

Hydroformylation of 1-hexene catalyzed with rhodium fluorinated phosphine complexes in supercritical carbon dioxide and in conventional organic solvents: effects of ligands and pressures

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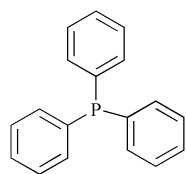
Rhodium-catalyzed hydroformylation of 1-hexene was investigated in compressed CO₂ and organic solvents using different fluorinated phosphine compounds as ligands at a temperature of 333 K. The reaction runs were conducted under conditions where the reaction mixtures were homogeneous in order to examine the activity of the rhodium complexes in different media. The effects of phosphine ligand, CO₂ pressure, syngas (H₂/CO) pressure and solvent on the hydroformylation activity were studied, along with FTIR examination of reaction mixtures. Such phosphine compounds as diphenyl(pentafluorophenyl)phosphine (**II**), bis(pentafluorophenyl)phenylphosphine (**III**), and tris(*p*-trifluoromethylphenyl)phosphine (**VI**) are effective ligands in scCO₂. Compound **II** is better since with it the undesirable isomerization side reaction is avoided. The *n*/*iso* ratio (heptanal/2-methylhexanal) does not change so much with the phosphine ligand used. It is interesting that the aldehyde yield goes through a minimum at about 9 MPa with increasing CO₂ pressure, and it tends to increase with an increase in the syngas pressure. The catalytic activities in scCO₂ are comparable with those in toluene and it is suggested that scCO₂ has some positive effects in promoting the hydroformylation.

Supercritical fluids have been attracting much attentions owing to their unique physical and chemical properties.¹ Supercritical fluids may be used as reaction media, having such merits as organic solvent replacement, better chemistry, and new chemistry, and they will contribute environmentally benign methods for chemical synthesis and processing. Highly pressurized carbon dioxide allows various chemical substances to dissolve in it but it simply separates from them by depressurization. This enables the easy separation of carbon dioxide used as a solvent and/or a reactant from other reactants, products, and catalysts that are liquid or solid. These features of carbon dioxide, in addition to its harmless nature, are of industrial and academic significance.

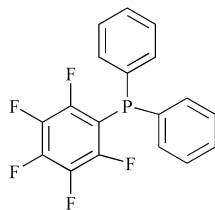
Organometallic complexes are effective catalysts for various chemical transformations in conventional solvents.² Several research groups have studied the combination of these catalysts and supercritical carbon dioxide (scCO₂) with the intention of making better use of both their high activities and its interesting properties.¹ It is possible to conduct homogeneous and heterogeneous catalytic reactions in scCO₂. For homogeneous reactions, organometallic complexes should show the same catalytic performance as obtained in conventional organic solvents but they should be soluble in scCO₂ to a certain extent. Often used metal complexes include phosphine compounds as ligands, which are less soluble in scCO₂. The fluorination of phosphine ligands can, however, lead to an increase in their solubility. According to Wagner *et al.*,³ for example, the solubility of triphenylphosphine in scCO₂ is $5.16 \times 10^{-3} \text{ mol L}^{-1}$ at 10.0 MPa and 310 K and, in contrast, the solubility increases to $60 \times 10^{-3} \text{ mol L}^{-1}$ at 10.1 MPa and 310 K for tris(*p*-fluorophenyl)phosphine and $228 \times 10^{-3} \text{ mol L}^{-1}$

at 9.5 MPa and 310 K for tris(pentafluorophenyl) phosphine. The solubility of organometallic catalysts is a factor in determining the overall rate of homogeneous reactions but the rate also depends on their specific activity. So, it is important to examine such activity in the new reaction medium that is scCO₂ for various chemical transformations.

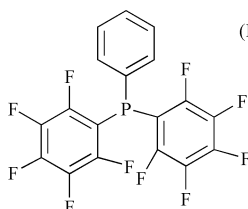
Recently, we have reported Heck reactions in scCO₂ using palladium complexes with several fluorinated phosphine compounds, as shown later in Scheme 1, which showed significant differences in their catalytic activity.⁴ In the present work, the same phosphine compounds have been applied for another type of chemical transformation, rhodium-catalyzed hydroformylation using 1-hexene as a substrate. Since CO and H₂ gases are present in addition to CO₂ in hydroformylation reactions, the environment around the organometallic catalysts is different from that in Heck reactions and so the influence of the phosphine ligands could be different. Several authors previously reported rhodium-catalyzed hydroformylation reactions using fluorinated phosphine ligands in scCO₂.^{5–11} Palo and Erkey studied the activities of rhodium complexes with various fluorinated phosphine compounds for hydroformylation of 1-octene.⁵ They have reported that the activity depends on the phosphine compound used and it increases with decreasing basicity. Osuna *et al.*⁶ and Koch and Leitner⁷ investigated hydroformylation of several olefins in scCO₂ with rhodium catalysts using variously modified phosphine ligands. Bach and Cole-Hamilton studied hydroformylation of 1-hexene with rhodium trialkylphosphine complexes in scCO₂ and in toluene, for which they reported similar TOF values.⁸ In the literature, there are reported other works on hydroformylation reactions in scCO₂¹² and a few authors use heterogeneous catalysts.¹³



