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Rhodium–tris(3,5-bis(trifluoromethyl)phenyl)phosphine catalyzed hydroformylation of dienes to dialdehydes in supercritical carbon dioxide with high activity

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Abstract—Rhodium-catalyzed hydroformylation of 1,5-hexadiene and 1,7-octadiene to corresponding dialdehydes was investigated in compressed CO_2 and in toluene using different fluorinated phosphine compounds as ligands. A rhodium complex using tris(3,5-bis(trifluoromethyl)phenyl)phosphine is highly effective in compressed CO_2 for double hydroformylation of 1,5-hexadiene, whose TOF value is much larger than those reported so far. It has been shown that this ligand is effective also for the hydroformylation of 1,7-octadiene and $scCO_2$ is a better solvent than a conventional organic solvent of toluene for the title reaction.
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Supercritical carbon dioxide ($scCO_2$) is gaining considerable interest as an ecologically benign and economically feasible new generation reaction medium, which can replace conventional toxic, flammable organic solvents.[1] It allows various chemical substances to dissolve in it but it simply separates from them by depressurization. It also has advantages of nonflammability, nontoxicity and absence of a gas–liquid phase boundary.

Dialdehydes are valuable intermediates for commercially important products and cross-linking agents for polymers and can be synthesized by double hydroformylation of diolefins. There are some reports concerning the hydroformylation of diolefins in organic solvents;[2] however, no one has carried out this reaction in $scCO_2$ so far. It has been pointed out that the purification of dialdehydes is troublesome due to their peculiar reactivity, in particular with conventional organic solvents.[2g] The merit of $scCO_2$ in the product–solvent separation described above should be beneficial to the syntheses of dialdehydes. For homogeneous organometallic catalysis in $scCO_2$, fluorinated phosphine ligands have been used instead of a conventional ligand such as triphenylphosphine (TPP) owing to their

high solubility in $scCO_2$.[3] In the present work, using phosphine compounds as shown in Scheme 1, the authors have studied the effectiveness of those compounds for the title reaction in $scCO_2$. It is shown that tris(3,5-bis(trifluoromethyl)phenyl)phosphine, **VII**, gives a highly effective rhodium complex catalyst for this reaction.
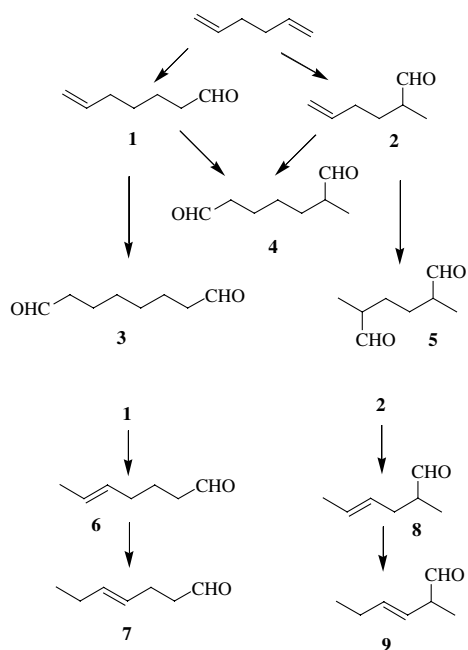
Under the present reaction conditions, the products 6-hepten-1-al (**1**), 2-methyl-5-hexen-1-al (**2**), 1,8-octanedial
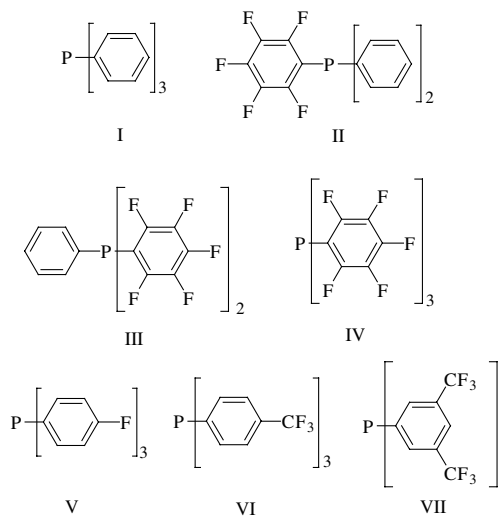
Scheme 1. Structure of phosphine ligands used.

Scheme 2. Hydroformylation of 1,5-hexadiene.

