

# Hydroformylation of alkenes in supercritical carbon dioxide catalysed by rhodium trialkylphosphine complexes †

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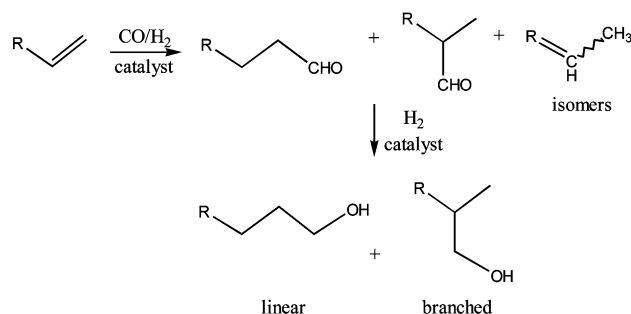
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Rhodium complexes modified by simple trialkylphosphines can be used to carry out homogeneous hydroformylation in supercritical carbon dioxide (scCO<sub>2</sub>). The catalyst derived from PEt<sub>3</sub> is more active and slightly more selective for the linear products in scCO<sub>2</sub> than in toluene, and under the same reaction conditions [100°C, 40 bar of CO/H<sub>2</sub> (1:1)] P(OPr<sup>i</sup>)<sub>3</sub> is also an effective ligand giving good catalyst solubility and activity. Other ligands such as PPh<sub>3</sub>, POct<sub>3</sub>, PCy<sub>3</sub>, and P(4-C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>)<sub>3</sub> are less effective because of the low solubility of their rhodium complexes in scCO<sub>2</sub>. P(4-C<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>n</sub>Ph<sub>3-n</sub> (*n* = 3 or 1) and P(OPh)<sub>3</sub> impart activity despite their complexes only being poorly soluble in scCO<sub>2</sub>. Under subcritical conditions, using PEt<sub>3</sub> as the ligand, C<sub>7</sub>-alcohols from hydrogenation of the first formed aldehydes are the main products whilst above a total pressure of 200 bar, where the solution remains supercritical (monophasic) throughout the reaction, aldehydes are obtained with 97% selectivity. High pressure IR studies in scCO<sub>2</sub> using PEt<sub>3</sub> as the ligand are reported.

## Introduction

The hydroformylation of alkenes is one of the world's most important homogeneous catalysed reactions, producing more than six million tons of aldehydes and alcohols annually.<sup>1,2</sup> In this reaction an alkene is transformed into a mixture of branched and linear aldehydes by addition of a molecule of CO and H<sub>2</sub> across the olefinic double bond (Scheme 1). Successive



**Scheme 1** Hydroformylation reaction scheme with subsequent hydrogenation to alcohol products.

hydrogenation of the aldehyde group is often used to produce alcohols, which are used as plasticisers or in the manufacture of soaps and detergents. Rhodium complexes are the most successful catalysts (in terms of selectivity to the desired linear products and mild operating conditions) for carrying out such a transformation and, indeed, are used in most processes involving low boiling products which can be easily separated from the

catalyst solution by distillation at atmospheric or reduced pressure.<sup>1,2</sup> When less volatile compounds are involved, such recovery of the catalyst is not possible because the thermally sensitive rhodium complexes decompose below the boiling point of the product. For the longer chain products, which are important in soap and detergent manufacture, cobalt catalysts are used despite their lower activity and selectivity.<sup>3</sup>

Because of the advantages of rhodium-based systems, there has been considerable interest in developing process conditions that will allow them to be used with long chain alkenes. The only process to be commercialised to date is the aqueous biphasic process developed by Rhône Poulenc and commercialised by Ruhr Chemie.<sup>4</sup> This involves a water soluble analogue of triphenylphosphine, for which the rhodium complex remains in the water at all times and the product aldehydes are separated from it because they are insoluble in water. The separation is by a simple decantation process. The catalysis takes place in the aqueous phase and the system works well for alkenes up to eight C atoms in length. Beyond this, the solubility of the alkene in water is too low for industrially important rates to be achieved. A process which is nearing commercialisation and is claimed to be suitable for alkenes up to C<sub>18</sub> involves the low pressure distillation of the products.<sup>5</sup>

Various other approaches to the separation problem are being investigated. These include (i) anchoring homogeneous catalysts to insoluble polymers or inorganic solid supports.<sup>6,7</sup> Although catalyst leaching is usually a problem, a recent report has described anchoring hydroformylation catalysts to a sol-gel-derived silica. This catalyst has been used for over a year under many different conditions with little or no catalyst leaching.<sup>8</sup> The linear selectivity is also very high as the rhodium-bound ligand is one of the Xantphos family of ligands, which are known to give very high selectivities.<sup>9</sup> (ii) 'Ship-in-a-bottle' catalysts, in which the catalyst is constructed within the pores of a zeolite and the size of the catalyst prevents it from leaving

† Electronic supplementary information (ESI) available: full analysis of products obtained from the hydroformylation of 1-hexene in scCO<sub>2</sub>. See <http://www.rsc.org/suppdata/dt/b2/b207747g/>

the pores.<sup>6,10-13</sup> The catalyst may also be covalently linked to the inner surface of the zeolite. However, leaching can still be a problem and substrates may be prevented from approaching the catalyst. Mesoporous solids can overcome this problem to some extent.<sup>12</sup> (iii) Anchoring homogeneous catalysts to dendrimer supports,<sup>14-25</sup> and removing the catalyst from the products by ultra-filtration.<sup>24</sup> The well defined geometry of the binding sites on the dendrimer surface and the possibility of multi-dentate coordination mean that higher linear selectivities can be achieved than expected from studies of small molecule analogues,<sup>16</sup> but there are problems with finding membranes that are compatible with the reaction conditions (organic solvents, elevated temperatures and pressures) and prevent leaching. Dendrimers grafted onto solid bead supports may be easier to separate by conventional filtration.<sup>15,21</sup> (iv) Fluorous biphasic systems, in which a catalyst is rendered soluble in fluorinated hydrocarbons, usually by adding fluororous tails to known active and selective catalysts, whilst the substrate and products are dissolved in the organic phase.<sup>26-31</sup> The great advantage of this type of system over the aqueous biphasic approach is that, by careful choice of the fluororous and organic solvents, a single phase is formed at the operating temperature but phase separation occurs on cooling. We have recently shown that, by operating in the absence of organic solvent and using triaryl phosphines with fluororous ponytails, it is possible to obtain high linear selectivities at low catalyst loadings in hydroformylation reactions with >99.5% retention of rhodium into the fluororous phase.<sup>30,31</sup> (v) Aqueous biphasic systems with 'smart catalysts'. These use the same principles as the Rhône Poulenc/Ruhr Chemie process, but the catalysts are derivatised with polyether chains. These undergo changes in their hydrogen bonding patterns with temperature, so that the catalyst is soluble in the organic phase under the reaction conditions, but moves back into the aqueous phase on cooling. Since the reaction takes place in the organic solvent, the water solubility of the substrate is not an issue and yet its partitioning back into water allows its ready separation.<sup>32</sup>

One other approach to solving the problem of separating rhodium-based catalysts from the aldehydes formed by hydroformylation of long chain alkenes involves the use of supercritical fluids, such as scCO<sub>2</sub>.<sup>7,26,33-64</sup> Supercritical fluids (scf) have been known since early in the 19th century but have been only lately rediscovered as an alternative solvent for environmentally more acceptable chemical processes. They now find applications from extraction and chromatography in analytical chemistry to reaction chemistry and preparation of new materials. These fluids are gases heated above their critical temperature ( $T_c$ ) and pressurised above their critical pressure ( $P_c$ ). Their densities are comparable to those of organic liquids, which allows them to solubilise a wide range of organic substrates, and the gas-like nature of the fluids renders them completely miscible with permanent gases such as H<sub>2</sub>.

