligand, which in turn would give heptanol as product at the end of the cycle. For simplicity only the route to the anti-Markownikoff product is shown.
- (3). Coordination of carbon monoxide.
- (4). Insertion of a carbonyl ligand into the metal-alkyl bond to give an acyl ligand.



Scheme 4.8.

(5). Protonation of the acyl oxygen to give a cationic rhodium hydroxy-alkyl-carbene species with an ethoxide counterion.

(6). The oxidative addition of ethanol-OD to the cationic species would probably be slow, yielding a charged six coordinate carbene species which would be followed by:

(7). migration of deuterium onto the carbene carbon.

(8).  $\beta$ -hydrogen abstraction from the ethoxide ligand would then allow:

(9). reductive elimination of heptanol, monodeuterated on the C<sub>1</sub> carbon. The cycle would then be completed by one of two routes.

The first route is that shown in steps (10) and (11), yielding ethyl ethanoate as by-product.

(10). If the coordinated ethanal produced in step (9) were to add oxidatively to the rhodium centre it would give an acyl ligand on the still charged metal species. This species would then be subject to:

(11). ethoxide attack from the counter ion on the acyl carbon which would cause the elimination of ethyl ethanoate and the return of the rhodium to its starting catalytic form.

Alternatively a neutral species could be generated as shown in steps (12), (13), (14) and (15):

(12). Ethoxide coordination to the metal centre followed by:

(13). elimination of ethanal.

(14).  $\beta$ -hydrogen abstraction from the ethoxide ligand with subsequent:

(15). elimination of a second molecule of ethanal and return to the starting catalytic species.

Both routes would yield a total of four hydrogen/deuterium atoms from the dehydrogenation of ethanol (initially reacting in steps (5) and (6)) as was required for the conversion of hexene to heptanol. The ethyl ethanoate was found to account for between 35% and 67%

of the required hydrogen at this catalyst concentration. It was not fully understood which conditions determined the final route taken to reconstitute the starting catalyst, though in reactions carried out with lower catalyst concentrations less ethyl ethanoate was formed.

As shown, scheme 4.8. would yield heptanol deuterated in the hydroxyl position and at carbon C<sub>1</sub> only. The major proportion of the product was found to be deuterated at carbon C<sub>2</sub> and so an exchange with the solvent ethanol-OD must have been taking place. This is unlikely to have been occurring due to tautomerism and exchange on free aldehyde as discussed in section 4.3.1. in view of the differing rates of hydrogenation of heptanal, and transfer hydroformylation of hexene seen here. The acyl species formed in step (4) is known to

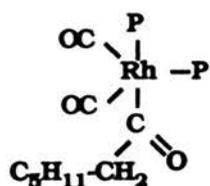
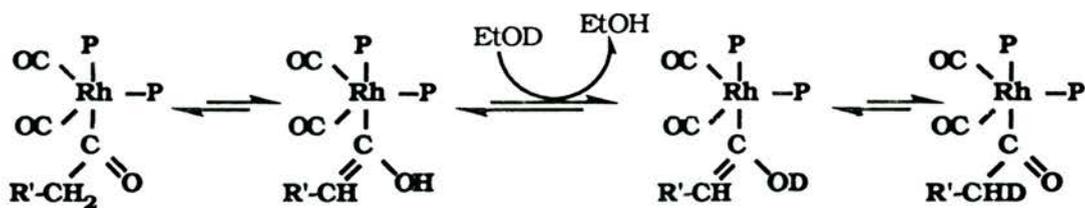


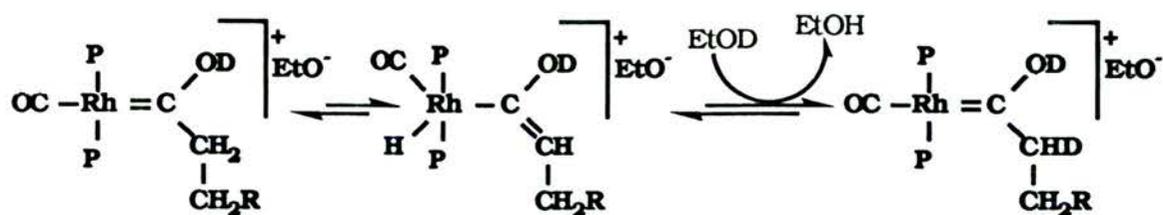
Figure 4.9.

coordinate a further CO to form a resting species as depicted in figure 4.9.. This species would be able to undergo keto-enol tautomerism and hydrogen/deuterium exchange with the solvent ethanol-OD as shown in scheme 4.9..



Scheme 4.9.

An alternative mechanism for this exchange is proposed in scheme 4.10. where the rhodium centre  $\beta$ -abstracts a hydrogen from the hydroxy-alkyl-carbene ligand, formed in step (5) of scheme 4.7., to form a five coordinate rhodium centre with an alkenyl ligand, the



Scheme 4.10.

species still being cationic. It is now proposed that the solvent exchanges its hydroxyl deuterium for the hydride ligand on the metal centre and in so doing reforms the carbene ligand but with deuterium on the  $\beta$ -carbon of this ligand. A possible intermediate for this exchange is shown in figure 4.10. which with electron redistribution as shown would lead to deuterium incorporation into the  $C_2$  position of the product heptanol.

The production of heptanal which was nondeuterated in the  $C_1$  position is still not accounted for by any of these mechanisms. This

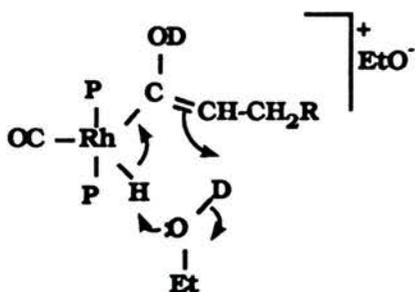


Figure 4.10.

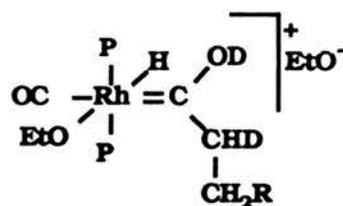


Figure 4.11.

could come about by ethoxide coordinating to the rhodium rather than abstracting the proton in the second step of scheme 4.10. to form the species shown in figure 4.11. This species is effectively the same as that formed in step (6) of scheme 4.8. but with deuterium on the  $\beta$ -carbon of the carbene ligand and a hydride rather than deuteride ligand on the rhodium. This species would proceed to give product hydrogenated in the  $C_1$  position.

The mechanism as shown would return to a starting species

with a hydride ligand. This would be the source of the hydrogen in the C<sub>3</sub> position of the product heptanol.  $\beta$ -shift intensities of the C<sub>4</sub> carbon showed that approximately 29% of product was monodeuterated in this position. Some of this deuterium incorporation would be accounted for by a slow step (4a) where ester formation could occur by nucleophilic attack by the solvent ethanol-OD to give ethyl heptanoate, a Reppe type product<sup>33</sup>, and deuteride ligand on the starting catalyst. A maximum of ~10% of the original hex-1-ene was converted to Reppe product and about 60% to C<sub>7</sub> alcohol so there must have been a further source of deuteride on some of the starting catalyst and it is possible that there was some slow exchange between the starting catalyst and the solvent.

As the reaction proceeded the proportion of C<sub>7</sub> alcohol relative to ethanol-OD would have increased, and it would have competed with ethanol in steps (4a), (5) and (6) to give the following products:

(4a) - heptyl heptanoate and its isomers derived from the 2-methylhexyl ligand and 2-methylhexoxy counter ion.

(5) - heptyl ethanoate and 2-methylhexyl ethanoate.

(6) - heptanal and 2-methylhexanal.

Small proportions of all these products were seen in reactions lasting 16 hours.

Two other factors were observed to alter the rate of this reaction. Firstly if the pressure of carbon monoxide was increased above 20 atmos. a lower percentage of hex-1-ene was converted to C<sub>7</sub> alcohol. Also if excess PEt<sub>3</sub> was added there was a higher conversion to C<sub>7</sub> alcohol apparent. The products of reactions carried out in ethanol-OD, with and without excess PEt<sub>3</sub> were compared and there was no significant variation in amount or positioning of the incorporated deuterium so it would appear that this reduction in reaction rate on increasing CO pressure or reducing free PEt<sub>3</sub>

concentration was due to removal of the active catalytic species due to an equilibrium between the active species and carbon monoxide with an inactive species and  $\text{PEt}_3$ . This equilibrium will be discussed further in chapter 5.

#### 4.4. Reactions involving gaseous $\text{D}_2$ and $\text{RhH}(\text{PEt}_3)_3$ (0.0008 moles $\text{dm}^{-3}$ ) as catalyst precursor.

It had been found that if  $\text{RhH}(\text{PEt}_3)_3$  (0.008 moles  $\text{dm}^{-3}$ ) was used as catalyst precursor (ie one tenth of the concentration previously employed) in hydroformylation reactions the product obtained was mainly aldehyde with only small quantities of alcohol observed. Assignments of the  $^{13}\text{C}$  nmr signals for heptanal and 2-methylhexanal were made using the formula published by Williams and Fleming<sup>31</sup> as before, and are shown in table 4.3.. Comparison was made between the products of a reaction of hex-1-ene in ethanol using firstly  $\text{CO}/\text{H}_2$  and then  $\text{CO}/\text{D}_2$  in the gas phase.

##### 4.4.1. Hex-1-ene with $\text{CO}/\text{H}_2$ in ethanol-OH.

Hex-1-ene in ethanol was reacted with  $\text{CO}/\text{H}_2$  (1:1) at 40 atmos., with the oven set at  $125^\circ\text{C}$ , for 3 hours, using  $\text{RhH}(\text{PEt}_3)_3$  (0.0008 moles  $\text{dm}^{-3}$ ) as catalyst precursor. The solvent was distilled off under vacuum and the aldehydic products were studied by  $^{13}\text{C}$  nmr to assign the peaks of 2-methylhexanal. 1,1-diethoxyheptane and 1,1-diethoxy-2-methylhexane were also seen in the nmr sample, the concentration of the former allowing assignment of its peaks as shown in table 4.4..

##### 4.4.2. Hex-1-ene with $\text{CO}/\text{D}_2$ in ethanol-OH.

The reaction of hex-1-ene in ethanol was carried out with  $\text{CO}/\text{D}_2$  (20:17) at 37 atmos., with the oven set at  $125^\circ\text{C}$ , for 2.5 hours, using  $\text{RhH}(\text{PEt}_3)_3$  (0.0008 moles  $\text{dm}^{-3}$ ) as catalyst precursor. The products

Table 4.3. Assignment of  $^{13}\text{C}$  nmr peaks for  $\text{C}_7$  aldehydes.

Heptanal.		2-methyl hexanal.						
$\text{O}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3.$		$\begin{array}{c} 3 \text{ CH}_3 \\   \\ \text{O}=\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3. \\ 1 \quad 2 \quad 4 \quad 5 \quad 6 \quad 7 \end{array}$						
	1	2	3	4	5	6	7	
	1/ppm	2/ppm	3/ppm	4/ppm	5/ppm	6/ppm	7/ppm	
heptanal - calculated value.	-	43.9	22.5	29.5	32.2	23.1	14.0	
heptanal - supplied sample.	202.72	43.98	22.15	28.95	31.67	22.56	14.04	
2-methylhexanal - calculated value.	-	49.3	12.3	30.5	29.5	23.1	14.0	

Table 4.4. Reactions catalysed by  $[\text{RhH}(\text{PET}_3)_3]$  at low concentration ( $\sim 0.0008$  moles  $\text{dm}^{-3}$ ).

	1/ppm	$J_{\text{C-D}}/\text{Hz}$	2/ppm	$J_{\text{C-D}}/\text{Hz}$	3/ppm	$J_{\text{C-D}}/\text{Hz}$	4/ppm	5/ppm	6/ppm	7/ppm
<u>Hex-1-ene + <math>\text{CO}/\text{H}_2</math> in ethanol giving:</u>										
heptanal.	203.37		44.08		22.25		29.07	31.80	22.68	14.07
2-methylhexanal .	205.76		46.50		13.38		30.44	29.37*	22.82	13.98
<u>Hex-1-ene + <math>\text{CO}/\text{D}_2</math> in ethanol giving:</u>										
heptanal - partially deuterated.	203.09		44.00		22.26		29.11	31.81	22.71	14.06
	202.82	t. 25.9	43.82	t. 3.2	21.90	t. 19.5	29.01			
2-methylhexanal - partially deuterated.	205.21	t. 25.3	46.43		13.09	t. 19.7	30.45	29.39*	22.94	13.97
			46.28	t. 2.8						
<u>Heptanal - ethanol -OD exchange giving :</u>										
heptanal - partially deuterated.	203.55		43.97		22.14		28.88	31.63	22.53	14.01
	203.46		43.59	t. 19.3	22.08					
	203.37				22.02					

Note: Acetals, mainly 1,1-diethoxyheptane, were also seen in the  $\text{C}_7$  fraction of products when they are distilled off the catalyst. The peaks for 1,1-diethoxyheptane were assigned as shown.

1,1-diethoxyheptane.		$(\text{CH}_3-\text{CH}_2-\text{O})_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3.$										
		B	A	1	2	3	4	5	6	7		
	1/ppm	$J_{\text{C-D}}/\text{Hz}$	2/ppm	$J_{\text{C-D}}/\text{Hz}$	3/ppm	$J_{\text{C-D}}/\text{Hz}$	4/ppm	5/ppm	6/ppm	7/ppm	A/ppm	B/ppm
1,1-diethoxyheptane - calculated.	114.7		36.4		20.7		29.7	32.5	23.1	14.0	57.1	14.7
$(\text{C}_2\text{H}_5\text{O})_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}_4\text{H}_9.$	97.88		37.44		25.06		29.37*	32.09	22.82	14.15	62.42	15.35
$(\text{C}_2\text{H}_5\text{O})_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}_4\text{H}_9.$	97.92		37.39		25.06		29.39*	32.11	22.85	14.14	62.35	15.39
$(\text{C}_2\text{H}_5\text{O})_2-\text{CD}-\text{CH}_2-\text{CHD}-\text{C}_4\text{H}_9.$	97.51	t. 24.3	37.30		24.67	t. 19.1	29.33					
1,1-diethoxyheptane -	98.17		37.45		24.83		29.21 $\S$	31.95 $\S$	22.86	14.09 $\S$	62.55 $\S$	15.31
partially deuterated at $\text{C}_2.$	97.95		37.06	t. 18.5	24.73							
					24.64							

\*  $\text{C}_5$  of 2-methylhexanal was superimposed on  $\text{C}_4$  of 1,1-diethoxyheptane.

$\S$  overlap with heptanol peaks.

Hex-1-ene with CO/D<sub>2</sub> in ethanol-OH.

<sup>13</sup>C{<sup>1</sup>H} nmr of products.

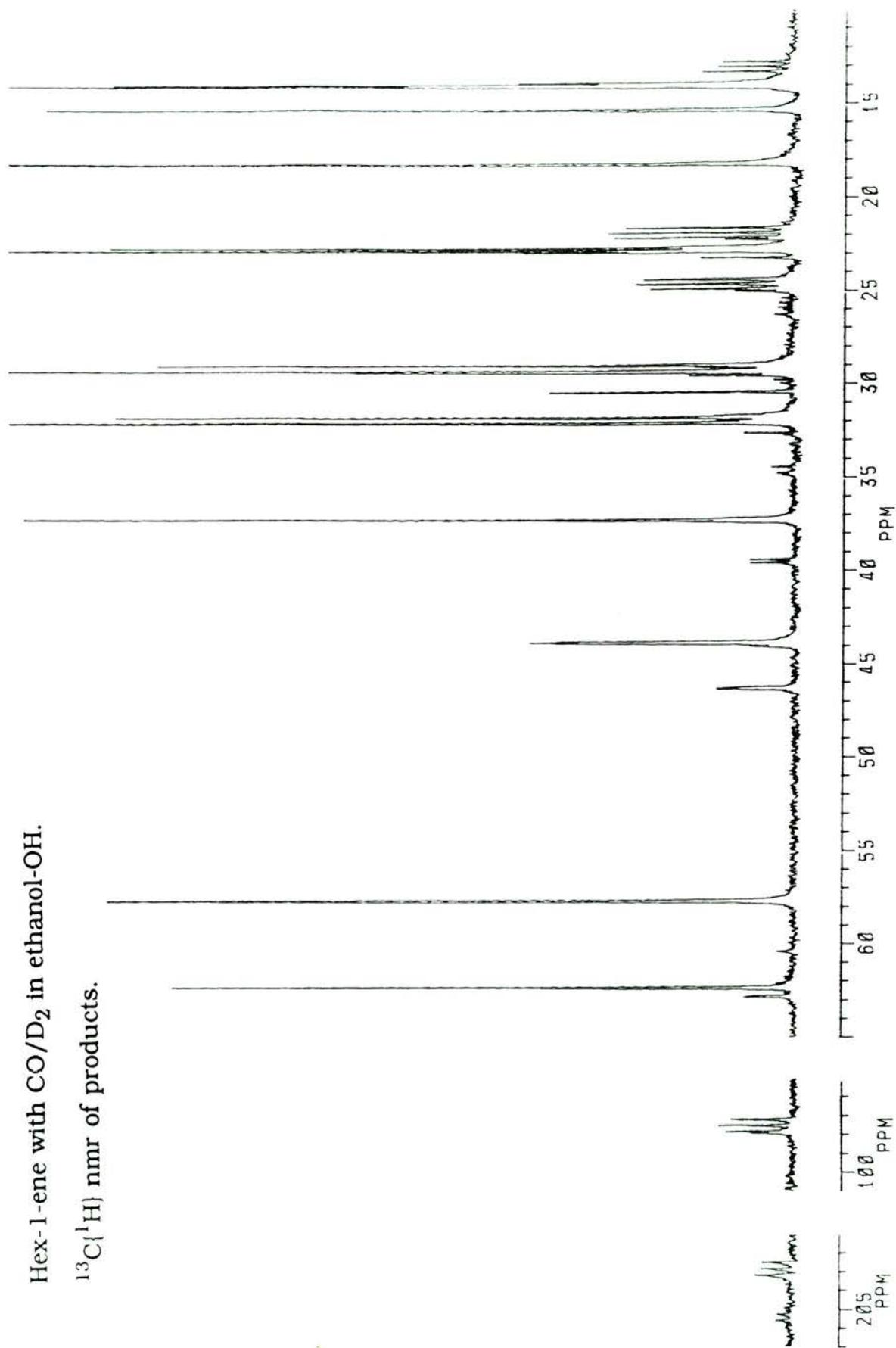


Figure 4.12.

were studied by  $^{13}\text{C}$  nmr after most of the solvent ethanol had been removed under vacuum. The spectrum is shown in figure 4.12. and the peak positions obtained are listed in table 4.4..

Comparison with products of the reaction with molecular hydrogen showed that deuterium incorporation had taken place at carbons  $\text{C}_1$  and  $\text{C}_3$ . The  $\text{C}_2$  signal of both heptanal and 2-methylhexanal appeared to indicate, by  $\beta$ -shift signals, that zero, one and two deuterium atoms had been incorporated onto the two adjacent carbon atoms in roughly equal quantities.

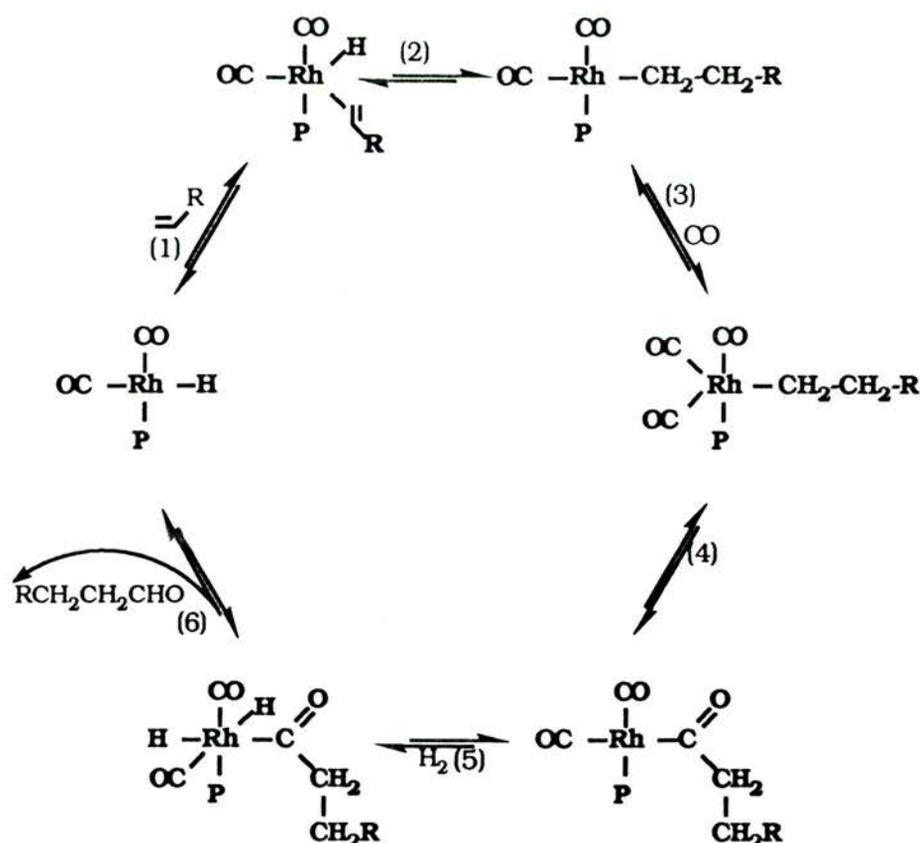
In the case of heptanal the main  $\text{C}_1$  signal was a triplet ( $J_{\text{C-D}} = 25.9$  Hz. and  $\alpha$ -shift of 0.27 ppm.) with only a small singlet signal due to only hydrogen being bonded to this carbon. Similarly the  $\text{C}_3$  signal showed only a weak singlet signal and a strong triplet ( $J_{\text{C-D}} = 19.5$  Hz. and  $\alpha$ -shift of 0.36 ppm.) while the  $\text{C}_4$  peak showed two signals with  $\beta$ -shift of 0.10 ppm. and intensities in the ratio 1.00 : 6.55. 2-methylhexanal also showed triplets for both carbons  $\text{C}_1$  ( $J_{\text{C-D}} = 25.3$  Hz.) and  $\text{C}_3$  ( $J_{\text{C-D}} = 19.7$  Hz.) with no singlet evident in either case. These observations pointed to the major product being dideuterated with one deuterium each on the  $\text{C}_1$  and  $\text{C}_3$  carbons. The splitting of the  $\text{C}_2$  carbon signal into a triplet for both heptanal ( ${}^2J_{\text{C-D}} \sim 3.2$  Hz.) and 2-methylhexanal ( ${}^2J_{\text{C-D}} \sim 2.8$  Hz.) must have been due to two bond coupling to the aldehydic deuterium. Either the enlarged bond angle, due to  $\text{sp}^2$  hybridisation of the aldehydic carbon, or the greater s character of the bonds, permitted the coupling to be large enough to be observed. A small singlet was observable for this carbon atom ( $\text{C}_2$ ) also slightly downfield from the triplet, the  $\beta$ -shift being 0.18 Hz. for heptanal and 0.15 for 2-methylhexanal. The singlet was due to incorporation of a small amount of hydrogen on the aldehydic carbon.

