

Efficient Hydroformylation in Dense Carbon Dioxide using Phosphorus Ligands without Perfluoroalkyl Substituents

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Abstract: Rhodium catalysts modified with triphenylphosphine, triphenyl phosphite, and tris(2,4-di-*tert*-butylphenyl) phosphite have been evaluated for their performance in the hydroformylation of 1-octene using carbon dioxide as the solvent. It is demonstrated that these catalysts are very efficient for the hydroformylation in carbon dioxide, although they are not designed for use in this medium. In particular, the catalyst prepared *in situ* from dicarbonyl(2,4-pentanedione)rhodium(I) and tris(2,4-di-*tert*-butyl-phenyl) phosphite gave rise to an initial turnover frequency in excess of $3 \times 10^4 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$. Such a reaction rate is unprecedented for hydroformylation in supercritical carbon dioxide-rich reaction mixtures.

Keywords: carbon dioxide; homogeneous catalysis; hydroformylation; phosphorus ligands; rhodium; supercritical fluids

Introduction

An important example of homogeneous catalysis carried out on an industrial scale is the hydroformylation reaction.^[1] Generally, cobalt or rhodium catalysts are used in the hydroformylation reaction, to convert an alkene, carbon monoxide, and hydrogen into an aldehyde product with a high atom economy.^[1]

During recent years, the use of carbon dioxide as a solvent for homogeneously catalyzed hydroformylation reactions^[2] and as a means to influence reaction selectivity or activity^[3] has received considerable attention. Advantages of using carbon dioxide as a solvent over traditional liquid (organic) solvents include

improved mass transfer rates, an environmentally benign character, convenient separation from reaction products by depressurization, and the possibility to create a monophasic reaction system.^[2a,4] Furthermore, the ongoing development of monodentate and multidentate phosphorus ligands has resulted in more efficient, selective, and versatile hydroformylation catalysts.^[5]

In general, many well-known hydroformylation catalysts have a poor solubility in carbon dioxide-rich reaction mixtures.^[4a] The catalyst solubility in carbon dioxide can be improved by attaching perfluoroalkyl substituents on the phosphorus ligands of the catalyst.^[6] Because the cost of perfluoroalkyl reagent starting materials increases with chain length,^[7] the development of inexpensive “non-fluorous” CO_2 -philic ligands is receiving increasing attention.^[8] Other ways to increase the solubility of higher molecular weight substances in carbon dioxide rich media are based on the use of cosolvents^[9] or auxiliary agents like peracetylated β -cyclodextrins.^[10] Moreover, for catalytic applications organic solvents expanded with carbon dioxide seem to combine both the advantages of organic solvents and carbon dioxide.^[11]

Examples of well-known hydroformylation catalysts are rhodium complexes with phosphorus ligands like triphenylphosphine or triphenyl phosphite. For a total pressure below 30 MPa the use of triphenylphosphine and triphenyl phosphite for the hydroformylation of 1-alkenes in carbon dioxide has resulted in moderate turnover frequencies^[12] (TOF) in the order of $100\text{--}200 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$.^[8a,b,e] One of the highest TOF values reported in the literature for the hydroformylation of a 1-alkene with a triphenylphosphine-modified rhodium catalyst in carbon dioxide is $174 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ at 80°C .^[8a] Recently, Galia

et al. have discussed the use of triphenylphosphine for the hydroformylation of 1-octene in carbon dioxide. They have reported a TOF of $116 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ at an initial total pressure in excess of 31 MPa and 60°C .^[8d] We have applied triphenylphosphine in the rhodium-catalyzed hydroformylation of 1-octene in carbon dioxide, which resulted in an initial rate of $460 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ at 70°C and a initial total pressure of about 50 MPa.^[13] It is noted that in these examples the reaction conditions vary with respect to the temperature, phase behaviour, and the amount of rhodium, phosphorus ligand, and reactants that have been used. This makes a direct comparison of the different results for the TOF difficult. However, it appears that the reaction conditions we have used allow for an effective use of triphenylphosphine-modified rhodium catalysts.

