

Hydroformylation of 1,5-Hexadiene Catalyzed by Rhodium Complexes in Supercritical Carbon Dioxide and in Toluene: Effects of Fluorinated Phosphane Ligands and Reaction Conditions

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Rhodium-catalyzed hydroformylation of 1,5-hexadiene to dialdehydes was investigated in compressed CO₂ and in toluene using different fluorinated phosphane compounds as ligands at a temperature of 60 °C. Product yields depend greatly on the ligand used and, of the ligands examined, tris[3,5-bis(trifluoromethyl)phenyl]phosphane is the most effective for the production of dialdehydes both in supercritical CO₂ (scCO₂) and in toluene. The total yield of the dialde-

hydes passes through a minimum at about 9 MPa as the CO₂ pressure is increased and increases appreciably as the H₂ pressure in scCO₂ increases. The effect of the syngas (H₂/CO) and H₂ pressures on the reaction in scCO₂ is different from that in toluene. It has been suggested that scCO₂ promotes the hydroformylation reaction.

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Introduction

Supercritical carbon dioxide (scCO₂) is gaining considerable interest as an ecologically benign and economically feasible new generation reaction medium that could replace conventional toxic, flammable organic solvents.^[1,2] Various chemical substances are soluble in scCO₂ and they can be easily separated by depressurization; scCO₂ is also nonflammable, nontoxic and has no gas/liquid phase boundary. The physicochemical properties of scCO₂ can be tuned within a certain range by adjusting the pressure and temperature, these also being the parameters for optimization of reactions in this solvent.

Organometallic complexes are effective catalysts for various chemical transformations in conventional solvents.^[3] Although homogeneous organometallic catalysis in scCO₂ is attractive, the organometallic complexes must be soluble in scCO₂. Phosphane ligands, such as triphenylphosphane (TPP), that are often used in these complexes are less sol-

uble in scCO₂ than in conventional solvents. However, fluorination of these ligands improves their solubility^[4] and hence metal complexes with fluorinated ligands can be effectively used as catalysts in scCO₂. The solubility of metal complexes is a determining factor in the overall reaction rate, but the rate also depends on their specific activity, which can be changed by fluorination of the ligands. Several groups, including us, have already reported hydroformylation,^[5–18] coupling reactions^[19–21] or hydrogenation^[22] in scCO₂ using metal complexes with different fluorinated phosphane compounds as ligands. Some of the fluorinated ligands are superior to TPP, when compared under homogeneous conditions, but the effectiveness of the fluorinated ligand is different for each reaction.

Dialdehydes are valuable intermediates in the preparation of commercially important products and as cross-linking agents for polymers.^[23] Hydroformylation of diolefins produces dialdehydes,^[23–32] but no one has investigated this reaction in scCO₂ so far. Very recently, we reported a preliminary investigation into the hydroformylation of diolefins in scCO₂^[33] and a detailed study of the title reaction is now reported here. We have studied the effectiveness of several phosphane compounds (shown in Scheme 1) in the hydroformylation of diolefins in scCO₂ and in toluene and the effect of CO₂, syngas (CO/H₂), H₂ and CO pressures on the reaction. The effects of pressure on this reaction have not been well studied so far.

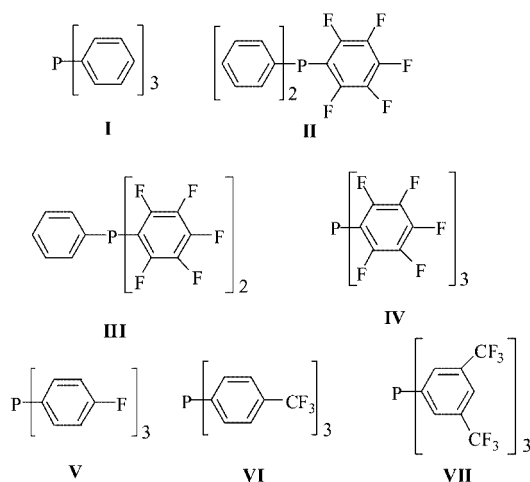
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Scheme 1. Structures of the phosphane ligands used in the hydroformylation reactions

