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Article

Highly efficient Rh(I)/tris- H_8 -binaphthyl monophosphite catalysts for hydroformylation of dicyclopentadiene to dialdehydes

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ABSTRACT

Novel catalytic systems for the Rh-catalyzed hydroformylation of dicyclopentadiene have been developed using tris- H_8 -binaphthyl monophosphite as ligands containing different ester substituents at the 2'-binaphthyl position (OCOMe, OCOPh, OCOAdamantyl and OCOPhCl). The catalysts exhibited high activity ($S/C = 4000$, $TON = 3286$) with good to excellent selectivity towards dialdehydes. Remarkably, the Rh(I) complex bearing the ligands with chlorophenyl ester substituents led to 99.9% conversion and 98.7% selectivity for dialdehydes under relatively mild conditions (6 MPa, 120 °C).

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1. Introduction

The hydroformylation of olefins, which was discovered by Roelen as early as 1938 in the course of his investigation on cobalt-catalyzed Fischer-Tropsch synthesis, has developed into one of the most widely applied homogeneously catalyzed processes in industry [1–8]. More importantly, the hydroformylation of olefins yields a mixture of aldehydes which can be further converted to carboxylic acids, alcohols or amines. These products are considered as important versatile intermediates that can be further transformed into a wide variety of high-performance chemicals, such as pharmaceuticals, agro-

chemicals, perfumes, and fine chemicals [9–15].

Dicyclopentadiene (DCPD) is one of the most important components of the C5 fraction in the cracking steam from naphtha and gas oils. It can be hydroformylated to tricyclodecanemonoaldehyde (TCDMA) or tricyclodecanedialdehyde (TCDDA) (Scheme 1), which offer a broad range of applications [5,11,16]. However, the main difficulties are related to the low selectivity of TCDDA. There are two unsaturated double bonds (on positions 3,4 and 8,9) in DCPD and the norbornenyl moiety is therefore more reactive than the cyclopentenyl part [17,18]. Firstly, hydroformylation might occur on the 8,9 double bond to generate monoaldehydes (TCDMA). Subsequently, the hy-

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Scheme 1. DCPD hydroformylation catalyzed by a rhodium/ligand complex and the products derived from TCDDA.

droformylation may take place at the cyclopentenyl moiety of TCDMA to form dialdehydes (TCDDA) [19]. The formation of TCDMA proceeds readily; however, the conversion of TCDMA to TCDDA is challenging [11,17–20].

Over the last few decades, many groups had been involved in the development of new catalytic systems for the hydroformylation of DCPD with high conversion and good selectivity [11,17,21–23]. When a non-ligand modified Rh catalyst was used in DCPD hydroformylation, the reaction conditions are often difficult. For instance, In 2007, Papp et al. [22,23] described that more than 90% yield of TCDDA was obtained via the hydroformylation of DCPD in the presence of a non-ligand modified Rh catalyst $\text{HRh}(\text{CO})_4$. However, the reaction conditions were quite harsh with a syngas pressure as high as 35 MPa in at least two reaction zones, and a required temperature in the range of 80 to 130 °C in the first reaction zone, which was adjusted from 120 to 150 °C in the subsequent zone. In 2011, Pi et al. [11] reported that the water-soluble rhodium complex $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ catalyzed the hydroformylation of DCPD in an aqueous/organic two-phase system containing cationic surfactants $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_2\text{C}_n\text{H}_{2n+1}\text{Br}$ ($n = 1, 8, 12, 16$) that were used to accelerate the reaction. Garlaschell et al. [17] used cobalt-rhodium catalytic systems that were promoted by triphenylphosphine (PPh_3) in the hydroformylation of DCPD with 94.5% selectivity of TCDDA under relatively mild conditions (4.0 MPa, 110 °C). However, this catalytic system required a large amount of bimetallic catalysts.

Thus, it is desirable to identify new ligands with rhodium complexes that lead to higher efficiency and better selectivity in the hydroformylation of DCPD under mild reaction conditions. In this context, P-donor ligands (phosphine, phosphites, phosphoramidites) have garnered much attention in recent decades. Among the aforementioned ligands, phosphites are extremely attractive because they can be simply prepared from readily accessible precursors. In addition, phosphites exhibit high resistance to oxidative destruction because of the absence of P–C bonds [24–32]. However, the phosphite ligands in the Rh-catalyzed hydroformylation of DCPD have been rarely studied. We have recently developed the synthesis of a new class of helical C_3 -symmetric monophosphite ligands, whose metal complexes show high activity and regioselectivity in the hydroformylation of styrene and other catalytic reactions [33]. Based on the synthesis and successfully application of phosphite, we considered that the ligands (**L1–L4**) (Fig. 1) containing different ester substituents at the 2'-binaphthyl position (OCOMe, OCOPh, OCOAdamantyl and OCOPhCl), possess obvious potential for the Rh-catalyzed hydroformylation of olefins.