Besides modifying the catalytic complex it is also possible to tune the properties of the supercritical fluid (SCF) to adjust the solubility and reactivity. The density of an SCF is an important parameter with respect to the solubility of large molecules. Usually, an increase in fluid density results in a higher solubility.^[6f] Increasing the temperature while keeping the fluid density constant results in a higher pressure and a significant increase in phosphorus ligand solubility.^[6f] The combination of high temperature and high pressure also facilitates the existence of a single phase reaction mixture.^[14,15] Laboratory-scale experiments at pressures in excess of 30 MPa are feasible and have been reported,^[16–18] but applying high pressure to improve catalyst solubility in an SCF is not a common strategy. This might be attributed to the perception that on an industrial scale high pressure processing is inherently uneconomical or unpractical. Nevertheless, there are examples of commercial large-scale processes carried out at high pressure.^[19]

The main objective of this work is to study the performance of a rhodium catalyst employing ligands without perfluoroalkyl substituents for the hydroformylation of 1-octene in carbon dioxide using a combination of high pressure (initial pressure $\geq 30 \text{ MPa}$) and temperature ($\geq 70^\circ\text{C}$). In particular, we have studied the use of hydroformylation catalysts generated *in situ* from triphenylphosphine (**L1**), triphenyl phosphite (**L2**), or the bulky phosphite tris(2,4-di-*tert*-butyl-phenyl) phosphite (**L3**) and the metal complex $[\text{Rh}(\text{CO})_2\text{acac}]$ (acac = 2,4-pentanedione). For comparison, results are presented for the CO_2 -philic tris(3,5-bis(trifluoromethyl)phenyl)phosphine (**L4**). **L3** has been used for the hydroformylation in organic solvents^[20] and CO_2 expanded organic solvents.^[21] To the best of our knowledge the application of the bulky phosphite **L3** for the hydroformylation in dense CO_2 has not been reported before.

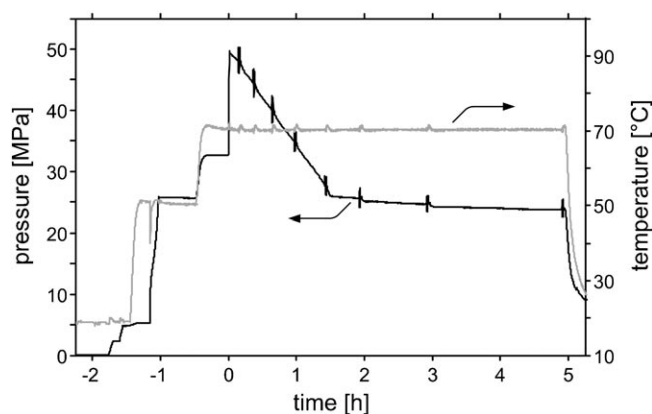


Figure 1. Pressure and temperature as a function of time during the hydroformylation in carbon dioxide with **L1** as the ligand (Table 1, entry 1).

Results and Discussion

During the batch experiments the temperature and pressure of the reaction mixture were monitored and logged. In Figure 1 a typical pressure and temperature profile is shown. These results were obtained for **L1** (*vide infra*, entry 1 in Table 1). In all cases, 1-octene was injected at $t = 0 \text{ h}$ to start the reaction. Before the hydroformylation reaction was started, the catalyst was prepared *in situ* ($t = -1.0$ to 0 h) in a supercritical mixture containing 14.4 mol L^{-1} carbon dioxide (Table 1), 1 mol L^{-1} carbon monoxide and 1 mol L^{-1} hydrogen. For the phosphite ligands (**L2** and **L3**) a somewhat longer catalyst formation time was applied (see Supporting Information). In Figure 1 it can be seen that conversion of 0.97 mol L^{-1} 1-octene (0.105 mol 1-octene in 0.108 L reactor volume), 1 mol L^{-1} carbon monoxide and 1 mol L^{-1} hydrogen results in a decrease in pressure of 24 MPa. It is noted that about 10% of the change in pressure can be attributed to sampling.^[18]