The absence of a gas-liquid phase boundary and the ability of supercritical fluids such as scCO<sub>2</sub> to support high concentrations of dissolved gases combined with facile product and catalyst separation make scCO<sub>2</sub> a competitive alternative to conventional solvents. Therefore the use of scCO<sub>2</sub> is becoming increasingly important as a reaction medium in metal-catalysed reactions<sup>65-69</sup> but has not yet provided industrial applications, although a pilot plant has now been constructed for continuous flow hydrogenation reactions using a heterogeneous catalyst and transferring the substrates and products using scCO<sub>2</sub> as the transport vector.<sup>70,71</sup>

The first catalytic applications of supercritical fluids as media for hydroformylation reactions involved unmodified cobalt catalysts.<sup>58,59</sup> Being non-polar and of relatively low molecular weight, they are readily soluble in scCO<sub>2</sub>. Most research in this area has, however, focussed on attempts to solubilise analogues of the successful rhodium/triphenylphosphine complexes in scCO<sub>2</sub>, since the parent compounds themselves show rather low

solubility and activity. Success has been achieved by a number of groups by attaching fluororous tails to the phenyl groups of the PPh<sub>3</sub> ligands. These ligands are analogous to those used for solubilising similar catalysts in fluororous solvents.<sup>26,27,41,50,51,56</sup>

Although the use of scCO<sub>2</sub> allows the ready separation of the solvent from the reaction products and catalysts, it does not easily address the real problem of separation of the products from the catalyst. Leitner and coworkers have proposed the use of temperature and pressure swings to achieve this separation,<sup>72</sup> but we<sup>35,44</sup> and others have realised that active catalysts that are *insoluble* in scCO<sub>2</sub> may have great advantages in terms of separation. Strategies that are being adopted include the use of insoluble coordination compounds,<sup>44</sup> the anchoring of ionic<sup>43,73</sup> or insoluble catalysts<sup>42,70</sup> to insoluble supports so that even if the catalysts break from the support, it will not be extracted into the supercritical phase, or immobilising the catalysts into an ionic liquid.<sup>35,74-76</sup> Both the supported catalysts<sup>43</sup> and those in the ionic liquids<sup>35</sup> have been used to demonstrate that hydroformylation of relatively long chain alkenes can be carried out in a continuous flow manner, with the catalyst-product separation being intrinsic to the process. Continuous operation for up to 3 days with minimal catalyst leaching has been achieved.<sup>35</sup>

The use of fluororous tails to render hydroformylation catalysts soluble in scCO<sub>2</sub> is effective, but the ligands can be difficult to prepare and are expensive. In addition, the high molecular weights of the ligands, and hence catalysts, means that relatively large amounts need to be used to obtain high reaction rates and linear selectivities. We have described the use of simple trialkylphosphine complexes in conventional solvents for hydroformylation reactions and have shown that they can show high activities.<sup>77-80</sup> In addition, in the presence of protic solvents, the chemoselectivity of the hydroformylation reactions can be changed so that alcohols rather than aldehydes become the only products.<sup>77</sup> Labelling studies have shown that the alcohols are not formed *via* the aldehydes, and studies on model complexes have shown that the key intermediates are hydroxycarbene complexes formed by protonation of acyl complexes as a result of the high electron density on the metal and hence acyl O atom and the availability of protons in solution.<sup>77</sup> Since these complexes show high solubility in hydrocarbons, we reasoned that they might also be soluble in scCO<sub>2</sub>, as is the case for, for example, PMe<sub>3</sub> ruthenium complexes, which have been successfully used for the hydrogenation of scCO<sub>2</sub>.<sup>57,81-84</sup> We now report details of the successful use of PET<sub>3</sub> as a solubiliser for rhodium-based hydroformylation catalysts in scCO<sub>2</sub>. Preliminary reports of some of these studies have appeared.<sup>54</sup>

## Experimental

Microanalyses were by the University of St. Andrews micro-analytical service. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AM 300 or a Varian 300 nmr spectrometer, with reference to tetramethylsilane (external). <sup>31</sup>P NMR spectra were referenced externally to 85% H<sub>3</sub>PO<sub>4</sub>. <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded with broad band proton decoupling. Infrared spectra were recorded using either a Perkin Elmer 1710 or a Nicolet 460 Protege FTIR spectrometer. Unless otherwise stated, analysis by gas chromatography (GC) was carried out using a Philips PU 4500 GC with a 25 m SGE BP1 column (100% dimethylsiloxane) and Chrompac software. The carrier gas was nitrogen (30 bar) and the temperature programme was 23 °C for 15 min. Gas chromatography-mass spectrometry (GCMS) analysis was carried out using helium as a carrier gas with a Hewlett-Packard 5890 GC fitted with an Incos 50 electric quadrupole mass spectrometer. A 25 m SGE BP1 column was used.

All manipulations were performed using standard Schlenk line and catheter tubing techniques under nitrogen purified by passing through a glass column containing Cr(II) adsorbed

onto silica. All solvents were freshly distilled and dried; petroleum ether (boiling range, 40–60 °C) and diethyl ether were distilled over sodium diphenylketyl, and dichloromethane and cyclohexane were distilled over calcium hydride. Ethanol and methanol were distilled over magnesium ethoxide and magnesium methoxide, respectively. Propanone was dried by refluxing over  $K_2CO_3$  for one hour.  $CD_3I$ , azoisobutyronitrile (AIBN), lithium iodide, anhydrous lithium iodide and sodium iodide (Aldrich); aqueous hydrogen chloride (11.6 mol  $dm^{-3}$ ), aqueous hydrogen bromide (8.8 mol  $dm^{-3}$ ) and aqueous hydrogen iodide (7.6 mol  $dm^{-3}$ ) (Fisons),  $[Rh_2(OAc)_4]$  (Alfa),  $PPh_3$ ,  $PEt_3$ ,  $POct_3$ , and  $PCy_3$ , (Strem) were used as supplied without further purification.  $P(4-C_6H_4SiMe_3)_3$ ,<sup>85</sup>  $P(4-C_6H_4CMe_3)_3$ ,<sup>86</sup> and  $Et_2P(CH_2)_5PEt_2$ ,<sup>87</sup> were prepared by standard literature methods. 4-Trimethylsilylbromobenzene was obtained by reaction of 4-bromophenylmagnesium bromide and chlorotrimethylsilane.<sup>88</sup>