1,1-Diethoxyheptane similarly showed deuterium incorporation with triplet signals for carbon  $\text{C}_1$  ( $J_{\text{C-D}} = 24.3$  Hz. and  $\alpha$ -shift of 0.41

ppm.) and carbon C<sub>3</sub> ( $J_{C-D} = 19.1$  Hz. and  $\alpha$ -shift of 0.39 ppm.). The C<sub>2</sub> signal showed two peaks with a  $\beta$ -shift of 0.09 ppm. and relative intensity 1.00 : 6.89 suggesting that 87% of the acetal was dideuterated. The carbon C<sub>4</sub> un- $\beta$ -shifted signal was under the C<sub>5</sub> carbon signal for 2-methylhexanal and so comparison could not be made to confirm the percentage of deuteration at position C<sub>3</sub>.

#### 4.4.3. Proposed reaction mechanism for hydroformylation of hex-1-ene to C<sub>7</sub> aldehydes using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.0008 moles dm<sup>-3</sup>) as catalyst precursor.

When hex-1-ene was hydroformylated with CO/H<sub>2</sub> using RhH(PEt<sub>3</sub>)<sub>3</sub> (0.0008 moles dm<sup>-3</sup>) as catalyst precursor, the products were found to be C<sub>7</sub> aldehydes. At this concentration of catalyst precursor the rhodium species present were not able to hydrogenate C<sub>7</sub> aldehyde, or form C<sub>7</sub> alcohol directly. The higher relative concentration of CO in solution could have shifted the equilibrium of initial hydridic species from predominantly RhH(CO)(PEt<sub>3</sub>)<sub>3</sub> to mainly RhH(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>. This eighteen electron species on loss of one PEt<sub>3</sub> ligand would form RhH(CO)<sub>2</sub>(PEt<sub>3</sub>) which could trap alkene and so initiate hydroformylation. A proposed route for the production of C<sub>7</sub> aldehyde by this species is shown in scheme 4.11.. Initial coordination of alkene, step (1), would be followed by insertion of alkene into the Rh-H bond to give an alkyl ligand, as shown in step (2). Coordination of CO, step (3), would then lead to insertion of CO into the rhodium-alkyl bond to form an acyl species, as shown in step (4). As this proposed species has one triethylphosphine and two carbonyl ligands it would have a lower electron density than the equivalent acyl species with two triethylphosphine and one carbonyl ligands, proposed in scheme 4.5. for the reaction at high concentration of catalyst precursor. Oxidative addition of hydrogen would now take



Scheme 4.11.

place (step (5)) followed by reductive elimination of heptanal (step (6)) and return to the starting hydridic species.

Thus it is proposed that the rhodium-acyl species formed at low concentrations of rhodium has a lower electron density at rhodium than that formed at high rhodium concentrations with  $\text{PET}_3$ . This allows conventional hydroformylation yielding aldehydes to take place, while the species formed at high catalyst concentrations has a higher electron density and forms alcoholic products directly. (The proposed route for alcohol production via a cationic rhodium species with a hydroxy-carbene ligand is discussed in section 4.2.6. above).

#### 4.4.4 Heptanal exchange with ethanol-OD.

As mentioned earlier in the discussion of the reduction of heptanal with ethanol-OD in section 4.3.1 some unreduced heptanal

Heptanal exchange with ethanol-OD.

$^{13}\text{C}\{^1\text{H}\}$  nmr of products.

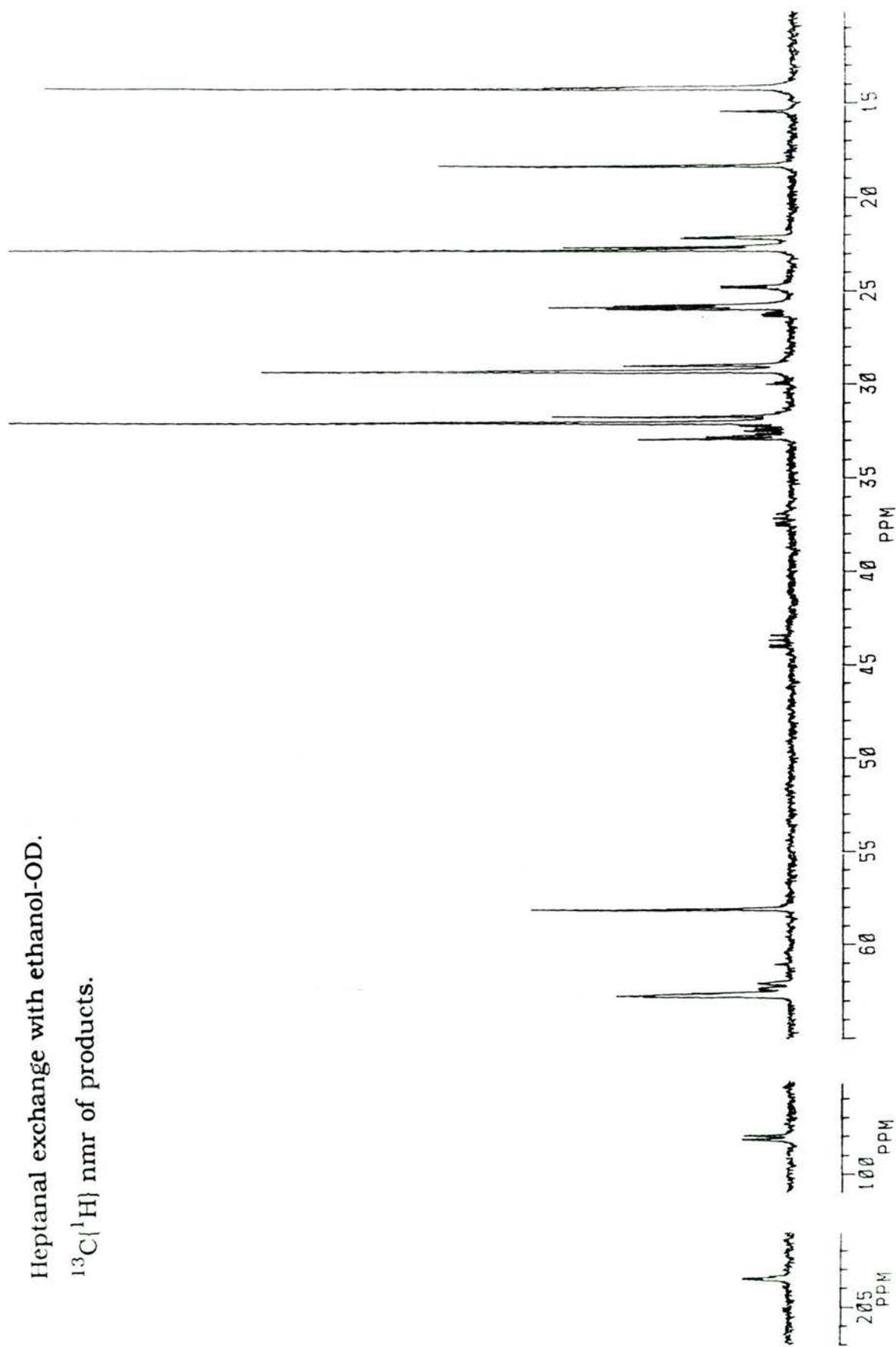


Figure 4.13.

was found to be deuterated in the C<sub>2</sub> position. It is of interest to note the <sup>13</sup>C nmr spectra of heptanal and 1,1-diethoxyheptane with deuterium in the C<sub>2</sub> position at this point. The spectrum obtained from the reaction mixture of heptanal reduction with ethanol-OD discussed in section 4.3.1. was not fully resolvable for the heptanal C<sub>2</sub> signal but a clearer spectrum was obtained from a reaction of heptanal in ethanol-OD with RhH(PET<sub>3</sub>)<sub>3</sub> (0.010 moles dm<sup>-3</sup>), PET<sub>3</sub> (0.10 moles dm<sup>-3</sup>) and CO at 20 atmos as catalyst precursor. The oven was set at 125°C and the autoclave was heated for 16 hours as it had been previously. At this concentration of catalyst there was evidence of non-, mono- and dideuteration on the C<sub>2</sub> carbon of the unreduced heptanal, as shown by non-β-shifted and β-shifted signals for carbons C<sub>1</sub> and C<sub>3</sub> (see figure 4.13.). The 1,1-diethoxyheptane observed showed similar deuteration on the C<sub>2</sub> carbon. The peak positions and couplings for C<sub>5</sub>H<sub>11</sub>CHDCHO and C<sub>5</sub>H<sub>11</sub>CHDCH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> obtained from this reaction are listed in table 4.4..

The carbon C<sub>2</sub> signal of heptanal showed a small singlet and a triplet ( $J_{C-D} = 19.3$  Hz.,  $\alpha$ -shift 0.38 ppm.), with the expected quintet due to dideuteration at this position being unresolved. The carbon C<sub>3</sub> signal, however, was split into three peaks of relative intensity 1.00 : 2.83 : 2.71 ( $\beta$ -shift 0.06 ppm.) indicating zero, one and two deuterium atoms on carbon C<sub>2</sub>. The signal from carbon C<sub>1</sub> was also split into three peaks with the intensities in reverse order 2.36 : 2.44 : 1.00. This would appear to indicate that there was a negative  $\beta$ -shift in this environment, ie as registered on the aldehydic carbon, of -0.09 ppm but it confirmed the presence of two, one and zero deuterium atoms on carbon C<sub>2</sub>. The difference in the intensity ratio values for C<sub>1</sub> and C<sub>3</sub> carbons may be due to the weaker signal obtained from carbonyl carbons due to their long relaxation times giving a less accurate reading of intensity at -CHO compared with -CH<sub>2</sub>- but it does give

confirmation that most of the carbon in the C<sub>2</sub> position was deuterated and only a small proportion remained bonded to hydrogen alone.

In the case of 1,1-diethoxyheptane the C<sub>2</sub> carbon signal showed a weak singlet and a triplet ( $J_{C-D} = 19.3$  Hz.,  $\alpha$ -shift 0.38 ppm.). The quintet due to dideuteration at the C<sub>2</sub> position was not resolvable. Zero, one and two deuterium atoms on the C<sub>2</sub> carbon were indicated by the carbon C<sub>3</sub> non- $\beta$ -shifted and  $\beta$ -shifted signals of intensities 1.00 : 3.44 : 3.42 ( $\beta$ -shift 0.06 ppm.). The C<sub>1</sub> signal only resolved to show the  $\beta$ -shifted peaks due to one and two deuterium atoms in the C<sub>2</sub> position.

#### 4.5. Summary of <sup>13</sup>C nmr data.

Table 4.5. shows the <sup>13</sup>C nmr coupling constants,  $\alpha$ -shifts and  $\beta$ -shifts for the partially deuterated compounds studied above.

The size of the coupling to deuterium was found to be determined by the environment of the carbon atom being studied. The largest coupling of 25.9 Hz. was found on the aldehydic carbon, with an sp<sup>2</sup> bonding orbital, and this was slightly larger for heptanal than for 2-methylhexanal. The coupling was smaller for the sp<sup>3</sup> bonded carbons being about 19.5 Hz for carbon bonded to carbon and hydrogen only but increasing to 21.6 Hz for carbon singly bonded to one oxygen and 24.3 Hz. when bonded to two oxygens. Two bond coupling was only observable on the carbon bonded to an aldehydic carbon. The wider bond angle due to the sp<sup>2</sup> hybridisation and/or the greater s character of these bonds probably accounts for its relatively large size.

There was a reverse trend in the  $\alpha$ -shifts observed with the greatest being seen for secondary alkyl carbon adjacent to a carbon bonded to at least one electronegative group (hydroxyl or ethoxy), and

Table 4.5. Summary of  $^{13}\text{C}$  nmr data.

Type of carbon observed.	$^1J_{\text{C-D}}$ /Hz.	$^2J_{\text{C-D}}$ /Hz.	$\alpha$ -shift /ppm.	$\beta$ -shift /ppm.
aldehydic	$25.6 \pm 0.3$		$\sim 0.27$	$-0.09$
secondary alkyl adjacent to C=O	$19.3 \pm 0.1$	$\sim 0.32$	$0.38 \pm 0.01$	$\sim 0.18$
tertiary alkyl adjacent to C=O		$\sim 0.28$		$\sim 0.15$
primary alcoholic	$21.6 \pm 0.2$		$0.39 \pm 0.02$	$0.05 \pm 0.01$
secondary alkyl adjacent to C-OH	$19.5 \pm 0.3$		$0.40 \pm 0.01$	$0.09 \pm 0.01$
tertiary alkyl adjacent to C-OH				$0.09 \pm 0.01$
secondary alkyl adjacent to $\text{CH}(\text{OEt})_2$ .	$\sim 18.5$		$\sim 0.39$	
primary alkyl	$19.4 \pm 0.3$			$0.12 \pm 0.01$
secondary alkyl	$19.4 \pm 0.3$		$0.39 \pm 0.03$	$0.11 \pm 0.01$
$-\text{CH}(\text{OEt})_2$ .	$\sim 24.3$		$\sim 0.41$	$0.20 \pm 0.01$

the smallest for the aldehydic carbon. The smallest  $\beta$ -shift observed was on a primary alcoholic carbon with the deuterium causing the shift bonded to a secondary carbon. It would therefore appear that the type and position of functional groups determines the size of coupling and extent of isotopic shift observed due to replacement of hydrogen by deuterium. The electronegative group has a deshielding effect on the carbon with which it is bonded but a shielding effect on the carbon next to that to which it is bonded.

## Chapter 5. Nmr studies of rhodium species.

### 5.1. Introduction.

The catalytic system that has been investigated for this work was based on  $\text{RhH}(\text{PEt}_3)_3$ . In order to try to identify key intermediates in the catalytic cycle, the nature of  $\text{RhH}(\text{PEt}_3)_3$  was investigated in both deuterated toluene and deuterated ethanol, and some difference was found on changing from one solvent to the other. The addition of CO to the system led to rapid reaction at room temperature and the equilibrium set up between the species formed was studied.

The species which were thought to be possible intermediates in the catalytic cycle were also studied, starting from the known compound  $\text{RhCl}(\text{CO})(\text{PEt}_3)_2$  and reacting this with methyl lithium to make  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  as a model alkyl species with which to work.

### 5.2. $\text{RhH}(\text{PEt}_3)_3$ in perdeuterotoluene without and with ethanol.

$\text{RhH}(\text{PEt}_3)_3$  is a known compound<sup>61</sup> with a recorded fluxional  $^{31}\text{P}\{^1\text{H}\}$  nmr spectrum (broad doublet  $\delta = 26.6$  ppm.) at room temperature which resolves at  $-40^\circ\text{C}$  into an  $\text{AB}_2\text{X}$  pattern at  $\delta = 28.8$  ppm.,  $J_{\text{Rh-P}_A} = 137$  Hz. and a higher field resonance at  $\delta = 25.4$  ppm.  $J_{\text{Rh-P}_B} = 152$  Hz.,  $J_{\text{P}_A-\text{P}_B} = 28.5$  Hz. The hydride resonance in the  $^1\text{H}$  nmr spectrum at  $-50^\circ\text{C}$  is a complex multiplet at  $\delta = -7.9$  ppm., which becomes a doublet ( $J_{\text{Rh-H}} = 18$  Hz.) when  $^{31}\text{P}$  decoupled. These data are tabulated in table 5.1. together with figures from our own measurements on fresh samples in deuterated toluene,  $\text{C}_7\text{D}_8$ . It was found that the  $^{31}\text{P}$  spectrum, which at room temperature had been a broad peak centred at  $\delta = 26.1$  ppm., when fully  $^1\text{H}$  decoupled, at  $-40^\circ\text{C}$  showed a doublet of doublets at  $\delta = 26.6$  ppm.  $J_{\text{Rh-P}_B} = 153$  Hz. and a doublet of triplets at  $\delta = 23.2$  ppm.  $J_{\text{Rh-P}_A} = 138$  Hz. with  $J_{\text{P}_A-\text{P}_B}$

Table 5.1.  $^1\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectral data of rhodium species derived from  $\text{RhH}(\text{PEt}_3)_3$ .

Rhodium species	solvent	Temp. / $^{\circ}\text{C}$	$^{31}\text{P}$ $\delta$ /ppm.	$^1\text{Rh-P}$ /Hz.	$\text{J}_{\text{P-P}}$ /Hz.	$^1\text{H}$ $\delta$ /ppm.	$\text{J}_{\text{Rh-H}}$ /Hz.	$\text{J}_{\text{P-H}}$ /Hz.	$^{13}\text{C}$ of CO peaks $\delta$ /ppm.	$\text{J}_{\text{Rh-C}}$ /Hz.
$\text{RhH}(\text{PEt}_3)_3$	$\text{C}_7\text{D}_8$	25	26.1 b			-8.4 bm				
<b>61</b>	$\text{C}_7\text{D}_8$	-40	26.6 dd 23.2 dt	153 138	28	-8.1 bd				~106
	$\text{C}_7\text{D}_8$	25	26.6 b							
		-40	28.8 m 25.4 m	137 152	28.5	-7.9 <sup>a</sup> m	18			
$\text{RhH}_2(\text{PEt}_3)_4^+$ $\text{EtO}^-$	$\text{C}_7\text{D}_8$	-40	19.5 dt 4.3 dt	101 89	21	-12.2 bd				~126
<b>62</b> $\text{BPh}_4^-$	thf-d8									
						-11.7 dd	11.0	124.5 16.0		
$\text{RhH}(\text{CO})(\text{PEt}_3)_3$ with EtOH	$\text{C}_7\text{D}_8$	25 -40	26.2 d 26.9 d	147 147					212.5 <sup>b</sup> d	62
<b>45</b>	$\text{C}_6\text{D}_6$					-11.1 qd -11.3 qd	~4 ~4	17 17		

<sup>a</sup> -50C. <sup>b</sup> in  $\text{C}_6\text{D}_6$ .

$^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_7\text{D}_8$  at  $-40^\circ\text{C}$ .

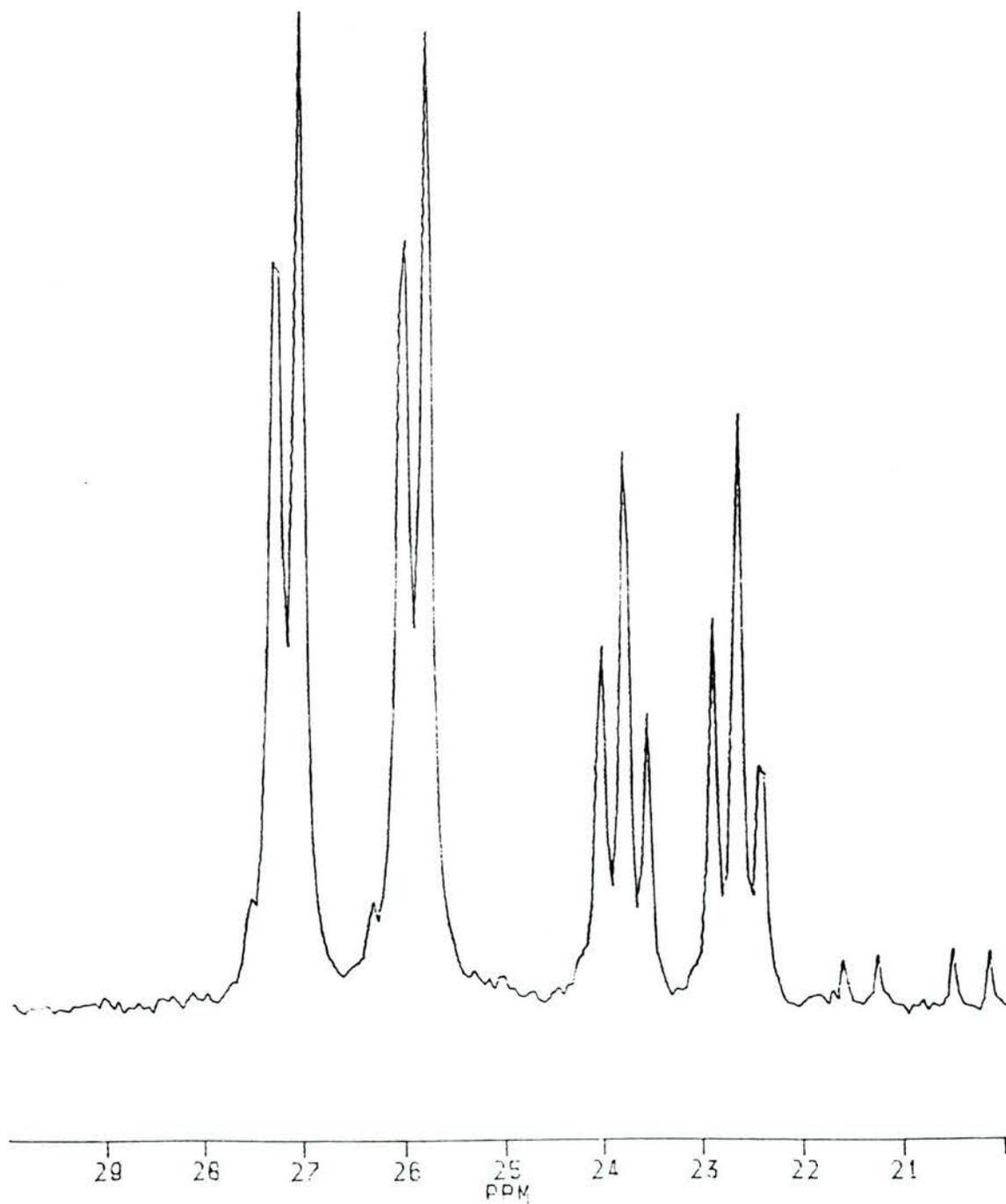


Figure 5.1.