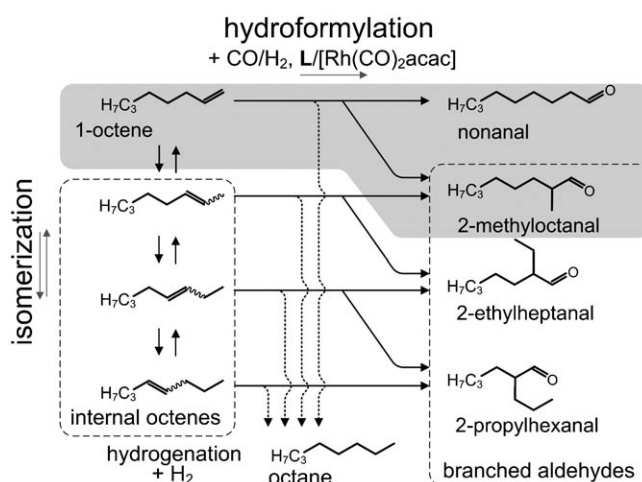
The period of time to allow for the *in situ* formation of the catalyst prior to reaction is an aspect in which our experimental procedure differs from most methods reported in the literature. Often the catalyst precursors and the reactants are already mixed together before the desired reaction conditions are reached. The advantage of the procedure we use is that possible influences of catalyst formation on the kinetics of the hydroformylation reaction are minimized.

In order to compare the ligands **L1** to **L4** we used a reaction temperature of 70°C and an initial maximum pressure of about 50 MPa as reference conditions. It has been established that with these conditions a single phase reaction system is present throughout the extent of the reaction.^[13] In Scheme 1, the most probable reaction pathways are depicted for the hydroformylation of 1-octene.

No.	L	<i>T</i> [°C]	<i>p</i> _{max} ^[b] [MPa]	n _{1-octene} [mmol]	1-oct- ene:Rh	L:Rh	TOF _{1-octene} ^[c,d]	TOF ^[c,e]	<i>t</i> _r [h]	Conv. [%]	Selectivity [%]			l:b ^[f] [-]
											linear ald.	branched ald.	octene iso- mers, octane	
1	L1	70	50.2	105	2030	4.2	832 (1190) ^[g]	819 (1190) ^[g]	1.01 2.97	44 93	74 73	25 24	1 3	2.9 3.0
2	L2	70	50.2	105	1910	5.1	1890	1820	1.04 3.11	83 99	68 67	28 26	4 7	2.4 2.6
3 ^[j]	L3	70	49.2	105	1940	4.0	37,400	31,400	0.05 1.00	88 100	58 58	26 33	16 9	2.2 1.7
4	L4	70	49.3	105	1970	4.1	7107	6710	0.98 3.03	98 100	66 65	23 24	12 11	2.9 2.7
5	–	70	49.8	105	2000	-	3120 (5320) ^[g]	2090 (3600) ^[g]	0.96 2.96	99 99	47 50	24 31	29 19	1.9 1.6
6 ^[j]	L1	90	46.7	100	3660	99	2840	2640	1.00 2.98	70 93	76 76	24 22	1 2	3.2 3.4
7 ^[i,k]	L3	70	25.7	106	1970	4.2	37,000	34,100	0.04 1.05	67 100	63 62	29 34	8 3	2.2 1.8

[k] CO_2 amount = 52 g.

The reaction using **L1** as the modifying ligand proceeds with a high chemoselectivity for aldehydes with nonanal and 2-methyloctanal as the main products (Table 1, entry 1, and Figure 2a). After a reaction time of one hour the selectivities for nonanal and 2-methyloctanal were 74% and 25%, respectively. At the moderate temperature of 70°C this aldehyde product distribution can be considered to be common for the **L1**-modified rhodium-catalyzed hydroformylation of 1-octene.^[22] Using **L1** only traces of 2-ethylheptanal (selectivity=0.1%) and 2-propylhexanal (selectivity=0.01%) were observed after three hours



Scheme 1. Reaction scheme for the hydroformylation of 1-octene. Following the coordination of 1-octene to the rhodium complex, hydride insertion can take place to form either the 1-octyl or 2-octyl rhodium intermediate. The main reaction products nonanal and 2-methyloctanal, depicted in the grey shaded area, are formed through the catalytic steps involving the 1-octyl and 2-octyl intermediates, respectively.

