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Hydroformylation of 1-Octene in Supercritical Carbon Dioxide and Organic Solvents using Trifluoromethyl-Substituted Triphenylphosphine Ligands

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Abstract: Two different *in situ* prepared catalysts generated from Rh(CO)$_2$acac and trifluoromethyl-substituted triphenylphosphine ligands have been evaluated for their activity and selectivity in the hydroformylation of 1-octene. The solvents used were supercritical carbon dioxide, hexane, toluene, and perfluoromethylcyclohexane. The highest value for the turnover frequency, 9820 $\mathrm{mol_{1\text{-}octene}\ mol_{Rh}^{-1}\ h^{-1}}$, has been obtained in supercritical carbon dioxide using ligand **I**, $P[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_3$. For both supercritical carbon dioxide and hexane employing ligand **II**, $P(C_6H_4\text{-}3\text{-}CF_3)_3$, a selectivity towards the linear aldehyde product, nonanal, and an *n:iso* ratio of 79.3 % and 4.6–4.8 have been obtained, respectively. These values are significantly higher than those obtained with triphenylphosphine as ligand (nonanal: 74–76 %, *n:iso*: 3.1–3.3). An increase in trifluoromethyl substitution on the triphenyl ligand results in an increase in the 1-octene conversion rate, an increase in the *n:iso* ratio and a decrease in the overall selectivity towards aldehydes. In terms of turn-over frequency and selectivity the three ligands give comparable results in supercritical carbon dioxide and hexane. This leads to the conclusion that the properties of supercritical carbon dioxide as a solvent for hydroformylation can be better compared with those of hexane rather than with those of toluene.

Keywords: fluorinated ligands; homogeneous catalysis; 1-octene hydroformylation; organic solvents; supercritical carbon dioxide

Supercritical carbon dioxide, scCO$_2$, has been established as an environmentally benign alternative to organic solvents in the field of homogeneous catalysis.[1] In terms of production volume, hydroformylation is one of the most important examples of homogeneous catalysis applied on an industrial scale.

Commercial hydroformylation processes are commonly carried out in a gas-liquid system or in a gas-liquid-liquid system. Rigorous mixing of the phases is required to reduce or prevent mass transfer limitations. The Ruhrchemie/Rhône–Poulenc (RCH/RP) hydroformylation process, in which propene is converted to butanal using a phosphine-modified rhodium catalyst, is an example of homogeneous catalysis in a gas-liquid-liquid system.[2] In this process, the sulfonated phosphine renders the catalyst preferentially soluble in the aqueous phase, facilitating easy catalyst separation and recovery through liquid-liquid phase separation. By this means one of the major disadvantages of homogeneous catalysis, which is the troublesome recovery of the catalyst, is overcome.

Research into hydroformylation reactions has focused on ligand design to make the catalyst complex more selective, more active, or better separable from the product.[3] To facilitate catalyst separation phosphine ligands have been covalently attached to a support, such that the catalyst complexes form a separate solid[4–8] or liquid[9] phase, which can be recovered by filtration or decantation, respectively. Another strategy is to design ligands that dissolve in an aqueous[2], fluorous[10–13], or ionic[14,15] solvent that is immiscible with an organic phase containing the product.

The RCH/RP process is limited to the conversion of short-chain alkenes, such as propene and 1-butene, because the solubility of longer-chain alkenes in water is too low to realize an acceptable reaction rate. Currently, industrial hydroformylation of long-chain alkenes, including 1-octene, is carried out using a cobalt catalyst. Although the cobalt-based processes have been optimized over the years, relatively harsh conditions, typically 30 MPa and 175 °C for the Exxon process, are required to keep the catalyst active and stable, while the activity and selectivity for linear aldehyde are lower than in rhodium-catalyzed hydroformylation.[2] Employing a rhodium catalyst and $scCO_2$ as the reaction medium could be advantageous for the hydroformylation of longer-chain alkenes when combined with a facile recovery of the expensive rhodium catalyst. The use of $scCO_2$ has the additional advantage that it reduces mass transfer limitations, resulting in a more efficient use of reactor volume at elevated process pressure. Moreover, the development in the synthesis of bulky phosphites and diphosphines has led to improved activity and regio- or stereoselectivity for rhodium-catalyzed hydroformylation reactions.[16] Furthermore, it has been shown that a homogeneous catalyst can be recovered using a microporous ceramic membrane in combination with $scCO_2$ as the reaction medium.[17,18]