### Diethyl(2-(tridecafluorohexyl)ethyl)phosphine

$Et_2PH$  (0.65  $cm^3$ , 7.8 mmol),  $C_6F_{13}CH=CH_2$  (2.0 g, 5.78 mmol) and AIBN (0.1 g) were dissolved in cyclohexane (10  $cm^3$ ) and heated at 80 °C for 8 h. The cyclohexane was removed *in vacuo* and the resulting oil found to be essentially pure by NMR.  $^1H$ :  $\delta$  0.86 dt ( $J_{HH} = 7.3$ ,  $J_{HP} = 14.6$  Hz), 6H,  $PCH_2CH_3$ ; 1.05 m, 4H  $PCH_2Me$ ; 1.41 second order multiplet, 2H,  $PCH_2CH_2C_6F_{13}$ ; 2.03 qm, 2H,  $PCH_2CH_2C_6F_{13}$ .  $^{19}F$ :  $\delta$  -82.1 t ( $J_{FF} = 9.9$  Hz); -115.9 q ( $J_{FF} = 13.9$  Hz); -123.1 m; -124.1 m; -124.38 m; -124.42 s, -127.4 q ( $J_{FF} = 7.9$  Hz).  $^{13}C$ :  $\delta$  9.7 d ( $J_{CP} = 13.1$  Hz),  $PCH_2CH_3$ ; 16.6 bd ( $J_{CP} = 18.0$  Hz),  $PCH_2CH_2C_6H_{13}$ ; 19.2 d ( $J_{CP} = 13.2$  Hz),  $PCH_2CH_3$ ; 28.6 dt ( $J_{CP} = 19.1$  Hz,  $J_{CF} = 22.81$  Hz),  $PCH_2CH_2C_6H_{13}$ . The  $CF_2$  and  $CF_3$  resonances are not observed as intense resonances in the  $\delta$  0–150 spectral range.

### 1,2-Bis(di-2-(tridecafluorohexyl)ethylphosphino)ethane

$H_2PCH_2CH_2PH_2$  (1 g, 2.1 mmol),  $C_6F_{13}CH=CH_2$  (4.5 g, 0.013 mol) and AIBN (0.1 g) were dissolved in cyclohexane (10  $cm^3$ ) and heated at 60 °C for 20 h. After cooling, a white solid precipitated and excess alkene and cyclohexane were removed *in vacuo*. The white solid was extracted with perfluoromethylcyclohexane (2  $\times$  10  $cm^3$ ). The resulting solution was filtered and evaporated to dryness to give the product as a white solid (yield 2.6 g, 85%). It was found to be essentially pure by NMR.  $^{31}P$ :  $\delta$  -24.1 s.  $^1H$ :  $\delta$  1.18 t ( $J_{PH} = 37.5$  Hz), 4 H,  $PCH_2CH_2P$ ; 1.38 dt ( $J_{PH} = 7$  Hz,  $J_{HF} = 7.5$  Hz), 8H,  $PCH_2CH_2C_6F_{13}$ ; 1.99 bm, 8H,  $PCH_2CH_2C_6F_{13}$ , apart from small amounts of cyclohexane ( $\delta$  1.26 s).

### Diphenyl(4-trimethylsilylphenyl)phosphine

To a solution of 4-trimethylsilylbromobenzene (1.74 g, 7.6 mmol) in  $Et_2O$  (40  $cm^3$ ) at -78 °C was slowly added n-butyllithium (7.6 mmol, 1.6 mol  $dm^{-3}$  in hexane). After slowly heating to room temperature, the resulting solution was cooled at -78 °C and then a solution of  $Ph_2PCl$  (1.68 g, 7.6 mmol) in  $Et_2O$  (10  $cm^3$ ) was added. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After addition of MeOH (1  $cm^3$ ) in order to eliminate unreacted  $^nBuLi$ , the mixture was filtered and the filtrate was concentrated. The resulting residue was extracted with petroleum ether, filtered under nitrogen and the solvent was removed from the filtrate to give a yellow oil, which was found to be pure by NMR spectroscopy, but its very high solubility in many solvents including hexane has precluded obtaining an analytically pure sample. Yield 1.87 g, 74%.  $^1H$  NMR (300 MHz,  $C_6D_6$ ):  $\delta$  7.64–7.16 (CH, Ph), 0.29 (s, 9,  $CH_3Si$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  141.1, 137.3, 133.9, 133.7 (s, Ph), 133.4 (d,  $J_{CP} = 24$  Hz, Ph), 132.8 (d,  $J_{CP} = 76$  Hz, Ph), 128.7, 128.5, 128.4 (s, Ph), -1.5 (s,  $CH_3Si$ ).  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  -4.95 (s). Found: C 74.09, H 7.44%.  $C_{27}H_{39}Si_3P$  requires: C 75.45, H 6.89%.

### Catalytic reactions in $scCO_2$

All catalytic reactions were carried out using a mechanically stirred Hastelloy autoclave (36 or 48  $cm^3$ ) fitted with a bursting disc, thermocouple, pressure transducer and gas inlet and outlet valves. The bottom of the autoclave was constructed from a sapphire window so that the reactions could be inspected visually. A typical procedure was as follows:  $[Rh_2(OAc)_4]$  (0.052 g, 0.118 mmol) was dissolved in  $PEt_3$  (0.1  $cm^3$ , 0.74 mmol) to give a red solution. Degassed 1-hexene (2  $cm^3$ , 16 mmol) was added and the mixture transferred to the autoclave, pressurised with CO and  $H_2$  and stirred at room temperature for 1 h. Liquid  $CO_2$  (18  $cm^3$ ) was then transferred to the autoclave using a cooled head hplc pump to give a total pressure of 65 bar above that of the  $CO/H_2$ . The autoclave was then heated to 100 °C for the desired reaction time, with the pressure and temperature being monitored throughout. The initial working pressure was typically 200 bar, although this dropped as gas was consumed. After the reaction, the autoclave was allowed to cool in dry ice to -50 °C. The  $CO_2$  was vented and the liquid product, typically 1.8  $cm^3$ , was collected and analysed by GC (quantitative analysis) and GCMS (identification of products).  $^{31}P$  NMR studies of the final liquid indicated that the major species in solution is  $[RhH(CO)_2(PEt_3)_2]$ .<sup>77</sup>

For reactions in toluene, the reaction was carried out in the 48  $cm^3$  autoclave using half the amounts of all the reagents in toluene (17  $cm^3$ ) and the same pressure of  $CO/H_2$  (40 bar, 1:1).  $ScCO_2$  was not used in this reaction.

### HPIR studies

A solution containing  $[Rh_2(OAc)_4]$  (0.051 g, 0.115 mmol),  $PEt_3$  (0.1  $cm^3$ , 0.74 mmol) and hexane (2  $cm^3$ ) was prepared. An aliquot of this solution (0.04  $cm^3$ ) was transferred into the IR cell, which had a volume of 0.7  $cm^3$ . It was pressurised with  $CO/H_2$  (1:1, 40 bar) and then  $CO_2$  was added (65 bar). The cell was heated in the IR spectrometer and spectra were recorded every 10 °C up to 100 °C. Variations in  $CO:H_2$  ratio were effected by adding more  $H_2$  and the Rh:P ratio was altered by adding more  $PEt_3$  before pressurising the reactor. Background spectra were taken at the same temperatures using all the components except the rhodium complex and  $PEt_3$ . These were subtracted from the experimental spectra of the complete system.