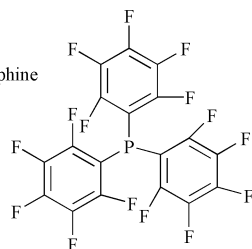
(I) Triphenylphosphine



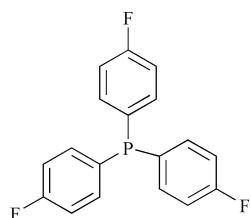
(II) Diphenyl(pentafluorophenyl)phosphine



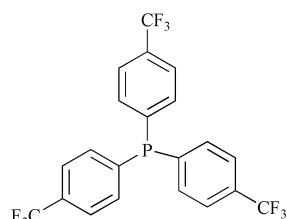
(III) Bis(pentafluorophenyl) phenylphosphine



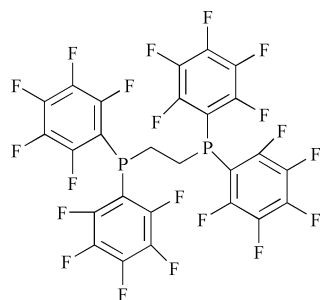
(IV) Tris(pentafluorophenyl)phosphine



(V) Tris(4-fluorophenyl)phosphine



(VI) Tris(p-trifluoromethyl phenyl)phosphine



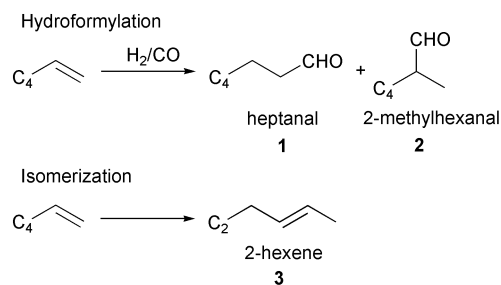
(VII) 1,2-Bis[bis(pentafluorophenyl)phosphino]ethane

Scheme 1 Phosphine compounds used as ligands in this work.

In the present work using such fluorinated phosphine compounds as shown in Scheme 1, most of which are different from those used in the above-mentioned previous works, the authors have studied the effectiveness of these compounds in scCO_2 and in organic solvents and the influence of CO_2 and syngas (CO/H_2) pressures for the hydroformylation of 1-hexene. Pressure effects have not been much studied so far in the literature.

Results and discussion

Under the present conditions, the products heptanal (**1**), 2-methylhexanal (**2**), and 2-hexene (**3**) were formed from



Scheme 2 Hydroformylation and isomerization of 1-hexene.

hydroformylation or isomerization, as shown in Scheme 2, and the product distribution was observed to change depending on the catalysts and pressures of CO_2 and syngas.

Reactions in scCO_2

Figure 1 shows the results obtained at CO_2 partial pressures of 8 MPa and 12 MPa and at a syngas partial pressure of 4 MPa. The phosphine compounds used as ligands markedly change the overall conversion of 1-hexene and the overall yield of aldehydes, while they do not affect the **1** : **2** ratio so much. The effectiveness of the ligands for the yield of aldehydes is **VI** > **II**, **III** > **V** > no ligand \approx **IV** > **I** > **VII** at CO_2 8 MPa and **VI** > **III** > no ligand \approx **IV** > **II** > **V** > **I** > **VII** at CO_2 12 MPa. The ligand **VI** is the most effective and the total aldehyde yield is about 65% with a **1** : **2** ratio of 2.3 but it also causes the isomerization giving **3**. Although the catalyst with the ligand **II** is slightly less active than that with the ligand **VI**, it gives little isomerization product **3**. The other fluorinated ligands, except for **VII**, are more effective compared with the reference phosphine **I**. An increase in CO_2 pressure has a significant effect on the overall conversion only in two cases, with