A number of researchers have illustrated the potential of $scCO_2$ as an alternative reaction medium for the hydroformylation long-chain alkenes, such as 1-octene.[19–21] Besides the requirement of a good selectivity and activity, it is important that the catalyst is also sufficiently soluble in the supercritical mixture.[19] Generally, it is concluded that the hydroformylation rates in $scCO_2$ are comparable or even exceed the rates observed in organic solvents. It has been demonstrated that the attachment of perfluoroalkyl substituents on a ligand improves the solubility in $scCO_2$ considerably.[19,22] Additionally, the attachment of perfluoroalkyl substituents on the aryl rings of triphenylphosphine has led to an improved catalytic activity.[23]

In terms of activity and selectivity the comparison between an organic solvent and $scCO_2$ as a reaction medium for hydroformylations has only been made to a limited extent. In general, toluene is used to benchmark the performance in $scCO_2$.[21,24] In this work the hydroformylation of 1-octene (**1a**), see Figure 1, is evaluated for four different solvents, including $scCO_2$, *n*-hexane, toluene, and perfluoromethylcyclohexane. Also, the effect of ligand modification is addressed. Beside triphenylphosphine, two different monodentate triarylphosphine analogues with trifluoromethyl substituents on the *meta* positions were used for hydroformylation of **1a**. The chemical structures of the three phosphines used are shown in Figure 2.

First, the hydroformylation in supercritical carbon dioxide is discussed. In all the experiments a high ligand to rhodium ratio was used, in the order of 50:1, which approaches conditions used on an industrial scale. A high ligand to rhodium ratio usually results in an increase in the selectivity towards the linear product.[2] Also, we chose a relatively high reaction temperature of 70 °C to ensure a high catalytic activity. Most results reported for the hydroformylation of 1-octene in $scCO_2$ were obtained at temperatures lower than 70 °C.[20,21] In Table 1 an overview is given of the experimental reaction conditions for the case $scCO_2$ or an organic solvent is used.

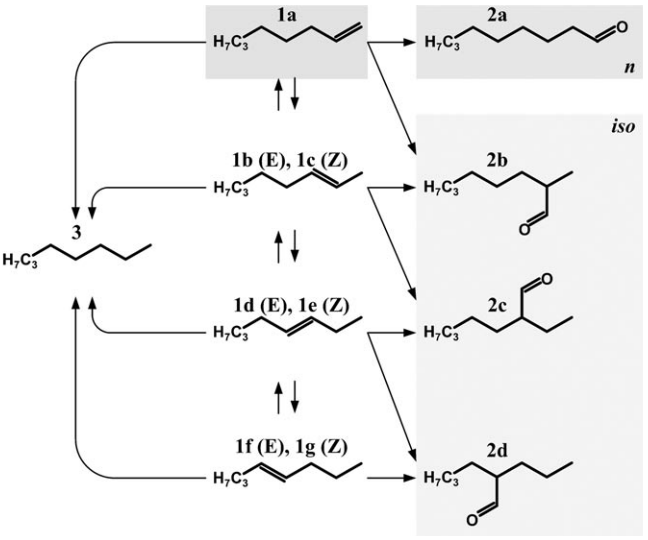

Figure 1. Reaction scheme for the hydroformylation of 1-octene (**1a**), with the two main products nonanal (**2a**) and 2-methyloctanal (**2b**). The side products are (*E,Z*)-2-octene (**1b**, **1c**), (*E,Z*)-3-octene (**1d**, **1e**), (*E,Z*)-4-octene, 2-ethylheptanal (**2c**), 2-propylhexanal (**2d**), and *n*-octane (**3**).

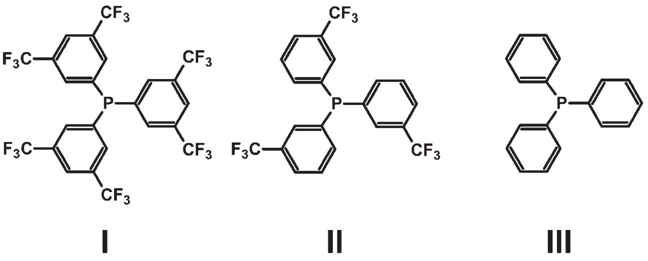

Figure 2. The three triphenylphosphine analogues used. **I** = tris[3,5-bis(trifluoromethylphenyl)]phosphine, **II** = tris(3-trifluoromethylphenyl)phosphine, **III** = triphenylphosphine.