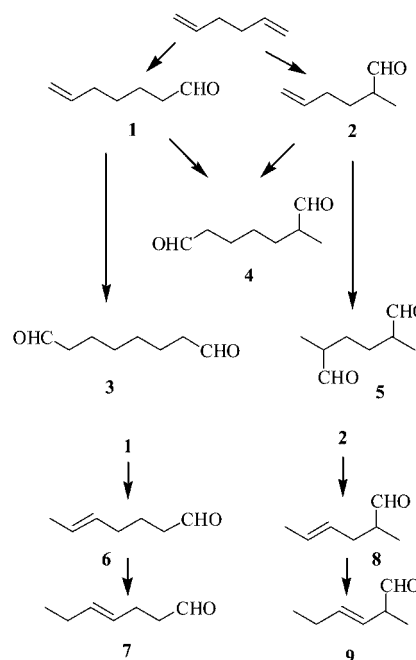
Results and Discussion

FT-IR Spectra of Rhodium Complexes with Various Ligands

Figure 1 shows IR spectra between 1800 and 2200 cm^{-1} for the catalytic species in 14 MPa of scCO_2 at a syngas (H_2/CO) pressure of 0.1 MPa. The spectrum of the rhodium complex with ligand **I** (a) has very weak bands at around 1900 cm^{-1} . The spectrum of the complex with ligand **IV** (d) has strong absorption bands at 2020 and 2089 cm^{-1} , ascribed to carbonyl stretching, and is the same as that of the precursor measured in air, indicating that this ligand does not form a complex with rhodium, in agreement with previous results.^[13,18] With ligand **III** (c), the spectrum shows a shoulder peak at 2009 cm^{-1} along with the two strong peaks of the rhodium precursor, suggesting that most of the precursors remain unchanged. In contrast, strong carbonyl absorption bands appear at 1995, 1989, 1996 and 2005 cm^{-1} with ligands **II** (b), **V** (e), **VI** (f) and **VII** (g), respectively. Thus, active species are formed with these ligands.

Hydroformylation of 1,5-Hexadiene in scCO_2 with Various Ligands

Under the reaction conditions used in this work, the products 6-hepten-1-al (**1**), 2-methyl-5-hexen-1-al (**2**), 1,8-octanediol (**3**), 2-methyl-1,7-heptanediol (**4**) and 2,5-dimethyl-1,6-hexanediol (**5**) were formed from the hydroformylation of 1,5-hexadiene, as shown in Scheme 2. Along with these compounds, 1,4-hexadiene and 2,4-hexadiene were formed by isomerization of the substrate, the former being the main product of this isomerization. Only small amounts of the monoaldehydes **1** and **2** were further isomerized to 5-heptene-1-al (**6**) or 4-heptene-1-al (**7**) and 2-methyl-4-hexene-1-al (**8**) or 2-methyl-3-hexene-1-al (**9**), respectively. Monoaldehyde **6** was the main product of the monoaldehyde isomerization. The product distribution was