= 28 Hz. (see figure 5.1.). (These  $J_{\text{Rh-P}}$  couplings are the reverse of those recorded by Yoshida et al. who used a spectrometer at 40.32 MHz. and so were analysing a second order spectrum). The  $^1\text{H}$  nmr spectrum at room temperature was a complex multiplet  $\delta = -8.4$  ppm. while at  $-40^\circ\text{C}$  it became a broad doublet at  $\delta = -8.1$  ppm..

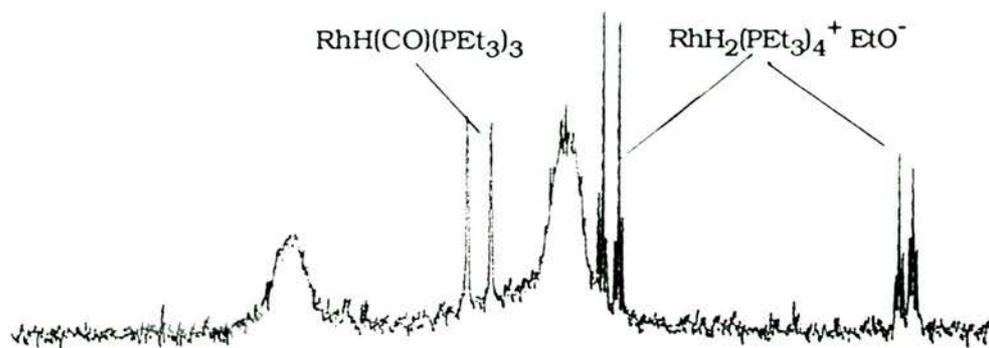
On addition of ethanol to a solution of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_7\text{D}_8$ , or when  $\text{RhH}(\text{PEt}_3)_3$  was dissolved in deuterated ethanol,  $\text{C}_2\text{D}_5\text{OH}$ , the rhodium species reacted slowly at ambient temperature with the ethanol to give  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  on decarbonylation of ethanol, as shown in equation 5.1.. The concentration of  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  increased with time until it was almost the sole species present. Analysis, by glc, of the gases which accumulated above a solution of  $\text{RhH}(\text{PEt}_3)_3$  in ethanol showed the presence of hydrogen and methane as expected.



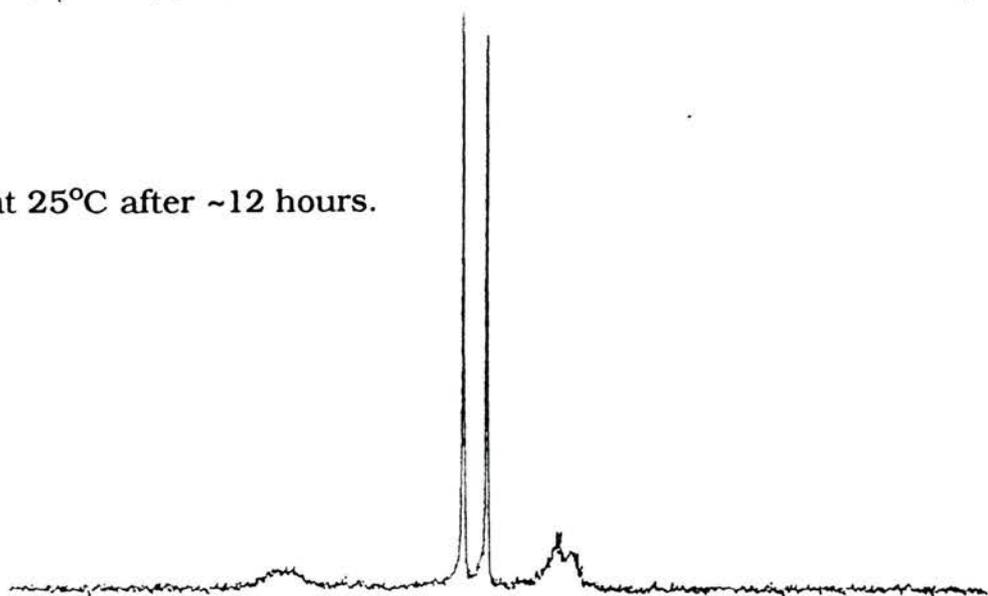
At  $25^\circ\text{C}$  two uncharacterised hydridic species, with broad  $^{31}\text{P}$  peaks centred at  $\delta = 21.2$  ppm. and  $\delta = 35.2$  ppm. and broad  $^1\text{H}$  peaks at  $\delta = -10.8$  ppm. and  $\delta = -10.05$  ppm. were also detected. At  $-40^\circ\text{C}$  these became a doublet at  $\delta = 21.2$  ppm.  $J_{\text{Rh-P}} = 94$  Hz. and a doublet of doublets at  $\delta = 39.5$  ppm.  $J_{\text{Rh-P}} = 107$  Hz. and  $J_{\text{P-P}} = 26$  Hz.. The expected second pairing coupled with the peaks at  $\delta = 39.5$  ppm. was not seen, probably because the signal was too weak. See figure 5.2.. The corresponding  $^1\text{H}$  peaks at  $\delta = -10.8$  ppm. (unresolved triplet) and  $\delta = -9.1$  ppm. (unresolved quintet) are shown in figure 5.3.. These were transient species, their intensities decreasing as that of  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  increased. A trace of  $[\text{RhH}_2(\text{PEt}_3)_4]^+ \text{EtO}^-$  was also detected.  $[\text{RhH}_2(\text{PEt}_3)_4]^+ \text{EtO}^-$  was seen as a major species in place of the two uncharacterised transient species mentioned above when  $\text{RhH}(\text{PEt}_3)_3$  was dissolved in ethanol in the presence of excess  $\text{PEt}_3$ ,

$^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_7\text{D}_8$  with ethanol.

i. at  $25^\circ\text{C}$  immediatly after addition of ethanol.



ii. at  $25^\circ\text{C}$  after ~12 hours.



iii. at  $-40^\circ\text{C}$  after 2 days.

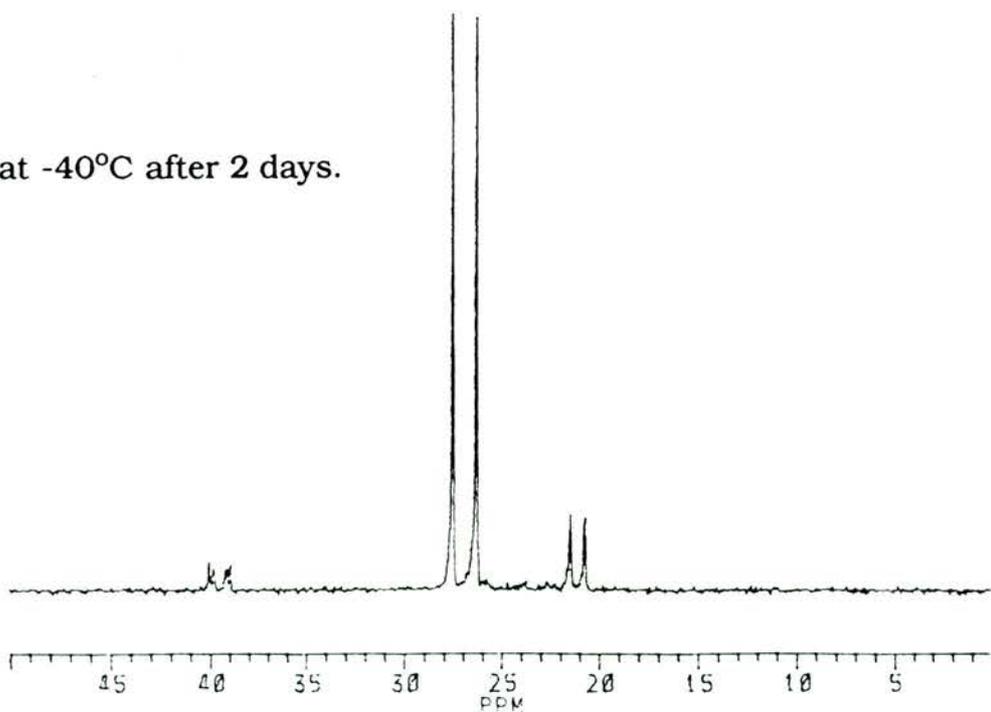
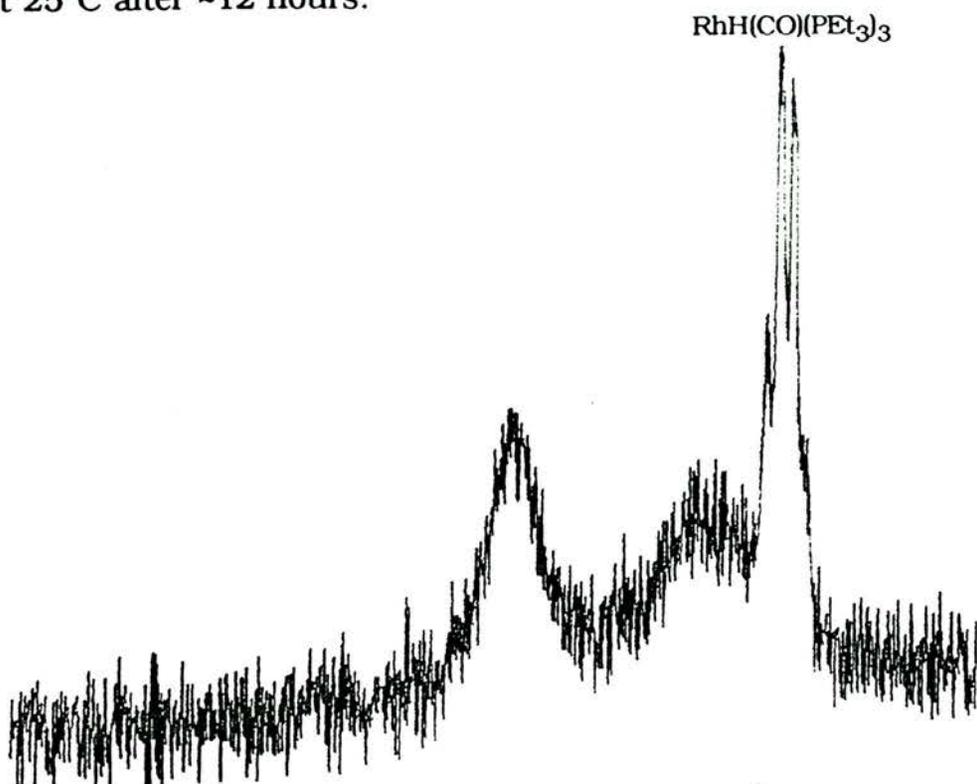


Figure 5.2.

Hydride resonance of the  $^1\text{H}$  nmr of  $\text{RhH}(\text{PEt}_3)_3$  in ethanol with  $\text{C}_7\text{D}_8$  at  $-40^\circ\text{C}$ .

i. at  $25^\circ\text{C}$  after  $\sim 12$  hours.



ii. at  $-40^\circ\text{C}$  after 2 days.

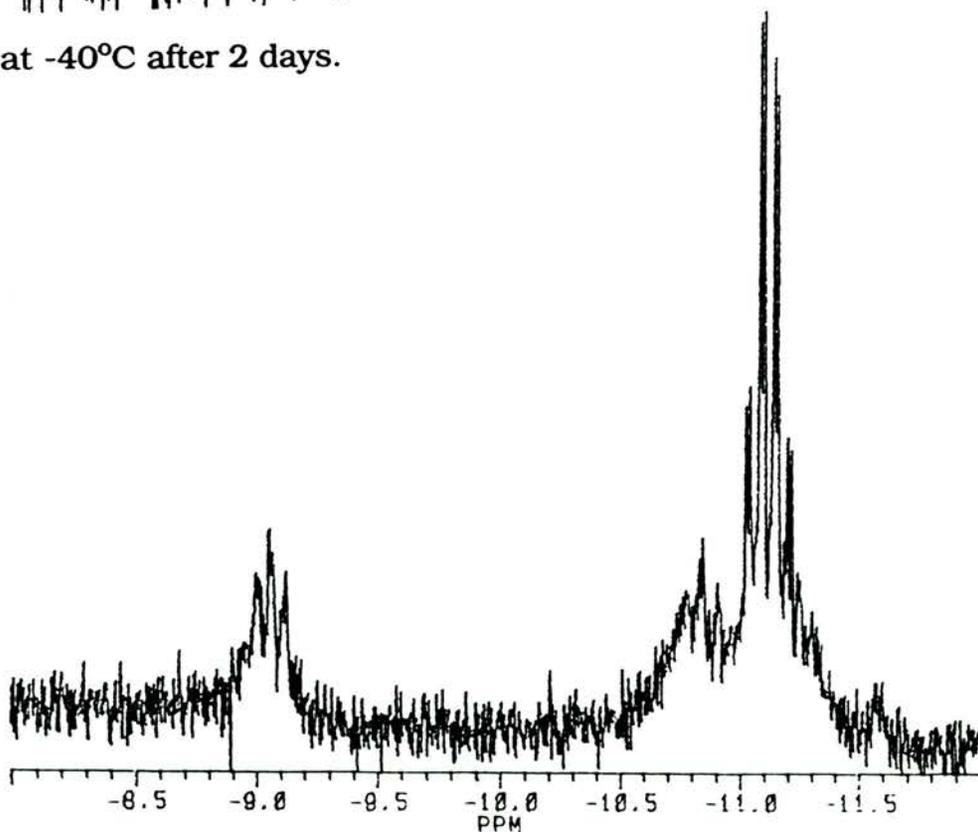
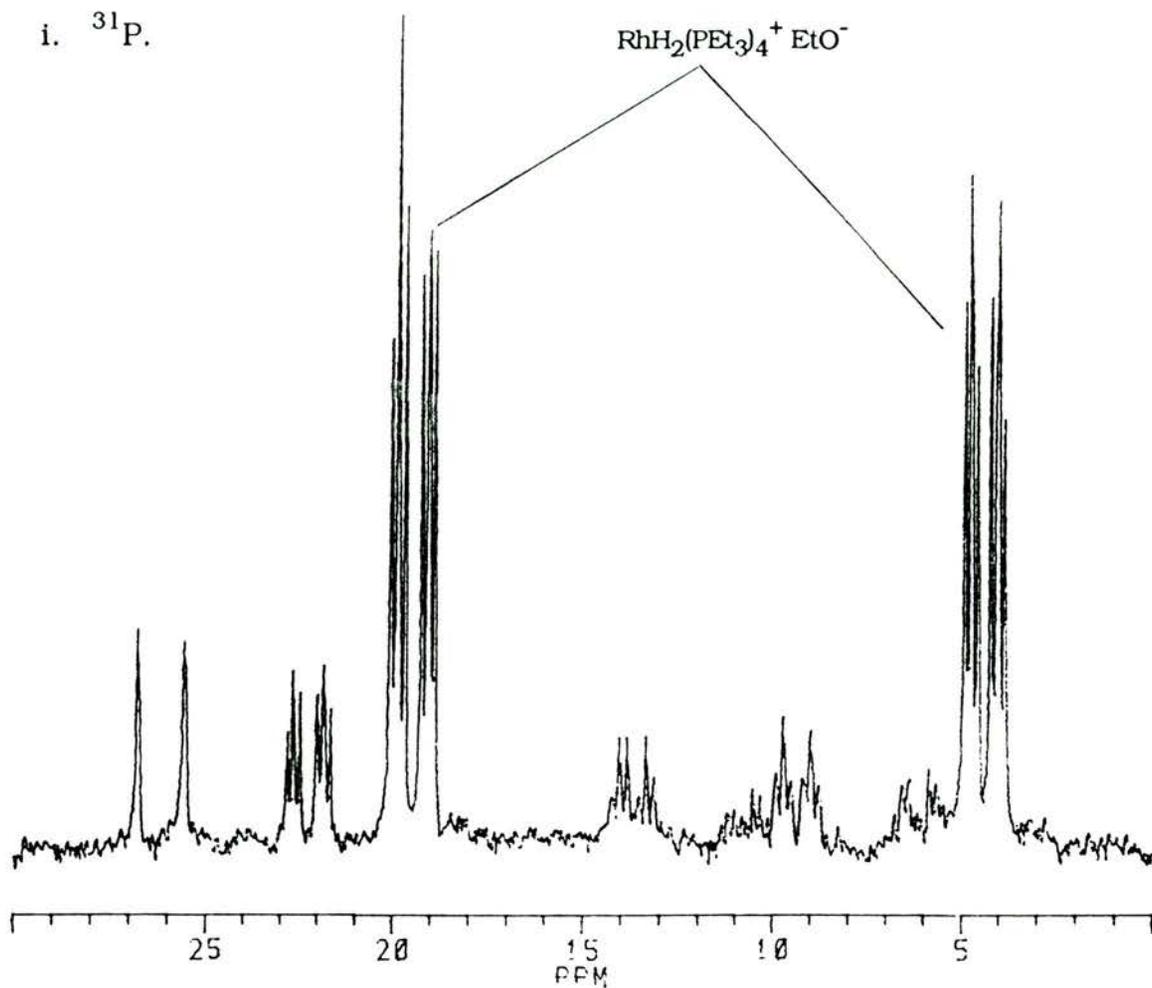


Figure 5.3.

$^{31}\text{P}\{^1\text{H}\}$  and hydride resonance of the  $^1\text{H}$  nmr of  $\text{RhH}(\text{PEt}_3)_3 + \text{PEt}_3$  in ethanol with  $\text{C}_7\text{D}_8$  at  $25^\circ\text{C}$ .

i.  $^{31}\text{P}$ .



ii.  $^1\text{H}$ .

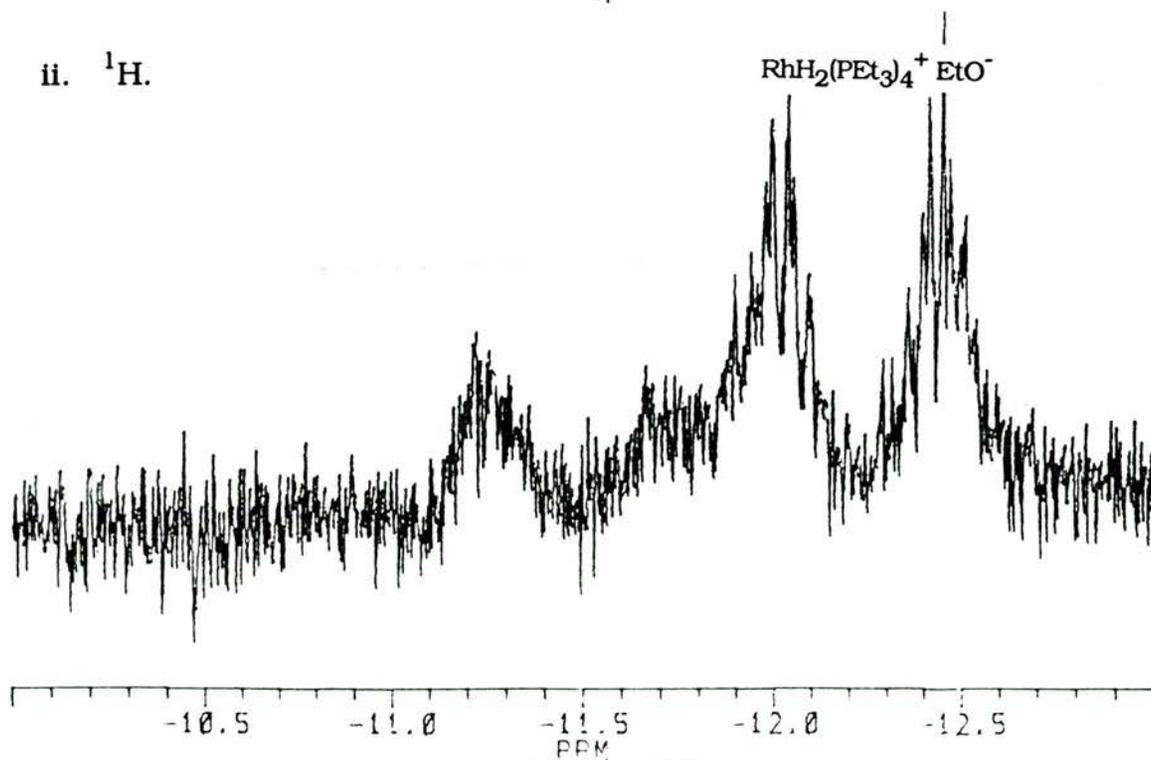


Figure 5.4.

with  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  again forming slowly at room temperature as ethanol was decarbonylated. Other unidentified species were also present, as seen figure 5.4.. The fully  $^1\text{H}$  decoupled  $^{31}\text{P}$  spectrum of  $[\text{RhH}_2(\text{PEt}_3)_4]^+ \text{EtO}^-$  at  $-40^\circ\text{C}$  showed a doublet of triplets at  $\delta = 19.5$  ppm.  $J_{\text{Rh-P}} = 101$  Hz. and a doublet of triplets at  $\delta = 4.3$  ppm.  $J_{\text{Rh-P}} = 89$  Hz. with  $J_{\text{P-P}} = 21$  Hz.. The  $^1\text{H}$  hydride signal was seen as a broad doublet at  $\delta = -12.2$  ppm.  $J_{\text{Rh-H}} = \sim 126$  Hz.