The batch reactors used did not allow for a visual inspection of the mixture during the catalyst pre-formation or the catalytic reaction. Prior to the reaction in $scCO_2$, the catalyst complex was formed *in situ* from $Rh(CO)_2acac$ (acac = acetylacetonate) and one of the phosphine analogues in the presence of CO, H_2 and CO_2 (under the conditions as stated in Table 1). The reaction was started upon addition of **1a**. We employed a CO_2 density of $0.63\,g\,mL^{-1}$, which was higher than the density used by Koch and Leitner, who observed a one-phase mixture.[21] Furthermore, employing a higher density and a higher temperature at the same concentration of solvent and reactants increases the likelihood that a one-phase mixture is present during the progress of the reaction.[25] The maximum initial total pressure obtained after addition of **1a** was *ca.* 50 MPa. This corresponds to a total reaction mixture density of approximately $0.78\,g\,mL^{-1}$. The total concentration (the sum of **1a** and its reac-

Table 1. Overview of experimental conditions.

	Symbol	Unit	ScCO$_2$	Organic solvent
Reactor temperature	*T*	[°C]	70	70
Reactor pressure	*P*	[MPa]	50[a]	1
Reactor volume	*V*	[mL]	107.6	100
Mode of operation			batch	semi-batch
Amount of solvent[b]		[mL]	87[c]	21[d]
Amount of **1a**[b]		[mmol]	105	25.0
Amount of syngas[e]	$P_{CO/H2}$	[MPa]	4.9[f]	1.0
Amount of Rh(CO)$_2$acac[b]	Rh	[μmol]	54.8	12.5
Ligand[b]	L	[mmol]	2.75	0.625

[a] Maximum pressure reached after injection of **1a**.

[b] Average value.

[c] At 20 °C and 6.0 MPa.

[d] 20 mL solvent plus 1.07 mL (5.5 mmol) *n*-decane as internal standard.

[e] Molar ratio CO:H$_2$ = 1:1.

[f] At 20 °C. This pressure corresponds with 110 mmol of syngas.

tion products, excluding CO and H$_2$, as measured using off-line GC) became constant after approximately 20 min and then did not deviate more than 12% from the initial concentration based on the amount of **1a** added to the reactor vessel. Furthermore, the homogeneity of the reaction mixture was confirmed by taking samples at different locations, i.e., the top and bottom, of the reactor. Considering these arguments it is likely that during the reactions there is a one-phase reaction system.

The normalized concentrations of the main reactant and products as a function of time for the experiment conducted in scCO$_2$ with **I** as the ligand are depicted in Figure 3, panel a. In Figure 3, panel b the normalized concentrations of the remaining octene isomers, aldehyde isomers, and octane are given. The catalyst derived from **I** gave rise to a significant amount of isomers of **1a**, resulting in a maximum concentration of about 6% and 5.5% for **1b** and **1c** after approximately 0.5 h of reaction, respectively. It can be seen that after almost complete conversion of **1a** the concentration of **2a** remains constant. However, as a result of the hydroformylation of **1b** and **1c** the concentrations of **2b** and **2c** still increase, respectively. After 2 h the hydroformylation product **2d** also starts to appear.

In Figure 4 the conversion of **1a** is plotted as a function of time for the reaction in scCO$_2$ for the different catalytic systems. No noticeable induction time has been observed at the sampling frequency used. Therefore, the slope of the conversion profile, the straight lines in Figure 4, is a measure of the initial activity. Although **III** is significantly less soluble in