Alternatively, a solution was prepared in an autoclave exactly as for the catalytic reactions, but replacing 1-hexene by hexane, and was pumped using the hplc pump through an IR cell held in the spectrometer beam. This proved to be less satisfactory because the metal-containing compounds precipitated in the head of the hplc pump.

## Results and discussion

### Hydroformylation reactions of 1-hexene in $scCO_2$ using various phosphines

Various tertiary phosphines and phosphites were examined in the presence of  $[Rh_2(OAc)_4]$  for their activity and selectivity in hydroformylation reactions and the results are collected in Fig. 1. As expected,<sup>51</sup> using  $PPh_3$ , rather low conversions (6.7%, Koch and Leitner obtained 26% conversion after 20 h at 65 °C, but with a higher substrate:Rh ratio)<sup>51</sup> were obtained and visual inspection confirmed that a significant amount of material remained undissolved. Similar heterogeneous solutions were obtained using  $PCy_3$  or  $[Rh_2(OAc)_4]$  alone without added phosphine, although the conversions were somewhat higher (60 and 50% respectively). Using  $PEt_3$ , on the other hand, a clear homogeneous yellow-orange solution was obtained and the conversion reached 84% [82% aldehydes, 2.3% alcohols, linear:branched (l:b) ratio = 2.4] in 1 h. A comparison between the reaction in  $scCO_2$  and one in toluene under comparable conditions (Table 1) revealed that the conversion was less in

**Table 1** Yields of products from the hydroformylation of 1-hexene (1 cm<sup>3</sup>, 7.8 mmol)<sup>a</sup>

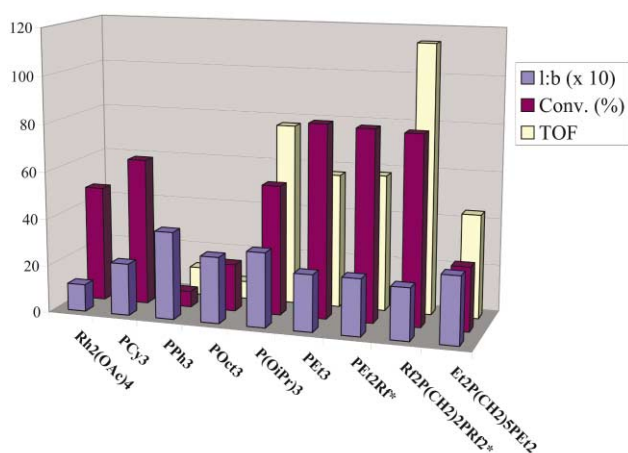
Solvent	[Rh]/mmol dm <sup>-3</sup>	Time/h	Aldehydes (%)	Alcohols (%)	TOF <sup>b</sup>	l:b <sup>c</sup>
Toluene <sup>d</sup>	6.58	1	74	4.8	53	2.1
scCO <sub>2</sub>	4.59	1	82	2.3	72	2.4
scCO <sub>2</sub>	4.60	2	89	8.1		2.5
scCO <sub>2</sub>	4.64	22	54	28		2.5
scCO <sub>2</sub> /EtOH <sup>e</sup>	4.59	1	60	3	56	2.4
scCO <sub>2</sub> /RfO <sup>e,f</sup>	4.54	1	82	11	62	2.5

<sup>a</sup> General reaction conditions: 100 °C, 230 bar, PEt<sub>3</sub>:Rh = 3,  $p_{\text{CO}} = p_{\text{H}_2} = 20$  bar at 293 K, autoclave volume = 48 cm<sup>3</sup>. <sup>b</sup> Average turnover frequency: mol of aldehyde formed (mol of catalyst)<sup>-1</sup> h<sup>-1</sup>. <sup>c</sup> Linear:branched aldehyde ratio. <sup>d</sup> 17 cm<sup>3</sup>, 1-hexene (0.5 cm<sup>3</sup>). <sup>e</sup> 2 cm<sup>3</sup>. <sup>f</sup> Rf = C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>.

**Table 2** Hydroformylation of 1-octene by Rh/PAr<sub>3</sub> in scCO<sub>2</sub><sup>a</sup>

Phosphine	P:Rh	$p_{\text{CO}_2}$ /bar	Time/h	Conversion (%) <sup>b</sup>	Aldehyde (%) <sup>c</sup>	l:b	TOF/h <sup>-1</sup>
PPh <sub>3</sub>	3.3	220	1	39.6	95	3.4	104
P(4-Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	3.3	220	1	82.4	97	4.0	221
P(4-Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	3.3	200	1	80	98	3.0	217
P(4-Me <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	3.3	220	1	1.8	68	2.7	3.4

<sup>a</sup> General reaction conditions: [Rh<sub>2</sub>(OAc)<sub>4</sub>] (20 mg, 0.046 mmol), 1-octene (2 cm<sup>3</sup>, 0.013 mol), 40 bar CO/H<sub>2</sub> (1:1), 100 °C, autoclave volume = 48 cm<sup>3</sup>. The products were analysed by GC. <sup>b</sup> Conversion of alkene. <sup>c</sup> Selectivity to aldehyde, remaining products are isomerised alkenes.



**Fig. 1** Yields of products, l:b ratio (× 10) and average Turnover Frequency (TOF) from the hydroformylation of 1-hexene in scCO<sub>2</sub> by catalysts derived from [Rh<sub>2</sub>(OAc)<sub>4</sub>] in the presence of various tertiary phosphines or phosphites. Rf = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>. Conditions as Experimental, but varying the phosphine.

toluene (74%) than in scCO<sub>2</sub> and the l:b ratio was also somewhat lower (2.1 *cf.* 2.4). These differences do not suggest any great rate enhancement in the scCO<sub>2</sub>. Such rate enhancements have been proposed as a potential advantage of using supercritical fluids for reactions involving gaseous reagents, because of the much greater solubility of the gases. However, the rate depends on the activity of the gas and this will be little different in the supercritical fluid from what it is in the gas or liquid states. The activities are identical for a gas in contact with a liquid under equilibrium conditions. We note that, for hydroformylation reactions, the order in  $p_{\text{CO}}$  is often negative so positive effects of increased [H<sub>2</sub>] would be moderated by negative effects of increased [CO]. In this particular system, however, we observe positive order in both gases (see below).