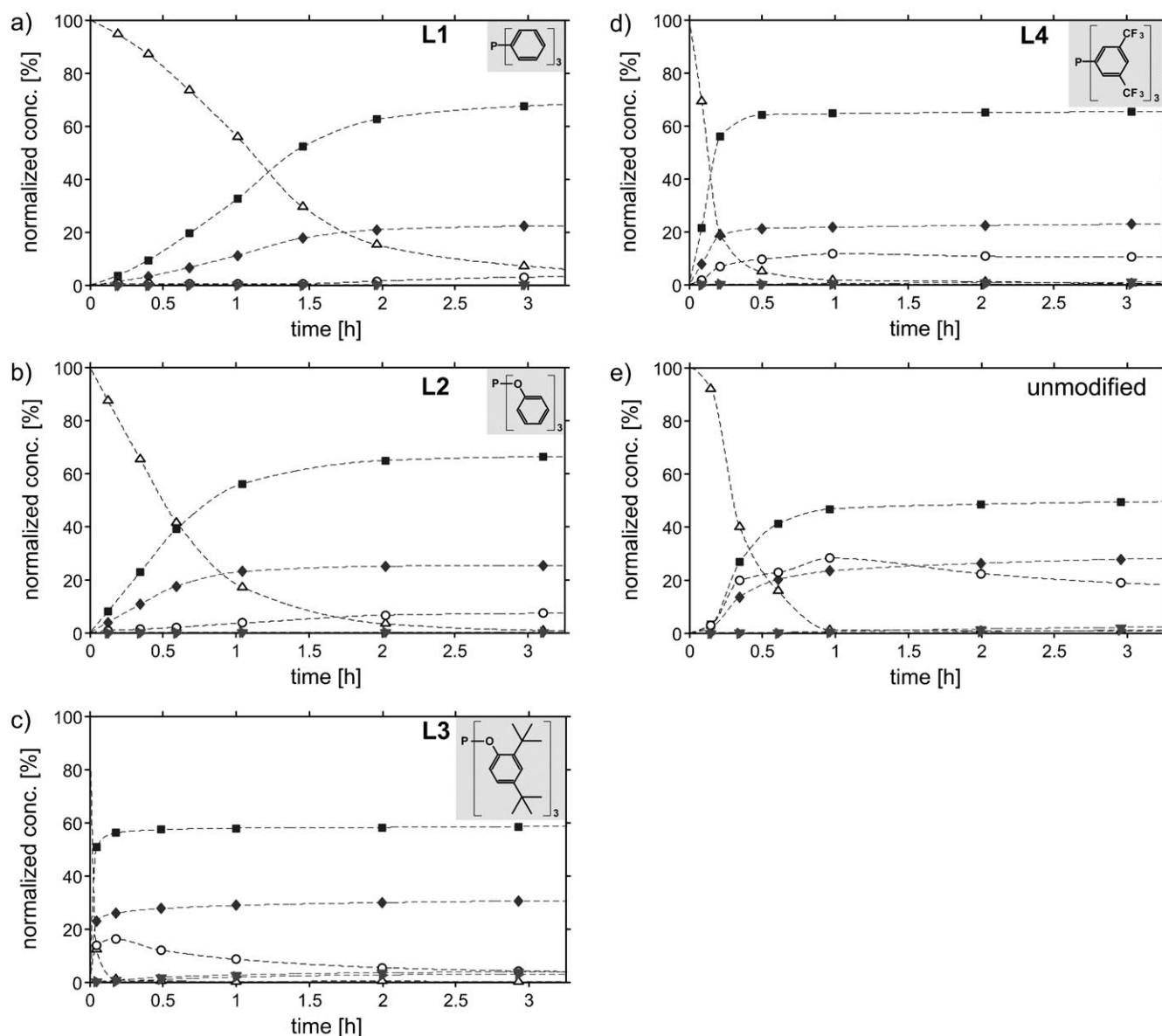


Figure 2. Kinetics of the rhodium catalyzed hydroformylation of 1-octene modified by **L1** (a), **L2** (b), **L3** (c), **L4** (d), or unmodified (e). Concentration profiles are obtained by sampling and GC analysis. Δ = 1-octene, $\circ$ = internal octene isomers, octane, $\blacksquare$ = nonanal, $\blacklozenge$ = 2-methyloctanal, $\blacktriangledown$ = 2-ethylheptanal, $\blacktriangleright$ = 2-propylhexanal. Reaction conditions are given in Table 1 (entries 1 to 5).

reaction time (t_r). It is noted that the amounts of reactants were near stoichiometric. At a high aldehyde yield, and a correspondingly low carbon monoxide and hydrogen concentration, isomerization of octene can become the dominant reaction.^[22] However, for **L1** the concentration of the octene isomers reached a significant value only after two hours of reaction. Furthermore, a maximum reaction rate of $1190 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ is observed, which is unprecedented for the hydroformylation of 1-octene in dense carbon dioxide (Table 1, entry 1).