L1–L4

R = Me, Ph, 1-adamantyl, PhCl.

Fig. 1. C_3 -symmetric tris- H_8 -binaphthyl monophosphite ligands.

In addition, although the phosphites with P–O bonds are sensitive to water, bulky phosphite ligands exhibit good stability and more resistant to hydrolysis in the case of Rh-catalyzed hydroformylation [5,34]. Moreover, bulky phosphite ligands have performed much better than PPh_3 in the enhancement of Rh-catalyzed hydroformylation reactions due to steric and electronic effects [34–36]. In the present work, we report on the highly efficient Rh-catalyzed hydroformylation of DCPD under mild conditions, wherein the rhodium complexes were prepared *in situ* from the ligands **L1–L4**.

2. Experimental

2.1. General

All experiments were performed in a nitrogen environment using standard Schlenk techniques. NMR spectra were recorded using Bulker 300 or 400 MHz spectrometers. ^1H and ^{13}C NMR spectra were reported with tetramethylsilane (TMS) as an internal standard. ^{31}P NMR spectra were reported with 85% (volume fraction) of H_3PO_4 as an external reference. The coupling constants (J) were reported in Hertz (Hz). Spin multiplicities were given as s (singlet), d (doublet), t (triplet) and m (multiplet). High resolution mass spectra (HRMS) were recorded using a Bulker microTOF-QII mass instrument. The melting points of the solid samples were determined with an X-4 digital melting point apparatus with an attached microscope. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter at 20 °C. Gas chromatography analysis was performed using a HP-Agilent 6890 chromatographer, equipped with a flame ionization detector (FID) and with a SE-54 column. GC-MS was performed on an Agilent 5975C with a Triple-Axis detector. Reactions were monitored using thin layer chromatography (TLC, silica gel GF254 plates). Column chromatography separations were conducted on silica gel (200–300 mesh). NEt_3 , THF, Et_2O and toluene were distilled with Na and benzophenone as an indicator, and CH_2Cl_2 was dried over CaH_2 before use. All the other chemicals were ob-

tained commercially and used without further purification.

2.2. General procedure of Rh(I)/monophosphate catalyzed hydroformylation

A 25-mL stainless steel autoclave was charged with DCPD (0.13 mL), toluene (2.5 mL), ligand (0.0038 mmol), and Rh(acac)(CO)₂ (0.0038 mmol) under a nitrogen atmosphere. The autoclave was pressurized with CO and H₂ (4 MPa, 1:1). The reaction mixture was stirred with a magnetic stirrer at the reaction temperature. After a prescribed reaction time, the autoclave was quickly cooled with water to room temperature and the residue gas was slowly released. The conversion of DCPD, the selectivity of aldehydes, and the molar ratio of TCDMA/TCDDA were determined by GC analysis with a SE-54 column (30 m × 0.25 mm).

3. Results and discussion

3.1. Synthesis of monodentate phosphite Ligands

The phosphite ligands **L1**-OCOMe, **L2**-OCOPh, **L3**-OCOAd and **L4**-OCOPhCl (Fig. 1) were synthesized from the corresponding mono-protected H₈-binaphthol derivatives and PCl₃ based on our recently published procedure [33]. The acquired spectroscopic data (¹H, ¹³C, ³¹P NMR and HRMS-ESI) were in agreement with previously reported results.

3.2. Rh(I)-catalyzed hydroformylation of DCPD

In order to evaluate the effects of the ligand's structure on the activity and selectivity of the rhodium catalytic system, a set of four tris-H₈-binaphthyl monophosphites containing different ester (–OCOR) appendices, **L1**-OCOMe, **L2**-OCOPh, **L3**-OCOAd and **L4**-OCOPhCl, were evaluated as ligands.

In a typical reaction, the autoclave was charged with the appropriate amount of phosphite ligand and [Rh(acac)(CO)₂] (in a 1:1 ratio) with toluene as the solvent. The reactor was then pressurized with an equimolar mixture of CO/H₂ (4 MPa), and the reaction was conducted at 110 °C under magnetic stir-

ring. The progress of the reaction was monitored via GC analysis (Table 1).