For reactions in scCO<sub>2</sub>, replacing one ethyl group of PEt<sub>3</sub> with CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub> made very little difference (yield = 81%, l:b = 2.4). The longer chain trioctylphosphine, however, afforded much lower conversions (20%, l:b = 2.8) and the reaction mixture contained a liquid as well as a gaseous/supercritical phase. IR studies, see later, suggest that very little of the rhodium complex was dissolved. This is somewhat surprising, as Smart *et al.* have studied the effect of alkyl chains on the solubility of a variety of phosphorus compounds in scCO<sub>2</sub> and concluded that solubility increases up to a carbon chain length of eight,

but then falls as the chain length is increased further.<sup>89</sup> This effect is mirrored in the hydroformylation activity in scCO<sub>2</sub> of triarylphosphines bearing alkyl chains, which increases up to a chain length of ten C atoms, but then dramatically decreases for compounds containing C<sub>16</sub> chains.<sup>26</sup> Some work on triarylphosphines containing trimethylsilyl groups has suggested that they may be capable of solubilising metal complexes in scCO<sub>2</sub>,<sup>90</sup> so we investigated P(4-C<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>3</sub> and Ph<sub>2</sub>P(4-C<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub>). These gave better activity (80 and 82.4%, l:b = 4.0 and 3.0, respectively) than PPh<sub>3</sub> (39.6%, l:b = 3.4) for the hydroformylation of 1-octene (Table 2), whereas P(4-C<sub>6</sub>H<sub>4</sub>CMe<sub>3</sub>)<sub>3</sub> gave a system that is almost inactive (1.8%, l:b = 2.7). Visual inspection (significant amounts of solid present in the reactor) and IR studies (very weak absorptions, see below) suggest that for the silylated phosphines, rather little is dissolved, so the activity may not simply arise because of increased solubility. We have shown that some complexes which are insoluble in scCO<sub>2</sub> can still give significant activity under similar conditions.<sup>44</sup>

We also examined some diphosphines (Fig. 1), and found significant activity in 1-hexene hydroformylation, although R<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub> (R = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>) (80% conversion) proved to be superior to Et<sub>2</sub>P(CH<sub>2</sub>)<sub>5</sub>PEt<sub>2</sub> (20%) in this case. Finally, we also investigated the use of triorganophosphites (Fig. 1). P(OPr<sup>i</sup>)<sub>3</sub> and its complex with rhodium were totally soluble in scCO<sub>2</sub> under these conditions and gave reasonable conversion (55%) and a rather better linear selectivity (l:b = 3.2) than most of the phosphines. Triarylphosphites gave very interesting results, with high yields and linear selectivities, despite their low solubility.<sup>44</sup> These results will be the subject of a separate report.

#### Alcohols as possible reaction products

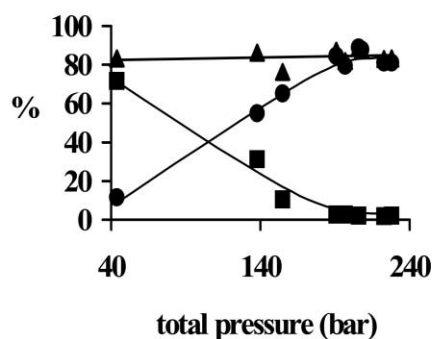
One possible advantage of using trialkylphosphine complexes is that alcohols may be products of hydroformylation reactions for rhodium-based catalysts.<sup>77–80</sup> In non-polar conventional solvents such as toluene, very little alcohol is produced even after extended reaction times, but in THF, complete conversion to alcohols is observed after 16 h at 120 °C, the reaction proceeding in this case *via* the aldehyde and sequential hydrogenation.<sup>77</sup> It can be seen from Table 1, that small amounts of C<sub>7</sub> alcohols are produced when the hydroformylation is carried out in toluene or scCO<sub>2</sub> and that the amount of alcohol product increases, clearly as a result of sequential hydrogenation of the C<sub>7</sub> aldehydes, as the reaction time in scCO<sub>2</sub> is prolonged. In protic solvents, alcohols are the only products of the hydroformylation reaction using PEt<sub>3</sub> as the ligand,<sup>77</sup> so we attempted

to increase the yield of alcohol by adding alcohols to the  $\text{scCO}_2$ . Although this was unsuccessful using ethanol, the fluorinated alcohol  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH}$  increased the yield of alcohols significantly (11%) after 1 h, despite the molar amount added being lower than for ethanol.

### Influence of reaction parameters on the reaction rate and product selectivity

(i) **CO<sub>2</sub> pressure.** Changes of the CO<sub>2</sub> pressure are sometimes responsible for changes in reactivity partly as a result of the variation of the density of the medium, so we carried out a series of experiments using  $\text{PEt}_3$  as the ligand and 1-hexene as the substrate but modifying the total pressure by varying the CO<sub>2</sub> loading and keeping all other parameters identical. When no CO<sub>2</sub> was present, *i.e.* the reaction was carried out in neat 1-hexene, the alkene conversion was high and C<sub>7</sub> alcohols were the major products. This is somewhat surprising since studies in toluene have shown that the same catalyst system gives aldehydes almost exclusively as the products, although sequential hydrogenation occurs in more polar aprotic solvents such as THF.<sup>77</sup> The different behaviour observed in this study probably arises because of the very high concentration of catalyst in the 1-hexene compared with that used in the studies carried out in toluene. For the studies in 1-hexene/ $\text{scCO}_2$ , the catalyst concentration was chosen to be similar to that used in the toluene studies if the catalyst were dissolved in the supercritical solution and distributed throughout the reactor (*i.e.* if the reaction volume were 36 cm<sup>3</sup>). For the reaction in the absence of CO<sub>2</sub>, the solution volume was 1 cm<sup>3</sup>, so that the catalyst concentration was 36× that used in our previous studies. Reactions in ethanol have been shown to give aldehydes at low catalyst concentrations, but alcohols at higher catalyst loading. The change in chemoselectivity occurs at much lower concentrations than those used in this study, but the reaction mechanism is also very different.<sup>77</sup>

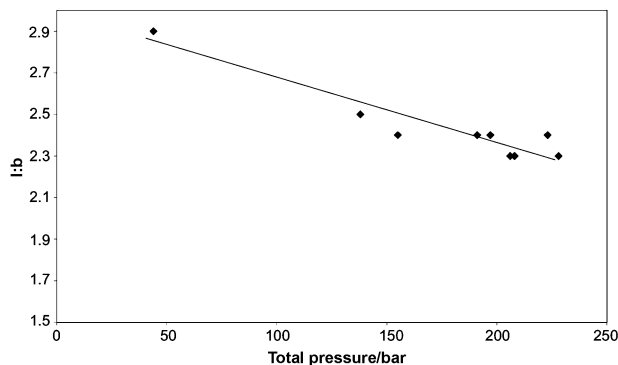
At all pressures of CO<sub>2</sub> between 50 bar (reaction in neat alkene) and 190 bar (at 100 °C), two phases were permanently present due to the poor solvating properties of the low pressure CO<sub>2</sub> phase. Observation through the sapphire window clearly showed a coloured liquid phase, which seemed to retain most of the catalyst. Under these conditions, alcohols were present in large amounts in the reaction products especially at low total pressure (see Fig. 2). Between 190 and 200 bar, a homogeneous