(3), 2-methyl-1,7-heptanedial (4) and 2,5-dimethyl-1, 6-hexanedial (5) were formed from the hydroformylation of 1,5-hexadiene (Scheme 2). Along with these compounds, 1,4-hexadiene and 1,3-hexadiene were formed via isomerization of the substrate and 1,4-hexadiene was the main product for this isomerization. Very small quantities 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 for the monoaldehyde isomerization. The product distribution was observed to change depending on the catalysts and the reaction conditions used.

Figure 1 shows the results of 1,5-hexadiene hydroformylation obtained at a CO_2 pressure of 12 MPa and at a syngas pressure of 4 MPa.[4] The phosphine compounds used as ligands markedly change the overall conversion of 1,5-hexadiene and the overall yield of dialdehydes. The effectiveness of the ligands for the overall yield of dialdehydes, 3, 4 and 5, is in an order of $VII > VI > II \gg IV > III > V > I$, no ligand. The fluorinated ligands are more effective as compared with the reference phosphine I. The catalyst using the ligand VII gives the highest total yield of the dialdehydes. Although not so significant, regio-selectivity is also different by the ligands. With the catalysts using the ligands II, IV and VII, the fraction of the linear dialdehyde 3 in all of the dialdehydes produced was 38%, 44% and 57%, respectively. Thus, the ligand VII is the most effective for the production of the linear dialdehyde 3. Probably, the high activity obtained with the ligand VII should result from its less basic property induced by fluorine atoms.[3g,k]

Palo and Erkey carried out the hydroformylation of a monoolefin of 1-octene in $scCO_2$ using several fluorinated ligands,[3g] some of which were the same as num-
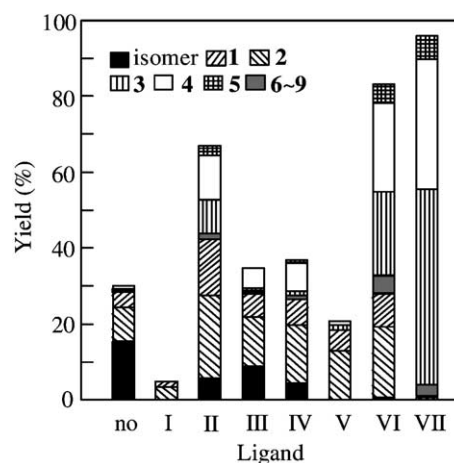

Figure 1. Influence of fluorinated phosphine ligands on hydroformylation of 1,5-hexadiene in $scCO_2$. Reagents and conditions: CO_2 pressure, 12 MPa; substrate, 11.5 mmol; CO/H_2 pressure, 4 MPa; catalyst, 12.4 μmol; temperature, 60 °C; reaction time, 2 h.

bered IV, VI and VII in the present study. They also showed that the ligand VII was the best and the effectiveness was $VII > VI \approx IV$ with respect to the initial rate at an elevated pressure of 27.3 MPa, which is slightly different from the present result of $VII > VI > IV$ at 16 MPa (Fig. 1). According to these authors the initial rate of 1-octene hydroformylation with VII is higher by a factor of 1.4 than that with VI. As shown in Figure 1, the overall conversions with the ligands VII and VI are comparable; however, the total yield of dialdehydes with VII is much higher than that with VI. The present authors also conducted the hydroformylation of 1-hexene using the same ligands as used in the present work.[3k,5] The effectiveness of the ligands for the aldehyde formation was $VII > VI > III$, $VI > II > V > I$ at 12 MPa. Thus, the influence of ligands on hydroformylation of diolefins in $scCO_2$ cannot be simply estimated from that of monoolefins in $scCO_2$ and from that in organic solvents as described in the following.

The reaction results obtained in toluene are shown in Figure 2. The effectiveness of the ligands for the total yield of dialdehydes is in an order of $VII > II$, $VI > V$, $I > III$, $IV > $ no ligand. In contrast to the results in $scCO_2$, the fluorinated ligands III and IV are less effective as compared with the reference ligand I and the ligand V. The reason for this is unknown at present, but the ability of these ligands to ligate rhodium may change by the solvent. The catalyst using the ligand VII gives the highest total yield of the dialdehydes and the highest yield of the linear dialdehyde 3. Thus, the ligand VII is the most effective for the production of the linear dialdehyde in toluene as well as in $scCO_2$.

