

# Rhodium-catalyzed biphasic hydroformylation of 4-octene using water-soluble calix[4]arene-phosphine ligands

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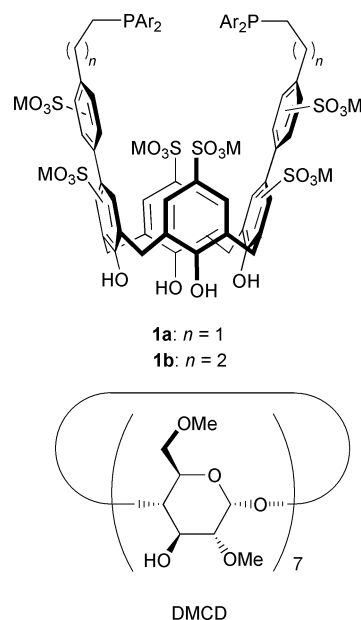
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The hydroformylation of water-insoluble internal olefins has been realized in biphasic systems via the use of rhodium complexes of water-soluble calix[4]arene-phosphines. This catalytic system resulted in a good level of activity and reusability.

The development of aqueous biphasic systems using water-soluble transition metal-complex catalysts has attracted a great deal of interest in both academic and industrial research.<sup>1</sup> Biphasic systems are superior to homogeneous catalytic systems, in that they permit facile product separation and catalyst recovery. The most spectacular examples of biphasic systems currently in industrial use include the Ruhrchemie/Rhône-Poulenc process<sup>2</sup> for the hydroformylation of propene, which is catalyzed by a water-soluble rhodium complex in which  $P(C_6H_4-m-SO_3Na)_3$  (TPPTS) serves as a ligand. Hydroformylation of internal short chain olefins, 2-pentenes, in an aqueous biphasic system with a cobalt-TPPTS complex has also been recently reported.<sup>3</sup> The applicability of this system, however, is limited to substrates which have appreciable water solubility. An important breakthrough in the biphasic hydroformylation of water-insoluble terminal olefins was achieved by Monflier and co-workers,<sup>4</sup> through the use of partially O-methylated  $\beta$ -cyclodextrins ( $\beta$ -CDs), which are used as inverse phase-transfer catalysts<sup>5</sup> along with a rhodium-TPPTS complex. This system works well only with terminal olefins. When internal olefins are used, very low reaction rates are observed.<sup>4b</sup> Reetz *et al.*<sup>6</sup> developed an improved system based on  $\beta$ -CD-modified diphosphine ligands.<sup>7</sup> With this system, even the reaction of internal olefins such as *trans*-3-hexene takes place cleanly to afford 2-ethylpentanal as the major product. Unfortunately, however, the catalytic activity is reduced to approximately 50% with reuse of the aqueous phase, which contains the catalyst.

We have recently reported that water-soluble calix[4]arene-phosphines **1a** and **1b** (Fig. 1) are excellent ligands for the rhodium-catalyzed biphasic hydroformylation of water-insoluble terminal olefins, such as 1-octene.<sup>8</sup> The rhodium complexes of **1a** and **1b** function as inverse phase-transfer

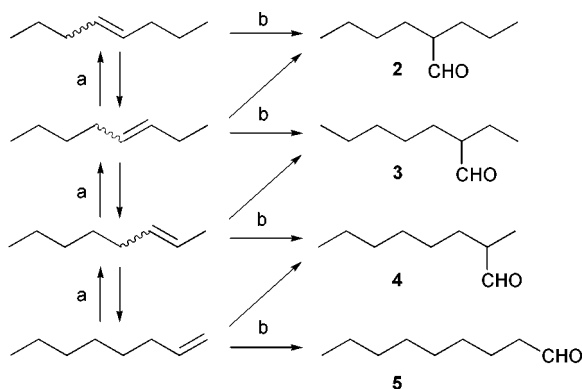


**Fig. 1** The structures of DMCD and of the water-soluble calix[4]arene-phosphines **1a** and **1b** ( $Ar = C_6H_4-m-SO_3M$ ); for **1a** and **1b** the ten M represent nine  $Na^+$  and one  $H^+$ , or ten  $Na^+$ , respectively.