**Fig. 2** Chemoselectivity as a function of the total pressure in the hydroformylation of 1-hexene (1 cm<sup>3</sup>, 7.8 mmol) in CO<sub>2</sub> catalysed by Rh/ $\text{PEt}_3$  complexes. 100 °C,  $[\text{Rh}_2(\text{OAc})_4]$  (30 mg, 0.066 mmol),  $\text{PEt}_3$ :Rh = 3,  $p_{\text{CO}} = p_{\text{H}_2} = 20$  bar at 293 K, autoclave volume = 36 cm<sup>3</sup>.

mixture was obtained at 100 °C, but precipitation of the organic products occurred during the reaction, indicating the lower solubility in CO<sub>2</sub> of the aldehyde products than of 1-hexene. Under these near critical conditions, the amount of alcohols produced decreased dramatically. When enough CO<sub>2</sub> was introduced to maintain a fully homogeneous mixture throughout the reaction, alcohols made up only a very small proportion of the

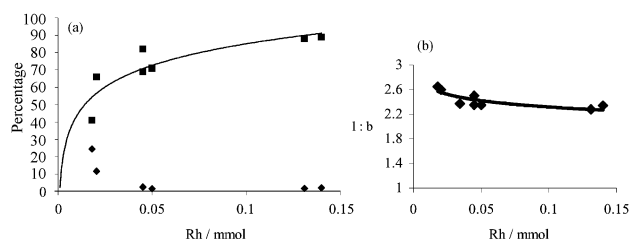
product mixture. Further increases of the CO<sub>2</sub> density had no effect on the selectivity. It is noteworthy that the conversion of 1-hexene after one hour was essentially independent of the total pressure (amount of CO<sub>2</sub> added) whilst the l:b ratio dropped slightly as the pressure was increased (Fig. 3)



**Fig. 3** l:b ratio as a function of the total pressure in the hydroformylation of 1-hexene in CO<sub>2</sub> catalysed by Rh/ $\text{PEt}_3$  complexes. Conditions as Fig. 2.

In a recent publication, one of us has reported the phase behaviour of the quaternary system (the 1-hexene, CO, H<sub>2</sub> and CO<sub>2</sub> system has been examined), with the critical points being determined using acoustic measurements.<sup>91</sup> These studies were carried out with 1-hexene:H<sub>2</sub>:CO ratios close to 1:1:1, whilst in the catalytic studies the ratio is 1:3:3. The critical point measurements all show that  $T_c$  is well below 100 °C,<sup>91</sup> so our measurements were taken well above  $T_c$ . Our reactions were carried out using a molar fraction of 1-hexene of 0.018. At this concentration, the measured values of  $p_c$  are all 80–120 bar.<sup>91</sup> However, it is expected that the critical pressure will increase as more CO/H<sub>2</sub> is added as the mixture of permanent gases effectively acts as an antisolvent and reduces the solubility of 1-hexene in CO<sub>2</sub>. Unfortunately, the very different relative concentrations used in the catalytic study compared with those used in the acoustic measurements do not allow for a more quantitative comparison. The lower solubility of the aldehyde in CO<sub>2</sub> than of the alkene accounts for the higher critical pressure of the system at the end of the reaction. Increases in  $p_c$  when aldehyde replaces alkene have been demonstrated in the system corresponding to propene hydroformylation, by measurements of the critical points of the mixture of CO<sub>2</sub>, CO, H<sub>2</sub> containing varying amounts of propene and butanal, but with the total molar fraction of the organic compounds being kept constant.<sup>92</sup>

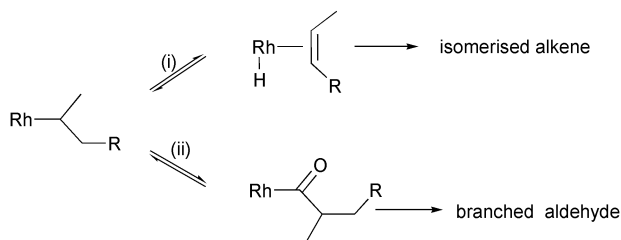
(ii) **Rhodium concentration.** By carrying out a series of reactions using different amounts of rhodium, a positive order with respect to rhodium was observed, although this tended towards saturation at higher [rhodium] [Fig. 4(a)]. It should be noted, however, that the L:Rh ratio was kept constant during this series of reactions so [L] is varying along with [Rh]. The reaction is inhibited by excess  $\text{PEt}_3$  (see below), which presu-



**Fig. 4** (a) Yields of aldehyde (■) and isomerised hexenes (◆), and (b) l:b ratio as a function of [rhodium] in the hydroformylation of 1-hexene (1 cm<sup>3</sup>, 7.8 mmol) catalysed by Rh/ $\text{PEt}_3$  (1:3) complexes in  $\text{scCO}_2$ . 100 °C, 230 bar, CO:H<sub>2</sub> (1:1, 40 bar at 25 °C), 1 h, autoclave volume = 36 cm<sup>3</sup>.



ably accounts for the less than first order behaviour observed. In all these experiments, the amount of alcohols formed was low with a maximum of 2% obtained at higher conversion. More significantly, up to 24.4% of alkene isomerisation/hydrogenation products were detected at low rhodium concentration (0.025 mmol, 0.69 mmol dm<sup>-3</sup>) (see ESI†). This side reaction is, however, strongly inhibited by just doubling the rhodium loading. There is a small decrease in the l:b ratio with increased rhodium (and phosphine) loading [Fig. 4(b)]. In part this may reflect the lack of formation of internal alkenes. Internal alkenes arise from the branched alkyl intermediate, which also gives rise to the branched aldehyde product. (Fig. 5)



**Fig. 5** Formation of isomerised alkene or branched aldehyde from the branched alkyl intermediate: (i) β-H abstraction; (ii) reaction with CO.

If the ratio of linear:branched alkyl intermediate remains constant, a decrease in isomerised alkene must be reflected in an increase in branched aldehyde. One possible reason for the formation of isomerised alkenes at low [rhodium] is that the formation of internal alkenes from the branched alkyl intermediate occurs by β-H abstraction in the branched alkyl intermediate, whilst the reaction to form the branched aldehyde occurs by reaction of the same intermediate with CO. Once the branched intermediate is formed, the rate of β-H abstraction, being unimolecular, will be independent on the rhodium concentration, whilst the reaction with CO, being bimolecular, will be slowed at lower [rhodium]. This explanation is not, however, sufficient to explain the very high amounts of isomerisation at very low catalyst loading. This probably arises because of the presence of significant amounts of rhodium complex containing no PEt<sub>3</sub>, which are known to produce significant amounts of isomerisation. (We note that the concentration of PEt<sub>3</sub> was also reduced, although the Rh:P ratio was held constant.)