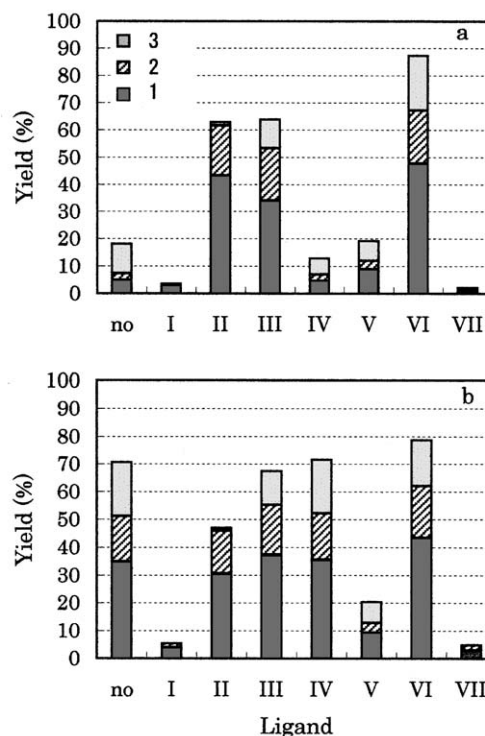


Fig. 1 Influence of fluorinated phosphine ligands on hydroformylation and isomerization of 1-hexene in condensed carbon dioxide at pressures of 8 MPa (a) and 12 MPa (b). Conditions: 1-hexene 0.318 mol L^{-1} , R_h $2.47 \times 10^{-2} \text{ mol L}^{-1}$, ligand/ R_h = 4, syngas (CO/H_2) partial pressure 4 MPa, 333 K, 2 h. Products: **1**: heptanal, **2**: 2-methylhexanal, **3**: 2-hexene.

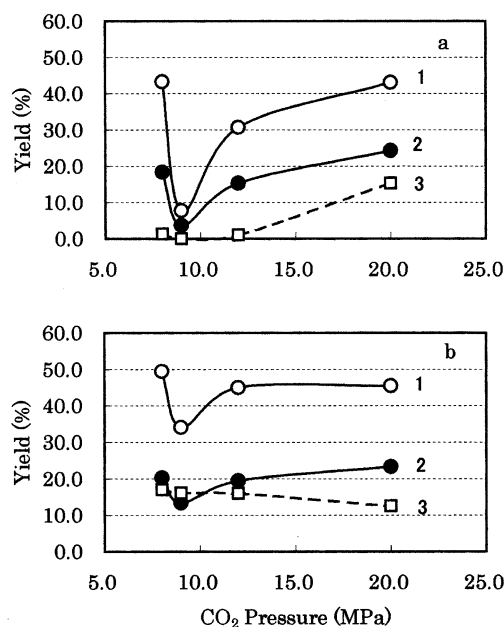


Fig. 2 Influence of CO₂ pressure on hydroformylation and isomerization of 1-hexene catalyzed by Rh complexes with the ligands **II** (a) and **VI** (b). Conditions: 1-hexene 0.318 mol L⁻¹, Rh 2.47 × 10⁻² mol L⁻¹, ligand/Rh = 4, syngas (CO/H₂) partial pressure 4 MPa, 333 K, 2 h. Products: 1: heptanal, 2: 2-methylhexanal, 3: 2-hexene.

the ligand **IV** and without any ligand. For the other ligands, the yields of aldehydes are similar at CO₂ partial pressures of 8 or 12 MPa. These effects of the phosphine compounds and CO₂ pressure observed are different from those previously reported for Heck reactions.⁴

The influence of CO₂ pressure has been examined with the catalysts using the phosphine compounds **II** and **VI** at a syngas partial pressure of 4 MPa. The results are given in Fig. 2, indicating that the yield of aldehydes goes through a minimum at about 9 MPa with CO₂ pressure for the both catalysts although the change is more significant for the phosphine **II**. For this ligand, isomerization does not occur at CO₂ pressures of 12 MPa or below while it proceeds at a higher CO₂ pressure of 20 MPa. For the phosphine **VI**, in contrast, the isomerization can occur even at 8 MPa CO₂ and the yield of the isomerization product decreases slightly with CO₂ pressure. Naked eye observations showed that the reaction mixtures were homogeneous at pressures used in the experiments of Fig. 2. It was also observed that solid rhodium complexes were seen to deposit after depressurization following the reactions only at a CO₂ pressure of 9 MPa. It is speculated that at this pressure some fraction of the catalysts precipitate from the CO₂ solvent or metal complexes such as dicarbonyls are also formed. This causes a decrease in the concentration of active species in the solvent, giving drastic decreases in the yields of aldehydes; in the other cases, the catalyst complexes were in the organic liquid phase after the reaction experiments. Probably the solvent nature of CO₂ at 9 MPa is significantly different compared with that at lower and higher pressures, resulting in the decrease in the yields of aldehydes. With increasing CO₂ pressure, the yields of aldehydes increase and show little change for the phosphines **II** and **VI**, respectively. These types of pressure dependence are interesting because the substrate and the catalyst are significantly diluted with increasing CO₂ pressure and thus the reaction would be expected to slow down. This dilution effect is likely to be cancelled or overcome by other effects; the details are not known at present but highly dense CO₂ should improve the specific activity of the catalysts for hydroformylation.