**Table 1** Rhodium-catalyzed biphasic hydroformylation of internal octenes<sup>a</sup>

Entry	Ligand/additive	Olefin	Conversion (%) <sup>b</sup>	Yield (%) <sup>b,c</sup>	2 : 3 : 4 : 5 (%) <sup>d,e</sup>
1	TPPTS <sup>f</sup>	<i>trans</i> -4-octene	12	trace	—
2	TPPTS <sup>f</sup> /DMCD <sup>g</sup>	<i>trans</i> -4-octene	74	16	23 : 20 : 35 : 22
3	<b>1a</b>	<i>trans</i> -4-octene	79	56	20 : 19 : 37 : 24
4	<b>1b</b>	<i>trans</i> -4-octene	75	55	19 : 19 : 37 : 25
5	<b>1a</b>	<i>cis</i> -4-octene	74	33	23 : 19 : 35 : 23
6	<b>1a</b>	<i>trans</i> -2-octene	81	52	13 : 17 : 42 : 28

<sup>a</sup> Ligand (0.016 mmol),  $[Rh(acac)(CO)_2]$  (0.008 mmol), molar ratio olefin : P : Rh = 500 : 4 : 1,  $H_2O$  (3 ml), decane (GC internal standard; 0.40 mmol),  $CO : H_2 = 1 : 1$ ,  $p = 4.0$  MPa,  $T = 140^\circ C$ ,  $t = 12$  h. <sup>b</sup> Determined by GC. <sup>c</sup> Yield of nonanals. <sup>d</sup> Percentage of each nonanal in all nonanals. <sup>e</sup> For structures of isomeric nonanals, see Scheme 1. <sup>f</sup>  $P(C_6H_4-m-SO_3Na)_3$  (0.032 mmol). <sup>g</sup> 2,6-Di-O-methyl- $\beta$ -cyclodextrin (0.016 mmol).



**Scheme 1** Hydroformylation of octenes with preceding isomerization; (a) isomerization; (b) hydroformylation.

catalysts.<sup>9</sup> We report herein that the rhodium(I) complexes of **1a** and **1b** continue to maintain high activity even in the case of water-insoluble internal olefins. Unlike the systems of precedent,<sup>4b,6</sup> a practical level of catalyst reusability was realized, in addition to high catalytic activity.

The results from the rhodium-catalyzed biphasic hydroformylation of internal octenes using **1a** and **1b** are summarized in Table 1. For comparison, data with respect to *trans*-4-octene using a TPPTS ligand and Monflier's combination of TPPTS and 2,6-di-*O*-methyl- $\beta$ -cyclodextrin (DMCD) (Fig. 1) under the same reaction conditions are also listed.

When *trans*-4-octene was treated with a 1 : 1 mixture of carbon monoxide and hydrogen (4.0 MPa) in water in the presence of 0.2 mol% of a  $[\text{Rh}(\text{acac})(\text{CO})_2]$ -TPPTS complex for 12 h at 140 °C,<sup>10</sup> trace amounts of nonanals were obtained along with a 12% conversion of *trans*-4-octene (Entry 1). The addition of DMCD to this reaction mixture increased the conversion to 74%, along with a mixture of nonanals in 16% total yield and isomerized olefins (Entry 2). Although the addition of DMCD accelerates the isomerization of *trans*-4-octene to other octenes (Scheme 1), a substantially lower yield of aldehydes was obtained. When the same reaction was carried out using the  $[\text{Rh}(\text{acac})(\text{CO})_2]$ -**1a** catalyst (Entry 3), a mixture of nonanals was obtained in a yield of 56% without detectable olefin hydrogenation and alcohol formation at 79% conversion. Thus, this catalytic system is more efficient than the DMCD system by a factor of 3.5 for the case of *trans*-4-octene. Although over 80% of all aldehydes, that is, nonanals **3–5** were formed from the isomerized olefins, the level of selectivity for 1-nonalal, which is a most desirable product in industry,<sup>11</sup> was not acceptable. The selectivity is substantially the same compared with that observed for the DMCD system. Comparable activity and selectivity were also obtained when the  $[\text{Rh}(\text{acac})(\text{CO})_2]$ -**1b** catalyst was used (Entry 4). Entries 5 and 6 show a slightly different result in the hydroformylation of *cis*-4-octene and *trans*-2-octene, respectively.