The hydroformylation of 1,7-octadiene was also carried out in $scCO_2$ and in toluene. The products were 8-nonen-1-al (10), 2-methyl-7-octen-1-al (11), 1,9-decanedial (12), 2-methyl-1,8-nonanedial (13) and 2,8-dimethyl-1,8-octanedial (14). Small amounts of the monoaldehydes were isomerized to 7-nonen-1-al (15), 6-nonen-1-al (16), 2-methyl-6-octen-1-al (17) and 2-meth-
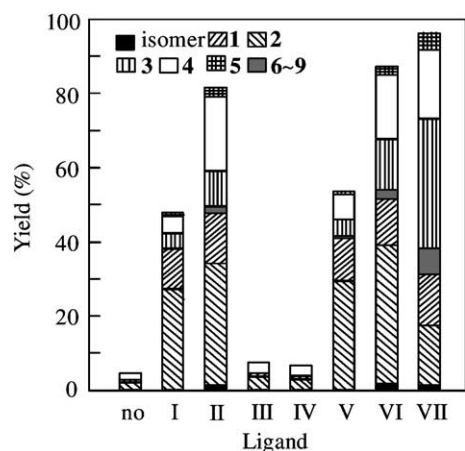
Figure 2. Influence of fluorinated phosphine ligands on hydroformylation of 1,5-hexadiene in toluene. Reagents and conditions: toluene, 5 mL; substrate, 11.5 mmol; CO/H$_2$ pressure, 4 MPa; catalyst, 12.4 µmol; temperature, 60 °C; reaction time, 2 h.

yl-6-octen-1-al (**18**). Along with these compounds, isomerization products of the substrate were also produced. Main products for the substrate isomerization and the monoaldehyde isomerization were 1,6-octadiene and 7-nonen-1-al, respectively. The reaction results obtained are listed in Table 1. The conversion levels of 1,7-octadiene are almost the same as those of 1,5-hexadiene shown in Figures 1 and 2; however, the total yields of dialdehydes are lower than those in the hydroformylation of 1,5-hexadiene irrespective of the ligands and the solvents. The reactivity of the monoaldehydes for the hydroformylation and/or the isomerization may depend on the carbon number of the substrates, resulting in the difference in the total yield of the dialdehydes. Even though the lower yields of dialdehydes are obtained from 1,7-octadiene, the effective-

ness of the ligands for the dialdehyde formation is in the same order as that for the reaction of 1,5-hexadiene in both scCO$_2$ and toluene. The ligand **VII** is the most effective for the dialdehyde production. When the reaction in scCO$_2$ is conducted using this ligand and under different reaction conditions where the amount of 1,7-octadiene is reduced to 7.4 mmol (Table 1), the total yield of dialdehydes formed in scCO$_2$ increases from 65% to 85% and that of isomerized monoaldehydes decreases from 20% to 3%. The ligand **VII** will be also effective for double hydroformylation of other diolefins, only if the reaction conditions are modified slightly.

Figures 1 and 2 show that the catalyst using the ligand **VII** in toluene gives the almost same conversion but less total yield of the dialdehydes, as compared with those obtained in scCO$_2$.[6] Since the reaction in scCO$_2$ proceeds in a homogeneous phase,[7] the concentrations of the catalyst and the substrate in scCO$_2$ in mol/L are smaller by a factor of about 1/7 than those in toluene. This can cause 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 at the same concentrations of the catalyst and the substrate as those employed in scCO$_2$. In Table 2, the result obtained is compared with that obtained in scCO$_2$. Under such conditions, the total yield of the dialdehydes produced in toluene is much lower than that in scCO$_2$ (entries 1, 2). It is suggested that scCO$_2$ has some promotional effect for the hydroformylation.

The reaction in scCO$_2$ was also carried out with a reduced amount of the catalyst (6.2 µmol) and for a shorter reaction time of 30 min using the ligand **VII**. Under these conditions and at the same H$_2$ and CO pressures as those in Figure 1, as expected, the substrate

Table 1. Influence of fluorinated phosphine ligands on hydroformylation of 1,7-octadiene in scCO$_2$ and in toluene

Ligand	Conversion (%)	Yield (%)						
		10	**11**	**12**	**13**	**14**	**15–18**	Isomer
In scCO$_2$								
I	6	3	1	1	0	0	0	1
II	72	27	14	9	6	6	2	8
III	30	15	8	1	<1	1	<1	5
IV	55	24	12	5	2	2	1	10
V	26	9	4	2	1	1	<1	8
VI	87	21	10	19	15	13	3	7
VII	92	4	1	20	34	26	5	2
VII[a]	92	2	1	3	46	33	6	<1
In toluene								
I	67	34	15	10	4	4	1	n.d.[b]
II	86	27	13	29	8	8	2	n.d.
III	10	6	4	<1	0	0	0	n.d.
IV	7	5	3	<1	0	0	0	n.d.
V	32	21	9	1	1	1	<1	n.d.
VI	82	34	15	18	7	6	2	n.d.
VII	93	29	12	26	13	11	2	n.d.