Figure 3 shows the influence of the syngas partial pressure for rhodium catalysts with the phosphines **II** and **VI** and

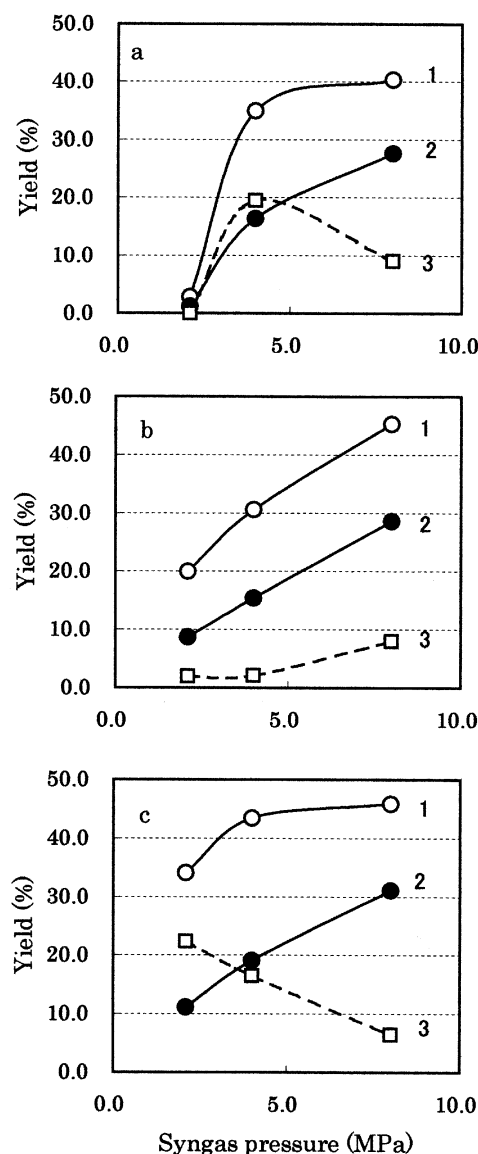


Fig. 3 Influence of syngas (CO/H₂) pressure on hydroformylation and isomerization of 1-hexene catalyzed by Rh precursor with no phosphine ligands (a) and Rh complexes with the ligands **II** (b) and **VI** (c). Conditions: 1-hexene 0.318 mol L⁻¹, Rh 2.47 × 10⁻² mol L⁻¹, ligand/Rh = 4, CO₂ partial pressure 12 MPa, 333 K, 2 h. Products: 1: heptanal, 2: 2-methylhexanal, 3: 2-hexene.

without any ligands at a CO₂ partial pressure of 12 MPa. For all the cases examined, the yield of aldehydes tends to increase with the syngas pressure but the 1 : 2 ratio decreases. This pressure dependence of the aldehyde yield is different from that reported by Koch and Leitner,⁷ who indicate that the yield decreases with the syngas pressure (3–6 MPa) for hydroformylation of 1-octene in scCO₂. Compared with the previous results with 1-octene and higher olefins,^{7,9} the extent of isomerization is large in the present study with 1-hexene. The pressure dependence of isomerization changes with the phosphine used; the yield of **3** has a maximum at about 4 MPa in the absence of phosphines, slightly increases for the phosphine **II**, but decreases for the phosphine **VI**. At a higher syngas pressure of 8 MPa, a hydrogenated product of hexane was observed to form in 10–15% yields, with a trace amount of 3-methylhexanal, for all the ligands.