**Table 2** Reuse of the aqueous phase containing rhodium-**1a** complex<sup>a</sup>

Cycle	Conversion (%) <sup>b</sup>	Yield (%) <sup>b,c</sup>	<b>2</b> : <b>3</b> : <b>4</b> : <b>5</b> (%) <sup>d,e</sup>
1	90	81	20 : 19 : 37 : 24
2	91	87	20 : 19 : 37 : 24
3	89	84	20 : 19 : 38 : 23
4	91	86	20 : 19 : 37 : 24
5	90	83	20 : 19 : 37 : 24

<sup>a</sup> Reaction conditions: *trans*-4-octene (4.0 mmol), **1a** (0.064 mmol),  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.008 mmol), molar ratio olefin : P : Rh = 500 : 16 : 1,  $\text{H}_2\text{O}$  (3 ml), decane (GC internal standard; 0.40 mmol),  $\text{CO} : \text{H}_2 = 1 : 1$ ,  $p = 4.0$  MPa,  $T = 140$  °C,  $t = 24$  h. <sup>b</sup> Determined by GC. <sup>c</sup> Yield of nonanals. <sup>d</sup> Percentage of each nonanal in all nonanals. <sup>e</sup> For structures of isomeric nonanals, see Scheme 1.

The reusability of the aqueous phase, which contains the rhodium-**1a** catalyst was also examined (Table 2). Activity was maintained after five reaction cycles. This result indicates that the catalyst is very stable and remains in the aqueous phase.

In conclusion, the biphasic hydroformylation of water-insoluble internal olefins was achieved using a rhodium complex with the water-soluble calix[4]arene-phosphines **1a** and **1b**. This catalytic system resulted in a good level of activity and reusability giving no emulsion, but the selectivity was similar to that obtained in Monflier's system. A study concerning the improvement of selectivity for linear aldehydes is currently in progress.

## Experimental

### General

TPPTS and  $[\text{Rh}(\text{acac})(\text{CO})_2]$  were purchased from Strem Chemicals, Inc. DMCD was purchased from Tokyo Kasei Kogyo Co., Ltd. These reagents were used without further purification. Calix[4]arene-phosphine ligands **1a** and **1b** were prepared by methods reported in the literature.<sup>8</sup> GC analyses were performed on a Hewlett-Packard Model 6890 gas chromatograph equipped with a flame ionization detector and a capillary column DB-1701 (0.25 mm  $\times$  30 m, 0.25  $\mu\text{m}$ ).

### Typical procedure for the hydroformylation of internal octenes

$[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.008 mmol) and **1a** or **1b** were dissolved in degassed water (3 ml) under argon. The resulting yellowish solution was then transferred to an autoclave. Internal standard (decane; 0.40 mmol) and *trans*-4-octene (4.0 mmol) were added. The autoclave was pressurized to 4.0 MPa of  $\text{CO} : \text{H}_2$  (1 : 1) and heated to 140 °C with stirring at 800 rpm. After the reaction, the autoclave was cooled to room temperature and the reaction mixture was extracted with chloroform (5 ml  $\times$  3). The combined extracts were dried over  $\text{Na}_2\text{SO}_4$  and analyzed by GC. For recycling experiments, after the reaction of each cycle, the autoclave was depressurized and the contents were transferred to a Schlenk flask under argon. After extraction with chloroform, the aqueous catalyst solution was reinjected into the autoclave for the next cycle.

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