As clearly shown in Table 1, distinct profiles were obtained for each different Rh(I)/monophosphite catalytic system. The conversion of DCPD is nearly 100% for all the ligands of **L1**–**L4**, but the selectivity of TCDDA was very different with the other ligands. The monodentate phosphites **L1**–**L4** showed better performance compared to PPh₃ in terms of selectivity towards TCDDA (Table 1, entries 1–5) for the ligands PPh₃ and **L1**–**L4**. In addition, the P atom in **L1**–**L4** is connected with a backbone via the O atom, while the P atom of PPh₃ is connected through a C atom. Van der Slot et al. [37] proved that the P–O bond could result in a lower electronic density for phosphorus compared to the P–C bond. The electron-deficient ligand with π -accepting-ability is good, which results in a suitable lower electron density around the rhodium metal and this, in turn, weakens the metal-carbonyl bond. Hence, the P atom connected with the backbone via the O atom is favorable for the dissociation of CO and thereby accelerates the catalysis reaction. The performance comparison between the rhodium catalyst modified by ligands **L3** and **L4** also confirmed that good π -accepting-ability of the ligand favored catalysis (Table 1, entries 3 and 4). Using the catalyst prepared *in situ* from Rh(acac)(CO)₂ and ligand **L4**, the hydroformylation of DCPD with different solvents was investigated, and a profound solvent effect on the reaction was observed (Table 1, entries 5–8). It is noteworthy that in the non-coordinating and relatively non-polar solvents of toluene and hexane, TCDDA was obtained at yields of 89.8% and 90.1%, respectively (Table 1, entries 5 and 6). The selectivity of TCDDA was 80.6% in toluene but only 49.4% in hexane. When the reactions were performed using the weakly coordinating solvent CH₂Cl₂, the yield and selectivity of TCDDA were 92.3% and 84.2%, respectively (Table 1, entry 7). In contrast, 91.2% yield and 88.8% selectivity of TCDDA were obtained in the highly polar and coordinating solvent THF (Table 1, entry 8). Therefore, THF was found to be the preferred solvent in terms of yield and selectivity in the hydroformylation of DCPD.

Since the hydroformylation reaction is highly dependent on the reaction conditions, we set out to determine the optimal conditions for the rhodium catalyst system with ligand **L4**. Representative results for temperature, P/Rh molar ratio, initial syngas pressure and reaction time are shown in Table 2. In the absence of the monophosphite ligand, the non-modified rhodium catalyst yielded only 32.1% of TCDDA, while TCDMA was formed at 67.9% (Table 1, entry 1). It can be seen that the selectivity to TCDDA increased as the P/Rh molar ratio was varied from 0.5 to 1. A further increase of the P/Rh molar ratio caused a reduction in the selectivity to TCDDA. The reaction temperature has a dramatic effect on the hydroformylation of DCPD. In the range of 90–120 °C (Table 2, entries 3–7) a good yield of 92.8% aldehydes was achieved, and an excellent selectivity of 91.1% was obtained at 120 °C (Table 2, entry 5). The total pressure of the syngas was also a key element in the hydroformylation of DCPD. The selectivity to TCDDA greatly increased in the pressure range from 2 to 6 MPa (Table 2, entries 5, 8 and 9). When the pressure was increased from 6 to 8 MPa,

Table 1

The Rh(I)-catalyzed hydroformylation of DCPD. ^a

Entry	Ligand	Solvent	Conversion ^b (%)	Aldehydes ^b (%)	TCDMA/TCDDA ^b
1	PPh ₃	toluene	99.9	92.8	58.7/41.3
2	L1	toluene	99.9	93.9	37.1/62.9
3	L2	toluene	99.9	92.4	43.2/56.8
4	L3	toluene	99.9	93.1	26.4/73.6
5	L4	toluene	99.9	89.8	19.4/80.6
6	L4	hexane	99.9	90.1	50.6/49.4
7	L4	CH ₂ Cl ₂	99.9	92.3	15.8/84.2
8	L4	THF	99.9	91.2	11.2/88.8

^a Reaction conditions: Rh(acac)(CO)₂ (3.8 × 10^{−3} mmol), DCPD (0.13 mL), S/C = 250, P/Rh = 1, P = 4 MPa, CO/H₂ = (1:1), T = 110 °C, t = 5 h, Solvent (2.5 mL).

^b Conversion of DCPD, the selectivity for aldehydes of DCPD, and molar ratio of TCDMA to TCDDA, determined by GC.

Table 2

Rh(I)-catalyzed hydroformylation of DCPD at different temperatures, pressures, and times.