Scheme 2. Hydroformylation of 1,5-hexadiene

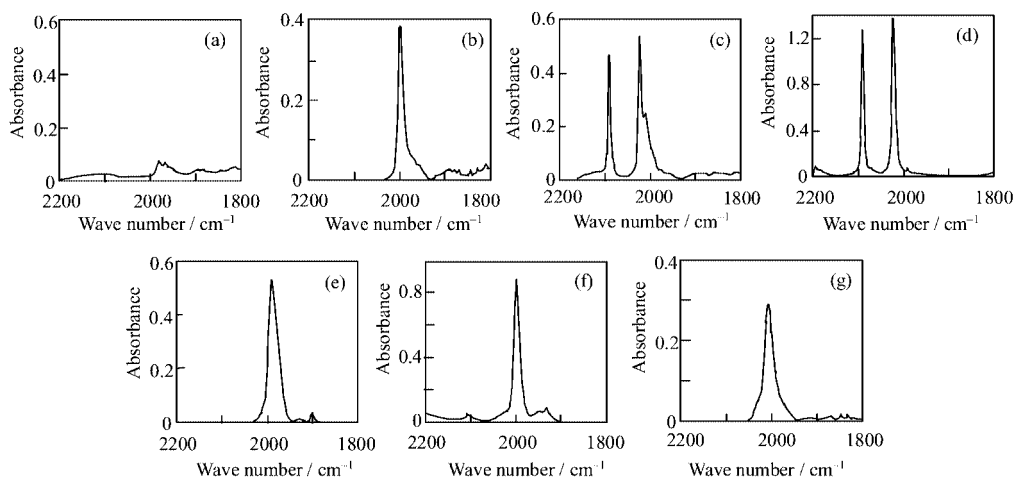


Figure 1. FT-IR spectra of rhodium complexes with ligands **I** (a), **II** (b), **III** (c), **IV** (d), **V** (e), **VI** (f) and **VII** (g) in scCO_2 . Reaction conditions: 3.9 mmol $[\text{Rh}(\text{CO})_2(\text{acac})]$, ligand/Rh = 4:1, 14 MPa CO_2 , 0.1 MPa CO/H_2 , temperature 60 $^\circ\text{C}$

observed to change depending on the nature of the catalyst and the reaction conditions used. The formation of these various compounds poses challenges for controlling the selectivity of the dialdehyde products.

Figure 2 shows the results obtained at a CO₂ pressure of 12 MPa and at a syngas pressure of 4 MPa. The phosphane ligands significantly changed the overall conversion of 1,5-hexadiene and the overall yields of the dialdehydes. The effectiveness of the ligands in the production of dialdehydes decreases in the order **VII** > **VI** > **II** >> **IV** > **III** > **V** > **I**, no ligand. The fluorinated ligands are more effective than the reference phosphane **I**. The catalyst with ligand **VII** gives the highest total yield of the dialdehydes **3**, **4** and **5**. The regioselectivity is also different for each ligand. With ligand **VII**, the linear dialdehyde **3** constitutes 57% of all the dialdehydes produced. With the other ligands, this fraction is below 45%. Thus, ligand **VII** is the most effective for the production of the linear dialdehyde **3**.

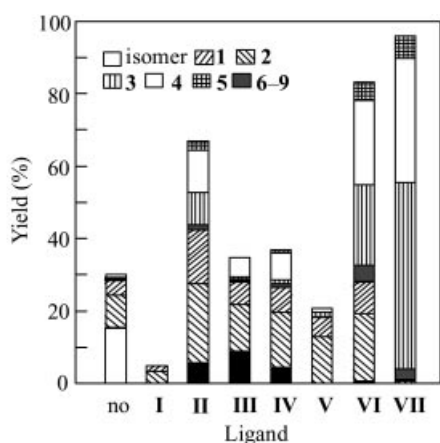


Figure 2. Effect of the fluorinated phosphane ligands on the hydroformylation of 1,5-hexadiene in supercritical carbon dioxide; reaction conditions: 11.5 mmol substrate, 12.4 μ mol catalyst, ligand/Rh = 4:1, 12 MPa CO₂, 4 MPa syngas, temperature 60 °C, time 2 h

As Figure 1 shows, the carbonyl absorption band appears at the largest wave number for the most active catalyst, that is, the catalyst with ligand **VII**. Palo and Erkey carried out the hydroformylation of 1-octene in scCO₂ using several flu-

orinated ligands.^[13] These ligands included the compounds **IV**, **VI** and **VII** used in this study. In agreement with the results obtained in this work, they reported that ligand **VII** showed the best activity of the ligands used. They also showed that the position of the carbonyl stretching band of the metal complex [HRhCOL₃] changed for each ligand used and correlated well with the activity of the complex; the carbonyl bands of the more active complexes appeared at larger wave numbers. We also obtained similar results for the hydroformylation of 1-hexene.^[18] It has been concluded that the ligand with the least basic properties induced by fluorine atoms gives the most active catalyst for the hydroformylation.^[13,18] We can draw the same conclusion for the (phosphane)rhodium complexes used in this study.