Concerning the influence of CO₂ pressure, it should be noted again that the yield of aldehydes, **1** + **2**, is minimized near the critical pressure of CO₂, as demonstrated in Fig. 2, in contrast with previous observations reported in the literature. Several

authors observed the occurrence of maximum reaction rates or maximum conversions near the critical pressure for several reactions.¹⁴ Although the present authors do not have a clear explanation for the minimum observed, a possibility is given hereafter, which invokes an inhibition effect of high CO concentration (pressure)¹⁰ and increased local concentration.¹⁵ It is postulated that the local concentration of CO around the rhodium complex catalyst is increased near the critical pressure of CO₂ and this decreases the rate of hydroformylation. In the initial stage of reaction, the reaction mixture was seen to be homogeneous in a single phase by naked eye observations, even at CO₂ pressures near the critical point. However, a fraction of the rhodium complex catalysts could have changed during the course of reaction due to the inhibition effect of CO and they precipitated and separated as solids from the organic liquid phase after reaction followed by depressurization, as described above. The inhibition effect is typical of hydroformylation kinetics in homogeneously catalyzed reactions with rhodium complex catalysts. Davis and Erkey reviewed the rate expressions for hydroformylation of olefins in organic solvents and scCO₂.¹⁰ There are large differences among the rate expressions in the literature, indicating differences in the mechanism and/or the rate-determining step, but these include the inhibition effect at higher CO partial pressures. They discussed possible explanations for this CO inhibition effect on the basis of a reaction mechanism. The local concentration concept has been proposed to explain unexpected types of behavior that are observed in supercritical fluids.¹⁵

IR spectroscopy in scCO₂

Figure 4 shows FTIR spectra from 2200 to 1800 cm⁻¹ for the catalytic species in scCO₂ at CO₂ and H₂/CO partial pressures of 12 MPa and 0.1 MPa, respectively. The absorbance with **I** (b) is very weak and the spectra with no ligands (a) and **IV** (e) have two peaks at 2020 and 2089 cm⁻¹ assigned to carbonyl.^{5,16} The latter two spectra were found to be the same as that of the rhodium precursor measured in air, indicating that the phosphine **IV** did not complex the metal, in agreement with the previous result of Palo and Erkey,⁵ and so the metal precursor remained unchanged. As a consequence, very similar reaction results were obtained in the absence of any phosphines and in the presence of the phosphine **IV**, as described

above. With **III** (d), a shoulder is seen at 2009 cm⁻¹, in addition to the two large peaks at 2020 and 2089 cm⁻¹, and so some metal precursors remained unchanged but the residual ones complexed the phosphine **III**, producing more active species. With **II** (c), **V** (f), and **VI** (g), in contrast, a single peak exists at different positions of 1995, 1989 and 1996 cm⁻¹, respectively. So, active species were formed with the phosphines **II**, **V**, and **VI**, for which the rhodium complex with the phosphine **V** is less active than those with the other two phosphines. The spectrum (h) is very different from the other spectra, having a peak at 1725 cm⁻¹ due to bridge-type carbonyl. The phosphine **VII** may coordinate with the metal but the complex formed is different from those with the phosphines **II**, **III**, **V**, and **VI** and it is much less active and its activity is comparable with that of the phosphine **I**.

According to Erkey and co-workers^{5,10} the basicity of the ligand affects the electronic nature of the metal and the absorption of carbonyl would shift to higher frequency with a decrease in the basicity. For the present cases in which metal-phosphine complexes are formed, the basicity is expected to be in the order of the phosphine **VI**, **II** > **V**, which corresponds to the order of the hydroformylation activity at a CO₂ pressure of 12 MPa. So, when the basicity of the ligand is weaker, the metal complex formed is more active in the present cases as well. It is interesting that the metal complex with the phosphine **II** is active for hydroformylation but it is much less active for isomerization, in contrast to the complexes with the phosphines **VI** and **V**.

Reactions in organic solvents

The results in organic solvents and under solvent-less conditions are shown in Fig. 5. The isomerization product was analyzed for the reactions in toluene and under solvent-less conditions but not for the others due to limitation of the analysis. Relatively high yields of aldehydes were obtained for the catalysts with the ligands **II**, **V**, and **VI**. The catalyst with the ligand **IV** is also effective but only in toluene. In toluene, hydroformylation took place but the isomerization did not occur for the catalysts with the ligands **IV** and **V**, in contrast to the results in scCO₂. The 1 : 2 ratio does not depend much on the solvent used.