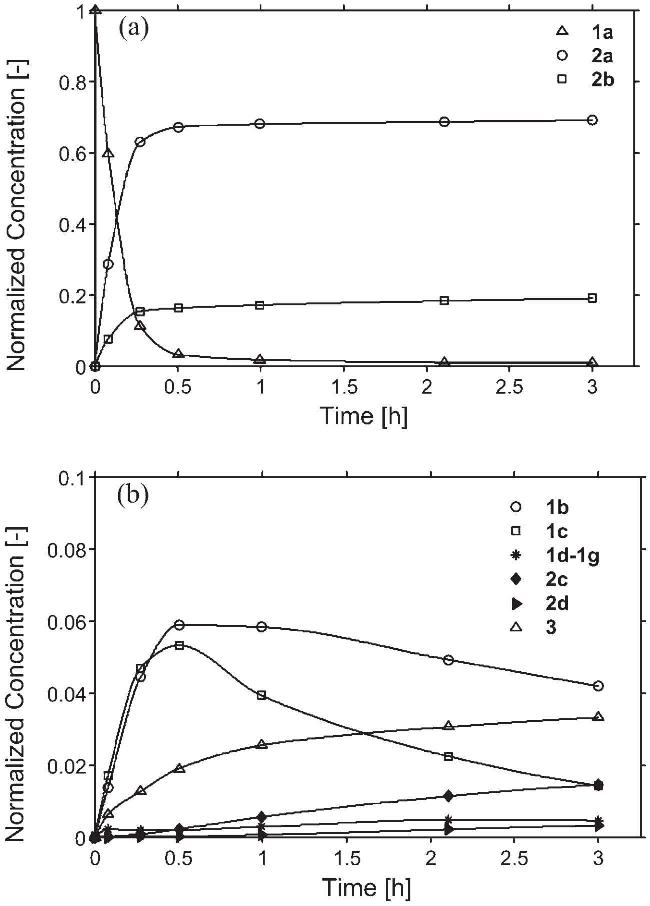

Figure 3. (**a**): Normalized concentrations of the main reactant and products and (**b**) normalized concentrations of isomers as a function of time for the experiment with ligand **I**. *Experimental conditions:* $T = 70\,°C$, $[\mathbf{1a}]_0 = 0.98$ mol/L, $[\mathbf{1a}]_0$:[Rh] = $2.0 \cdot 10^3$, [CO$_2$] = 14.5 mol/L, $[CO]_0 = [H_2]_0 = 1$ mol/L.

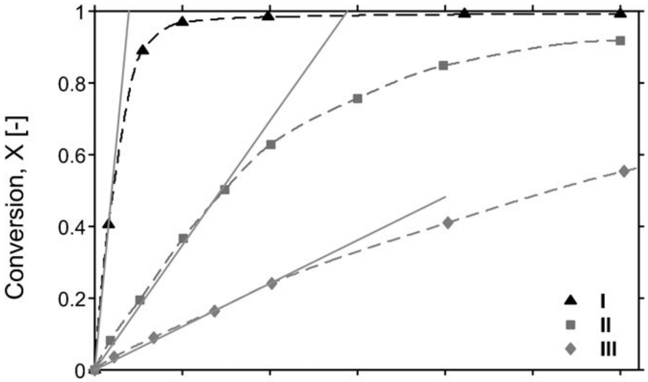

Figure 4. Conversion of 1-octene as a function of time using **I**, **II**, and **III** with an L:Rh ratio of 50:1. The markers indicate the times at which samples were taken. *Experimental conditions:* $T = 70\,°C$, $[\mathbf{1a}]_0 = 0.974 \pm 0.005$ mol/L, $[\mathbf{1a}]_0$:[Rh] = $2.0 \cdot 10^3$, [CO$_2$] = 14.3 ± 0.2 mol/L, $[CO]_0 = [H_2]_0 =$ 1 mol/L.

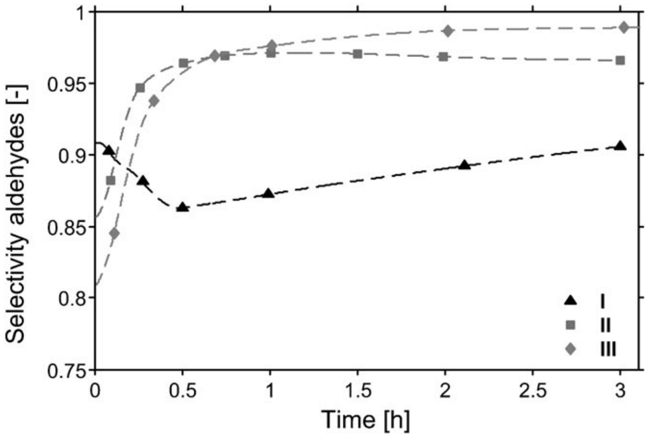

Figure 5. The overall selectivity for aldehydes as a function of time using **I**, **II**, and **III** with an L:Rh ratio of 50:1. The markers indicate the times at which samples were taken. *Experimental conditions:* $T=70\,°C$, $[\mathbf{1a}]_0=0.974\pm0.005$ mol/L, $[\mathbf{1a}]_0$:[Rh]$=2.0\cdot10^3$, $[CO_2]=14.3\pm0.2$ mol/L, $[CO]_0=[H_2]_0=1$ mol/L.