Table 5.1. shows the chemical shifts and couplings of these characterised compounds together with literature values where known. The presence of an ethoxide counter ion, compared with tetraphenylborate,  $\text{BPh}_4^-$  counter ion for the sample of  $[\text{RhH}_2(\text{PEt}_3)_4]^+$  quoted in the literature (at unspecified temperature)<sup>62</sup>, altered the position of the  $^1\text{H}$  hydride signal by 0.5 ppm. upfield. The  $^{31}\text{P}$  spectrum of  $[\text{RhH}_2(\text{PEt}_3)_4]^+ \text{BPh}_4^-$  was not quoted.

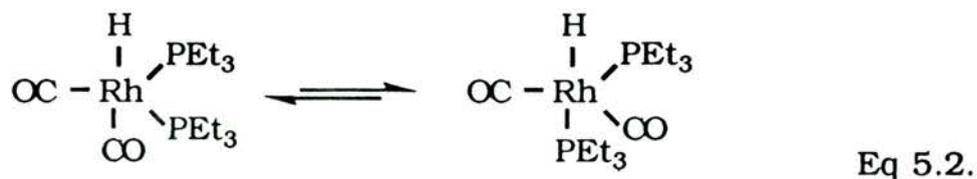
The  $^{31}\text{P}$  nmr spectrum of  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  showed a doublet at  $\delta = 26.2$  ppm.  $J_{\text{Rh-P}} = 147$  Hz. when fully  $^1\text{H}$  decoupled (see figure 5.2.) and a  $^1\text{H}$  hydride signal as a broad quartet at  $\delta = -11.1$  ppm. (see figure 5.3.). At  $-40^\circ\text{C}$  the hydride signal resolved into a quartet of doublets with  $J_{\text{Rh-H}} = \sim 4$  Hz. and  $J_{\text{P-H}} = \sim 17$  Hz. . The  $^{13}\text{C}$  spectrum at  $25^\circ\text{C}$  showed a weak carbonyl peak as a doublet at  $\delta = 212.5$  ppm.  $J_{\text{Rh-C}} = \sim 62$  Hz., with no coupling to phosphorus evident at this concentration and temperature. The chemical shift and coupling constants of the  $^1\text{H}$  hydride signal correspond well with the value reported by Ugo et al<sup>45</sup>.. This, together with the solution I.R. spectrum of this compound dissolved in EtOH with  $\text{C}_6\text{D}_6$  which showed absorptions at  $\nu(\text{CO}) = 1964 \text{ cm}^{-1}$  and  $\nu(\text{Rh-H}) = 1884 \text{ cm}^{-1}$  (lit<sup>45</sup>. thin film  $1952 \text{ cm}^{-1}$ ,  $1880 \text{ cm}^{-1}$  respectively) confirmed the production of  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  from  $\text{RhH}(\text{PEt}_3)_3$  in ethanol.

### 5.3. Reaction of RhH(PET<sub>3</sub>)<sub>3</sub> with CO.

#### 5.3.1. Reaction of RhH(PET<sub>3</sub>)<sub>3</sub> with CO in perdeuterotoluene.

CO was bubbled through a solution of RhH(PET<sub>3</sub>)<sub>3</sub> in C<sub>7</sub>D<sub>8</sub> in an nmr tube for ~ 5 minutes and the <sup>31</sup>P, <sup>13</sup>C and <sup>1</sup>H spectra were then studied. Three distinct rhodium species were evident together with free PET<sub>3</sub> which had been displaced from the rhodium centre by CO. These three species were RhH(CO)(PET<sub>3</sub>)<sub>3</sub>, RhH(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> and Rh<sub>2</sub>(CO)<sub>4</sub>(PET<sub>3</sub>)<sub>4</sub> and their spectra are listed in table 5.2.. They are analogous to the species formed when CO reacts with RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> and an equilibrium is allowed to be set up<sup>55</sup>.

As described in section 5.2. the <sup>31</sup>P spectrum of RhH(CO)(PET<sub>3</sub>)<sub>3</sub> showed a doublet while the <sup>1</sup>H spectrum was a broad quartet. The higher field peak of the <sup>31</sup>P spectrum of RhH(CO)(PET<sub>3</sub>)<sub>3</sub> overlapped with the lower field peak of RhH(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> with which it was in equilibrium. RhH(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> showed a <sup>31</sup>P spectrum with a doublet at δ = 25.1 ppm. J<sub>Rh-P</sub> = 130 Hz. which at -40°C broadened into a weak signal at δ = ~21.8 ppm.. The <sup>1</sup>H spectrum was a broad triplet at δ = -10.1 ppm. which at -40°C became a broad triplet J<sub>P-H</sub> = ~30 Hz. This suggests fluxionality at room temperature between the two species shown in equation 5.2..



The third species included in the equilibrium was Rh<sub>2</sub>(CO)<sub>4</sub>(PET<sub>3</sub>)<sub>4</sub> the concentration of which gradually built up with time, due to combination of two RhH(CO)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> molecules with loss of hydrogen and some precipitation of this species. Its <sup>31</sup>P spectrum showed a doublet at δ = 4.4 ppm. J<sub>Rh-P</sub> = 158 Hz. The solution I.R. of this species in C<sub>6</sub>D<sub>6</sub> showed both terminal and bridging carbonyl

Table 5.2.  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectral data of rhodium species derived from  $\text{Rh}(\text{PEt}_3)_3$  with  $\text{CO}$ .

Rhodium species	solvent	Temp. / $^{\circ}\text{C}$	$^{31}\text{P}$		$^1\text{H}$		$^{13}\text{C}$ of CO peaks	
			$\delta$ /ppm.	$J_{\text{Rh-P}}$ /Hz.	$\delta$ /ppm.	$J_{\text{Rh-H}}$ /Hz.	$\delta$ /ppm.	$J_{\text{Rh-C}}$ /Hz.
$\text{RhH}(\text{CO})(\text{PEt}_3)_3$	$\text{C}_7\text{D}_8$	25	26.2 d	149	-11.1 bq			
		-40	27.0 d	147	-11.1 qd	~5	~18	
$\text{RhH}(\text{CO})(\text{PEt}_3)_3$ with EtOH	$\text{C}_7\text{D}_8$	25	26.2 d	147	-11.1 bq			
		-40	26.9 d	147	-11.2 qd	~5	~17	212.5 <sup>a</sup> d 62
$\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$	$\text{C}_7\text{D}_8$	25	25.1 d	130	-10.1 b			
		-40	23.5 b		~-9.6 bt	~-30		
$\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$ with EtOH	$\text{C}_7\text{D}_8$	25	24.5 d	127	~-10.2 b			
		-40	23.1 b		~-9.8 b			
$\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$	$\text{C}_7\text{D}_8$	25	4.4 d	158				227.8 bm
								228.7 <sup>a</sup>
$\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$ with EtOH	$\text{C}_7\text{D}_8$	25	4.2 d	158				
		-40	4.6 d	158				229.5 <sup>a</sup> bm
species (A) with EtOH	$\text{C}_7\text{D}_8$	25	16.8 d	96				
		-40	18.7 d	93				196.7 bd 62
	$\text{C}_2\text{D}_5\text{OD}$	25	17.5 d	96				200.2 bd 53
		-60	20.5 d	92				197.7 bd 63

<sup>a</sup> in  $\text{C}_6\text{D}_6$ .

Variable temperature  $^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$  in  $\text{C}_7\text{D}_8$ .

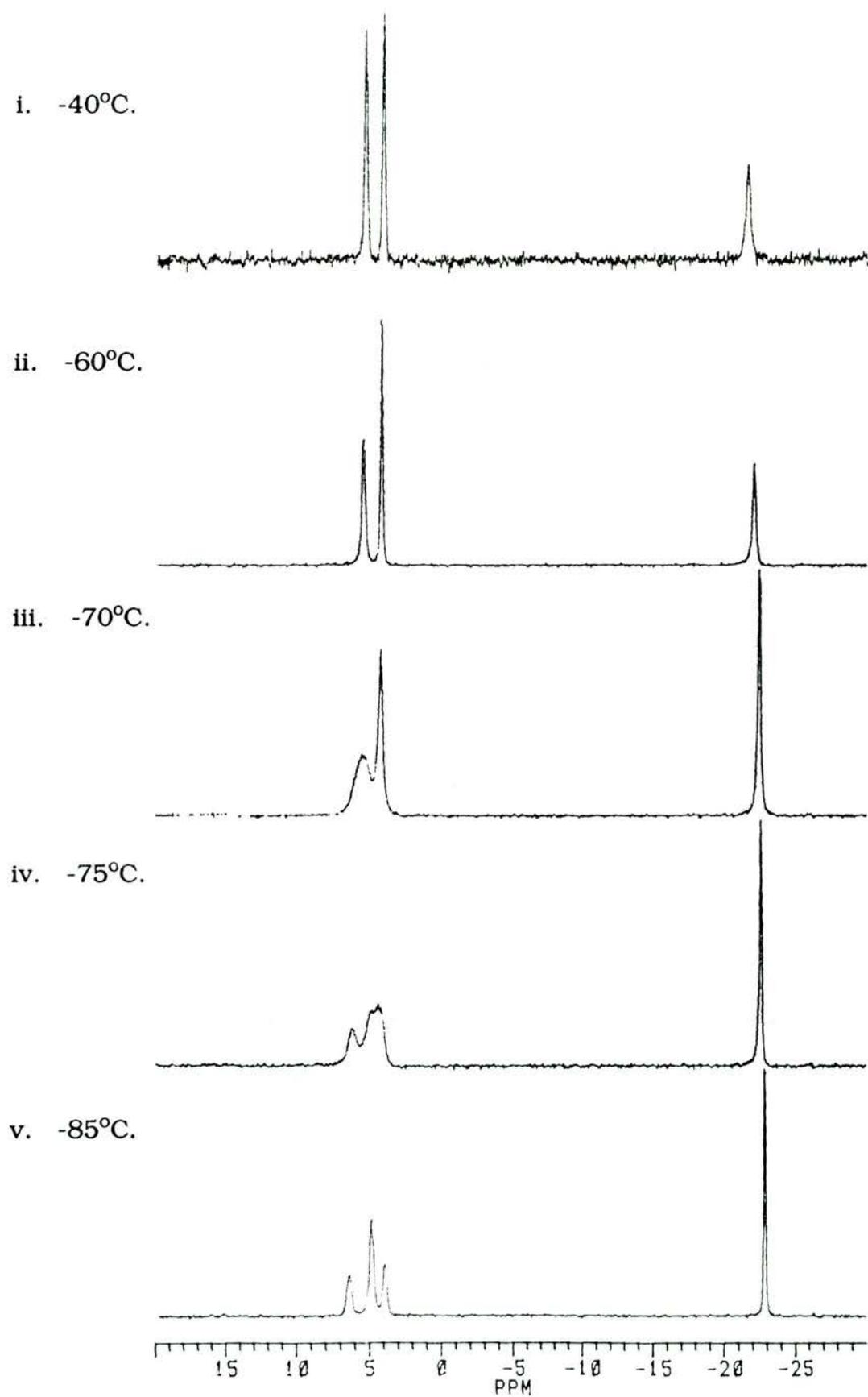


Figure 5.5.

absorptions at  $\nu_{\text{CO}} = 1957, 1939, 1742$  and  $1721 \text{ cm}^{-1}$ , while the  $^{13}\text{C}$  spectrum showed one unresolved multiplet signal at  $\delta = 228.7 \text{ ppm}$ . ( $227.9 \text{ ppm}$ . in  $\text{C}_7\text{D}_8$ ), between the usual positions for terminal ( $180\text{--}200 \text{ ppm}$ .) and bridging ( $230\text{--}240 \text{ ppm}$ .) carbonyl ligands<sup>63</sup>, indicating CO exchange between these two sites.  $^{13}\text{C}$  spectra run at lower temperatures ( $-40^\circ\text{C}$  and  $-80^\circ\text{C}$ ) did not show carbonyl peaks so a species with distinct terminal and bridging carbonyls could not be 'frozen' out.

The  $^{31}\text{P}$  spectrum at low temperature showed some change below  $-40^\circ\text{C}$  but was not fully resolved at  $-85^\circ\text{C}$ , see figure 5.5.. This sequence of spectra shows that at room temperature the phosphine ligands were equivalent, and not exchanging with free  $\text{PEt}_3$ . At low temperature there were two distinct environments for the phosphine ligands, probably due to a slowing of the exchange between terminal and bridging carbonyl ligands, as suggested above. The couplings observed at  $-85^\circ\text{C}$  were  $J_{\text{Rh-P}} = 115 \text{ Hz}$ . for the signal centred at  $\delta = 5.6 \text{ ppm}$ ., and  $J_{\text{Rh-P}} = 184 \text{ Hz}$ . for the signal centred at  $\delta = 4.4 \text{ ppm}$ . but the peaks were still fairly broad, probably due to unresolved P-P coupling. The difference in Rh-P coupling for the two sites is the cause of the differing coalescence temperatures of the two signals with the doublet having the wider coupling coalescing at  $-70^\circ\text{C}$  while the doublet with the narrower coupling coalesced at  $-75^\circ\text{C}$ .

There are two possible dimeric structures which would fit these data as shown in figures 5.6., with a square pyramidal configuration around the rhodium atoms, and 5.7., with the rhodium atoms surrounded by a trigonal bipyramidal configuration of ligands. The latter would have the terminal carbonyl ligands well positioned for terminal/bridge position exchange and would have the phosphine ligands in distinct axial and equatorial sites. The Rh-P couplings, however, are similar to those found at  $-65^\circ\text{C}$  for the related dimer

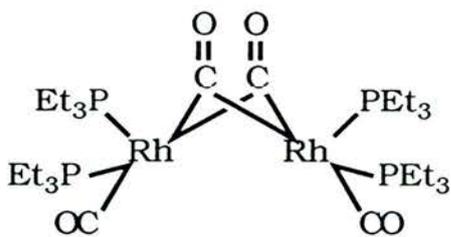


Figure 5.6.

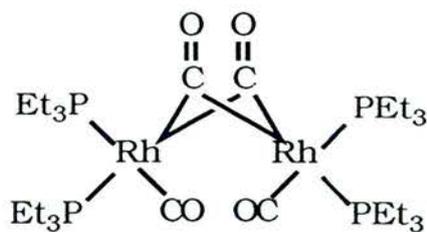


Figure 5.7.

$\text{Rh}_2(\text{CO})_4(\text{dppp})_2$ <sup>64</sup> (where dppp = 1,3-bis(diphénylphosphino)propane) which has  $J_{\text{Rh-P}} = 109 \text{ Hz. and } 181 \text{ Hz.}$  The crystal structure of  $\text{Rh}_2(\text{CO})_4(\text{dppp})_2$ <sup>64</sup> shows that the ligands surrounding the two rhodium atoms are in square pyramidal configurations which share the edge of a basal plane, defined by the two bridging carbonyl carbons. Thus the rhodium atoms are in a pseudooctahedral configuration, with a bent Rh-Rh bond trans to one of the phosphines of each chelating ligand. This would suggest that the structure shown in figure 5.6. is that taken up by  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$ .

### 5.3.2. Reaction of CO with $\text{RhH}(\text{PEt}_3)_3$ in perdeuterotoluene with ethanol.

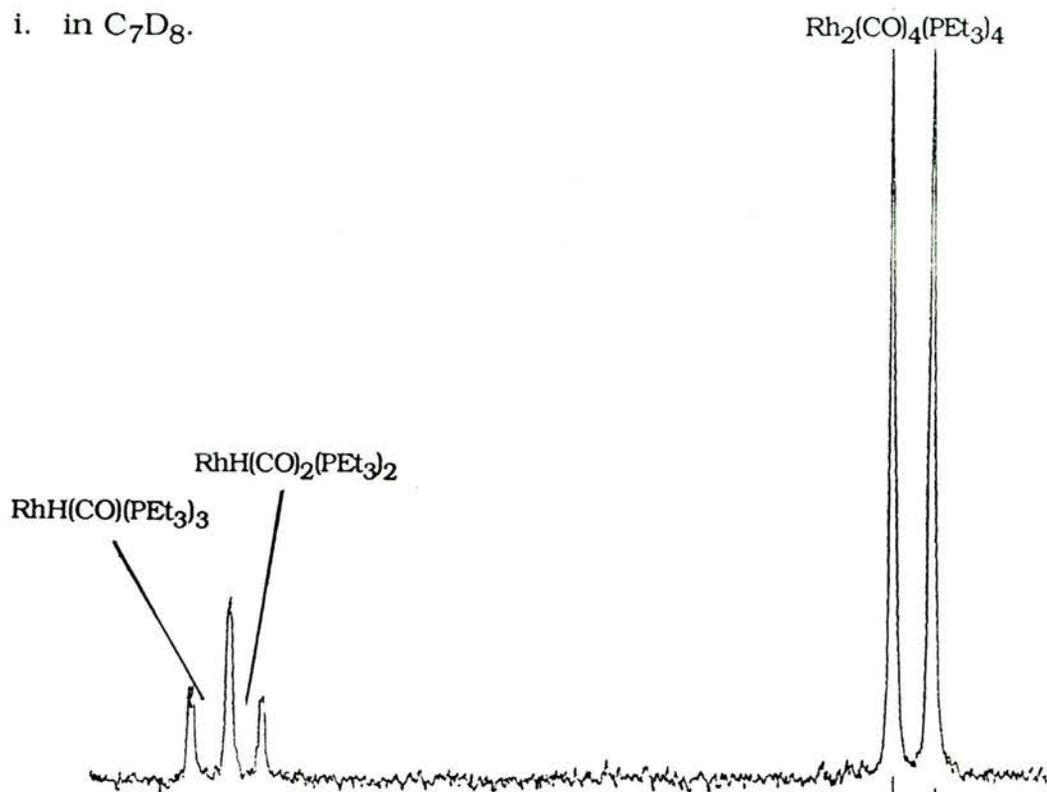
When CO was bubbled through a solution of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_7\text{D}_8$  to which ethanol had been added the same three species as discussed above were detected, with some slight variation in their spectra due to solvent effects, together with a fourth species. See figure 5.8. for comparison of the species present in  $\text{C}_7\text{D}_8$  alone and in  $\text{C}_7\text{D}_8$  with ethanol.

The signal for  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  was almost unchanged as a doublet at  $\delta = 26.2 \text{ ppm.}$   $J_{\text{Rh-P}} = 147 \text{ Hz.}$  with its  $^1\text{H}$  spectrum a broad quartet at  $\delta = -11.1 \text{ ppm.}$ , which resolved into a quartet of doublets  $J_{\text{Rh-H}} = \sim 5 \text{ Hz.}$  and  $J_{\text{P-H}} = \sim 17 \text{ Hz.}$  at  $-40^\circ\text{C.}$

The signal for  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  had shifted by 0.6 ppm. upfield to  $\delta = 24.5 \text{ ppm.}$   $J_{\text{Rh-P}} = 127 \text{ Hz.}$  and now showed no overlap with

$^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{RhH}(\text{PEt}_3)_3 + \text{CO}$  in  $\text{C}_7\text{D}_8$  without and with ethanol.

i. in  $\text{C}_7\text{D}_8$ .



ii. in  $\text{C}_7\text{D}_8$  with ethanol.

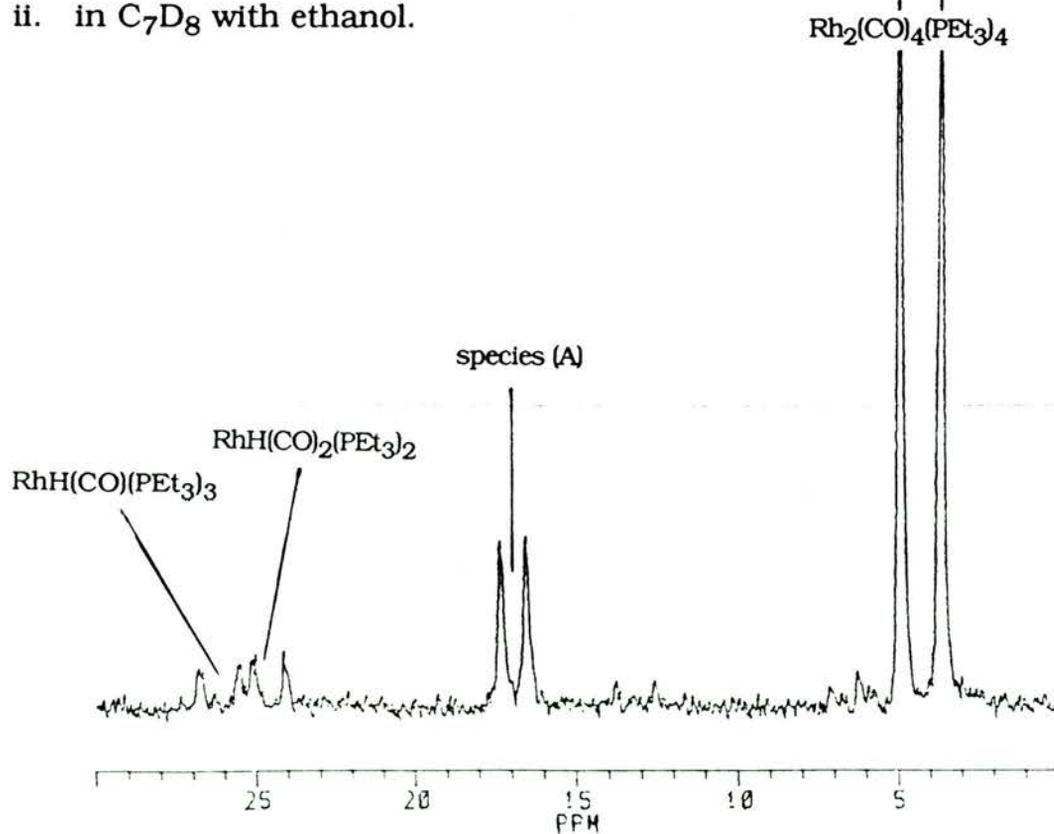


Figure 5.8.