Effect of the Reaction Conditions on the Reaction in scCO₂

The effects of various reaction conditions were investigated using the most effective ligand **VII** under conditions in which the amount of catalyst was reduced to half so that low conversion of the substrate was obtained. Table 1 shows the effect of the reaction time and catalyst loading on the reaction. As the reaction time is lengthened, the total yield of the dialdehydes increases and that of the monoaldehydes decreases (Entries 1–3). However, the total yield of the dialdehydes is below 70% and the monoaldehydes still remain in the reaction mixture, even when the reaction is carried out for 4 h. As expected, the dialdehydes are obtained in high yields by using increasing amounts of catalyst (Entries 1, 5 and 6). Increasing the catalyst loading instead of the reaction time improves dialdehyde production. The fraction of the linear dialdehyde **3** in all the dialdehydes produced does not change with catalyst loading. Table 1 also shows that substrate isomerization can be reduced by increasing the catalyst loading. A similar effect of catalyst loading on the isomerization has been reported for the hydroformylation of 1-hexene in scCO₂ by Sellin et al.^[17]

The effect of CO₂ pressure has been examined using the catalyst with ligand **VII** at a syngas pressure of 4 MPa. The results are given in Figure 3 and indicate that the conversion passes through a minimum at 9 MPa of CO₂ pressure. The product distribution also changes with CO₂ pressure. The total yield of the dialdehydes is also a minimum at 9

Table 1. Effect of the reaction time and catalyst loading on hydroformylation of 1,5-hexadiene catalyzed by a rhodium complex with ligand **VII** in scCO₂

Entry ^[a]	Time [h]	Catalyst loading [μ mol]	Yield (%)			
			1 + 2 (1/2)	3 + 4 + 5 (3/4/5)	6–9 ^[b]	Isomer
1	0.5	6.2	47 (74:26)	22 (55:37:8)	0.8	1.6
2	1	6.2	43 (73:27)	42 (54:38:8)	1.5	4.0
3	2	6.2	16 (69:31)	66 (54:39:7)	4.7	2.5
4	4	6.2	19 (69:31)	64 (52:41:7)	6.2	4.4
5	0.5	12.4	21 (70:30)	72 (58:36:6)	2.8	0.4
6	0.5	24.8	1.5 (53:47)	90 (58:36:6)	6.0	0.2

^[a] Reaction conditions: 11.5 mmol substrate; ligand/Rh = 4:1; 12 MPa CO₂; 4 MPa syngas; temperature, 60 °C. ^[b] Total yield of the monoaldehydes **6**, **7**, **8** and **9**.

MPa and the fraction of the linear dialdehyde tends to decrease with increasing CO₂ pressure. On the other hand, the total yields of the monoaldehydes and of the substrate isomers only increase slightly with increasing CO₂ pressure.

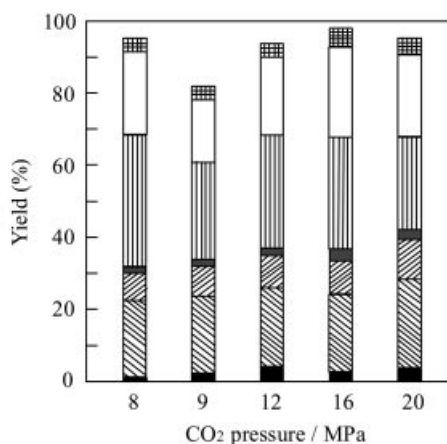


Figure 3. Effect of CO₂ pressure on the hydroformylation of 1,5-hexadiene catalyzed by a rhodium complex with ligand **VII**; reaction conditions: 11.5 mmol substrate, 6.2 μ mol catalyst, ligand/Rh = 4:1, 4 MPa syngas, temperature 60 °C; time 1 h; bars represent the same products as those in Figure 1