$scCO_2$ than **I** or **II**, a reasonable activity is observed for this ligand. A TOF of 470 $mol_{\mathbf{1a}}\ mol_{Rh}^{-1}\ h^{-1}$ was obtained. The number of trifluoromethyl groups per ligand follows the order: **I** > **II** > **III**. Figure 4 shows that the activity of the corresponding catalytic system follows the same sequence. The highest activity, a TOF of 9820 $mol_{\mathbf{1a}}\ mol_{Rh}^{-1}\ h^{-1}$, was observed for the catalyst derived from **I**.

In Figure 5 the overall selectivity towards aldehydes is given as a function of time. Davis and Erkey have reported a minimum overall selectivity of 95% towards aldehydes at a TOF of *ca.* 1500 $mol_{\mathbf{1a}}\ mol_{Rh}^{-1}\ h^{-1}$ by applying **I**, with L:Rh = 3:1, at a temperature of 50 °C at similar reactant concentrations.[26] We obtained an overall selectivity of 90.5% towards aldehydes at a TOF of 9820 $mol_{\mathbf{1a}}\ mol_{Rh}^{-1}\ h^{-1}$. This difference can be explained by the higher temperature applied in our experiments, which leads to more isomerization of **1a**.[2] The catalyst derived from **I** shows a good activity for the hydroformylation of internal alkenes, **1b** and **1c**. This has also been observed in a study on the hydroformylation of dienes where the same catalyst was used.[24]

To be able to make a comparison with the results in $scCO_2$, the three ligands have also been used to prepare the catalysts, *in situ*, for the hydroformylation of **1a** in the organic solvents toluene, hexane, and the fluorinated solvent perfluoromethylcyclohexane (pfmch). In this case the reactions were performed under a constant syngas pressure (molar ratio H_2:CO = 1:1) of 1.0 MPa, whereas during the reactions in $scCO_2$ no additional syngas was added (4.9 MPa initial syngas pressure, a near stoichiometric amount). In Table 2a detailed comparison is made of the reaction rates and selectivities obtained for the three catalyst systems in the four solvents. Additionally, results are given for experiments in toluene where an L:Rh ratio of 100 was used.

Table 2. Comparison of different ligands and solvents.

Entry	Solvent	Ligand	$[\mathbf{1a}]_0$ (mol/L)	$[\mathbf{1a}]_0$:[Rh] (10^3)	L:Rh	TOF[a] ($10^3\ h^{-1}$)	X[b] (%)	*n:iso*[b,c]	S[b,d]			
									2a (%)	**2a–d** (%)	**1b–g** (%)	**3** (%)
1	$scCO_2$	**I**	0.98	2.0	50	9.82	99.2	3.33	69.6	90.5	6.1	3.3
2	$scCO_2$	**II**	0.97	1.9	50	1.33	91.7	4.59	79.3	96.6	2.9	< 1
3	$scCO_2$	**III**	0.97	2.0	51	0.47	55.3	3.33	76.0	98.8	< 1	< 1
4	toluene	**I**	0.96	2.0	50	5.90	98.1	3.7	71.5	90.6	7.5	1.9
5	toluene	**II**	0.96	2.0	50	3.66	97.9	4.0	76.0	95.1	4.2	< 1
6	toluene	**III**	0.96	2.0	50	1.15	93.1	2.8	73.7	98.6	< 1	< 1
7	toluene	I	1.0	2.0	100	5.90	98	4.5	75	91	7	1
8	toluene	**II**	1.0	2.0	100	1.70	97	5.3	80	95	4	< 1
9	toluene	**III**	1.0	2.0	100	0.90	89	3.1	74	97	2	< 1
10	hexane	**I**	1.0	2.0	50	8.96	98.7	3.9	74.4	93.7	5.3	1.0
11	hexane	**II**	1.0	2.0	50	1.80	98.9	4.8	79.3	95.7	4.1	< 1
12	hexane	**III**	1.0	2.0	50	1.12	90.6	3.1	74.0	98.0	1.5	< 1
13	pfmch[e]	**I**	1.0	2.0	50	0.55	91.5	2.4	28.9	41.1	53.6	5.2
14	pfmch	**II**	1.0	2.0	50	1.20	99.3	3.2	72.2	94.7	4.6	< 1
15	pfmch	**III**	1.0	2.0	50	< 0.04	9.2	1.5	9.5	15.7	84.3	nd[f]