The application of **L2** results in a different type of kinetics, as compared to the application of **L1**. For **L2**

a TOF of $1820 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ was obtained, which was considerable higher than the TOF obtained with **L1** (Table 1, entry 2). Additionally, a lower selectivity for the linear product and a higher selectivity for the octene isomers was obtained, as compared to the results obtained with **L1** (Figure 2b, Table 1, entry 2). For the **L2**-modified catalyst traces of 2-ethylheptanal (selectivity = 0.2%) and 2-propylhexanal (selectivity = 0.01%) were observed after three hours reaction time. Finally, also for **L2** the values for the TOF seem to be exceptionally high in comparison with literature data on hydroformylation in supercritical media.^[8c]

In Figure 2c the results obtained with **L3** are depicted. It is clear that the use of **L3** results in a very high hydroformylation rate in combination with an isomerization rate considerably higher than that observed for **L2**. The yield of aldehydes determined from GC (gas chromatography) analysis was equal to 74% within 3 min of reaction time (Table 1, entry 3, $t_r = 0.05$ h). This corresponds to an initial TOF of $31,400 \text{ mol}_{\text{aldehyde}} \text{ mol}_{\text{Rh}}^{-1} \text{ h}^{-1}$ at the relatively mild initial reaction temperature of 70°C . At this reaction time the selectivity for 2-methyloctanal was 26% and traces of 2-ethylheptanal (selectivity = 0.1%) and 2-propylhexanal (selectivity = 0.01%) were observed. The normalized concentration of octene isomers increased to 16% at 11 min (0.18 h) and then decreased to a value of 4% at $t_r = 2.93$ h. At a high 1-octene conversion, the Rh catalyst modified with **L3** also started to convert the internal octene isomers. At the end of the reaction ($t_r = 2.93$ h) the yield of 2-methyloctanal was 31%, the yield of 2-ethylheptanal was 4%, and the yield of 2-propylhexanal was 3%. The total aldehyde yield of 96% at the end of the reaction is quite remarkable, considering that only a small excess of carbon monoxide and hydrogen is present at the start of the reaction. In particular, for the catalyst modified with **L3** one would expect that at a low carbon monoxide and hydrogen concentrations isomerization should be more prevalent than the hydroformylation of internal octenes.^[23] Finally, it should be noted that in the initial stage of the reaction the fluid temperature rose from 70 to about 81°C . Thus, the values for TOF given in Table 1 do not strictly represent the activity of the catalyst at 70°C .

The use of **L4**, Figure 2d, has resulted in a more active catalyst than the application of **L1**, **L2**, or the situation where no ligand was used. The rhodium catalyst based on **L4** has the ability to hydroformylate internal octenes.^[13a,18] However, when comparing Figure 2c and Figure 2d, the use of **L3** appeared to result in a faster hydroformylation of internal alkenes than the use of **L4**. For **L4** after three hours reaction time selectivities of 0.9% and 0.2% for 2-ethylheptanal and 2-propylhexanal were found, respectively.

For the fifth case, where the unmodified Rh-catalyst has been used (Figure 2e, Table 1, entry 5) the results for the hydroformylation show the lowest selectivity for nonanal and a significant tendency for isomerization of 1-octene. A maximum normalized concentration of 28% of octene isomers at $t_r = 0.96$ h was found (Figure 2e) and the selectivity for nonanal was 50% at $t_r = 2.96$ h (Table 1, entry 5). For the reaction with the unmodified catalyst the hydroformylation of internal octenes appeared to be slower than for the situation where the **L3**-modified catalyst has been applied. At $t_r = 2.96$ h the selectivity for the branched aldehydes (31% in total) is distributed as follows: 28% for 2-methyloctanal, 2% for 2-ethylheptanal, and 1%

for 2-propylhexanal. Clearly, after approximately three hours reaction time the selectivity for the branched aldehydes was lower for the unmodified catalyst in comparison with the **L3**-modified catalyst.