Figure 4 shows photographs of the reaction mixture taken at various CO₂ pressures. Initially, the reaction mixture is homogeneous at all the pressures examined in Figure 3 (Figure 4, a). However, its state changes as the reaction proceeds depending on the CO₂ pressure. At 8 MPa, the homogeneous phase changes to a gas/liquid system within 5 min (Figure 4, b). At 9 MPa, the liquid phase could be observed after 15 min. In both cases, the amount of liquid increased with the reaction time. At 12 MPa, a very small amount of the liquid phase was observed after 50 min and still less liquid was produced as the reaction time further increased. Above 16 MPa, the reaction mixture is completely homogeneous even after 2 h (Figure 4, c). The solubility of the aldehydes in scCO₂ depends on its pressure, which accounts for the differences in the phase behavior in this system. We previously observed that CO₂ pressure has

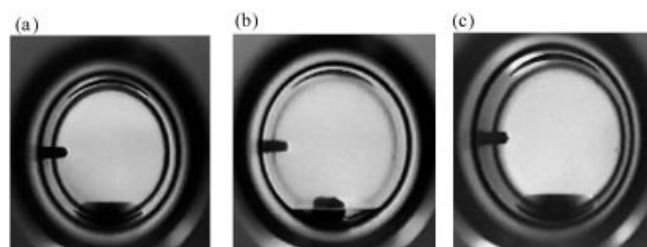


Figure 4. Photographs of the reaction mixture taken after the reaction was carried out for (a) 1 min at 8 MPa of CO₂, (b) 20 min at 8 MPa, (c) 2 h at 16 MPa; the black object at the bottom is a stirrer bar, which is “moving” in photographs (a) and (c); reaction conditions: 2.48 μ mol [Rh(CO)₂(acac)], 9.9 μ mol ligand **VII**, 4 MPa CO/H₂, temperature 60 °C

a similar effect on the hydroformylation of 1-hexene; solid particles were formed only after the reaction was carried out at 9 MPa.^[18] We speculated that some of the rhodium complex precipitated from scCO₂. In the present reaction, the formation of solid particles was not observed; however, the solvent nature of CO₂ at 9 MPa must be significantly different from that at lower and higher pressures, which results in the decrease in the yields of dialdehydes.

In other reactions in scCO₂, a decrease in the product yield with increasing CO₂ pressure was sometimes observed.^[34–40] This has been ascribed to a dilution effect of scCO₂. However, this dilution effect is not significant for the title reaction, as indicated in Figure 3. The dilution effect is likely to be cancelled or overcome by other effects; the details are not known now but scCO₂ may improve the overall reaction rate of hydroformylation at higher pressures.

The influence of syngas (CO/H₂), H₂ and CO pressures was also investigated at a CO₂ pressure of 12 MPa. The results obtained are summarized in Table 2. The syngas pressure has no significant influence on the total yields of the mono- and dialdehydes (Entries 1–3), although a slight decrease in the total yield of the dialdehydes and a slight increase in the substrate isomer are observed at 6 MPa (Entry 3). When the H₂ pressure is changed from 2 MPa to 4 MPa, the dialdehyde yields are enhanced significantly (Entries 2 and 4). However, a further increase in H₂ pressure causes a slight decrease in the total yield of the dialdehydes due to the isomerization of the monoaldehydes produced; the total yields of the mono- and dialdehydes are constant above 6 MPa (Entries 5 and 6). This suggests that the hydroformylation rate reaches a maximum at high H₂ pressure. On the other hand, a higher CO pressure retards the reaction and this effect is more significant for the yields of dialdehydes than for the monoaldehydes (Entries 2, 7 and 8). Conversely, the total yield of the substrate isomers increases with increased CO pressure.