Entry	P/ Rh	T/ (°C)	P/ (MPa)	t/h	Conversion ^a (%)	Aldehydes ^a (%)	TCDMA/TCDDA ^a
1 ^b	–	110	4	5	99.9	92.1	67.9/32.1
2	0.5	110	4	5	99.9	92.5	30.5/69.5
3	1	110	4	5	99.9	91.2	11.2/88.8
4	2	110	4	5	99.9	93.4	36.1/63.9
5	1	120	4	5	99.9	92.8	8.9/91.1
6	1	100	4	5	99.9	91.6	26.2/73.8
7	1	90	4	5	99.9	90.8	61.1/38.9
8	1	120	2	5	99.9	91.7	48.1/51.9
9	1	120	6	5	99.9	95.4	1.3/98.7
10	1	120	8	5	99.9	96.8	1.1/98.9
11	1	120	6	3	99.9	93.7	5.2/94.8
12	1	120	6	1	99.9	92.6	71.7/28.3

Reaction conditions: Rh(acac)(CO)₂ (3.8 × 10^{−3} mmol), DCPD (0.13 mL), S/C = 250, CO/H₂ = 1:1, THF (2.5 mL).^a See Table 1.^b The reaction with unmodified rhodium catalyst Rh(acac)(CO)₂.

a similar increase was observed in the selectivity, which afforded in the corresponding adduct TCDDA with 98.7% and 98.9% selectivity, respectively (Table 2, entries 9 and 10). When the reaction time for hydroformylation was reduced from 5 h to 3 h at 120 °C and 6 MPa, the selectivity to TCDDA was slightly reduced from 98.7% to 94.8% (Table 2, entries 9 and 11). It was found that the selectivity to TCDDA decreased dramatically to 28.3% when the reaction time was further shortened to 1 h, but increased the selectivity to TCDMA from 1.3% to 71.7% (Table 2, entries 9 and 12).

Next, we studied the influence of different rhodium precursors on the Rh-catalyzed hydroformylation of DCPD. In this case, rhodium complexes in different oxidation states were examined (Table 3). Among the tested catalytic precursors, almost all Rh(I) precursors such as Rh(acac)(CO)₂, Rh(cod)₂BF₄, and [Rh(cod)Cl]₂ afforded better yields of the aldehydes and a higher selectivity to the desired product TCDDA (Table 3, entries 1, 3 and 4). In particular, the yield of aldehyde and the selectivity of TCDDA exhibited maximum values of 95.4% and 98.7% respectively, when Rh(acac)(CO)₂ was used as the catalyst precursors. On the contrary, the conversion, the yield and the selectivity of TCDDA sharply decreased to 17.5%, and 7.5% and 16.9% respectively, when

Table 3

The Rh(I)-catalyzed hydroformylation of DCPD with different Rh precursors.

Entry	Rh precursor	Conversion ^a (%)	Aldehydes ^a (%)	TCDDA/TCDDA ^a
1	Rh(acac)(CO) ₂	99.9	95.4	1.3/98.7
2	RhCl ₃ ·3H ₂ O	17.5	7.5	83.1/16.9
3	Rh(cod) ₂ BF ₄	99.9	89.1	5.2/94.8
4	[Rh(cod)Cl] ₂	99.9	65.7	12.8/87.2

Reaction conditions: Rh precursor (3.8 × 10^{−3} mmol, 1 mg), DCPD (0.45 mmol, 0.13 mL), S/C = 125, P/Rh = 1, P = 6 MPa, CO/H₂ = (1:1), T = 120 °C, t = 5 h, THF (2.5 mL).^a See Table 1.**Table 4**

The Rh(I)-catalyzed hydroformylation of DCPD under different molar ratio of S/C.

Entry	S/C	Conversion ^a (%)	Aldehydes ^a (%)	TCDDA/TCDDA ^a	TON (TCDDA) ^b
1	250	99.9	95.4	1.3/98.7	224
2	500	99.9	95.2	2.4/97.6	464
3	1000	99.9	94.8	7.4/92.6	877
4	2000	99.9	93.5	15.5/84.5	1580
5	4000	40.8	28.1	90.1/9.9	111
6 ^c	4000	99.9	90.8	9.5/90.5	3286

Reaction conditions: Rh(acac)(CO)₂ (3.8 × 10^{−3} mmol), P/Rh = 1, P = 6 MPa, CO/H₂ = (1:1), T = 120 °C, t = 5 h, THF (2.5 mL).^a See Table 1.^b Turnover number of TCDDA.^c The reaction time was 20 h.