Assuming that the catalytic species are dissolved and homogeneously dispersed, the differences in results obtained with the four different ligands can be explained in terms of electronic and steric ligand effects. It seems that for the hydroformylation in supercritical CO_2 rich media a similar reasoning holds as for the hydroformylation in organic solvents. The electron density on the phosphorus of **L2** is lower than the electron density on the phosphorus of **L1**, which usually results in a faster hydroformylation.^[24,25] From Table 1 it follows that indeed **L2** leads to a more active catalyst at a moderate ligand excess, as compared to **L1**. **L3** is a bulky phosphite and has *tert*-butyl substituents at the *ortho* positions of the aryl rings. This results in a ligand with a cone angle^[26] considerable larger than that of **L2**. For hydroformylation in organic solvents it has been demonstrated that the use of this type of bulky ligand results in an extremely active catalyst.^[24] Under hydroformylation conditions usually only one **L3** can coordinate to rhodium.^[25] **L2** is less sterically demanding than **L3** and therefore can even completely replace carbon monoxide as a ligand. Using a large excess of **L2** can result in a catalyst with a relatively low activity.^[24]

Our results obtained with **L2** and **L3**, under supercritical conditions, reflect the difference in steric conformation between **L2** and **L3**. The catalyst based on a ligand closely related to **L3**, tris(2-*tert*-butyl-4-methylphenyl) phosphite, has a well-known ability to hydroformylate substituted alkenes.^[27] The decrease in concentration of internal octene isomers over time and the yield of branched aldehydes obtained after three hours of reaction (Figure 2c) confirm this feature. Trifluoromethyl substituents also have an electron-withdrawing effect and it is known that the application of **L4** results in a more active catalyst, as compared to the use of **L1**.^[6e,13a,28,29] Consequently, the difference between the results obtained for **L1** and **L4** in a supercritical medium can be expected, based on reaction rate data reported in the literature for related catalysts applied in organic solvents.

Our reactor does not allow for a visual observation of the phase behaviour of the reaction mixture. For **L1** and **L4** it can be readily assumed that the catalyst is dissolved in the supercritical reaction mixture based on literature reports.^[6b,e,f,g,8d] However, for **L2** and **L3** no detailed studies for the solubility of these two ligands in an SCF have been reported. Sellin and Cole-Hamilton observed that ligand **L2** and the catalyst formed a separate liquid phase at 100°C and 22 MPa total pressure during Rh-catalyzed hydroformylation of 1-nonene in carbon dioxide.^[8e] Furthermore, they found that other insoluble metal complexes modified

with monodentate phosphorus ligands could catalyze the hydroformylation although with moderate values for the TOF.^[8c] Typically, they observed values for the TOF between 25 and 120 mol_{aldehyde} mol_{Rh}⁻¹ h⁻¹. Compared to the conditions used by Cole-Hamilton and co-workers, we used a significantly higher CO₂ density. Based on literature dealing with the solubility of phosphorus ligands and the corresponding catalysts it is expected that under the conditions we have applied the solubility of the rhodium catalyst modified with **L2** has been higher than under the conditions used by Cole-Hamilton and co-workers.^[6f,g]

As the result obtained with **L3** was most remarkable, we performed a preliminary solubility study. It was determined that for pure **L3**, as ligand and not the rhodium complex, the saturation concentration in carbon dioxide at 20 MPa and 70 °C was about 2.5×10^{-3} mol L⁻¹. This implies that pure **L3** could be completely soluble at the reaction conditions applied in this study. In comparison with **L2**, **L3** contains six additional *tert*-butyl substituents. There have been some investigations into whether alkylation of ligands can lead to an improvement in ligand and catalyst solubility in CO₂.^[6d,8b,d] For the case of triarylphosphines Galia et al. concluded that attaching *tert*-butyl groups to **L1** did not appear to affect the solubility.^[8d] It, therefore, remains unclear whether the rhodium catalyst based on **L2** and **L3** dissolves in the supercritical phase or that a biphasic system, consisting of an organic catalyst rich phase and a carbon dioxide rich phase, is formed.

The results for the TOF (Table 1, entries 1 to 4) in combination with the results for the reaction rate and the selectivity presented for related catalysts in literature suggest that the catalysts are dissolved at the conditions we have applied.^[8b,c,13a,23,29,30] On the other hand, it is known that efficient homogeneous catalysis can be carried out using multiphase systems.^[31] Determining the distribution of metal complexes between the phases and establishing the nature of the catalytic species in these phases requires further study.

In addition to the reference conditions of 70 °C and a maximum initial total pressure of 50 MPa (see Table 1), we have explored two alternative sets of reaction conditions using ligand **L1** and **L3**. These conditions and the corresponding results are given as entries 6 and 7 in Table 1.