[a] The initial turn-over frequency, TOF, is given by the product of the slope of the linear fit and the (initial) substrate to catalyst ratio.

[b] Conversion (X), the *n:iso* ratio, and the selectivity (S) shown here are at approximately 3 h of reaction.

[c] *n:iso* = [**2a**]/([**2b**] + [**2c**] + [**2d**]).

[d] The overall selectivity for a product(s) at a certain time: $S_i(t)=[i](t)/\{[\mathbf{1a}]_0-[\mathbf{1a}](t)\}$, where i = **1b–d**, **2a–d**, and **3**.

[e] Perfluoromethylcyclohexane.

[f] The **3** signal overlaps with the **1a** signal.

For the hydroformylation in $scCO_2$ the parent phosphine, triphenylphosphine **III**, offers a better total aldehyde selectivity than **I** or **II**, but this is at the cost of a lower activity and, when compared to **II**, a lower *n:iso* ratio resulting in less linear aldehyde. For **I** the total aldehyde selectivity drops in the early phases of the reaction only to recover slowly over the course of the reaction. This is caused by the formation of isomers of **1a** and subsequent hydroformylation of these isomers to aldehydes. The observed trend for the activity as a function of the number of trifluoromethyl substituents could be a result of differences in solubility of the different ligands. It can be expected that the solubility increases with the number of trifluoromethyl groups on the ligand. For **III** a solubility of 0.101 mol/L in pure carbon dioxide at 25.2 MPa and 57 °C was reported.[22] However, the presence of carbon monoxide and hydrogen could have an opposite antisolvent effect. The amount of phosphine applied corresponds to a concentration of 0.025 mol/L assuming total solubility. This value is four times lower than the reported solubility value; this implies that **III** is most likely completely dissolved under the conditions applied. The addition of **1a** will probably improve the solubility of the ligand and its corresponding complex due to co-solvent effects. The observation that there is no, or very little, induction time is another indication that the catalyst is completely dissolved before the addition of **1a**. Therefore, it is concluded that the observed reaction rates represent the real activity of the complex. Furthermore, comparable activities with the same dependence on the ligand were found in hexane, supporting this conclusion.

The dependence of the activity on the number of fluorine atoms in the phosphines corresponds with results obtained by Palo and Erkey (50 °C, L:Rh = 3:1, P = 27.3 MPa) but absolute activities were significantly lower under these conditions (TOF = 500–900 mol_{1a} mol_{Rh}^{-1} h^{-1}).[23] Also, they obtained relatively low *n:iso* ratios in the range 3.0–3.3 for **I, II**, and $P(C_6H_4\text{-}4\text{-}CF_3)_3$ while the concentration of rhodium was comparable to that in our experiments. The optimum in *n:iso* ratio obtained for **II**, both in $scCO_2$ (*n:iso* = 4.6) and organic solvent (*n:iso* = 4.0–4.8) can thus be considered as quite remarkable. Moreover, this indicates that the *n:iso* ratio becomes sensitive to variation in perfluoralkylation at higher L:Rh ratios, while the higher activity obtained with tris(trifluoromethylaryl)-phosphines is essentially maintained.