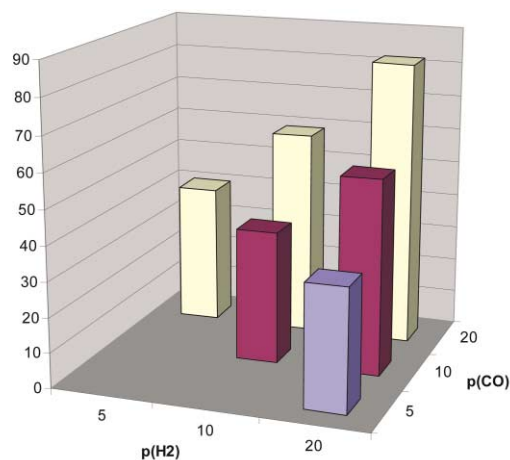
**(iii) Phosphine concentration.** The addition of excess PEt<sub>3</sub> (PEt<sub>3</sub>:Rh = 9 instead of 3) considerably retards both hydroformylation (yield 5.5%, *cf.* 50%) and hydrogenation/isomerisation (0%, *cf.* 12%). This is as expected, as excess PEt<sub>3</sub> will inhibit the loss of PEt<sub>3</sub> from [RhH(CO)(PEt<sub>3</sub>)<sub>3</sub>], and hence less rhodium will be in a catalytically active state. More surprisingly, addition of excess PEt<sub>3</sub> reduces the l:b ratio (from 2.6 to 1.9). This may be because these studies were carried out at low rhodium loading (0.02 mmol) when the lower PEt<sub>3</sub> concentration gives significant amounts of isomerised alkenes (see above and Fig. 4). No isomerised alkene was observed at the higher concentration of PEt<sub>3</sub> so that the branched alkyl must all proceed to the branched aldehyde and give a reduced l:b ratio. Under these conditions, all of the catalyst is likely to be coordinated to PEt<sub>3</sub>, thus reducing the tendency to promote isomerisation.

#### Effect of CO/H<sub>2</sub> pressure

A positive order is observed on both  $p_{\text{CO}}$  and  $p_{\text{H}_2}$  (Fig. 6). For hydrogen, this is as expected because less of the rhodium is tied up as the inactive dimer [Rh<sub>2</sub>(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>6</sub>] and more is in a catalytically active state at the higher  $p_{\text{H}_2}$ . For CO, various orders have been observed in other systems.<sup>2</sup> Often, there is a negative rate dependence on  $p_{\text{CO}}$ , because CO blocks active sites and inhibits the coordination of alkene, thus removing rhodium from its catalytically active forms. When a positive order is

**Table 3** l:b ratio as a function of  $p_{\text{H}_2}$  and  $p_{\text{CO}}$  on yields of aldehyde from the hydroformylation of 1-hexene in scCO<sub>2</sub> catalysed by Rh/PEt<sub>3</sub> complexes, conditions as Fig. 6

$p_{\text{H}_2}$ /bar	$p_{\text{CO}}$ /bar	l:b
5	20	2.3
10	20	2.3
20	20	2.4
20	10	2.4
20	5	2.6
10	10	2.5

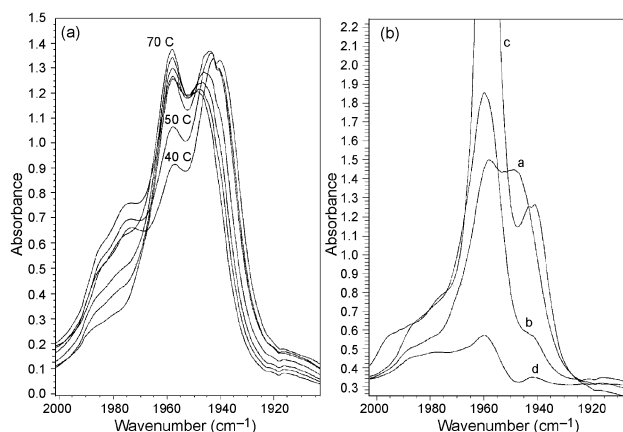


**Fig. 6** Influence of  $p_{\text{H}_2}$  and  $p_{\text{CO}}$  on yields of aldehyde from the hydroformylation of 1-hexene (2 cm<sup>3</sup>, 0.016 mol) in scCO<sub>2</sub> catalysed by Rh/PEt<sub>3</sub> complexes. Conditions as Experimental, autoclave volume = 48 cm<sup>3</sup>.

observed, this indicates that CO coordination to the alkyl intermediate is rate determining and dominates any effect of site blocking by CO. As in these studies, this dependence usually occurs when the partial pressure of CO is low. It may also be the case that CO<sub>2</sub>, which is present in a very high concentration, can also act as a blocking ligand. Since IR studies (see below) do not suggest coordination of CO<sub>2</sub>, we do not favour this explanation. The l:b ratio is not much affected by the change in partial pressure (Table 3), although there is a small increase at higher  $p_{\text{H}_2}$ .

#### High-pressure infrared spectroscopy of the Rh/PEt<sub>3</sub> system

In order to determine whether or not the catalysts were soluble in scCO<sub>2</sub> and to attempt to identify the species present in solution during the catalytic reactions, we have carried out high-pressure IR studies of the [Rh<sub>2</sub>(OAc)<sub>4</sub>]/PEt<sub>3</sub> system in scCO<sub>2</sub> under the conditions used for the hydroformylation reactions but in the absence of 1-hexene. Hexane was added instead to minimise any differences in medium polarity. After the catalyst precursor, free ligand, gases and liquid CO<sub>2</sub> had been charged, the cell (see Experimental section for details) was heated and spectra recorded every 10 °C. During heating, absorptions were observed between 1600 and 1700 cm<sup>-1</sup> as well as between 2100 and 1900 cm<sup>-1</sup>. Two strong CO stretching vibrations appeared at 1723 and 1775 cm<sup>-1</sup>. The peak at 1723 cm<sup>-1</sup> reached a maximum at 60 °C and disappeared on further heating whilst the peak at 1775 cm<sup>-1</sup> continued to grow until 80 °C, when it became stable. Since this peak is also present in scCO<sub>2</sub> systems where the complex is insoluble ([Rh<sub>2</sub>(OAc)<sub>4</sub>]/POct<sub>3</sub>), we assign it to ethanoic acid derived from the catalyst precursor. Matrix isolated monomeric ethanoic acid has  $\nu_{\text{C=O}}$  at 1780 cm<sup>-1</sup>.<sup>93</sup> More significant changes were recorded in the 2100–1900 cm<sup>-1</sup> spectral window [Fig. 7(a)] as various rhodium-carbonyl species were formed and further investigations were carried out to analyse the effect of an increase of the H<sub>2</sub>:CO ratio, from 1:1 to 3:1 at constant pressure [Fig. 7(b), spectrum b], the effect of

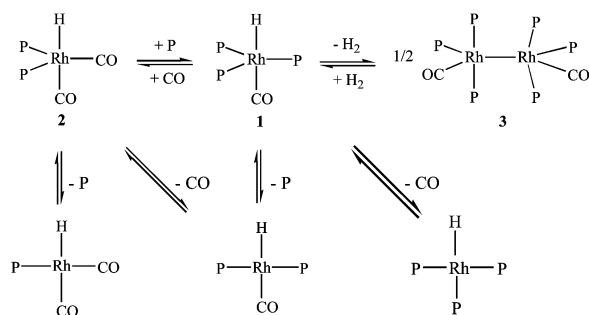


**Fig. 7** HPIR studies of complexes prepared from  $[\text{Rh}_2(\text{OAc})_4]$  and  $\text{PEt}_3$  in  $\text{CO}_2$  containing hexane. (a) Conditions as in Experimental, spectra recorded at various temperatures. (b) Spectrum a as Fig 7(a) at  $100^\circ\text{C}$ ; spectrum b as spectrum a but  $p_{\text{CO}} = 10$  bar and  $p_{\text{H}_2} = 30$  bar; spectrum c as spectrum a but  $\text{PEt}_3:\text{Rh} = 6$ ; spectrum d as spectrum a, but the  $[\text{Rh}]$  and  $[\text{PEt}_3]$  were  $0.25 \times$  those used for spectrum a.

an increase of the ligand concentration, L:Rh = 6 instead of 3 [Fig. 7(b), spectrum c], and of a reduced concentration of rhodium (Rh:P = 1:3) [Fig. 7(b), spectrum d], on the various rhodium species present.