First, **L1** was used with a phosphorus to rhodium ratio close to 100 at a temperature of 90 °C (Table 1, entry 6). With an increase in temperature from 70 to 90 °C an increase in reaction rate can be expected. However, a higher concentration of **L1** usually results in a lower reaction rate in combination with a higher selectivity.^[32] The maximum total pressure applied at 90 °C was lower than for the experiments at 70 °C. Despite the large excess of **L1** an initial TOF of 2640 mol_{aldehyde} mol_{Rh}⁻¹ h⁻¹ has been obtained

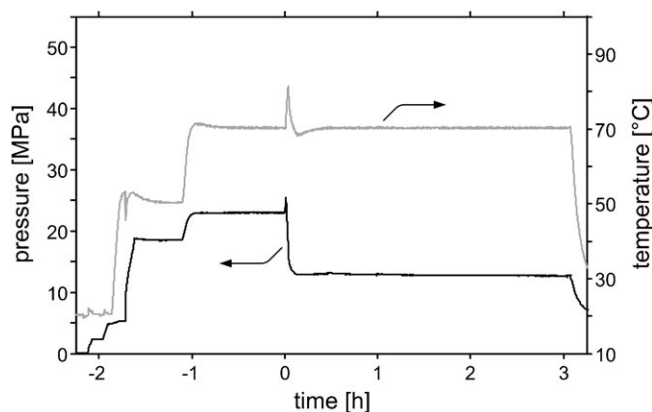


Figure 3. The pressure and temperature as a function of time when using **L3** for the hydroformylation of 1-octene and a lower CO₂ amount. The corresponding conditions and results are given in Table 1, entry 7.

(Table 1, entry 6), which is unparalleled for this ligand when using carbon dioxide as a solvent. As a result of the excess of **L1**, isomerization is almost completely suppressed and a selectivity of 76% for the linear aldehyde is obtained.

Second, **L3** was applied at a lower total pressure. By using a smaller amount of CO₂ a lower total pressure was achieved, while the amount of reactants and catalyst precursors was kept constant (Table 1, entry 7). The objectives of using a lower pressure were three-fold. First, we wanted to work with an initial total pressure, which was in the range of pressures usually encountered in reports on hydroformylation in carbon dioxide. Second, we wanted to establish whether the use of **L3** also would result in a high reaction rate under these conditions. Third, we were interested in the global phase behaviour under these conditions.

In Figure 3 the pressure-time and temperature-time histories are given for the hydroformylation of 1-octene using 52 g of CO₂ (Table 1, entry 7). After initiation of the reaction (at $t = 0$ h) the pressure decreased rapidly from 25.7 MPa to 12.8 MPa within 8 min. Again a very high initial TOF of 34,100 mol_{aldehyde} mol_{Rh}⁻¹ h⁻¹ was obtained (Table 1, entry 7). Notably, based on the similar initial TOFs observed using either a lower or higher pressure, it appears that catalyst formation at a lower pressure proceeds just as effectively as when a higher pressure is used. Based on the total amount of 1-octene injected, 106 mmol, into the reactor of volume 0.108 L a total concentration of about 1 mol L⁻¹ can be expected when 1-octene and the reaction products are homogeneously dissolved in a single phase supercritical medium. By GC analysis of the samples it was derived that the sum of the concentrations of 1-octene and reaction products at the bottom part of the reactor was about 2 to 3 mol L⁻¹ (see the Experimental Section for de-

tails on the sampling procedure). This implies that applying a smaller amount of CO₂ has resulted in a two-phase reaction mixture with an organic rich phase at the bottom part of the reactor, assuming that the catalyst completely dissolves and does not form a third phase. For the other cases reported here (Table 1, entries 1–6) a total concentration, sum of 1-octene and products, close to 1 mol L⁻¹ was derived by GC analysis. Using a lower pressure and consequently a two-phase reaction system (Table 1, entry 7) appeared to have a positive effect on the selectivity in comparison with the single phase condition (Table 1, entry 3). At t_r = 1.05 h, the selectivity for the linear aldehyde was 62%.