Few results have been reported on the use of **III** as a ligand for homogeneous hydroformylation catalysts in $scCO_2$ because of its limited solubility and poor activity. Sellins and co-workers have used **III** for the hydroformylation of **1a** in $scCO_2$ at 100 °C using $Rh_2(OAc)_4$ as the metal precursor with L:Rh = 3.3.[27] They obtained a low activity, (TOF = 104 $mol_{aldehyde}$ mol_{Rh}^{-1} h^{-1}) but a comparable *n:iso* ratio of 3.4 and a slightly lower selectivity towards aldehydes at a conversion of 39.6%. The observed differences in activity and selectivity are probably a result of the higher temperature and the lower initial pressure used than in our experiments. This could have resulted in a lower solubility for **III** and its corresponding catalyst complex. Kainz et al. have reported a conversion of 26% and an *n:iso* ratio of 3.5 after 19 h for the hydroformylation of **1a** with a concentration of 0.48 mol/L at 60 °C using **III** and $Rh(hfacac)(\eta^4\text{-}C_8H_{12})$ with a 6:1 ratio.[19] The density of the mixture applied there was approximately 0.75 $g\,mL^{-1}$, which is similar to the density applied in our case. The experimental conditions we applied, a high density combined with a relatively high temperature, can account for the higher activity of **III**/$Rh(CO)_2acac$ observed as compared to these previously reported values.

From Table 2 it follows that, despite the experimental differences, the results obtained in $scCO_2$ and the organic solvents hexane and toluene are comparable, while the fluorous solvent pfmch gives rise to inferior results. Clearly, the three catalysts systems employed are not fluorous enough to completely dissolve in pfmch. For **I**/$Rh(CO)_2acac$ the highest TOFs are observed in $scCO_2$ and hexane. For **II**/$Rh(CO)_2acac$ and **III**/$Rh(CO)_2acac$ the activity order $scCO_2 <$ hexane $<$ toluene and $scCO_2 <$ hexane $\approx$ toluene, respectively, is observed. The trends in *n:iso* ratio as well as the total aldehyde selectivity are essentially reproduced in all 4 solvent systems. The highest *n:iso* selectivity towards **2a** is always obtained with **II** in $scCO_2$ and hexane. It can be seen in Table 2 that in toluene this high selectivity with **II**/$Rh(CO)_2acac$ can only be reached when the amount of ligand is increased to an L:Rh ratio of 100. For the total selectivity towards the aldehydes, **2a–d**, **III** gives the best result. The formation of octene isomers and their successive hydroformylation has an unfavorable effect on the *n:iso* ratio. For the different solvents, $scCO_2$, hexane, and toluene, similar trends in activity and selectivity are observed, indicating that the extent and location of trifluoromethylation, rather than difference in solubility are responsible for the variations observed.

The hydroformylation in $scCO_2$ was performed batch-wise, while for the organic solvents the reaction was performed semi-batch. As can be derived from Table 2 the difference in the mode of operation has a small effect on the overall outcome of the reaction. The fact that the syngas pressure on the reaction rate is almost zero-order seems to be a plausible explanation for this phenomenon.[2] Furthermore, the effects of the partial pressure of hydrogen and carbon monoxide are opposite, and it is to be expected that for an equimolar syngas mixture the partial pressure effects will cancel each other out.

From the different results the following can be concluded in terms of the effect of the solvent and the effect of the ligand. The activity increases up to one order of magnitude with the number of trifluoromethyl substituents attached to the *meta* positions on the aryl rings for $scCO_2$, hexane and toluene in the order **I** > **II** > **III**. The highest activity was found for **I**, using $scCO_2$. Similar ligand-dependent trends in activity and selectivity were observed for the hydroformylation in $scCO_2$, toluene and hexane, with the results in hexane matching closest those obtained in $scCO_2$.

The catalyst **II/**$Rh(CO)_2acac$ gives the best compromise between activity and selectivity towards the linear aldehyde. Conditions were found, using hexane and $scCO_2$ as a reaction medium, where **II/**$Rh(CO)_2acac$ gives a 2.5-fold higher activity and a 5% higher selectivity for the linear aldehyde than **III/**$Rh(CO)_2acac$. A similar selectivity for **2a** with **II/**$Rh(CO)_2acac$ can also be reached using the solvent toluene. However, this required a much higher L:Rh ratio of 100. The combined selectivity towards the aldehydes (linear and branched as well as other isomers) in $scCO_2$, hexane, and toluene follow the order: **III** > **II** > **I**. The higher 1-alkene isomerization activity of the catalyst systems resulting from ligands **I** and **II** is responsible for this effect. The difference in experimental procedure for $scCO_2$ and the organic solvents has a small effect on the overall performance of the hydroformylation of **1a**. This leads to the general conclusion that hexane, rather than toluene, best matches the solvent properties of $scCO_2$ in the context of hydroformylation catalysis.

