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Hydroformylation reactions in supercritical carbon dioxide using insoluble metal complexes

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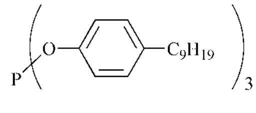
$P(OPh)_3$, $P(OC_6H_4$-4-$C_9H_{19})_3$ (1) and $Ph_2PCH_2CH(CO_2C_{16}H_{33})CH_2CO_2C_{16}H_{33}$ (2) provide rhodium catalysts which are insoluble in $scCO_2$ but which can show high activity and selectivity in the hydroformylation of hex-1-ene; removing the products from the reaction by flushing them into a second autoclave and decompressing gives the aldehyde product containing undetectable amounts of rhodium and the catalyst can be reused several times.

Supercritical fluids, especially CO_2, are finding increasing use in homogeneous catalysis because they are environmentally friendly and because their total miscibility with permanent gases (*e.g.* H_2 or CO) removes problems associated with interfacial gas transport.[1] In some cases enhanced selectivity compared with that obtained in conventional solvents can be obtained[2,3] and the separation of the catalyst and the products from the solvent can be easily achieved by decompression. However, the real problem for homogeneous systems, that of the separation of the products from the catalyst remains problematic. Leitner and co-workers have introduced a process involving changes in temperature and/or pressure, which leads to selective precipitation of the catalyst,[4,5] but it would be desirable to identify systems where the separation occurs under the reaction conditions, so that they could be adapted for use in flow systems. One such system has been reported for a hydrogenation reaction; the catalyst precipitates once all the hydrogen has been consumed.[6] Another approach has been to use supported catalysts[7–10] and to flow the reagents dissolved in $scCO_2$ over the catalyst bed,[7–9] or to remove the products by flushing with $scCO_2$ at the reaction temperature and pressure.[10] High throughput of the substrate is possible and leaching is minimal.

We now report an alternative approach to the hydroformylation of long chain alkenes using rhodium catalysts. Currently, these types of reaction are carried out using cobalt based catalysts, which require high temperatures and pressures, give poor selectivities to the desired linear aldehyde product and have a complicated catalyst recycle.[11] We have found that rhodium complexes prepared *in situ* from $[Rh_2(OAc)_4]$ and $P(OPh)_3$, **1** or **2**, which are insoluble in $scCO_2$, give good activity and, for the phosphites, excellent linear selectivity. Furthermore, the products can be flushed away from the catalyst using $scCO_2$ at the reaction temperature and pressure with no rhodium leaching.



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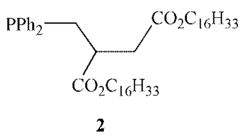

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Using hex-1-ene as a model substrate, the reactions are carried out in a stirred autoclave, the bottom of which consists of a sapphire window so that the reaction can be observed while it is progressing. Catalysts prepared from $[Rh_2(OAc)_4]$ and $P(OPh)_3$, phosphite **1**, or phosphine **2** appear as a liquid drop on the window of the reactor, whilst the rest of the reaction mixture is a single phase under the conditions that we have used. Comparing the reaction in toluene using **1** and $scCO_2$ under similar conditions, the yield is reduced in $scCO_2$ but the ratio of linear to branched aldehyde (l:b ratio) is increased. The results in toluene are similar to those reported by others for ligand **1**.[12] Rhodium complexes of all three ligands give good conversions; **1** and $P(OPh)_3$ give good selectivites to the desired straight chain product.

The activity and selectivity of the catalysts are influenced by a variety of parameters. For example, as with conventional solvents,[13] the l:b ratio increases with increasing overall ligand concentration (Entries 3,4,5 and 8,9 Table 1); but perhaps the most dramatic is that of $H_2:CO$ ratio. As the H_2 pressure is increased while keeping the total pressure of CO + H_2 constant, the yield of aldehyde drops slightly, there is a small increase in the amount of isomerised and hydrogenated hexene produced, but the l:b ratio increases to as high as 26:1 at an $H_2:CO$ ratio of 7.5:1 (see Fig. 1 for the $P(OPh)_3$ based catalyst). Similar high selectivities have been obtained in benzene using $[Rh(acac)(P(OPh)_3)_2]$ as a catalyst precursor, but only under very much lower temperatures and pressures of H_2/CO[14] or in the presence of large excesses of $P(OPh)_3$.[13] Under these conditions, the reactions are generally very slow and isomerisation (14–80%) is highly significant or even dominant.[14] Increasing the $H_2:CO$ ratio has been shown to increase the l:b ratio, but the maximum observed in that study was 9:1.[13] In benzene the species present at the end of the reaction are $[RhH(CO)(P(OPh)_3)_3]$ and $[RhH(P(OPh)_3)_4]$; we also observe these two complexes by ^{31}P NMR spectroscopy as the predominant species at the end of the catalytic runs in $scCO_2$. We have also investigated these systems for the hydroformylation of non-1-ene as a representative long chain alkene. Once again high selectivites to the linear aldehyde are obtained and conversions are high using either **1** or $P(OPh)_3$ (Table 2).