Table 2. Effect of syngas, H₂ and CO, pressures on the hydroformylation of 1,5-hexadiene catalyzed by a rhodium complex with ligand **VII** in scCO₂

Entry ^[a]	Pressure [MPa]		Yield (%)			
	H ₂	CO	1 + 2 (1/2)	3 + 4 + 5 (3/4/5)	6–9 ^[b]	Isomer
1	1.25	1.25	47 (76:24)	23 (54:38:8)	1.1	0.6
2	2	2	47 (74:26)	22 (55:37:8)	0.8	1.6
3	3	3	46 (73:27)	18 (53:39:9)	0.5	3.5
4	4	2	12 (66:34)	80 (56:38:7)	3.0	0.1
5	6	2	13 (66:34)	74 (53:40:8)	6.1	0.4
6	8	2	13 (67:33)	73 (54:39:7)	6.6	0.2
7	2	4	43 (74:36)	11 (50:43:7)	0.8	8.7
8	2	6	28 (70:30)	5 (44:46:9)	0.1	11

^[a] Reaction conditions: 11.5 mmol substrate; 6.2 μ mol catalyst; ligand/Rh = 4:1; 12 MPa CO₂; temperature, 60 °C; time, 0.5 h. ^[b] Total yield of the monoaldehydes **6**, **7**, **8** and **9**.

Note that the turnover frequency (TOF) of the overall dialdehyde formation, determined from the result of Entry 4 in Table 2, is 3000 h^{-1} , which is much larger (by factors of 38–300) than those reported by Botteghi et al.^[23] and by Trzeciak and Ziolkowski^[26] for the double hydroformylation of 1,5-hexadiene in organic solvents. Although they obtained 100% yield of dialdehyde, the reaction time and substrate/catalyst ratio were longer and smaller, respectively, than those for Entry 4 in Table 2.

Hydroformylation of 1,5-Hexadiene in Toluene

The results of the reaction in toluene are shown in Figure 5. The effectiveness of the ligands in the production of the dialdehydes decreases in the order **VII** > **II**, **VI** > **V** > **I** > **III**, **IV** > no ligand. In contrast to the results in scCO_2 , the fluorinated ligands **III** and **IV** are less effective than the reference ligand **I**. The catalyst with ligand **VII** gives the highest total yield of the dialdehydes and the highest yield of the linear dialdehyde **3**. Thus, ligand **VII** is the most effective for the production of the linear dialdehyde in toluene as well as in scCO_2 .

The effect of syngas, H_2 and CO pressures on the reaction in toluene has also been examined using the catalyst with ligand **VII** (Table 3). By increasing the syngas pressure, the total yields of both mono- and dialdehydes are enhanced, but the effect is less marked for the dialdehydes (Entries 1–3). The total yield of the dialdehydes gradually increases with increasing H_2 pressure (Entries 2, 4 and 5). Thus, the nature of the dependence of the reaction on the syngas and H_2 pressures are different from those of the reaction in scCO_2 . On the other hand, an increase in the CO pressure retards the reaction, similar to the results obtained in scCO_2 (Entries 6 and 7).

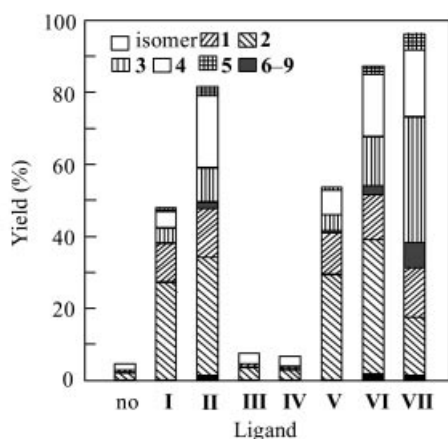


Figure 5. Effect of fluorinated phosphane ligands on hydroformylation of 1,5-hexadiene in toluene; reaction conditions: 5 mL toluene, 11.5 mmol substrate, 12.4 μmol catalyst, ligand/Rh = 4:1, 4 MPa syngas, temperature $60\text{ }^\circ\text{C}$, time 2 h