$\text{RhH}(\text{CO})(\text{PEt}_3)_3$ . Its  $^1\text{H}$  hydride signal was a broad peak at  $\delta = -10.2$  ppm.. The dimer signal had also moved slightly upfield to  $\delta = 4.2$  ppm.  $J_{\text{Rh-P}} = 158$  Hz., with the  $^{13}\text{C}$  carbonyl, an unresolved multiplet peak at room temperature, shifting downfield to  $\delta = 229.5$  ppm..

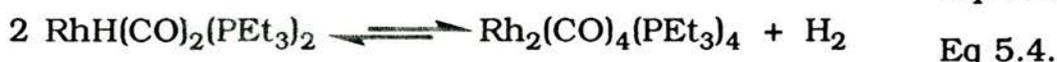
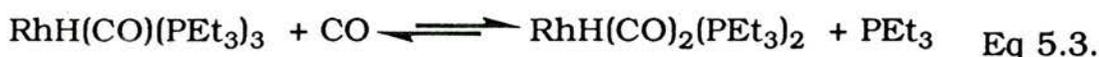
The most noticeable difference in the  $^{31}\text{P}$  spectrum of the solution containing ethanol was a new peak from an unknown species, (A), at  $\delta = 16.8$  ppm.  $J_{\text{Rh-P}} = 96$  Hz.. At  $-40^\circ\text{C}$  this peak centred at  $\delta = 18.7$  ppm. with coupling to rhodium reducing to  $J_{\text{Rh-P}} = 93$  Hz.. A similar downfield shift at reduced temperature was seen when  $\text{C}_2\text{D}_5\text{OD}$  was used as solvent. At  $25^\circ\text{C}$  the carbonyl region of its  $^{13}\text{C}$  nmr spectrum in  $\text{C}_2\text{D}_5\text{OD}$  showed a fairly broad doublet at  $\delta = 200.2$  ppm.,  $J_{\text{Rh-C}} = 53$  Hz. which remained a similar shape at  $-60^\circ\text{C}$ , but shifted upfield to  $197.7$  ppm.  $J_{\text{Rh-C}} = 63$  Hz.. A solution of this species (A) in  $\text{C}_2\text{D}_5\text{OD}$  showed an I.R. absorption for  $\nu_{\text{CO}} = 1962$   $\text{cm}^{-1}$  indicating only terminal carbonyl groups on this species.

The formation of species (A) giving this signal, with its narrower coupling to rhodium, required the presence of ethanol. It appeared when ethanol was added to an equilibrium mixture as described above, and also when CO was bubbled through a solution of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_2\text{D}_5\text{OD}$ . When an excess of  $\text{PEt}_3$  was added to a solution of  $\text{RhH}(\text{PEt}_3)_3$  in  $\text{C}_2\text{D}_5\text{OD}$  which had been reacted with CO this species (A) gradually became the sole species present, but when  $\text{H}_2$  was bubbled through a solution of (A) in  $\text{C}_2\text{D}_5\text{OD}$  with excess  $\text{PEt}_3$  present  $\text{RhH}/\text{D}(\text{CO})(\text{PEt}_3)_3$  was generated. This species (A) may be  $\text{Rh}_2(\text{CO})_2(\text{PEt}_3)_6$  as it formed as the major species on dehydrogenation of  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  in the presence of excess  $\text{PEt}_3$ . Its absence in the absence of ethanol could indicate that it is stabilised by ethanol. It does not appear to have bridging carbonyl groups, (cf. I.R. and  $^{13}\text{C}$  nmr carbonyl data). Booth et al.<sup>65</sup> found a similar species,  $\text{Rh}_2(\text{CO})_2(\text{PBu}_3)_6$ , after work up of the products formed on addition of  $\text{PBu}_3$  to a solution

of  $\text{Rh}_4(\text{CO})_{12}$  in benzene.  $\text{Rh}_2(\text{CO})_2(\text{PBU}_3)_6$  has a single I.R. absorption for  $\nu_{\text{CO}} = 1959 \text{ cm}^{-1}$ .

### 5.3.3. Equilibrium of carbonyl species.

The three species,  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$ ,  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  and  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$  when dissolved in  $\text{C}_7\text{D}_8$ , were shown to be in equilibrium as indicated in equations 5.3. and 5.4..

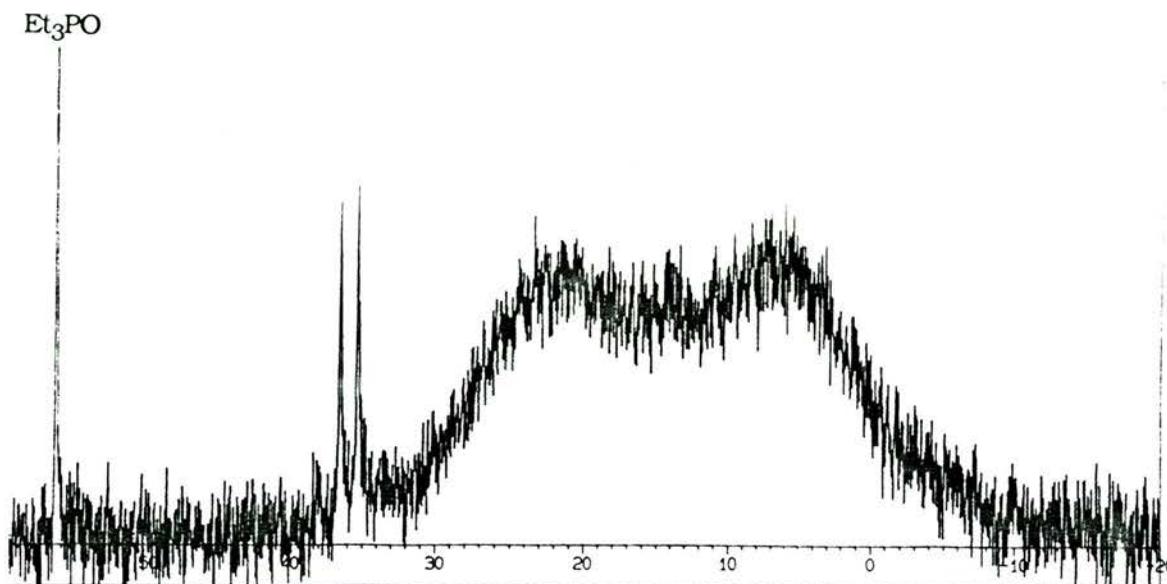


On bubbling CO through a solution containing a mixture of all three species the  $^{31}\text{P}$  nmr signal for  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$  was seen to increase in intensity, and this species come out of solution as a yellow precipitate, while the peaks for  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  and  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  reduced in intensity. The the intensity of the signal for free  $\text{PEt}_3$  ( $\delta = -18.6 \text{ ppm.}$  - exchanging and so broad) also increased. When hydrogen was subsequently bubbled through this solution rich in  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$  for ~10 minutes, all the free  $\text{PEt}_3$  was taken up and  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  now became the major species with the signal from  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  increasing slightly. The formation of  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  will have taken place because some  $\text{PEt}_3$  had been oxidised to triethylphosphine oxide,  $\text{Et}_3\text{PO}$ , and was no longer available for ready coordination to rhodium. This solution, with  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  as the major species present, now had CO bubbled through it for ~10 minutes. The intensity of the signal from  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$  decreased to about half that of  $\text{RhH}(\text{CO})_2(\text{PEt}_3)_2$  which had increased in intensity, with free  $\text{PEt}_3$  being released, and  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$  again becoming the major species present.

In the presence of ethanol with excess  $\text{PEt}_3$  the species (A) became the sole species present when a solution containing a mixture

$^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{RhH}(\text{PEt}_3)_3 + \text{CO} + \text{H}_2$  in ethanol with  $\text{C}_7\text{D}_8$ .

i. at  $100^\circ\text{C}$ .



ii. at  $25^\circ\text{C}$ .

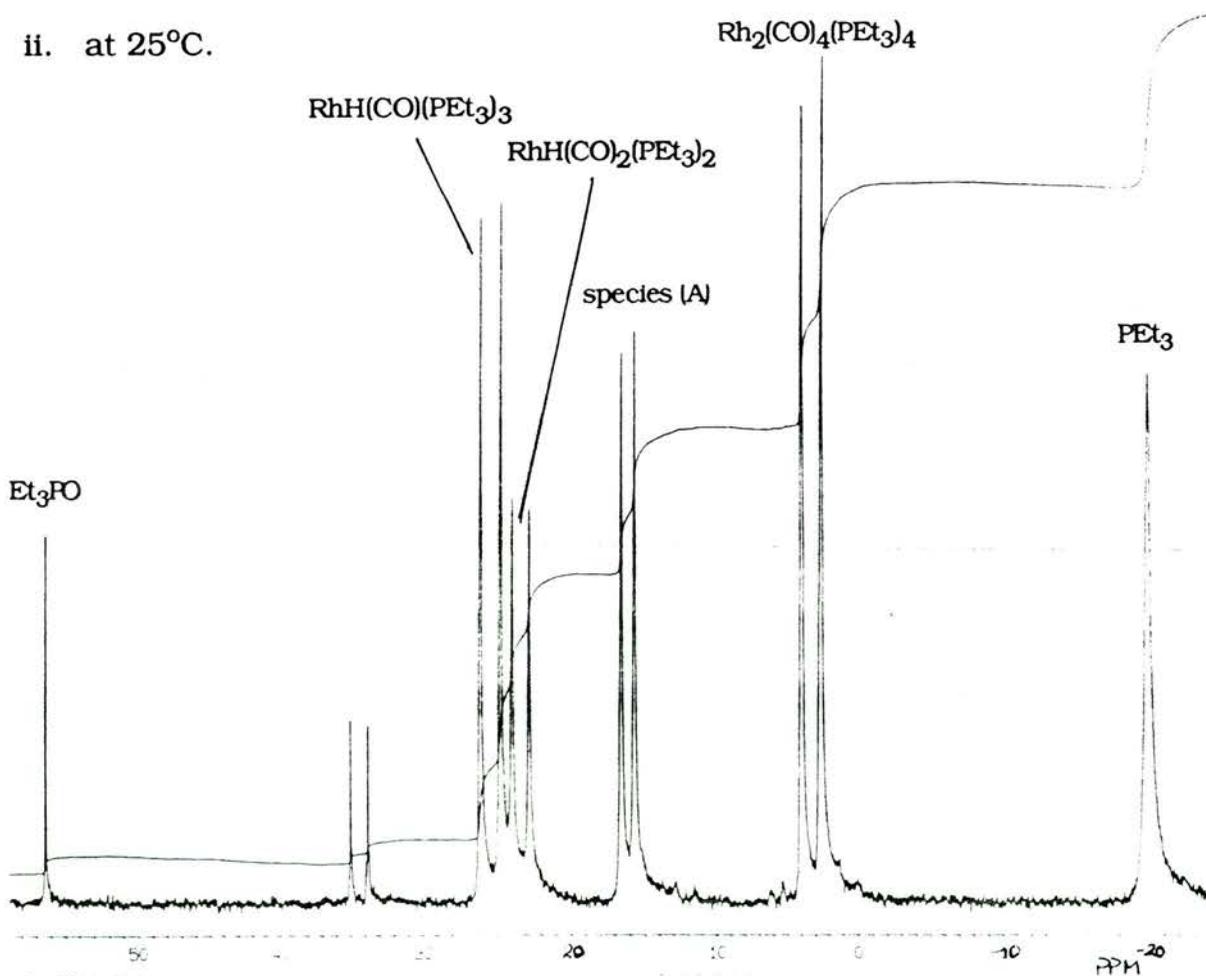


Figure 5.9.

of all four components contributing to the equilibrium was allowed to stand for several weeks. When  $H_2$  was bubbled through this solution for 10 minutes, complete conversion to  $RhH(CO)(PEt_3)_3$  took place. Addition of CO (bubbling through the solution for 2 minutes) now gave a mixture of  $RhH(CO)(PEt_3)_3$ ,  $RhH(CO)_2(PEt_3)_2$ ,  $Rh_2(CO)_4(PEt_3)_4$  and the species (A), with an increase in the intensity of  $PEt_3$ . The species (A) was the major species present.

Thus, without ethanol, a solution in toluene shows three species in equilibrium while with ethanol in the solution a fourth species also forms. These four species are all shown to exchange at higher temperature. Figure 5.9. shows the  $^{31}P$  spectra of such a mixture formed when  $RhH(PEt_3)_3$  in ethanol with  $C_7D_8$  (3:1 by volume) was pressurised with  $CO/H_2$  (~1:1), with the spectra recorded at  $25^\circ C$  and  $100^\circ C$ . Such a mixture will have been present in catalytic solutions for hydroformylation in ethanol with  $CO/H_2$ .

Three solutions were studied on completion of catalytic runs. That from hydroformylation in ethanol with  $CO/H_2$  showed a  $^{31}P$  spectrum with a doublet at  $\delta = 16.4$  ppm.  $J_{Rh-P} = 95$  Hz. indicating the presence of species (A). Solutions from hydroformylation reactions using ethanol as the source of hydrogen showed different species depending on the presence or absence of excess  $PEt_3$ . In the absence of  $PEt_3$  the  $^{31}P$  spectrum showed a doublet at  $\delta = 24.6$  ppm.  $J_{Rh-P} = 124$  Hz. indicating  $RhH(CO)_2(PEt_3)_2$  as the major species present, with a possible trace of species (A) at  $\delta = 16.3$  ppm.  $J_{Rh-P} = \sim 91$  Hz.. In the presence of free  $PEt_3$  species (A), a doublet at  $\delta = 16.4$  ppm.  $J_{Rh-P} = 97$  Hz., was again the only species detected. This would appear to indicate that species (A) was either taking part in the catalysis or, as seems more likely, was a resting species which, as was shown by addition of hydrogen, could easily be converted into  $RhH(CO)(PEt_3)_3$ . This on loss of one triethylphosphine ligand would

give the undetected species,  $\text{RhH}(\text{CO})(\text{PEt}_3)_2$ , proposed to trap alkene in the mechanistic cycle (see sections 4.2.6 and 4.3.4.).

#### 5.4. Models for proposed catalytic intermediates.

##### 5.4.1. Rhodium alkyl species.

Assuming that the catalytic cycle is similar to that which occurs for  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ , at least in its early stages, coordination of alkene to  $\text{RhH}(\text{CO})(\text{PEt}_3)_2$  followed by insertion of alkene into the Rh-H bond would give an alkyl intermediate of the form  $\text{Rh}(\text{alkyl})(\text{CO})(\text{PEt}_3)_2$ . In order to study reactions of a model compound of this form,  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  was synthesized by reaction of  $\text{RhCl}(\text{CO})(\text{PEt}_3)_2$  with methyl lithium,  $\text{CH}_3\text{Li}$ , in ether. Methyl was chosen as the alkyl group since the complex is likely to be more stable than others because it is stabilised against  $\beta$ -hydrogen abstraction. The  $^{31}\text{P}$  spectrum of  $\text{RhCl}(\text{CO})(\text{PEt}_3)_2$  and the  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  spectra of the product in  $\text{C}_7\text{D}_8$ , both without and with ethanol in solution, are listed in table 5.3..  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  was found to have spectra fully consistent with equivalent, mutually trans triethylphosphine ligands.

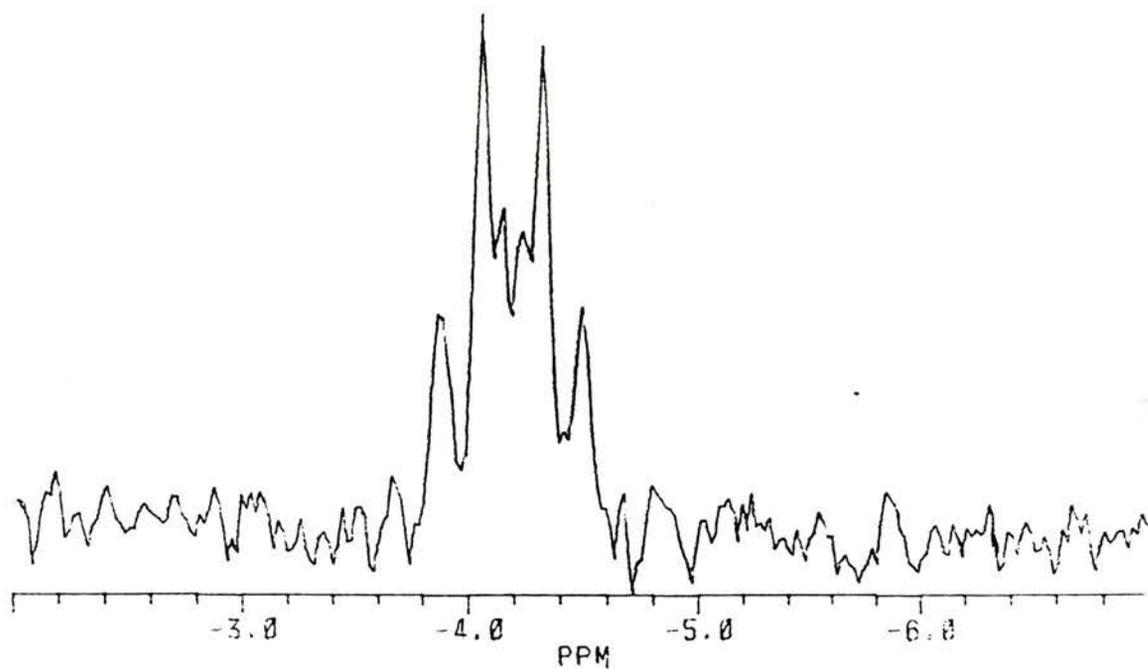
In  $\text{C}_7\text{D}_8$  without ethanol, the  $^1\text{H}$  spectrum showed a triplet of doublets at  $\delta = -0.35$  ppm.  $J_{\text{Rh-H}} = 1.6$  Hz.  $J_{\text{P-H}} = 8.2$  Hz. as would be expected of a methyl group on rhodium attached to two equivalent phosphines. The  $^{31}\text{P}$  signal was a doublet 2 ppm. further downfield and with a wider coupling to rhodium at  $\delta = 26.6$  ppm.  $J_{\text{Rh-P}} = 140$  Hz. than was found for  $\text{RhCl}(\text{CO})(\text{PEt}_3)_2$ . The  $^{13}\text{C}$  carbonyl signal showed as doublet of triplets at  $\delta = 192.8$  ppm.  $J_{\text{Rh-C}} = 57$  Hz.  $J_{\text{P-C}} = 14$  Hz. at room temperature and the methyl carbon showing as a triplet of doublets at  $\delta = -4.2$  ppm.  $J_{\text{Rh-C}} = 20$  Hz.  $J_{\text{P-C}} = 13$  Hz. (see figure 5.10.). Addition of ethanol to a solution of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  in  $\text{C}_7\text{D}_8$  caused the phosphorus signal to move upfield by 0.3 ppm. and the proton signal of the methyl group to also shift upfield by 0.15 ppm. as

Table 5.3.  $^3\text{1P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectral data of rhodium species derived from  $\text{RhCl}(\text{CO})(\text{PEt}_3)_2$  with  $\text{CH}_3\text{I}$  and then  $\text{CO}$ .

Rhodium species	solvent	Temp. / $^{\circ}\text{C}$	$^3\text{1P}$		$^1\text{H}$		$^{13}\text{C}$		$\text{J}_{\text{Rh-C}}$ /Hz.	$\text{J}_{\text{P-C}}$ /Hz.
			$\delta$ /ppm.	$\text{J}_{\text{Rh-P}}$ /Hz.	$\delta$ /ppm.	$\text{J}_{\text{Rh-H}}$ /Hz.	$\delta$ /ppm.	$\text{J}_{\text{P-H}}$ /Hz.		
$\text{RhCl}(\text{CO})(\text{PEt}_3)_2$	$\text{C}_6\text{D}_6$ $\text{thf-d}_8$	25	24.6 d	119						
		25	25.1 d	116						
$\text{RhCH}_3(\text{CO})(\text{PEt}_3)_2$	$\text{C}_7\text{D}_8$	25	26.6 d	140	$\text{CH}_3$ -0.35 dt	1.6	8.2	$\text{CO}$ 192.8 dt	57	14
$\text{RhCH}_3(\text{CO})(\text{PEt}_3)_2$ with EtOH	$\text{C}_7\text{D}_8$	25	26.3 d	140	$\text{CH}_3$ -0.50 dt	1.6	8.2	$\text{CH}_3$ -4.2 dt	20	13
		-70	11.0 d	144	$\text{CH}_3$ ~-0.2 b					
$\text{RhCH}_3(\text{CO})(\text{PEt}_3)_3$ with EtOH	$\text{C}_7\text{D}_8$	-70	11.0 d	145	$\text{CH}_3$ ~-0.2 b					
		25	~14.3 bd		$\text{COCH}_3$ 2.7			$\text{CO}$ 200.1 b		
$\text{Rh}(\text{CH}_3\text{CO})(\text{CO})_2(\text{PEt}_3)_2$	$\text{C}_7\text{D}_8$	-60	17.8 dd	71	$\text{COCH}_3$ 2.9			$\text{COCH}_3$ 53.0 b		
			12.1 dd	140				$\text{CO}$ 200.5 dt	75 21	
$\text{Rh}(\text{CH}_3\text{CO})(\text{CO})_2(\text{PEt}_3)_2$ with EtOH	$\text{C}_7\text{D}_8$	25	~14.3 bd		$\text{COCH}_3$ 2.5 b			$\text{COCH}_3$ 238.0 ddd	78	21&9
		-60	18.0 dd	72	$\text{COCH}_3$ 2.7			$\text{COCH}_3$ 53.8 dd	32.7	4
			10.3 dd	137				$\text{CO}$ 199.9 dt	73	21
							$\text{COCH}_3$ 246.8 ddd	81	21&9	
							$\text{COCH}_3$ 53.4 d	30.2		

$^{13}\text{C}\{^1\text{H}\}$  nmr of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  in  $\text{C}_7\text{D}_8$  at  $25^\circ\text{C}$ .

i. methyl carbon.



ii. carbonyl carbon.