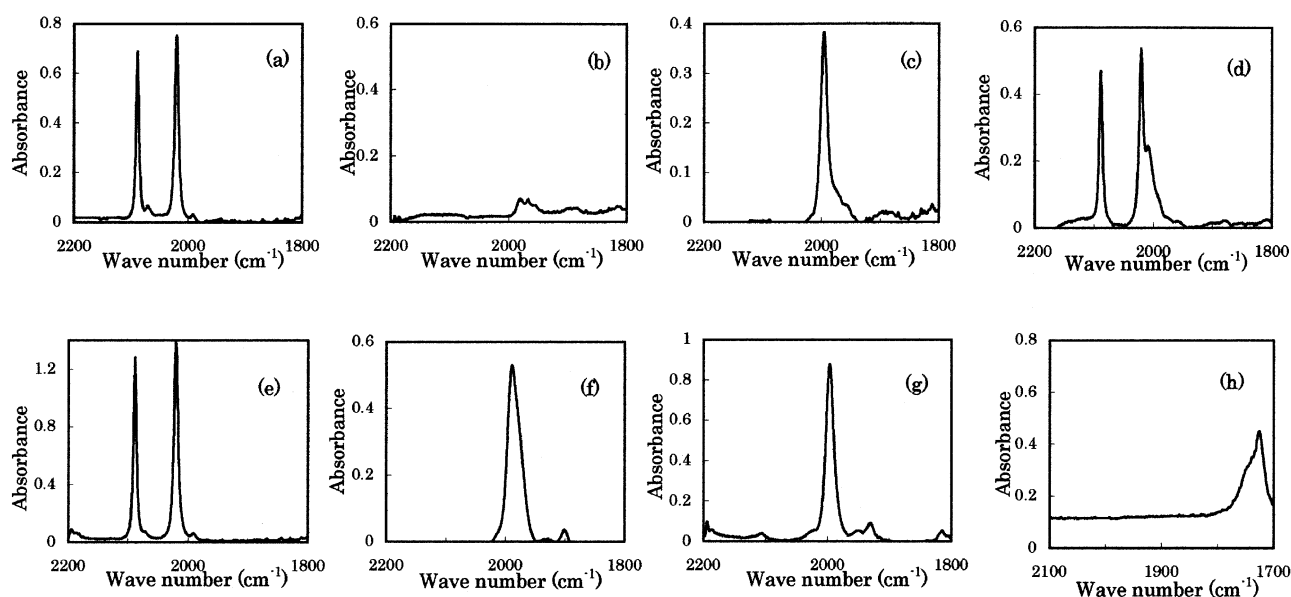


Fig. 4 FTIR spectra for Rh precursor with no phosphine ligands (a) and Rh complexes with the phosphines **I** (b), **II** (c), **III** (d), **IV** (e), **V** (f), **VI** (g), and **VII** (h) in scCO₂ at 333 K. Conditions: rhodium 2.59×10^{-3} ml L⁻¹, phosphine/rhodium = 4, CO₂ 12 MPa, syngas (CO/H₂) 0.1 MPa.