Table 3. Effect of syngas, H_2 and CO , pressures on the hydroformylation of 1,5-hexadiene catalyzed by a rhodium complex with ligand **VII** in toluene

Entry ^[a]	Pressure [MPa]		Yield (%)			
	H_2	CO	1 + 2 (1/2)	3 + 4 + 5 (3/4/5)	6–9 ^[b]	Isomer
1	1.25	1.25	35 (78:22)	10 (34:61:4)	0.5	1.2
2	2	2	47 (76:24)	20 (42:51:7)	0.7	0.9
3	3	3	52 (73:27)	24 (44:48:8)	0.6	0.8
4	4	2	40 (73:27)	53 (50:43:7)	3.0	0.2
5	6	2	17 (70:30)	75 (50:42:8)	6.8	0.1
6	2	4	38 (73:37)	12 (34:61:5)	0.3	0.2
7	2	6	26 (71:29)	6 (44:46:9)	0.1	0.1

[a] Reaction conditions: 11.5 mmol substrate; 6.2 μmol catalyst; ligand/Rh = 4:1; 12 MPa CO_2 ; temperature, $60\text{ }^\circ\text{C}$; time, 1 h. [b] Total yield of the monoaldehydes **6**, **7**, **8** and **9**.

Comparison of the Reactions in scCO_2 and Toluene

As shown above, the catalyst with ligand **VII** in toluene gives similar conversion levels but lower yields of the dialdehydes compared with those obtained in scCO_2 . Since the reaction in scCO_2 proceeds in a homogeneous phase, the concentrations of the catalyst and substrate in scCO_2 (in $\text{mol}\cdot\text{L}^{-1}$) are smaller by a factor of about 1/7 than those in toluene. This can cause a decrease in the total conversion of the substrate for the reaction in scCO_2 . To eliminate the effects of the differences in the concentrations, one experiment was conducted in toluene using the same concentrations of catalyst and substrate as those in scCO_2 . Under such conditions the total yield of the dialdehydes produced in toluene is much lower than that in scCO_2 (Table 4). On the basis of Henry's constants for H_2 and CO given by Bhanage et al.,^[41] the concentrations of H_2 and CO in toluene were estimated to be 0.032 and $0.107\text{ mol}\cdot\text{L}^{-1}$, respectively, at a syngas pressure of 4 MPa. The substrate and the syngas completely dissolve in scCO_2 and the concentration of H_2 or CO , roughly estimated on the basis of the van der Waals equation, was $0.76\text{ mol}\cdot\text{L}^{-1}$. Thus, the differences in the yields of the aldehydes. However, taking into account the negative effect of CO described above, it is suggested again that scCO_2 enhances the overall rate of hydroformylation.

Table 4. Comparison between scCO_2 and toluene as the solvent

Solvent ^[a]	Yield (%)			
	1 + 2 (1/2)	3 + 4 + 5 (3/4/5)	6–9 ^[b]	Isomer
scCO_2	1.3 (77:23)	91 (56:37:7)	3.1	0.1
Toluene	47 (69:31)	42 (28:67:5)	1.4	0

[a] Reaction conditions: 50 mL solvent; 11.5 mmol substrate; 12.4 μmol catalyst; ligand/Rh = 4:1; 12 MPa CO_2 ; 4 MPa syngas; temperature, $60\text{ }^\circ\text{C}$; time, 2 h. [b] Total yield of the monoaldehydes **6**, **7**, **8** and **9**.