At low temperature, with a Rh:P ratio of 1:3, two major peaks were observed at  $1942$  and  $1958\text{ cm}^{-1}$  together with two shoulders at  $1973$  and  $1982\text{ cm}^{-1}$ . On heating, the peak at  $1958\text{ cm}^{-1}$  increased together with the two shoulders at  $1973$  and  $1982\text{ cm}^{-1}$ , at the expense of the peak at  $1942\text{ cm}^{-1}$ , which nevertheless did not disappear. On addition of excess  $\text{PEt}_3$  [Fig. 7(b), spectrum c], the peak at  $1958\text{ cm}^{-1}$  was greatly increased in intensity relative to all the other peaks, although they remained visible. Addition of excess  $\text{H}_2$  [reduced  $p_{\text{CO}}$ , Fig. 7(b), spectrum b] led to a spectrum in which the major peak was at  $1958\text{ cm}^{-1}$ , the two shoulders at  $1973$  and  $1982\text{ cm}^{-1}$  were significant and the peak at  $1942\text{ cm}^{-1}$  had almost disappeared. The spectrum taken at  $100^\circ\text{C}$  but with reduced  $[\text{Rh}]$  and  $[\text{PEt}_3]$  [Fig. 7(b), spectrum d] was very similar to that at the higher concentration [Fig. 7(b), spectrum a], except that all the peaks were much reduced in intensity and the shoulders at  $1973$  and  $1982\text{ cm}^{-1}$  were more pronounced. A spectrum taken in toluene under conditions analogous to those of spectrum c of Fig. 7(b) is very similar to that obtained in  $\text{scCO}_2$  with absorptions at  $1927$ ,  $1958$  and  $1974\text{ cm}^{-1}$ .

We have previously shown<sup>77</sup> that three species (Scheme 2) predominate in toluene under similar conditions,  $[\text{RhH}(\text{CO})(\text{PEt}_3)_3]$  (lit.  $\nu_{\text{CO}} 1964$ ,<sup>77</sup>  $1952$ ,<sup>94</sup>  $\nu_{\text{RhH}} 1884$ ,<sup>77</sup>  $1880$ ,<sup>94</sup>),  $[\text{RhH}(\text{CO})_2(\text{PEt}_3)_2]$  and a species believed to be  $[\text{Rh}_2(\text{CO})_2(\text{PEt}_3)_6]$  (lit.  $\nu_{\text{CO}} 1962$ );<sup>77</sup> so the various peaks can probably be assigned to varying amounts of these species. However, there is significant overlap between the IR spectra of these species and the peaks in the HPIR spectra are very broad, so absolute assignments are difficult. What the studies do show is that rhodium/ $\text{PEt}_3$



**Scheme 2** Intermediates and their conversion to active species in the reaction.

complexes are soluble in  $\text{scCO}_2$  and that addition of excess  $\text{PEt}_3$  or of  $\text{H}_2$  allows species with  $\nu_{\text{CO}}$  at  $1958\text{ cm}^{-1}$  to predominate. With the excess  $\text{H}_2$  it is reasonable to assume that this peak arises for one or both of the hydrides, whereas with excess  $\text{PEt}_3$  it is presumably species with three  $\text{PEt}_3$  groups on Rh that are formed.  $^{31}\text{P}$  NMR studies of a product from a catalytic solution obtained after cooling and decompression showed the presence of  $\text{Et}_3\text{PO}$  and  $[\text{RhH}(\text{CO})_2(\text{PEt}_3)_2]$  ( $\delta 24.5$ ,  $J_{\text{PRh}} = 124\text{ Hz}$ ; lit.  $\delta 23.2$ ,  $J_{\text{PRh}} = 117\text{ Hz}$ <sup>77</sup>).

HPIR studies under similar conditions in  $\text{scCO}_2$  but using trioctylphosphine in place of triethylphosphine showed almost no absorption in the metal carbonyl region, apart from the peak at  $1775\text{ cm}^{-1}$ , previously assigned to ethanoic acid, indicating that the trioctylphosphine complexes are essentially insoluble in  $\text{scCO}_2$ . We assume that this accounts for their low reactivity in the hydroformylation reactions. Other studies have shown that as the length of the alkyl chains is increased, the solubility of compounds containing them passes through a maximum and then decreases because of the high molar volume of the chain.<sup>89</sup> With triphenylphosphine, there are peaks in the aromatic  $\nu_{\text{CH}}$  region ( $3060\text{--}3070\text{ cm}^{-1}$ ) when just  $\text{PPh}_3$  is present indicating that  $\text{PPh}_3$  is soluble in  $\text{scCO}_2$  to some extent, but these are unchanged when rhodium is present and only very weak peaks are observed in the  $\nu_{\text{CO}}$  region, showing that the rhodium/ $\text{PPh}_3$  complex has very low solubility in  $\text{scCO}_2$ . The situation is similar for  $\text{P}(4\text{-C}_6\text{H}_4\text{SiMe}_3)_3$ , although an extra peak in the  $\nu_{\text{CH}}$  region ( $2948\text{ cm}^{-1}$ ) and a slightly more significant peak at  $1950\text{ cm}^{-1}$  suggest that there may be some solubility for the rhodium complex in this case.

## Conclusions

Triethylphosphine provides an inexpensive method for rendering rhodium complexes soluble in  $\text{scCO}_2$ , and allowing hydroformylation of alkenes to be carried out. Below the critical point of the mixture alcohols are significant products, but above the critical point aldehydes are exclusively formed. The changes in the relative amounts of alcohol and aldehyde products with pressure and phase behaviour suggest that aldehydes are formed exclusively in the supercritical phase but that further hydrogenation occurs in the liquid phase if it is present. IR studies suggest that the complexes present during the reactions are similar to those present during liquid phase hydroformylation. Rhodium complexes of longer chain alkylphosphines are effectively insoluble in  $\text{scCO}_2$  and show little hydroformylation as are those of  $\text{P}(4\text{-C}_6\text{H}_4\text{Bu}^t)_3$ . Using  $\text{P}(4\text{-C}_6\text{H}_4\text{SiMe}_3)_3$  as a ligand, on the other hand, does impart some hydroformylation activity to rhodium complexes in  $\text{scCO}_2$ .

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