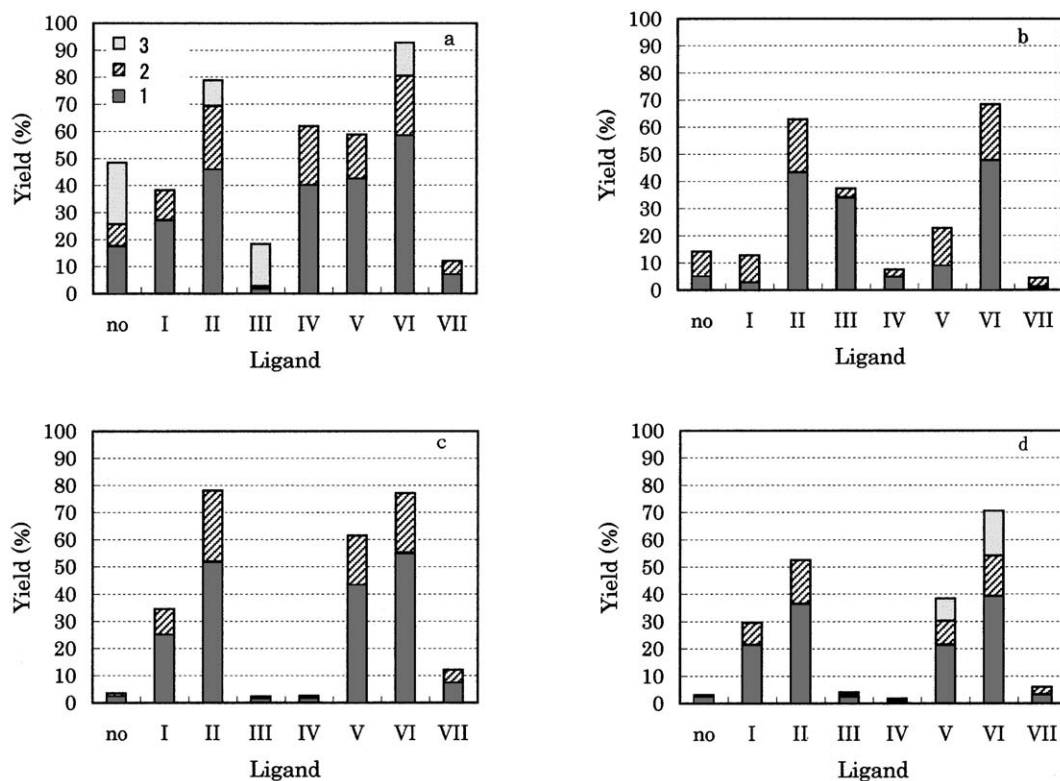


Fig. 5 Influence of fluorinated phosphine ligands on hydroformylation and isomerization of 1-hexene in different organic solvents: (a) toluene, (b) ethyl acetate, (c) hexane, (d) without solvent. Conditions: 1-hexene 7.95 mol L^{-1} , Rh $1.77 \times 10^{-3} \text{ mol L}^{-1}$ (a,b,c), $6.20 \times 10^{-3} \text{ mol L}^{-1}$ (d), ligand/Rh = 4, syngas (CO/H_2) 4 MPa, 333 K, 2 h. Products: **1**: heptanal, **2**: 2-methylhexanal, **3**: 2-hexene.

The influence of syngas pressure has been examined in toluene in the presence of the phosphines **II** and **VI** and in the absence of any phosphines (Table 1). The yield of aldehydes at 8 MPa is larger but the selectivity of **1** at 8 MPa is smaller compared with those at a lower syngas pressure of 4 MPa. These trends are in agreement with those observed in scCO_2 .

Comparison between scCO_2 and organic solvents

The results in scCO_2 and organic solvents using the phosphine compound **VI** are compared in Table 2. Under the conditions used, the reaction was seen to occur in a single homogeneous phase. The organic solvents except for NMP give only slightly higher yields of aldehydes than scCO_2 . Turnover numbers (TON) for 2 h in scCO_2 are 865 and 800 at CO_2 partial pressures of 8 and 12 MPa, respectively. In agreement with the previous report of Bach and Cole-Hamilton,⁸ these TON values are comparable with those in organic solvents, for which TON is 1031 in toluene, 918 in ethyl acetate and 990 in hexane. Turnover frequency (TOF) in scCO_2 is 433 h^{-1} at 8 MPa and 400 h^{-1} at 12 MPa. These TOF values are higher by about one order of magnitude than those reported previously¹³ for

hydroformylation of 1-hexene in scCO_2 using $\text{Rh-P}(\text{C}_2\text{H}_5)_3$ catalyst at a somewhat higher temperature of 363 K. Of course, the TON and TOF values depend on reaction conditions. The concentrations of the catalyst and the substrate in scCO_2 in mol L^{-1} are smaller by a factor of about 1/7 than those in the organic solvents. This will decrease the total conversion of the substrate in scCO_2 ; however, the concentration of the syngas is increased with disappearance of the gas-liquid interface and complete dissolution of the syngas into the scCO_2 solvent. This may partially explain that the total conversion data in scCO_2 and organic solvents are comparable. On the basis of mole fraction, there are larger differences between the organic solvents and scCO_2 . Estimates of mole fractions of reactants and catalyst are given in Table 2. It is again indicated that scCO_2 has a positive effect, enhancing the specific activity of the catalysts, which exceeds the dilution effect with increasing pressure.

Conclusions

The present results demonstrate that the phosphine compounds **II**, **III**, and **VI** are effective ligands for the rhodium complexes that are active for the hydroformylation of 1-hexene in scCO_2 . Compound **II** is better in that the complex formed catalyzes little isomerization. The 1:2 ratio does not change much with the phosphine ligand used. The yield of aldehydes (**1** + **2**) goes through a minimum at about 9 MPa with increasing CO_2 pressure. The yield of the isomerization product **3** changes with CO_2 pressure in different ways depending on the phosphine ligand used. The yield of aldehydes tends to increase with an increase in the syngas (H_2/CO) pressure, while the yield of **3** changes differently with the syngas pressure depending on the ligand used. The results obtained in scCO_2 are comparable with those in toluene and it is suggested that scCO_2 has some positive effects in promoting the hydroformylation.