The total yield of the dialdehydes produced in scCO_2 is saturated at H_2 pressures above 4 MPa (Table 2, Entries 4–6); however, this yield increases up to 6 MPa of H_2 pressure in toluene (Table 3, Entries 4 and 5). Palo and Erkey^[10] showed that the reaction order in H_2 pressure for the hydroformylation of 1-octene in scCO_2 is smaller than those in organic solvents in which the reactions are usually first order in H_2 pressure. They proposed that the rate-determining step in the catalytic cycle changes in scCO_2 due to a higher H_2 concentration in scCO_2 and/or an scCO_2 solvent effect. This difference in the reaction order in H_2 pressure probably causes the difference in the effects of H_2 pressure on the total yield of the dialdehydes. Since CO has a negative effect on the reaction both in scCO_2 and in toluene, the combination of the effects of CO and H_2 could result in the differences in the effects of syngas pressure on the reaction.

Conclusions

The results presented here demonstrate that the phosphane compound **VII** is effective as a ligand in the rhodium-catalyzed double hydroformylation of 1,5-hexadiene in scCO_2 . The TOF obtained with this ligand for the overall dialdehyde formation from 1,5-hexadiene is much larger than those reported so far. The total yield of the dialdehydes passes through a minimum at about 9 MPa as the CO_2 pressure is increased and increases appreciably as the H_2 pressure in scCO_2 increases. The effect of the syngas (H_2/CO) pressure on the reaction in scCO_2 is different from that in toluene. It has been suggested that scCO_2 promotes the hydroformylation reaction.

Experimental Section

Seven phosphane compounds, as shown in Scheme 1, were used as ligands, of which ligand **VI** was purchased from Strem and the others from Aldrich. These compounds were used without further purification. Hydroformylation experiments were conducted batchwise in a 50-mL high-pressure stainless-steel reactor with a magnetic stirrer, a high-pressure liquid pump, and a back-pressure regulator.^[21,42] The reactor was charged with 1,5-hexadiene (11.5 mmol), $[\text{Rh}(\text{acac})(\text{CO})_2]$ (12.4 μmol) and the phosphane ligand (ligand/ Rh = 4:1) and heated to a reaction temperature of 60 °C using a water bath. Then the reactor was charged with syngas (H_2/CO , 1:1 unless otherwise indicated) to a certain pressure (4 MPa in many cases) followed by the introduction of liquid CO_2 . 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 using a gas chromatograph packed with a capillary column using a flame-ionization detector and a mass spectrometer. **1**: MS: m/z (%) = 27 (44), 29 (37), 39 (52), 41 (100), 42 (30), 43 (30), 55 (47), 67 (47), 68 (77), 79 (28). **2**: MS: m/z (%) = 27 (28), 29 (25), 39 (41), 41 (87), 55 (56), 57 (26), 58 (100). **3**: MS: m/z (%) = 27 (47), 29 (68), 39 (36), 41 (100), 42 (27), 43 (61), 44 (65), 54 (41), 55 (67), 57 (88), 80 (26), 81 (79). **4**: MS: m/z (%) = 27 (37), 29 (50), 39 (29), 41 (100), 43 (69), 55 (35), 57 (60), 58 (83), 69 (29). **5**: MS: m/z (%) = 27 (32), 29 (44), 39 (30), 41 (61), 43 (100), 55 (67), 57

(49), 58 (77), 71, (40), 84, (51). The phase behavior of the reaction mixture was examined in a 10-mL high-pressure reactor with sapphire windows and a magnetic stirrer. The reactor was charged with 1,5-hexadiene (2.3 mmol), $\text{Rh}(\text{acac})(\text{CO})_2$ (2.1 μmol) and a phosphane ligand (ligand/ Rh = 4:1) and heated to 60 °C; the temperature was controlled with a heated oil circulating system. Then the reactor was charged with syngas (4 MPa) and pressurized by introducing liquid CO_2 to the desired pressure. The mixture in the reactor was examined by the naked eye and also recorded with a video recorder. The FT-IR spectra of the rhodium complexes were recorded using a 1.5-mL high-pressure in-situ cell with a path length of 4 mm. The cell was charged with the rhodium precursor (3.9 μmol) and a phosphane ligand (ligand/ Rh = 4:1) followed by the introduction of syngas (0.1 MPa) and liquid CO_2 (14 MPa). The spectra were recorded at 60 °C.

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