Conclusions

In conclusion, the reaction conditions reported here, allow for a more efficient use of the rhodium catalysts modified with **L1**, **L2** or **L3**, than the conditions reported previously in other investigations into Rh-catalyzed hydroformylation of long-chain alkenes in the presence of carbon dioxide. The catalyst derived from **L3** has shown to be a very effective catalyst at different carbon dioxide densities. Applying **L3** resulted in the highest TOF reported for homogeneous hydroformylation catalysts in supercritical CO₂-rich systems. The favourable results obtained with **L1**, **L2**, and **L3** could indicate that the reaction conditions used here could be suitable for application of other related commercially available ligands. Therefore, the results reported here can direct to further advancement of the use of carbon dioxide rich reaction systems for hydroformylation and related reactions using ligands without perfluoroalkyl substituents.

Experimental Section

Materials

Carbon dioxide, carbon monoxide, and hydrogen, grades 5.0, 4.7 and 5.0, respectively, were obtained from Hoekloos (The Netherlands). Prior to use CO₂ was passed over a Messer Oxisorb filter to remove oxygen and moisture. 1-Octene obtained from Aldrich, was passed over activated alumina, dried with pre-treated molecular sieves 3 Å (Aldrich, 4–8 mesh), and stored under argon. The rhodium precursor, dicarbonyl(2,4-pentanedione)rhodium(I), ([Rh(CO)₂(acac)]), was obtained in the form of dark green crystals from Fluka. Tris[3,5-bis(trifluoromethyl)phenyl]phosphine is a white to light yellow solid and was supplied by Arkema (Vlissingen, The Netherlands). Triphenylphosphine (white to off-white powder, reagent plus, 99% purity), triphenyl phosphite (colourless liquid, 97% purity), and tris(2,4-di-*tert*-butyl-phenyl) phosphite (white powder, 98% purity) were all obtained from Aldrich. All catalyst precursors were stored under argon. The solvents toluene (Merck, analytical

grade), *n*-heptane (Merck, analytical grade), the internal standard *n*-decane (Aldrich, >99% purity) and the substances involved in the reaction, *n*-octane (Aldrich, >99%), 2-octene (ABCR, mixture of *E* and *Z*, 98%) and nonanal (Fluka, >95%) used for the GC analysis (gas chromatography with flame ionization detection) were used as received.

Hydroformylation in Carbon Dioxide

Details on the reactor system, the general procedures applied during the hydroformylation experiments and the analysis have been reported in detail in refs.^[13,18] **Important note:** the risks of using of the very toxic flammable carbon monoxide gas and the highly flammable hydrogen gas in combination with the use of high pressure were extensively assessed. A variety of safety measures were taken including using detection for carbon monoxide and hydrogen, working in a fume hood, using pressure relief devices, and using equipment with a pressure rating 10 to 40 MPa above the maximum allowable working pressure of the reactor. Blank reaction runs were performed regularly. In the Supporting Information the pressure and temperature profiles are given for the experiments corresponding to entries 1–7 in Table 1. The procedure for sampling the reactor contents started with rinsing the contents of the tubing connecting the sample volume and reactor with a small volume high-pressure syringe pump. The sample could be taken from either the top or the bottom part of the reactor. For the experiments corresponding to entries 1–6 in Table 1 samples were taken from the top part of the reactor. For the experiment corresponding to entry 7 a two-phase reaction system was anticipated, because a considerably smaller amount of carbon dioxide was applied in comparison with the other experiments. Therefore, sampling was done from the lower part of the reactor in that case. After taking the high pressure sample the content of the sample volume (0.192 mL) was carefully bubbled through a vial with a solution of *n*-decane in toluene and afterwards rinsed with additional toluene solution to collect 1-octene and its reaction products quantitatively. The amount of the toluene solution used, containing 0.01 mol L⁻¹ of *n*-decane as a standard, was determined. By means of GC analysis the concentration of 1-octene and the reaction products in the toluene solution could be determined. Subsequently, the concentrations of 1-octene and reaction products present in the sample volume could be calculated.

Determination of Solubility of **L3**

First, **L3** (3.5 g) was loaded in the reactor, the reactor was heated to 70 °C, and consequently carefully pressurized up to 20 MPa with carbon dioxide. The system was allowed to stabilize at a stirring rate of 140 rpm. Samples were taken from the top of the reactor. The sample volume was depressurized and rinsed with *n*-heptane. The resulting solution of **L3** in heptane was weighed. Subsequently, the solution was analyzed using a UV-vis spectrophotometer (Shimadzu UV-2501 PC). The concentration of **L3** in heptane was calculated by means of a calibration line obtained by measuring heptane solutions with known **L3** concentrations.

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