Reagents and conditions: CO$_2$ pressure, 12 MPa; toluene, 5 mL; catalyst, 12.4 µmol; substrate, 11.5 mmol; CO/H$_2$ pressure, 4 MPa; temperature, 60 °C; reaction time, 2 h.
[a] Substrate, 7.5 mmol.
[b] Not determined.

Table 2. Comparison of $scCO_2$ and toluene and influence of H_2 pressure on hydroformylation of 1,5-hexadiene

Entry	Solvent	Pressure (MPa)		Yield (%)						
		H_2	CO	1	2	3	4	5	6–9	Isomer
1	$scCO_2$	2	2	1	1	51	34	6	3	Trace
2	Toluene	2	2	32	15	8	20	2	1	0
3[a]	$scCO_2$	2	2	35	12	12	8	2	<1	2
4[a]	$scCO_2$	4	2	8	4	45	30	6	3	0

Reagents and conditions: toluene, 50 mL (increased from 5 mL used in Fig. 2); substrate, 11.5 mmol; catalyst, 12.4 μmol; temperature, 60 °C; reaction time, 2 h; CO_2 pressure, 12 MPa.
[a] Catalyst, 6.2 μmol; reaction time 0.5 h.

conversion and the total yield of the dialdehydes decrease from 96% to 72% and from 91% to 22%, respectively (Table 2, entries 1, 3). However, these values reach to 96% and 80%, respectively, when the H_2 pressure is raised to 4 MPa while keeping the CO pressure at 2 MPa (entry 4). In spite of the high H_2/CO ratio of 2, hydrogenation and isomerization of the substrate were not observed and the total yield of the isomerized monoaldehydes is below 3%.

For the result of entry 4 in Table 2, the turnover frequency (TOF) of the overall dialdehyde formation was estimated to be 3000 h^{-1}. Trzeciak and Ziolkowski[2a] and Botteghi et al.[2g] carried out double hydroformylation of 1,5-hexadiene in organic solvents. Although they obtained 100% of the total dialdehyde yield, the reaction time and the substrate/catalyst ratio was longer and smaller compared with those for the entry 4 in Table 2. TOF values obtained by them were 80 and 10 h^{-1}, respectively. Thus, the TOF value of 3000 h^{-1} obtained in the present study is much larger by factors of 300–38 compared with those reported by them.

In conclusion, this is the first paper on the hydroformylation of diolefins in $scCO_2$. Among the ligands used, tris(3,5-bis(trifluoromethyl)phenyl)phosphine gives the best rhodium catalyst. TOF obtained with this catalyst for the overall dialdehyde formation from 1,5-hexadiene is much larger than those reported so far. Hence, $scCO_2$ is a better solvent than toluene for the reaction.

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4. Experimental: 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. The reactor was charged with 1,5-hexadiene (11.5 mmol), Rh(acac)(CO)$_2$ (12.4 μmol) and the phosphine ligand (P/Rh = 4) and heated to a reaction temperature of 333 K using a water bath. Then a syngas (H_2/CO = 1:1) was charged into the reactor to a certain pressure (4 MPa in many cases) followed by 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 by gas chromatograph packed with a capillary column using a flame ionization detector and a mass spectrometer. For the reaction in toluene, 5 mL of toluene was used instead of CO_2.
5. Since we did not use the ligand **VII** in the previous study on the hydroformylation of 1-hexene,[3k] we carried out the reaction using this ligand separately.
6. In separate runs, it was confirmed that the reaction in toluene was carried out under the conditions where the stirring speed had no effect on the reaction results. Hence, the possibility that diffusion between gas–toluene phases is the rate-determining step for the overall reaction rate can be neglected.
7. Phase behaviour of the reaction mixture was investigated by naked eyes using a reactor attached with sapphire windows and recorded on a video recorder. It was found that the reaction mixture consisted of a homogeneous phase at the initial stage of the reaction.