Table 1 Influence of syngas pressure on hydroformylation of 1-hexene in toluene^a

Phosphine ligand	Yield of aldehydes (%)		Product ratio 1/2	
	4 MPa	8 MPa	4 MPa	8 MPa
None	25.7	57.4	2.13	1.42
II	69.3	79.7	1.94	1.65
VI	80.4	85.1	2.65	1.70

^a Conditions: rhodium $1.77 \times 10^{-3} \text{ mol L}^{-1}$, 1-hexene 2.27 mol L^{-1} , ligand/rhodium = 4, temperature 333 K, time 2 h. Syngas: $\text{CO}:\text{H}_2 = 1:1$.

Table 2 Comparison of yields of **1** + **2** and **3** in hydroformylation and isomerization of 1-hexene catalyzed with the Rh complex containing the ligand **VI**, tris(*p*-trifluoromethyl phenyl) phosphine, in different solvents^a

Solvent	Concentration (mol L ⁻¹)		H ₂ ^b	CO ^b	Yield (%)	
	1-Hexene	Rh			1 + 2 (1/2)	3
CO ₂ , 8 MPa	0.318 (0.05) ^c	0.247 × 10 ⁻³ (4.0 × 10 ⁻⁵) ^c	0.761 (0.12) ^c	0.761 (0.12) ^c	67.2 (2.44)	20.1
CO ₂ , 12 MPa	0.318 (0.03) ^c	0.247 × 10 ⁻³ (2.1 × 10 ⁻⁵) ^c	0.761 (0.06) ^c	0.761 (0.06) ^c	62.2 (2.31)	16.5
Toluene	2.27 (0.25) ^c	1.77 × 10 ⁻³ (1.9 × 10 ⁻⁴) ^c	0.032 ^d (0.004) ^c	0.107 ^d (0.012) ^c	80.4 (2.65)	14.5
Ethyl acetate	2.27	1.77 × 10 ⁻³	—	—	71.6 (2.45)	—
Hexane	2.27	1.77 × 10 ⁻³	—	—	77.2 (2.51)	—
NMP	2.27	1.77 × 10 ⁻³	—	—	0 (—)	—

^a Reaction conditions: 1-hexene/Rh = 1280, syngas (H₂/CO) 4 MPa, 333 K, time 2 h. ^b Rough estimates based on van der Waals equations of state for H₂ and CO (ref. 17). ^c Mole fraction. The density of CO₂ was obtained from ref. 18. ^d Estimates using Henry's constants for H₂ and CO from ref. 19.

Experimental

Seven phosphine compounds, as shown in Scheme 1, were used as ligands, of which the ligand **VI** was purchased from Strem and the others from Aldrich. These were used without further purification.

Hydroformylation experiments were conducted batchwise in a 50 cm³ high-pressure stainless steel reactor with a magnetic stirrer, a high-pressure liquid pump, and a back-pressure regulator.^{4,20} The reactor was charged with 1-hexene, Rh(acac)(CO)₂ (both from Wako), and a phosphine ligand and heated to a reaction temperature of 333 K using a water bath. Then syngas (H₂ : CO = 1:1) was charged into the reactor to a certain pressure (4 MPa in many cases) followed by introduction of liquid CO₂. The reaction was continued for 2 h. After the reaction, the reactor was cooled by ice water to near room temperature and depressurized with the back-pressure regulator. The reaction mixture was analyzed by a gas chromatograph packed with a capillary column using a flame ionization detector and a mass spectrometer.

The phase behavior was examined with a 10 cm³ high-pressure stainless steel reactor with sapphire windows and a magnetic stirrer. The reactor was charged with 1-hexene (3.18 × 10⁻³ mol), Rh(acac)(CO)₂ (2.48 × 10⁻⁶ mol), and a phosphine ligand (9.92 × 10⁻⁶ mol) and heated to 333 K, which was controlled with a heated oil circulating system. Then the syngas was charged into the reactor and pressurized by introducing liquid CO₂ to a given pressure. The mixture in the reactor was examined by the naked eye and also recorded on a video recorder.

The Rh complexes in scCO₂ were examined with an *in situ* FTIR using a 1.5 cm³ high-pressure cell with a path length of 4 mm. The cell was charged with Rh(acac)(CO)₂ (3.88 × 10⁻⁶ mol) and phosphine ligand (1.55 × 10⁻⁵ mol) followed by introduction of the syngas (0.1 MPa) and liquid CO₂ (14 MPa). The FTIR measurements were made at 333 K.

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