Experimental Section

Ligands **I** and **II** were supplied by Arkema (Vlissingen). Ligand **III** was purchased from Aldrich. Rhodium(I) dicarbonylacetylacetonate [$Rh(CO)_2acac$] was obtained from Fluka. Ligands **I** and **II** and $Rh(CO)_2acac$ were stored under argon; **1a** was purchased from Aldrich, dried over molecular sieves and stored under argon.

$ScCO_2$ Hydroformylation Procedure

The general procedure for a hydroformylation experiment started with conveying 54.8 ± 0.6 μmol of $Rh(CO)_2acac$ and 27.5 ± 0.6 mmol of fluorinated phosphine ligand into the reactor. After closing the reactor, the reactor volume was carefully flushed with argon and evacuated three times. Next, the stirrer was turned on with a revolution speed of 700 rpm and the desired amount of carbon monoxide and hydrogen gas were fed to the reactor at room temperature. A total pressure of 4.9 MPa was used to obtain a concentration of 1 mol/L for both CO and H_2. The reactor content was then heated to a temperature of 50 °C and subsequently CO_2 was pumped into the reactor to a pressure of 26 MPa. These conditions were maintained for at least half an hour before heating further to the desired reaction temperature. An hour in total, 30 min at 50 °C and 30 min at 70 °C, was considered sufficient to allow the active catalyst complexes to be formed *in situ* from the $Rh(CO)_2(acac)$ precursor and the different fluorous ligands. The **1a** in the feed pump was then compressed to a pressure just above the pressure present in the reactor. The reaction was subsequently initiated by opening the valve between pump and reactor, causing a fast pressure equalization, and by consecutively pumping the desired volume of **1a** into the reactor, which as a rule did not take more than 30 s. Initially, high pressure samples were taken every 10–30 min. At higher conversions the sampling frequency was reduced to 1 per h. The content of the sample volume was carefully bubbled through a vial with a solution of *n*-decane in toluene, and after depressurization the sample volume was rinsed with additional toluene solution to collect **1a** and its reaction products quantitatively. Subsequently the sample volume was dried by alternately applying an argon flow and vacuum. A reaction time of 3 h was observed.

Organic Solvent Hydroformylation Procedure

$Rh(CO)_2(acac)$ (12.5 μmol; S/C = 2000; 1 mL stock solution in toluene) and ligand (0.625 mmol; 50 equivs.) were mixed in 10 mL of degassed toluene and stirred for 0.5 h at 67 °C under an atmosphere of 0.8 MPa syngas. Then **1a** and *n*-decane (25 + 5.5 mmol; 5.0 mL of a standard mixture) were added *via* a short column of alumina, followed by degassed toluene (10 mL). The mixture was pressurized with 10 bar of 1:1 synthesis gas and stirred at 70 °C. Additional syngas was added to maintain the pressure at 1 ± 0.1 MPa. Samples were taken at regular intervals. Conversions and selectivities were determined after a reaction time of 3 h. The TOF was determined after 15 min.

For experiments with hexane or perfluoromethylcyclohexane (pfmch) as solvent a slightly different procedure was followed. $Rh(CO)_2(acac)$ (12.5 μmol; S/C = 2000; 1 mL stock solution in MTBE) and ligand (0.625 mmol; 50 equivs.) were mixed in 5 mL of degassed Et_2O and stirred for 0.5 h at 70 °C under an atmosphere of 0.8 MPa syngas. Volatiles were removed under vacuum and then **1a** and *n*-decane (25 + 5.5 mmol; 5.0 mL of a standard mixture) were added *via* a short column of alumina, followed by degassed hexane or pfmch (20 mL). The remainder of the experiments was carried out following the procedure applied using toluene as the solvent.

Analysis

The samples were analyzed off-line using a Fisons Instruments GF-FID equipped with a Restek Rtx-5 column (fused silica, length 30 m, internal diameter 0.53 mm) where helium was the carrier gas. Calibration was done for **1a**, **3** and **2a**. The sensitivity coefficients for the octene (**1b–g**) and aldehyde isomers (**2b–d**) were taken to be equal to those of **1a** and **2a**, respectively.

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