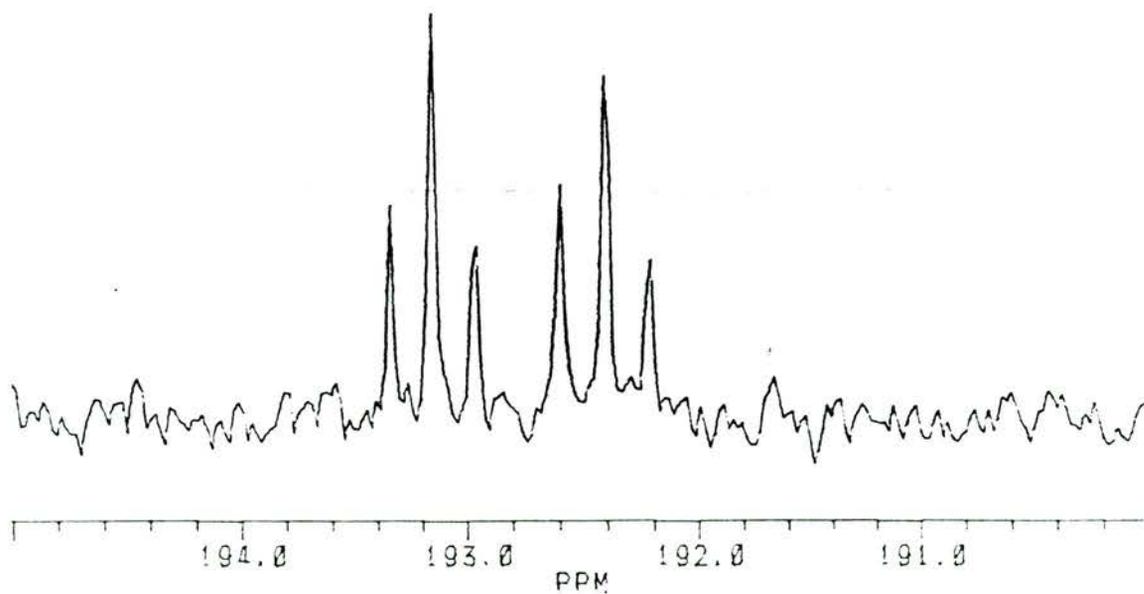
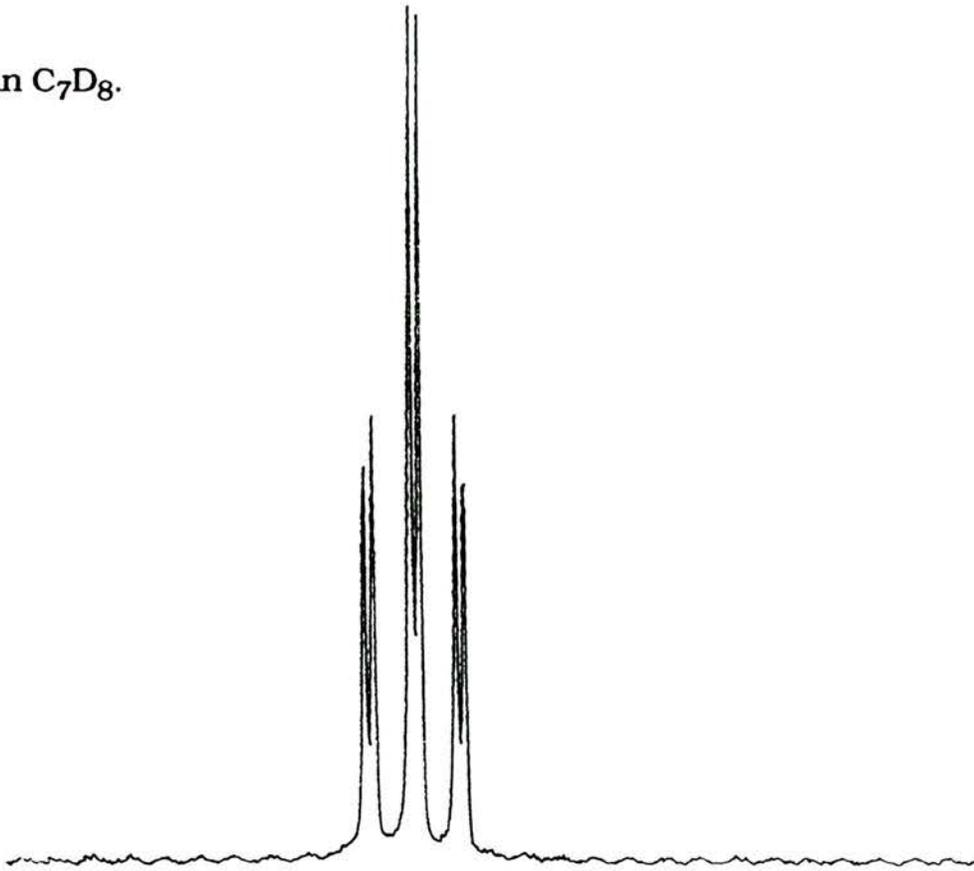


Figure 5.10.

$^1\text{H}$  nmr of  $\text{CH}_3$  signal of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  at  $25^\circ\text{C}$ .

i. in  $\text{C}_7\text{D}_8$ .



ii. in ethanol.

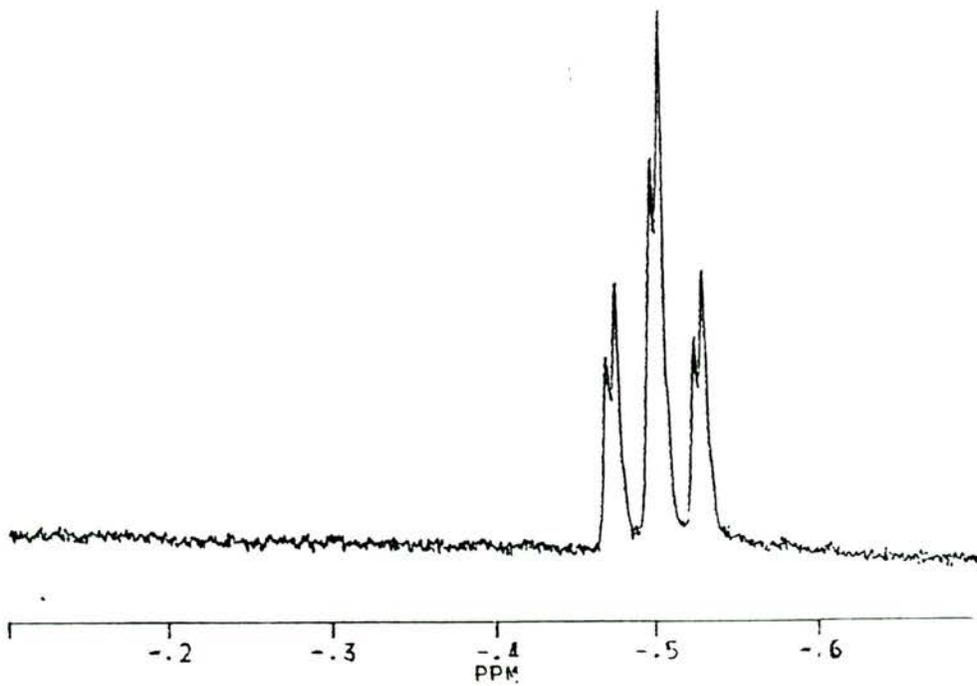


Figure 5.11.

shown in figure 5.11.. Alterations in the  $^{13}\text{C}$  spectrum on addition of ethanol were not measured but ethanol is seen to have some solvent effect on this compound.

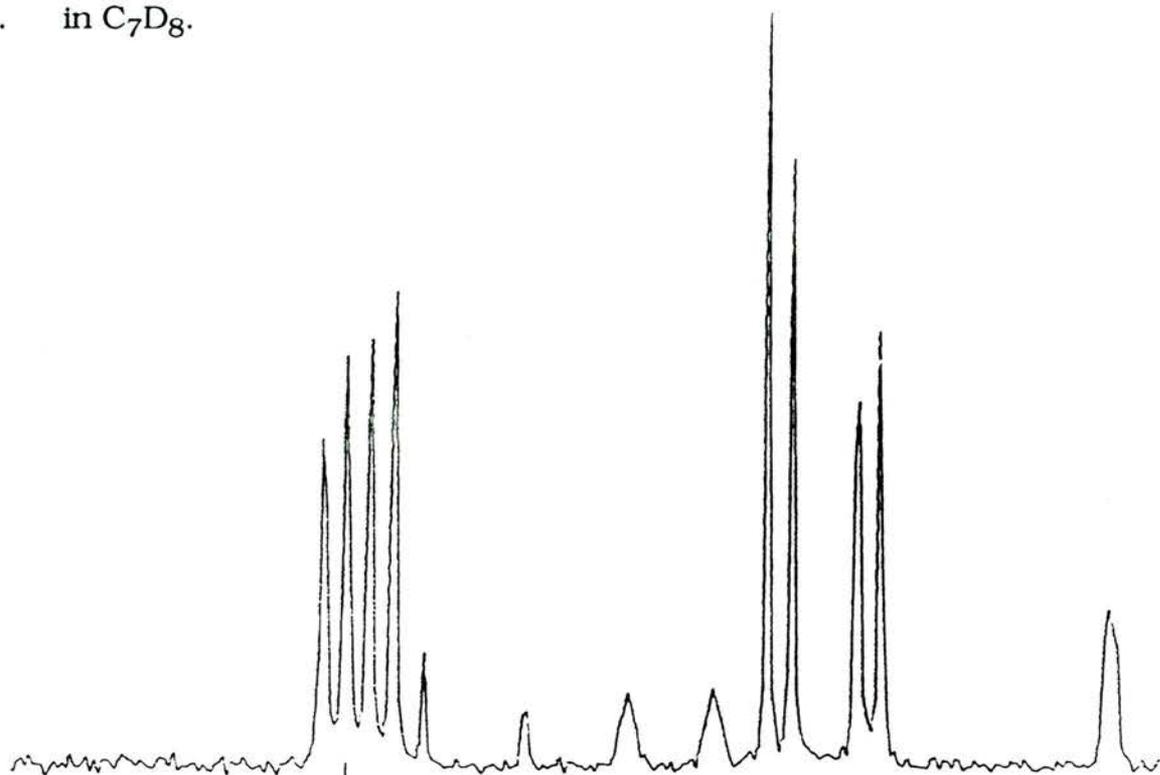
A solution of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  in  $\text{C}_7\text{D}_8$  with a twofold excess of  $\text{PEt}_3$  showed a broad  $^{31}\text{P}$  signal at  $\delta = \sim 3$  ppm. at room temperature due to coordination of, and exchange with, free  $\text{PEt}_3$  giving  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_3$ , which at  $-70^\circ\text{C}$  resolved into a doublet at  $\delta = 11.0$  ppm.  $J_{\text{Rh-P}} = 144$  Hz. indicating equivalent phosphine ligands. The  $^1\text{H}$  spectrum showed a broad peak at  $\delta = \sim -0.2$  ppm.. These spectra were unaltered by the addition of ethanol to the solution. Fast exchange with free  $\text{PEt}_3$  by this type of species will greatly reduce the rate of  $\beta$ -hydrogen abstraction from the alkyl ligand, thus reducing the rate of isomerisation, as was found to be the case in the presence of excess triethylphosphine during catalysis. Other catalytic systems with excess substituted phosphine ligands present are also known to undergo reduced isomerisation of substrate alkene<sup>37,66</sup>.

#### 5.4.2. Rhodium acyl species.

$\text{CO}$  was bubbled through a solution of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  in  $\text{C}_7\text{D}_8$  to give  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$ . The  $^{31}\text{P}$  spectrum of this product at room temperature was found to be a broad doublet, centred at  $\delta = \sim 14.3$  ppm.. At  $-60^\circ\text{C}$  this resolved into two doublets of doublets at  $\delta = 17.8$  ppm.  $J_{\text{Rh-P}} = 71$  Hz. and  $\delta = 12.1$  ppm.  $J_{\text{Rh-P}} = 140$  Hz.  $J_{\text{P-P}} = 36$  Hz., as shown in figure 5.12. and listed in table 5.3.. In the presence of ethanol at  $-60^\circ\text{C}$  the  $^{31}\text{P}$  spectrum showed two doublets of doublets at  $\delta = 18.0$  ppm.  $J_{\text{Rh-P}} = 72$  Hz. and  $\delta = 10.3$  ppm.  $J_{\text{Rh-P}} = 137$  Hz.  $J_{\text{P-P}} = 36$  Hz.. Thus ethanol caused one of the phosphine signals to move 1.8 ppm. upfield and reduced the coupling to rhodium slightly. There was a similar upfield shift of the  $^1\text{H}$  signal of the  $\text{COCH}_3$  group at  $-60^\circ\text{C}$  from  $\delta = 2.9$  ppm. without ethanol, to  $\delta = 2.7$  ppm. with

$^{31}\text{P}\{^1\text{H}\}$  nmr of  $\text{CH}_3$  signal of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  at  $-60^\circ\text{C}$ .

i. in  $\text{C}_7\text{D}_8$ .



ii. in  $\text{C}_7\text{D}_8$  with  
20% ethanol.

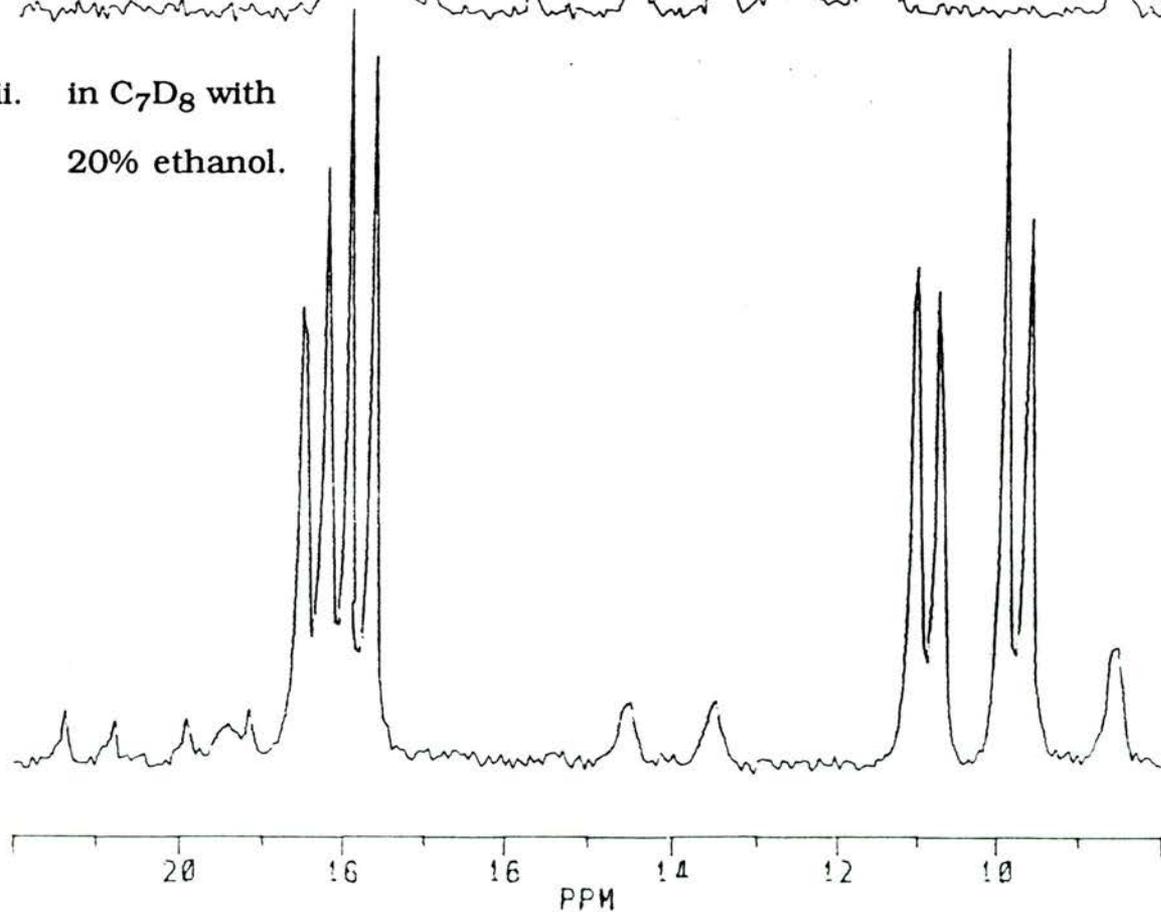
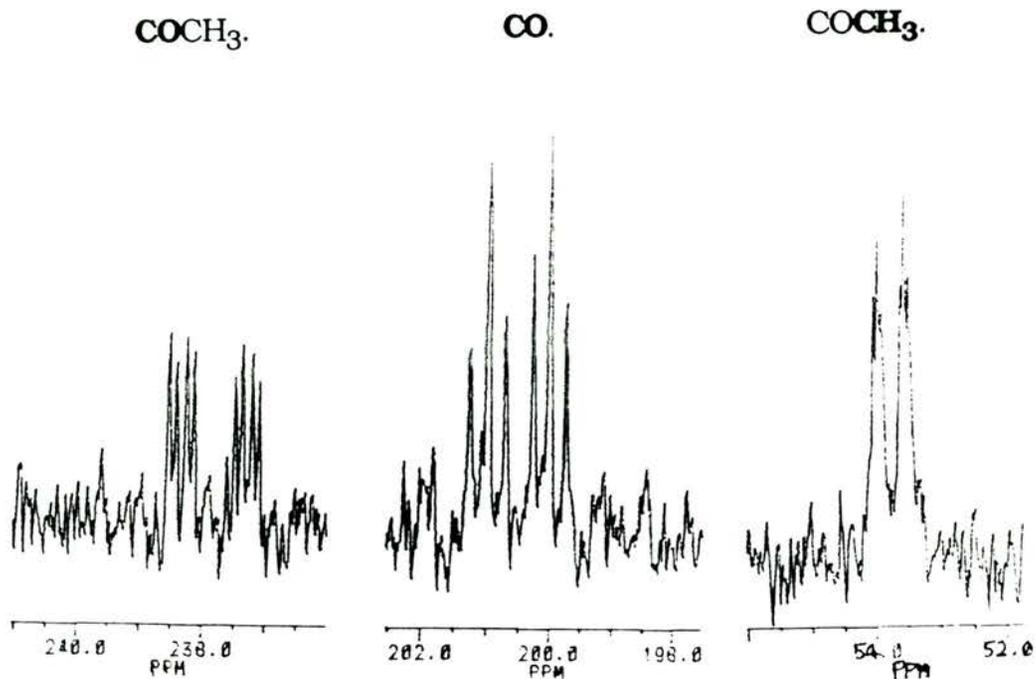


Figure 5.12.

$^{13}\text{C}\{^1\text{H}\}$  nmr of  $\text{CH}_3$  signal of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  at  $-60^\circ\text{C}$ .

i. in  $\text{C}_7\text{D}_8$ .



ii. in  $\text{C}_7\text{D}_8$  with 20% ethanol.

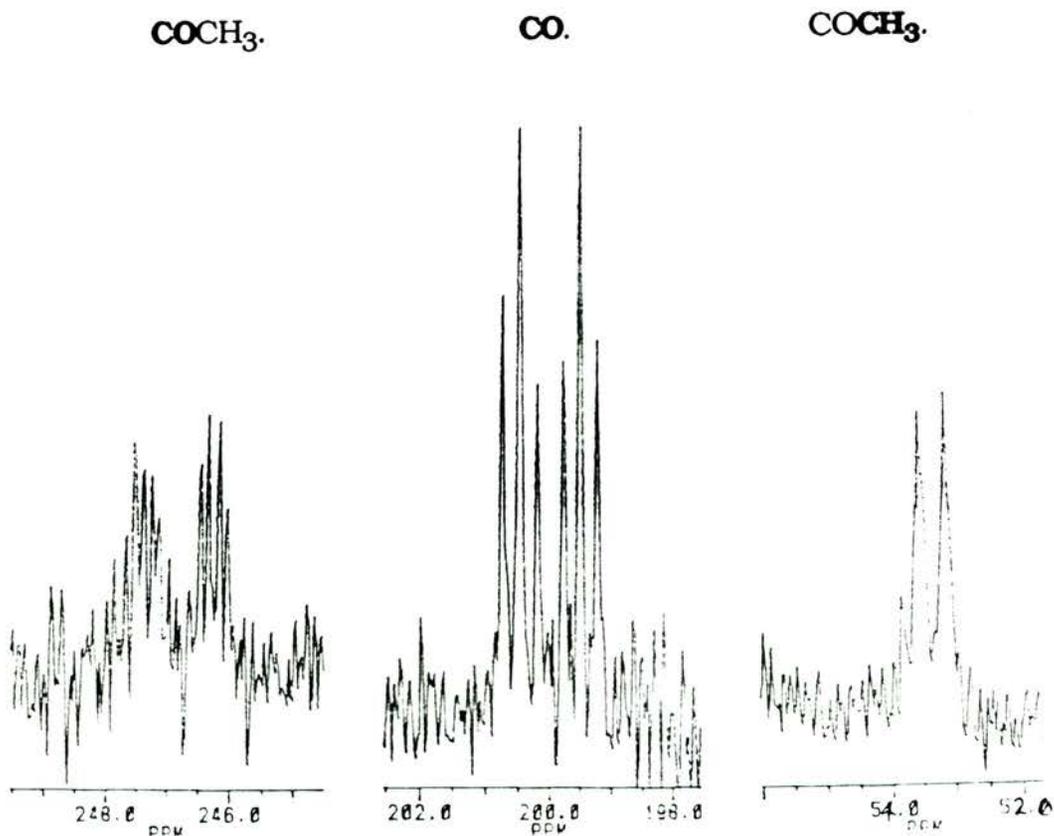


Figure 5.13.

ethanol in the solution. The largest shift on the addition of ethanol was seen in the  $^{13}\text{C}$  nmr of the  $\text{COCH}_3$  acyl peak which shifted downfield from  $\delta = 238.0$  ppm. without ethanol to  $\delta = 246.8$  ppm with ethanol (~20%) in the solution. This indicated some deshielding of the acyl carbon probably due to significant interaction with the ethanol. There was only a slight shift of the carbonyl signal (0.6 ppm. upfield to  $\delta = 199.9$  ppm. with  $J_{\text{Rh-C}} = 73$  Hz.) on addition of ethanol. The  $^{13}\text{C}$  nmr spectra of the acyl, carbonyl and methyl carbons of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_3$ , both in  $\text{C}_7\text{D}_8$  and in  $\text{C}_7\text{D}_8$  with ethanol, are shown in figure 5.13.. When more ethanol was added to the solution to give ~40% ethanol the carbonyl signal remained at  $\delta = 199.9$  ppm. with  $J_{\text{Rh-C}} = 72$  Hz. but the acyl carbon signal moved further downfield to  $\delta = 248.3$  ppm. with  $J_{\text{Rh-C}} = 72$  Hz. and  $J_{\text{P-C}} = 23$  Hz. and 10 Hz.. The methyl shift remained unaltered at  $\delta = 53.4$  ppm but the coupling to rhodium was reduced to 26.1 Hz.. This would appear to indicate further change in the nature of the rhodium to acyl carbon bond.