Since these catalysts appear to be insoluble in the $scCO_2$, we attempted to separate the products from the catalyst by flushing with $scCO_2$. After carrying out a reaction using **1** and $[Rh_2(OAc)_4]$ for 2 h, the stirrer was stopped and pure supercritical CO_2 at the reaction temperature and pressure was passed into the bottom of the reactor, passing the solution of products still in the supercritical phase into a cooled second reactor where it was decompressed. The products were collected and analysed for their rhodium content and for their organic composition. Once all the products had been removed from the reactor, it was depressurised, recharged with fresh alkene, CO, H_2 and CO_2 and the process repeated. The results of these experiments are collected for hex-1-ene in Table 2 (A1–5). Rhodium was not detectable in the recovered products (<0.01% of Rh charged) and the catalyst continued to show good activity with the l:b ratio remaining high. Although the activity remained similar, there was a drop off in l:b ratio in the later runs (A4, A5) and this, together with the appearance of the phenol in the gc of the products, but with no observable

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Table 1 Hydroformylation of hex-1-ene (1 h at 100 °C, $p_{CO} = p_{H_2} = 20$ bar at 290 K) catalysed by rhodium complexes

No.	Autoclave volume/cm^3	Solvent	Ligand (L)	Rh/ mmol	L:Rh	Hex-1-ene/ cm^3	p at T/bar	Yield (%)	l:b	Isomerisation (%)	TOF[c]
1	49	toluene	**1**	0.103	3	1	42	63	1.4[a]	5.6	49
2	49	scCO$_2$	**1**	0.206	3	2	246	38.1	3.4	5.1	30
3	36	scCO$_2$	**1**	0.145	3	1	198	52.4	5.5[b]	8.5	30
4	36	scCO$_2$	**1**	0.052	3	1	196	40.7	3.5[b]	7.8	63
5	36	scCO$_2$	**1**	0.052	9	1	224	16.5	5.1	1.5	25
6	36	scCO$_2$	P(OPh)$_3$	0.145	3	1	205	57	6.8	8.6	32
7	36	scCO$_2$	P(OPh)$_3$	0.049	3	1	224	53.5	6.5	5.9	95
8	36	scCO$_2$	P(OPh)$_3$	0.045	9	1	216	38	9.2	4.5	68
9	36	scCO$_2$	P(OPh)$_3$	0.048	13.7	1	218	47.1	10.2	3.7	81
10	36	scCO$_2$	**2**	0.127	3	1	195	62	2.8	2.6	39
11	36	scCO$_2$	**2**	0.042	4	1	195	61.1	2.6	2.6	116

[a] Includes 2-ethylpentanal (5.7%). [b] Includes 2-ethylpentanal (0.5%). [c] Turnover frequency/mol product (mol catalyst)$^{-1}$ h^{-1}.

Table 2 Hydroformylation in scCO$_2$, with supercritical product separation catalysed by insoluble rhodium complexes

Run no.	Substrate	Ligand	Yield of aldehyde (%)	l:b	Isomerisation (%)	Rh leached (%)[b]
A1[a]	hex-1-ene	**1**	83.6	5.6	3.3	n/d
A2	hex-1-ene	**1**	31.2	5.9	30.8	n/m
A3[c]	hex-1-ene	**1**	72.1	6.5	n/d	n/m
A4	hex-1-ene	**1**	83.9	5.1	3.2	n/d
A5	hex-1-ene	**1**	76.8	3.3	2.3	n/d
B1[d]	non-1-ene	P(OPh)$_3$	80.7	8.0	10.6	n/d
B2[d]	non-1-ene	P(OPh)$_3$	33.6	4.5	12.2	n/d
B3[d]	non-1-ene	P(OPh)$_3$	5.0	3.2	4.7	n/d
C1[e]	non-1-ene	**1**	85.2	5.5	12.9	n/d
C2[e]	non-1-ene	**1**	83	4.6	15.6	n/d
C3[e]	non-1-ene	**1**	69.0	2.6	26.2	0.02
C4[e]	non-1-ene	**1**	42.4	2.5	11.3	n/d