Attempts were made to see if any change in the chemical shift of the  $^{13}\text{C}$  signal of the acyl carbon and the  $^{31}\text{P}$  signals of  $\text{Rh}(\text{COC}_6\text{H}_{13})(\text{CO})_2(\text{PPh}_3)_2$  in  $\text{C}_7\text{D}_8$ , on the addition of ethanol. Unfortunately the solubility of this species, without the insertion of  $^{13}\text{C}$  enriched CO, was too low for the  $^{13}\text{C}$  signal of the acyl carbon to be detectable at  $-60^\circ\text{C}$ . The  $^{31}\text{P}$  spectrum at  $-60^\circ\text{C}$  showed two weak doublets of doublets at  $\delta = 27.5$  ppm. with  $J_{\text{Rh-P}} = 68$  Hz. and at  $\delta = 25.1$  ppm. with  $J_{\text{Rh-P}} = 131$  Hz. and  $J_{\text{P-P}} = 32$  Hz.. On the addition of ethanol these peaks were detected at  $\delta = 27.2$  ppm. with  $J_{\text{Rh-P}} = 70$  Hz. and at  $\delta = 24.7$  ppm. with  $J_{\text{Rh-P}} = 132$  Hz. and  $J_{\text{P-P}} = 32$  Hz.. This change in chemical shift is not significant and would indicate that this species is not greatly altered by the addition of ethanol. The recorded  $^{31}\text{P}$  spectrum for the the related species  $\text{Rh}(\text{COC}_8\text{H}_{17})(\text{CO})_2(\text{PPh}_3)_2$  at  $-95^\circ\text{C}$ <sup>67</sup> is that of two inequivalent nuclei at  $\delta = 36$  ppm. with  $J_{\text{Rh-P}} =$

140 Hz. and  $\delta = 30$  ppm. with  $J_{\text{Rh-P}} = 70$  Hz. with  $J_{\text{P-P}}$  not listed. These two couplings are the reverse of those found in this work for  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  and for the possible spectrum of  $\text{Rh}(\text{COC}_6\text{H}_{13})(\text{CO})_2(\text{PPh}_3)_2$ .

I.R. studies of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_3$  in thf-d8 showed an acyl absorbance for  $\nu\text{CO}$  at  $1627\text{ cm}^{-1}$ . When  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_3$  was dissolved in  $\text{C}_7\text{D}_8$  with ethanol (~4:1) the frequency of this absorbance shifted to  $1603\text{ cm}^{-1}$ . This is further evidence of the solvent effect of ethanol on this acyl C-O bond, indicating possible weakening due to hydrogen bonding between the acyl oxygen and the hydroxyl hydrogen of ethanol.

Conductivity measurements in ethanol on the solution of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  ( $1 \times 10^{-3}$  moles  $\text{dm}^{-3}$ ) in  $\text{C}_7\text{D}_8$  with 20% ethanol did not indicate the presence of any ionic species in sufficient concentration to increase the conductivity over that of a similar amount of the same solvent mixture.

It was also noticed that when CO was bubbled through a solution of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_2$  in  $\text{C}_7\text{D}_8$  a trace of ethanal was detected in the  $^1\text{H}$  spectrum, while none was observed in the presence of ethanol. This indicates that the presence of ethanol stabilised the acyl species in some way and prevented reductive elimination of ethanal. There was no obvious source of the aldehydic hydrogen required for formation of ethanal in  $\text{C}_7\text{D}_8$ , unless a trace of water was present in solution, whilst ethanol would be a possible source of hydrogen for formation of ethanal, where none was found to form.

When CO was bubbled through a solution of  $\text{Rh}(\text{CH}_3)(\text{CO})(\text{PEt}_3)_3$  with excess  $\text{PEt}_3$  in  $\text{C}_7\text{D}_8$  slower conversion to  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  took place than when ethanol was present. After 3 days no  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  remained in solution and  $^{31}\text{P}$  nmr of this solution with ethanol showed a mixture of  $\text{Rh}_2(\text{CO})_4(\text{PEt}_3)_4$ , species

$^{31}\text{P}\{^1\text{H}\}$  nmr run at  $-60^\circ\text{C}$  of species formed on reaction of  $\text{RhH}(\text{PEt}_3)_3$  with  $\text{CO} + \text{H}_2 + \text{ethene}$  after heating briefly to  $100^\circ\text{C}$ .

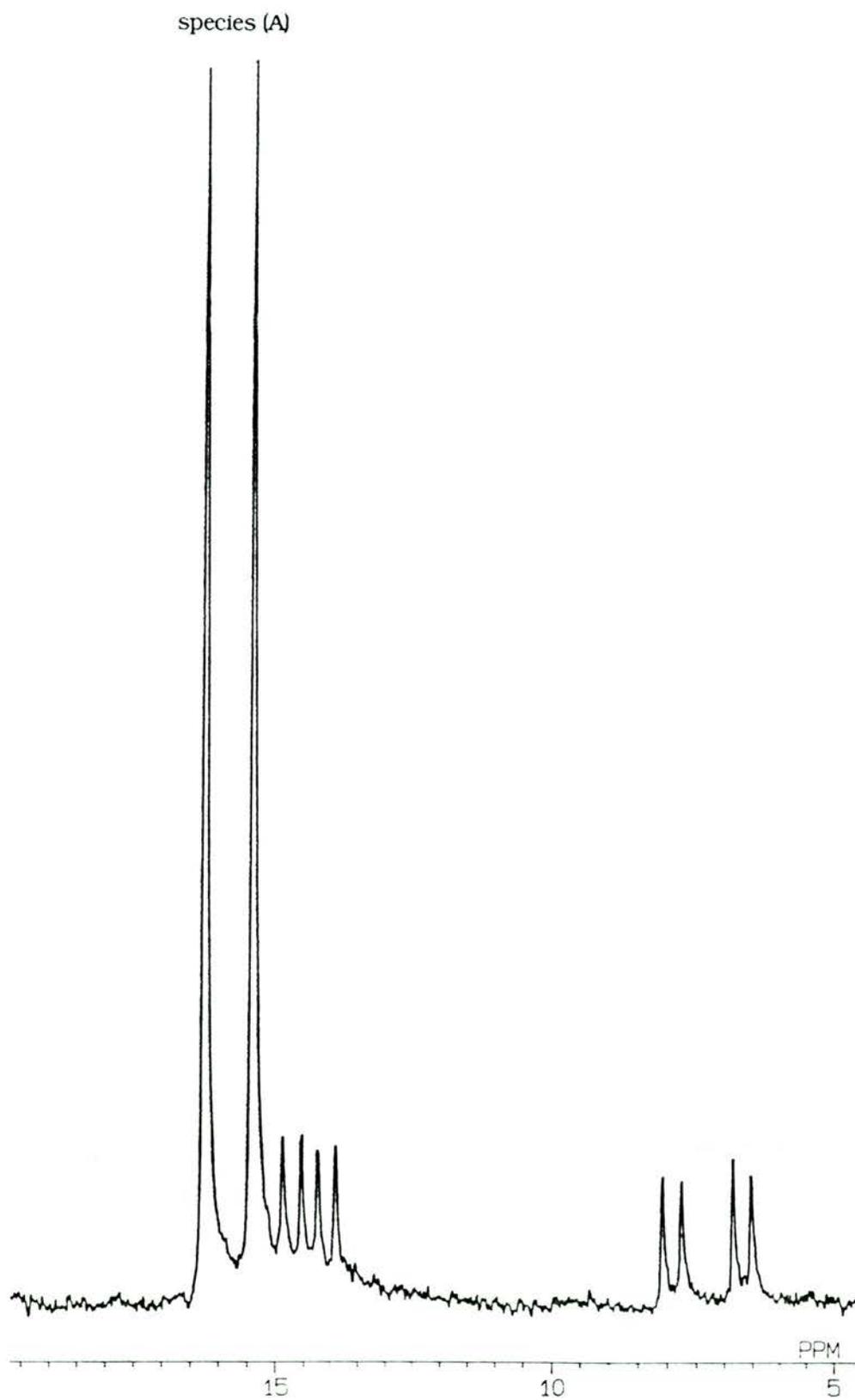


Figure 5.14.

(A) and a little  $\text{RhH}(\text{CO})(\text{PEt}_3)_3$ , with free  $\text{PEt}_3$ . The expected product, ethanol (see chapter 3.), would not be detectable as it would be mixed with the ethanol already present in the solvent mixture. Thus free  $\text{PEt}_3$  in the solution both aided the carbonyl insertion into the  $\text{Rh}-\text{CH}_3$  bond and also the return of the rhodium to the probable starting catalytic species.

The  $^{31}\text{P}$  nmr spectrum was run of a solution of  $\text{RhH}(\text{PEt}_3)_3$  in ethanol pressurised with a mixture of  $\text{CO}/\text{H}_2/\text{C}_2\text{H}_4$ . After heating briefly to  $100^\circ\text{C}$  the spectrum at  $-60^\circ\text{C}$  showed amongst others, a signal very similar in form to that observed at  $-60^\circ\text{C}$  for  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  but with different chemical shifts (due to presetting the  $\text{Et}_3\text{PO}$  peak). This spectrum is shown in figure 5.14.. Chemical shift values, corrected to external  $\text{H}_3\text{PO}_4$  standard, for the  $^{31}\text{P}$  nmr of this acyl species were  $\delta = 17.2$  ppm.  $J_{\text{Rh-P}} = 69$  Hz. and  $\delta = 10.1$  ppm.  $J_{\text{Rh-P}} = 135$  Hz. and  $J_{\text{P-P}} = 36$  Hz., which are very similar to the values obtained for the equivalent rhodium acyl complex formed by  $\text{CO}$  insertion into the  $\text{Rh}$ -methyl bond (see table 4.3.). This was thought to be an indication of the formation of  $\text{Rh}(\text{COCH}_2\text{CH}_3)(\text{CO})_2(\text{PEt}_3)_2$  following coordination of ethene, its reduction to an ethyl ligand and insertion of  $\text{CO}$  to give this acyl species.

In the catalytic system based on  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  comparable resting acyl species,  $\text{Rh}(\text{COR})(\text{CO})_2(\text{PPh}_3)_2$ , have also been observed<sup>58,68</sup> and found to have a similar structure to that found here for  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$ .

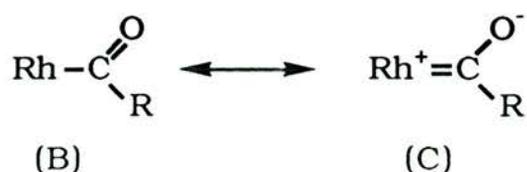
#### 5.4.3. Possible rhodium carbene species.

Although the  $^{13}\text{C}$  spectrum of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  in the presence of ethanol showed a downfield shift in the position of the acyl carbon signal this was probably due to hydrogen bonding rather

than protonation of this dicarbonyl species as the chemical shift was not lowfield enough to indicate a rhodium carbene species. The recorded  $^{13}\text{C}$  chemical shift for the carbene carbon of  $\text{W}\{\text{C}(\text{OH})\text{CH}_3\}(\text{CO})_5$ , which has the carbene ligand as that expected here, is  $\delta = 334.4$  ppm.<sup>69</sup> On protonation of an anionic acyl species to give a neutral alkoxy-carbene species when bound to chromium or tungsten there has been found to be a downfield shift of  $\sim 50$  and  $\sim 33$  ppm, respectively<sup>69</sup>, so a similar shift might be expected here if  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  were to be protonated to give  $[\text{Rh}\{\text{C}(\text{OH})\text{CH}_3\}(\text{CO})_2(\text{PEt}_3)_2]^+$ . This would require a chemical shift for the carbene signal to be at  $\delta = 300\text{-}280$  ppm.

It is clear from these stoichiometric studies that  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  undergoes an interaction with ethanol which probably involves hydrogen bonding of ethanol to the acyl oxygen atom and that similar species are present in the catalytic cycle. It is also clear from the in situ studies that the rate determining step for the catalytic cycle must be oxidative addition of  $\text{H}_2$ , if present, or of solvent alcohol.

The hydrogen bonding of ethanol to the acyl oxygen atom must arise because  $\text{PEt}_3$  is not a good  $\pi$ -acceptor ligand, but is a good  $\sigma$ -donor, so that there is a high electron density on the metal. This is then transmitted to the acyl oxygen to give a higher contribution from the carbenoid canonical form:



The rate determining oxidative addition will occur to a 16-electron complex,  $\text{Rh}(\text{COR})(\text{CO})_2(\text{PEt}_3)_2$  which, having one less CO ligand will be even more electron rich at the metal centre and give an

even greater contribution from (C), possibly even giving rise to complete protonation of (C). In order to try to isolate a complex similar to  $[\text{Rh}(\text{C}(\text{OH})\text{CH}_3)(\text{CO})(\text{PEt}_3)_2]^+$ , an ethanolic solution of  $\text{Rh}(\text{COCH}_3)(\text{CO})_2(\text{PEt}_3)_2$  was treated with  $\text{Na}^+ \text{BPh}_4^-$  in ethanol. A pale yellow precipitate formed immediately and this was filtered and dried under vacuum. It appeared to be very air sensitive, as some dark brown material formed on the addition of a filter stick to the Schlenk tube prior to filtration, probably due to reaction of the ionic product with traces of oxygen.  $^{31}\text{P}$  nmr on a solution of this yellow solid showed a doublet at  $\delta = 22.1$  ppm.  $J_{\text{Rh-P}} = 141$  Hz. The  $^{13}\text{C}$  spectrum at  $-40^\circ\text{C}$  showed no carbonyl, acyl or carbene peak, possibly because the solution was too weak. Clearly it is possible to isolate a cationic complex from this solution but its nature is not known.

It may be concluded that the acyl species formed in the catalytic cycle during hydroformylation of alkenes in alcoholic solvents catalysed by  $\text{RhH}(\text{PEt}_3)_3$  is substantially hydrogen bonded to the alcohol and may even be protonated by it. After rate determining addition of  $\text{H}_2$ , hydrogen transfer to the carbene-like carbon atom will give a hydroxyalkyl-like intermediate, rather than reductive elimination of aldehyde, so that aldehyde will not be formed as an intermediate in the reaction. These results add weight to the mechanistic proposals made in chapter 4..

## Chapter 6. Experimental Techniques and Preparation of Starting Materials.

### 6.1. Product analysis.

#### 6.1.1. Gas Chromatography - Mass Spectroscopy, GCMS.

Qualitative analysis of products from catalytic runs was carried out by GCMS on an INCOS 50 GCMS system with a Hewlett Packard 5890 gas chromatograph. The g.c. was run with a silica capillary column using a methyl siloxane stationary phase. Helium at 9 psi was used as carrier gas and the injector temperature was 200°C. The g.c. temperature program was set to run at 30°C for 5 minutes and was then ramped, at 20°C min<sup>-1</sup>, to 200°C, where it was held for 10 minutes. All samples were run undiluted, as reaction mixtures, on removal from the autoclave.

#### 6.1.2. Gas liquid chromatography, glc.

Products of catalytic runs were analysed quantitatively by glc. on a Philips PU 4500 chromatograph using nitrogen as the carrier gas, with the injector temperature set at 150°C and a flame ionisation detector at 200°C. Reaction solutions (100 µl) were diluted with an ethanolic solution of octanol (20% by volume), as internal standard, (100 µl) prior to injection. Standard solutions, with known percentage volumes of:

- i). heptanal, 2-methylhexanol, heptanol, ethyl heptanoate and heptyl ethanoate, with octanol (10%) as internal standard,
- ii). hex-1-ene with octanol (10%) as internal standard,
- iii). ethyl ethanoate with octanol (10%) as internal standard

were made up and run on the appropriate columns for use in calculations of percentage yield of products. Materials for which known samples were not available were assumed to have the same

response factors as injected samples as follows:

2-methylhexanal - heptanal,

ethyl 2-methylhexanoate - ethyl heptanoate,

2-methylhexyl ethanoate - heptyl ethanoate

and yields were calculated accordingly.

Quantitative analysis of product C<sub>7</sub> aldehydes, C<sub>7</sub> alcohols, and the esters of C<sub>7</sub> alcohols and C<sub>7</sub> acids, was carried out using an injection (0.1 µl) of prepared sample onto a capillary column with methyl siloxane as stationary phase with a temperature program set such that the oven temperature was held at 75°C for 1 minute and then ramped at 16°C min<sup>-1</sup> to 130°C, where it was then held for 2-6 minutes depending on the reaction products.

Quantitative analysis of unreacted hexenes was carried out using an injection (0.5 µl) of prepared sample on a glass column, packed with SP2340 as stationary phase. The temperature program was set such that the oven was held at 100°C for 2 minutes and then ramped, at 16°C min<sup>-1</sup>, to 130°C, where it was then held for a further 2 minutes. Ethyl ethanoate was analysed quantitatively, using the same sample preparation and injection size as for hexene analysis, using a glass column packed with carbowax as stationary phase. The temperature program was set such that the oven was held at 80°C for 2 minutes and then ramped at 16°C min<sup>-1</sup> to 160°C, where it was then held for 2 minutes.

### 6.1.3. Gas chromatography.

Detection of methane and hydrogen was carried out on a Pye-Unicam series 204 gas chromatograph, using a glass column packed with 5A molecular sieve as stationary phase and nitrogen as carrier gas. The column was held at 80°C, while the injector and thermocouple detector were maintained at 100°C.

#### 6.1.4. Nuclear magnetic resonance spectroscopy, nmr.

All nmr spectra run at St Andrews were recorded on a Bruker AM 300 Spectrometer ( $^1\text{H}$ , 300.1 MHz.;  $^{31}\text{P}$ , 121.5 MHz.;  $^{13}\text{C}$ , 75.5 MHz.) in 5 mm glass tubes.

The reaction mixtures were fractionally distilled from the catalyst.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were run on the solvent and reaction product fractions dissolved in deuteriochloroform,  $\text{CDCl}_3$ , with chemical shifts quoted relative to tetramethylsilane, TMS, as internal standard.

$^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  spectra of rhodium compounds were dissolved in either perdeuterotoluene,  $\text{C}_7\text{D}_8$ , perdeuterotetrahydrofuran,  $\text{C}_4\text{D}_8\text{O}$ , thf-d8 or perdeuteroethanol,  $\text{C}_2\text{D}_5\text{OD}$ . The high field signal of the solvent was set relative to TMS such that;

the methyl signal of  $\text{C}_7\text{D}_8$  for  $^1\text{H} = 2.1$  ppm. and  $^{13}\text{C} = 20.4$  ppm.,

the higher field signal of thf-d8 for  $^1\text{H} = 1.8$  ppm. and  $^{13}\text{C} = 26.7$  ppm. and

the methyl signal of  $\text{C}_2\text{D}_5\text{OD}$  for  $^1\text{H} = 1.2$  ppm. and  $^{13}\text{C} = 17.9$  ppm..

$^{31}\text{P}$  spectra were run relative to external  $\text{H}_3\text{PO}_4$ .

Nmr spectra run at B.P. Research Centre, Sunbury were recorded on a JEOL GSS270 Spectrometer ( $^1\text{H}$ , 270 MHz.;  $^{31}\text{P}$ ; 109 MHz.) in 5 mm sapphire pressure tubes.

#### 6.1.5. Infra-red spectroscopy, I.R..

All I.R. spectra were run on a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer in the range 4000-400  $\text{cm}^{-1}$ . Spectra were recorded either as nujol mulls between KBr disks, or as solutions in a KBr solution cell.

#### 6.1.6. Elemental analysis.

C-H microanalysis was carried out using a Carlo Erba MOD 1106

elemental analyser.

## 6.2. Equipment and reagents.

### 6.2.1. Vacuum Lines.

The vacuum work carried out for this thesis was carried out on a standard Schlenk line (with greaseless PTFE taps and ball and socket compression joints), with catheter tubing techniques. An inert atmosphere was provided by use of either nitrogen or, preferably, argon (both white spot grade) which had been dried by passage through a column packed with chromium (II) absorbed on silica.

### 6.2.2. Solvents.

Alcoholic solvents were dried by distillation, over magnesium, under an atmosphere of nitrogen or argon. Ether, petrol (40-60°C boiling range) and thf were dried by distillation from sodium benzophenoneketyl under a nitrogen atmosphere. Toluene was dried by distillation over sodium under an atmosphere of nitrogen.

### 6.2.3. Substrates.

Hex-1-ene, Hex-2-ene and styrene were degassed under vacuum but otherwise used as supplied. Heptanal was dried over anhydrous magnesium sulphate, filtered and then distilled under argon prior to use.

## 6.3. Catalytic experiments.

### 6.3.1. Preparation of catalyst solutions.

Catalytic solutions of  $\text{RhH}(\text{PEt}_3)_3$  were prepared by weighing  $\text{RhH}(\text{PEt}_3)_4$  (pale yellow crystals) under vacuum and then converting this to  $\text{RhH}(\text{PEt}_3)_3$  (oil, appearing dark green by reflected light and red by transmitted light) by pumping under vacuum at 65-70°C for at

least 30 minutes. The  $\text{RhH}(\text{PEt}_3)_3$  was dissolved in dried, degassed solvent to give a solution of  $0.010 \text{ moles dm}^{-3}$  concentration.

When ligands other than  $\text{PEt}_3$  were being used, a solution of  $\text{Rh}_2(\text{OAc})_4$  in degassed ethanol, with added phosphine ligand in the correct ratio, was made up under an argon atmosphere, such that the concentration of rhodium in solution was  $0.010 \text{ moles dm}^{-3}$ . Alternatively in some reactions the  $\text{Rh}_2(\text{OAc})_4$ , and when  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  was used as catalyst, the rhodium species was weighed directly into the autoclave liner, degassed during the autoclave purge and then dissolved in ethanol, with the added ligand as required, in situ.

### 6.3.2. Autoclave reactions.

The autoclave was closed and then purged with reactant gas to be used in the catalytic experiment, by pressurising to  $>20$  atmos. and then venting the autoclave. This process was carried out three times, to remove air, then the removable cap was taken off and a gentle flow of reactant gas allowed to pass through the vessel, while the catalyst solution ( $4\text{cm}^3$ ), (excess  $\text{PEt}_3$  ( $59 \mu\text{l}$ ) if used) and substrate ( $1\text{cm}^3$ ) were injected into the autoclave. The removable cap was then tightened and the autoclave pressurised with reactant gas to the required pressure. The autoclave was then sealed and placed in a preheated oven for a timed period. At the end of the reaction the autoclave was removed from the oven and placed in a cold water bath for  $\sim 20$  minutes, until cool. The reactant gases were then gently vented, the autoclave opened and the reaction mixture removed for analysis.

#### 6.4. Preparation of rhodium species.

##### 6.4.1. RhH(PEt<sub>3</sub>)<sub>4</sub>, Rh<sub>2</sub>(OAc)<sub>4</sub>, RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> and [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub>.

RhH(PEt<sub>3</sub>)<sub>4</sub><sup>61</sup>, Rh<sub>2</sub>(OAc)<sub>4</sub><sup>70</sup>, RhH(CO)(PPh<sub>3</sub>)<sub>3</sub><sup>71</sup> and [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub><sup>72</sup> were prepared by standard literature methods. (Samples of RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> were kindly provided by I. Utuk).

##### 6.4.2. Rh(Cl)(CO)(PEt<sub>3</sub>)<sub>2</sub>.

Rh(Cl)(CO)(PEt<sub>3</sub>)<sub>2</sub> was prepared by stirring chlorobis-(cyclooctene)rhodium, [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub>, (2.0 g) suspended in degassed petrol (50 cm<sup>3</sup>) with PEt<sub>3</sub> (1.7 cm<sup>3</sup>) in an argon atmosphere at ambient temperature for 20 hours. The solvent volume was reduced under vacuum and the product was then dissolved in ether (20 cm<sup>3</sup>). Carbon monoxide was then bubbled through this solution for 5 minutes during which time there was a colour change from deep orange/red to yellow. The volume of the solution was reduced (to ~4 cm<sup>3</sup>) and the product, Rh(Cl)(CO)(PEt<sub>3</sub>)<sub>2</sub>, was allowed to crystallise overnight under an atmosphere of argon, at -30°C. The product was filtered cold (~-50°C) and washed with cold ether before drying under vacuum. Yield 1.91 g, 85%; m.p. 71-72°C, (lit. 75-75.5°C)<sup>73</sup>; I.R., nujol mull, νCO 1958 cm<sup>-1</sup>, (lit. 1953 cm<sup>-1</sup>)<sup>73</sup>.

<sup>31</sup>P nmr, in thf-d<sub>8</sub>, d, δ = 25.1 ppm., J<sub>Rh-P</sub> = 116 Hz., (lit. in CD<sub>2</sub>Cl<sub>2</sub>, δ = 23.7 ppm. J<sub>Rh-P</sub> = 116 Hz.)<sup>74</sup>.

<sup>1</sup>H nmr, in thf-d<sub>8</sub>, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> m, δ = 1.9 ppm. and m, δ = 1.3 ppm..

Analysis; calculated for C<sub>13</sub>H<sub>30</sub>ClOP<sub>2</sub>Rh = 38.78% C; 7.51% H. Found = 39.08% C; 7.61% H.

##### 6.4.2. Rh(CH<sub>3</sub>)(CO)(PEt<sub>3</sub>)<sub>2</sub>.

Rh(CH<sub>3</sub>)(CO)(PEt<sub>3</sub>)<sub>2</sub> was prepared by reacting Rh(Cl)(CO)(PEt<sub>3</sub>)<sub>2</sub> (1.08g) dissolved in degassed ether (5 cm<sup>3</sup>) with methyl lithium, CH<sub>3</sub>Li, (2.0 cm<sup>3</sup>, 1.4 molar in ether) under an atmosphere of argon.

The yellow solution was filtered from the precipitated LiCl, and reduced in volume. Petrol (5 cm<sup>3</sup>) was added to the solution which was then refiltered, reduced (to ~2 cm<sup>3</sup>) and allowed to crystallise under argon at -30°C. The product was filtered and used unwashed.

m.p. 28-31°C; I.R., nujol mull,  $\nu_{\text{CO}}$  1938 cm<sup>-1</sup>.

<sup>31</sup>P nmr, in C<sub>7</sub>D<sub>8</sub>, d,  $\delta$  = 26.6 ppm.,  $J_{\text{Rh-P}}$  = 140 Hz..

<sup>1</sup>H nmr, in C<sub>7</sub>D<sub>8</sub>, Rh-CH<sub>3</sub> td,  $\delta$  = -0.35 ppm.,  $J_{\text{Rh-H}}$  = 1.6 Hz.,  $J_{\text{P-H}}$  = 8.2 Hz.; P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> m,  $\delta$  = 1.6 ppm. and m,  $\delta$  = 1.0 ppm..

<sup>13</sup>C nmr, in C<sub>7</sub>D<sub>8</sub>, Rh-CH<sub>3</sub> td,  $\delta$  = -4.2 ppm.,  $J_{\text{Rh-C}}$  = 20 Hz.,  $J_{\text{P-C}}$  = 13 Hz.; Rh-CO dt,  $\delta$  = 192.8 ppm.,  $J_{\text{Rh-C}}$  = 57 Hz.,  $J_{\text{P-C}}$  = 14 Hz.; P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> t,  $\delta$  = 18.1 ppm. and s,  $\delta$  = 8.9 ppm..

Analysis; calculated for C<sub>14</sub>H<sub>33</sub>OP<sub>2</sub>Rh = 43.98% C; 8.64% H. Found = 42.72% C; 9.36% H.

#### 6.4.3. Rh(COCH<sub>3</sub>)(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>.

Rh(COCH<sub>3</sub>)(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> was prepared in situ by bubbling CO through a solution of Rh(CH<sub>3</sub>)(CO)(PEt<sub>3</sub>)<sub>2</sub> (~0.1 moles dm<sup>-3</sup>) in C<sub>7</sub>D<sub>8</sub> for 1-5 minutes; I.R., solution in thf-d<sub>8</sub>,  $\nu_{\text{CO}}$  2002, 1977 cm<sup>-1</sup>;  $\nu_{\text{COCH}_3}$  1627 cm<sup>-1</sup>.

<sup>31</sup>P nmr, at -60°C in C<sub>7</sub>D<sub>8</sub>, dd,  $\delta$  = 17.8 ppm.,  $J_{\text{Rh-P}}$  = 71 Hz. and dd,  $\delta$  = 12.1 ppm.,  $J_{\text{Rh-P}}$  = 140 Hz.,  $J_{\text{P-P}}$  = 36 Hz..

<sup>1</sup>H nmr, at -60°C in C<sub>7</sub>D<sub>8</sub>, COCH<sub>3</sub>  $\delta$  = 2.9 ppm.; P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> m,  $\delta$  = 1.4 ppm., m,  $\delta$  = 1.1 ppm. and m,  $\delta$  = 0.9 ppm..

<sup>13</sup>C nmr, at -60°C in C<sub>7</sub>D<sub>8</sub>, COCH<sub>3</sub> ddd,  $\delta$  = 238.0 ppm.,  $J_{\text{Rh-C}}$  = 78 Hz.,  $J_{\text{P-C}}$  = 21 and 9 Hz.; COCH<sub>3</sub> dd,  $\delta$  = 53.8 ppm.,  $J_{\text{Rh-C}}$  = 32.7 Hz.,  $J_{\text{P-C}}$  = 4 Hz.; Rh-CO dt,  $\delta$  = 200.5 ppm.,  $J_{\text{Rh-C}}$  = 75 Hz.,  $J_{\text{P-C}}$  = 21 Hz.; P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> s,  $\delta$  = 17.0 and 16.8 ppm. and s,  $\delta$  = 7.4 and 8.1 ppm..

#### 6.4.4. Attempted preparation of $\text{Rh}(\text{COC}_6\text{H}_{13})(\text{CO})_2(\text{PPh}_3)_2$ .

$\text{Rh}(\text{COC}_6\text{H}_{13})(\text{CO})_2(\text{PEt}_3)_2$  was prepared in situ by bubbling CO through a solution of  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  ( $\sim 0.035$  moles  $\text{dm}^{-3}$ ) in  $\text{C}_7\text{D}_8$ , to which hex-1-ene (17  $\mu\text{l}$ ) had been added, for  $\sim 3$  minutes at ambient temperature. A precipitate, possibly of  $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]_2$ , formed slowly in the nmr tube.

## Chapter 7. Summary.

### Hydroformylation with CO/H<sub>2</sub>.

RhH(PEt<sub>3</sub>)<sub>3</sub> acted as a catalyst precursor for the hydroformylation of alkenes (ethene, propene, hex-1-ene, hex-2-ene, styrene and 3,3-dimethylbut-1-ene) with CO/H<sub>2</sub> (1:1, 20-80 atmos; 1:2, 15-45 atmos) in the gas phase within the temperature range 60-145°C. Either C<sub>7</sub> aldehydes or C<sub>7</sub> alcohols could be produced from hex-1-ene by manipulation of the solvent and or RhH(PEt<sub>3</sub>)<sub>3</sub> and free PEt<sub>3</sub> concentration.

With ethanol as solvent and [RhH(PEt<sub>3</sub>)<sub>3</sub>] < 0.001 moles dm<sup>-3</sup> (or in toluene with [RhH(PEt<sub>3</sub>)<sub>3</sub>] at 0.008 moles dm<sup>-3</sup>) hex-1-ene was readily hydroformylated to C<sub>7</sub> aldehydes. If the catalyst concentration was increased to > 0.004 moles dm<sup>-3</sup> with ethanol as solvent, C<sub>7</sub> alcohols were formed as product. At this higher catalyst concentration heptanal was also readily hydrogenated to heptanol by this same system.

Deuteration studies with CO/D<sub>2</sub> in the gas phase showed that hex-1-ene was converted to C<sub>4</sub>H<sub>9</sub>CHDCH<sub>2</sub>CD<sub>2</sub>OH/D and C<sub>4</sub>H<sub>9</sub>CH(CH<sub>2</sub>D)CD<sub>2</sub>OH/D exclusively while heptanal was reduced to a mixture of C<sub>4</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>CHDOH/D and C<sub>4</sub>H<sub>9</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH/D. Reduction of heptanal with CO/H<sub>2</sub> using ethanol-OD as solvent showed similar incorporation of deuterium into the product. This indicated that the solvent was an active participant in the hydrogenation of heptanal. Consequently it was deduced that C<sub>7</sub> aldehyde was not formed as a reaction intermediate in the hydroformylation, with hydrogenation, of hex-1-ene to heptanol and 2-methylhexanol under these conditions.

The catalyst turnover rates, as indicated in table 7.1., were fast when the reaction was carried out in a stirred autoclave.

Table 7.1.

Substrate	Catalyst turnover rate.
ethene	900 min <sup>-1</sup> = 15sec <sup>-1</sup>
propene	58 min <sup>-1</sup>
hex-1-ene	38 min <sup>-1</sup>

The n:i ratio of products remained in the range 2.2-2.8 under the reaction conditions studied, even when excess PEt<sub>3</sub> was added.

The one step production of C<sub>7</sub> alcohols from hex-1-ene was dependent on the presence of an alcoholic solvent and basic phosphine ligand, and the concentration of catalyst precursor. When PEt<sub>3</sub> was used as phosphine ligand, with CO/H<sub>2</sub> 1:1 at 40 atmos, a ratio of PEt<sub>3</sub>:Rh ≥ 3 and [RhH(PEt<sub>3</sub>)<sub>3</sub>] > 0.004 moles dm<sup>-3</sup> were required to yield C<sub>7</sub> alcohols.

#### Transfer hydroformylation.

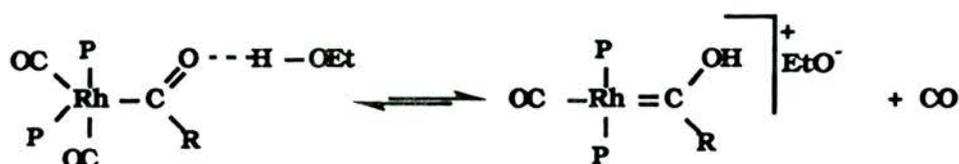
When ethanol was used as the solvent/hydrogen source hex-1-ene was again hydroformylated/hydrogenated to heptanol and 2-methylhexanol in 40-80% yield when the reaction was carried out in the temperature range 110-140°C. C<sub>7</sub> aldehyde and esters (ethyl heptanoate, ethyl 2-methylhexanoate, heptyl ethanoate and 2-methylhexyl ethanoate) were all formed in lesser yield (individually no more than 10% of overall yield of C<sub>7</sub> alcohol). The dehydrogenation products of ethanol were ethanal and ethyl ethanoate.

With [RhH(PEt<sub>3</sub>)<sub>3</sub>] at 0.008 moles dm<sup>-3</sup> the optimum CO pressure was shown to be ~20 atmos. The presence of excess PEt<sub>3</sub> increased the yield of C<sub>7</sub> alcohol, probably by reducing the isomerisation of the substrate and enhancing the dehydrogenation of the ethanol.

This system gave some hydrogenation of heptanal to heptanol but at a slower rate than that at which hydroformylation of hex-1-ene to C<sub>7</sub> alcohol took place. This indicates that aldehyde did not leave the catalytic centre as an intermediate prior to hydrogenation, with C<sub>7</sub> alcohol formation, when hex-1-ene was used as substrate.

Deuteration studies on hex-1-ene, with ethanol-OD as solvent/'hydrogen' source, showed deuterium incorporation at the C<sub>3</sub>, C<sub>2</sub> and C<sub>1</sub> carbons, that at carbon C<sub>2</sub> taking place due to β-exchange. The slow step in the catalytic cycle appeared to be the oxidative addition of ethanol to the metal centre allowing β-exchange at carbon C<sub>2</sub> to take place. This β-exchange was not observable in the reactions with CO/D<sub>2</sub> in the gas phase.

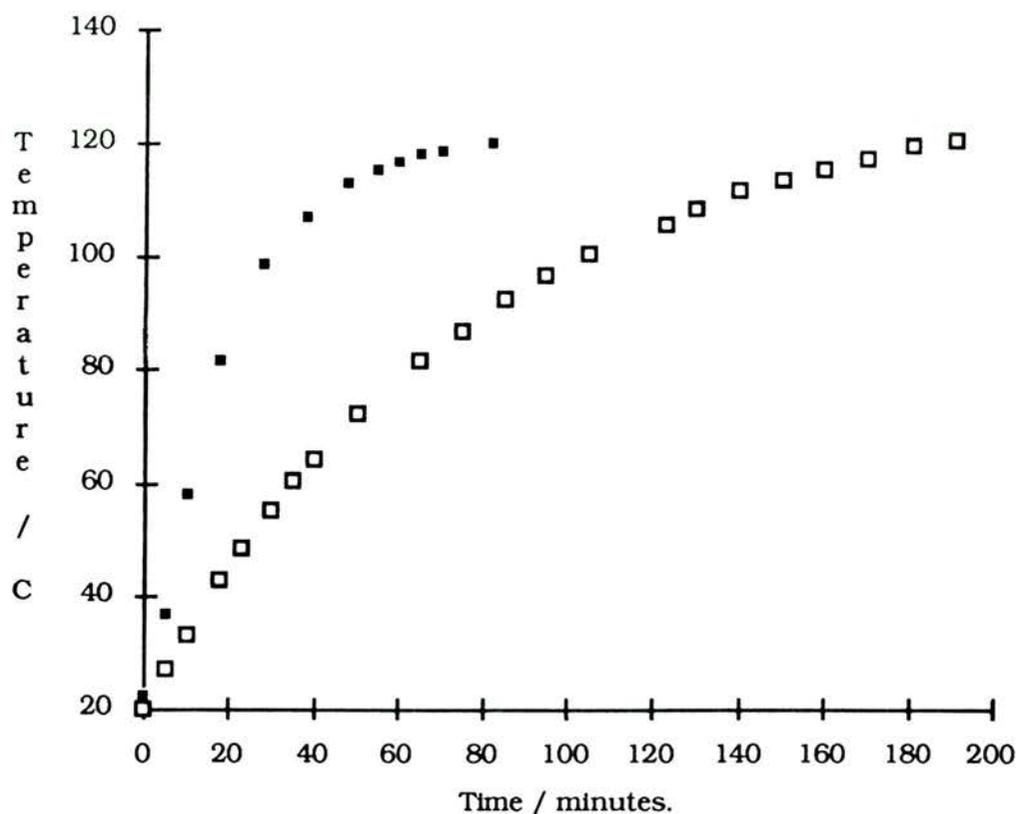
Nmr studies on possible reaction intermediates showed interaction between ethanol and the acyl species, Rh(COCH<sub>3</sub>)(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>3</sub>, indicating hydrogen bonding to the acyl oxygen. Loss of CO from this species would give greater electron density at the rhodium centre, possibly allowing protonation by ethanol. The proposed rhodium-hydroxycarbene intermediate thought to enable direct formation of C<sub>7</sub> alcohols from hex-1-ene is shown in scheme 7.1. For this species to form, an alcoholic solvent and the presence of a basic phosphine ligand in sufficient concentration are required in the reaction mixture.



Scheme 7.1.

## Appendix 1. Rate of internal heating in autoclave.

### Rate of internal heating in autoclave.



fan-assisted oven set at 120°C.  
non-fan-assisted oven set at 125°C.

These two experiments were run with an autoclave fitted with a probe containing a thermocouple so that the internal temperature of the autoclave could be monitored. The autoclave was primed with ethanol (5 cm<sup>3</sup>) and pressurised with CO to 20 atmos. It was then placed in a preheated oven and the rise in temperature within the autoclave was monitored. In a fan-assisted oven the autoclave contents took ~1.25 hours to reach the external oven temperature of 120°C, while in a non-fan-assisted oven the contents of the autoclave took over 3 hours to reach the external oven temperature of 125°C.

Appendix 2. Worked example. Calculation of percentage of deuterium incorporated into product by comparison of the intensities of non-β-shifted and β-shifted signals in the  $^{13}\text{C}\{^1\text{H}\}$  nmr spectrum.

The reaction of heptanal with  $\text{CO}/\text{D}_2$  in ethanol with  $\text{RhH}(\text{PEt}_3)_3$  as catalyst precursor gave a mixture of :



The peaks detected are shown in the table below.

carbon position	$\delta$ /ppm.	intensity	carbon environment	$\alpha/\beta$ shift /ppm.
1	62.39		$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{OH/D}$	-
	62.02 t		$-\text{CH}_2\text{-}\underline{\text{C}}\text{HDOH/D}$	$\alpha$ 0.37
2	32.82	15.5	$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_2\text{OH/D}$	-
	32.71	11.0	$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CHDOH/D}$	$\beta$ 0.09
3	26.02		$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-}$	-
4	29.41		$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-}$	-
5	32.11		$\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_2\text{-}$	-
6	22.83		$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_3$	-
7	14.14		$-\text{CH}_2\text{-}\underline{\text{C}}\text{H}_3$	-

The two species gave two signals for carbon in position  $\text{C}_1$ , a singlet at  $\delta=62.39$  ppm. due to hydrogenated product and a triplet at  $\delta=62.02$  ppm.,  $J_{\text{C-D}} = 21.4$  Hz., due to one deuterium atom being bonded to this carbon. This signal was not suitable for integration as these two carbons are not in identical local environments and so will have different relaxation times and be subject to differing NOEs.

The carbons at position  $\text{C}_2$ , which are in the same local environment, being bonded to two carbons and two hydrogens in both the nondeuterated and the deuterated species, are split into two

peaks by the absence and presence of a deuterium atom on the adjacent carbon C<sub>1</sub>. These two signals are directly comparable and so the intensities of the non-β-shifted and the β-shifted signals may be used to calculate the distribution of deuterium at carbon C<sub>1</sub>. This sample gives the following distribution:

$$\text{Total intensity} = 15.5 + 11.0 = 26.5.$$

$$\% \text{ non-}\beta\text{-shifted species} = \frac{15.5 \times 100}{26.5} = 58\%$$

$$\text{and } \% \beta\text{-shifted species} = 42\%.$$

ie. 58% of the product was hydrogenated and 42% was monodeuterated at carbon C<sub>1</sub>.

If a second deuterium had also been bonded to carbon C<sub>1</sub> a third peak would have been seen at carbon C<sub>2</sub> with a β-shift equal to twice that of the monodeuterated species.

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