[a] [Rh$_2$(OAc)$_4$] (0.022 g, 0.1 mmol Rh), **1** (0.7 g, 1.0 mmol), hex-1-ene (2 cm^3), CO/H$_2$ (1 : 1, 40 bar), T = 100 °C, t = 2 h, p_{tot} = 220 bar, products removed by flushing into a second autoclave with more scCO$_2$. A2–A5 were carried out using the same batch of catalyst, recharging with hex-1-ene. [b] n/m Not measured, n/d not detected [detection limit (hexene) = 0.2 ppm = 0.01% of rhodium charged, (nonene) = 0.05 ppm, 0.02% of Rh charged]. [c] t = 5 h. [d] As footnote *a* but using non-1-ene (2 cm^3), [Rh$_2$(OAc)$_4$] (0.01 g, 0.045 mmol Rh), P(OPh)$_3$ (0.2 g, 0.7 mmol), t = 1 h. [e] As footnote *a* but using non-1-ene (2 cm^3), [Rh$_2$(OAc)$_4$] (0.01 g, 0.045 mmol Rh), **1** (0.5 g, 0.8 mmol), t = 1 h.

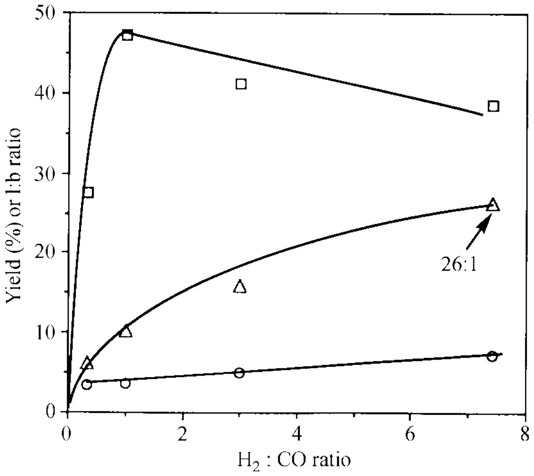

Fig. 1 Effect of CO : H$_2$ ratio on the products obtained from hydroformylation of hex-1-ene (1 cm^3) catalysed by Rh/P(OPh)$_3$ in scCO$_2$ ([Rh$_2$(OAc)$_4$] 0.045 mmol, P(OPh)$_3$ 0.65 mmol, 100 °C, $p_{CO} + p_{H_2}$ 40 bar at 293 K, total p at 100 °C 220–240 bar, 1 h). (□) Conversion to aldehyde; (○) isomerisation of alkene; (Δ) l : b ratio.

^{31}P NMR resonances in the product solution, shows that the phosphite is being slowly hydrolysed during the reaction. Using non-1-ene and a catalyst derived from P(OPh)$_3$, this problem is more severe; the catalyst turns black during the second pressurisation with CO and little activity is observed thereafter (Table 2, B1–3). With ligand **1** and non-1-ene, the situation is improved, with three successive reactions being successfully carried out. The catalyst turns black during the third run and the activity drops thereafter (Table 2, C1–4). Another advantage of this kind of reaction, where no organic solvent is used, is apparent because, on standing the products from experiments B1, B2, C1 and C2 at room temperature, decanal hydrate crystallises and can be separated from the other products by filtration, thus confirming the easy separation of the desired product not only from the catalyst, but also from the solvent (scCO$_2$) and side products.

A possible explanation of the way the reaction occurs in the two phase system is that the excess ligand, which dissolves the rhodium complex, acts as a solvent in which the catalytic reaction takes place and the scCO$_2$ acts as a vector for transporting the reagents into, and the products out of, the liquid phase. The reaction could be also occurring at the phase boundary between the supercritical fluid and the insoluble catalytic phase, in a manner similar to that which has been observed when using solid phase transfer catalysts for halide exchange or cyanation reactions in scCO$_2$.[15,16]

We conclude that these systems provide a method for the hydroformylation of alkenes which show high activity and selectivity (much higher selectivity towards the straight chain product than under comparable conditions in conventional organic solvents), but especially that they provide a facile method for the separation of the reaction products from the catalyst and from the solvent. The decanal produced is sufficiently pure that it crystallises directly from the product mixture. The ligand degradation (hydrolysis) observed after extensive usage is currently under further investigation. Such systems are environmentally beneficial because the need for volatile organic compounds as solvents is removed.

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