Rh(III) precursor RhCl₃·3H₂O was applied to the reaction (Table 3, entry 2). Some of the DCPD may be converted to the hydrogenation products dihydrodicyclopentadiene (3,4- or 8,9-dihydrodicyclopentadiene) or tetrahydrodicyclopentadiene or their mixture, because of the competition between hydroformylation and hydrogenation.

The data in Table 4 show the influence of different molar ratios of substrate to catalyst (S/C) on the hydroformylation of DCPD. The substrate can be converted completely (Table 4, entries 1–5). Under otherwise identical conditions, the increase of the S/C ratio from 250 to 2000 resulted in a considerable decrease of selectivity towards TCDDA from 98.7% to 84.5%, but the turnover number (TON) of TCDDA increases from 224 to 1580 (Table 4, entries 1 and 4), whereas a further increase of the S/C ratio to 4000 induced a significant decrease in both the selectivity and TON of TCDDA (Table 4, entries 4 and 5). This result may be due to the mutation of the increase in the concentration of DCPD, which causes a dramatic drop in the TON of TCDDA and further leads to the hydrogenation of a portion of DCPD. However, when the reaction time was increased from 5 to 20 h, the selectivity towards TCDDA increased to 90.5%, and the TON of TCDDA was up to 3286 (Table 4, entry 6). Therefore, increasing the reaction time could effectively increase the selectivity of TCDDA and TON in the case of high S/C ratio. In other words, when **L4** was used as a ligand, the rhodium catalyst showed high catalytic activity and good stability in the hydroformylation of DCPD to produce TCDDA.

3.3. NMR studies of [Rh(acac)(CO)₂/tris-H₈-binaphthyl monophosphate] complexes

The [Rh(acac)(CO)₂/monophosphate] complexes were accessed by solution ³¹P NMR spectroscopy. In a typical experiment the complexes were generated *in situ* by the reaction of the rhodium precursor Rh(acac)(CO)₂ and tris-H₈-binaphthyl monophosphite in CDCl₃ under N₂ atmosphere. The ³¹P NMR spectra of the resulting solutions were acquired while the mixture was stirred at room temperature for 5–30 min. Using equimolar amounts of [Rh(acac)(CO)₂] and monophosphite ligands **L1**-OCOMe, **L2**-OCOPh, **L3**-OCOAd or **L4**-OCOPhCl in CDCl₃, the spectra showed the formation of a specie assigned to

Fig. 2. ^{31}P NMR spectra (region 108–138 ppm) at 25 °C, in CDCl_3 of: (A) $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]$ species, obtained by reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with **L2-OCOPh** in equimolar amounts after 5 min; (B) $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]/[\text{Rh}(\text{acac})(\text{CO})(\text{L4-OCOPhCl})]$ (1:0.8), obtained by addition of one equivalent of **L4-OCOPhCl** to a $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]$ solution after 50 min.

the P–Rh coordination mode (^{31}P doublet in the range 114–116 ppm with $J(^{103}\text{Rh}-^{31}\text{P}) = 289\text{--}295\text{ Hz}$) (Fig. 2). The ^{31}P NMR spectrum obtained for the Rh(I) complexation with **L2-OCOPh** evidenced the formation of species (Fig. 2(A)). In order to evaluate the relative stability of the $[\text{Rh}(\text{acac})(\text{CO})_2/\text{monophosphate}]$ complexes, the ligand **L4-OCOPhCl** which was used as an internal standard was added to a CDCl_3 solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]$. After 50 min, considerable ligand exchange resulted in the formation of a ca. 1:0.8 mixture of $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]/[\text{Rh}(\text{acac})(\text{CO})(\text{L4-OCOPhCl})]$, in addition to the non-coordinated ligands **L2-OCOPh** and **L4-OCOPhCl**, as demonstrated by ^{31}P NMR spectroscopy (Fig. 2(B)). This suggests that $[\text{Rh}(\text{acac})(\text{CO})(\text{L4-OCOPhCl})]$ is more stable than $[\text{Rh}(\text{acac})(\text{CO})(\text{L2-OCOPh})]$.

From these studies, we considered that the lower activity

Fig. 3. ^{31}P NMR spectra in CDCl_3 at 25 °C for monophosphite **L4-OCOPhCl** (1), complex $[\text{Rh}(\text{acac})(\text{CO})(\text{L4-OCOPhCl})]$ ($\text{P/Rh} = 1$) (2), and equimolar mixture of monophosphite **L4-OCOPhCl** and the complex $[\text{Rh}(\text{acac})(\text{CO})(\text{L4-OCOPhCl})]$ ($\text{P/Rh} = 2$) (3).

and selectivity obtained with $\text{Rh}(\text{I})/\text{L2-OCOPh}$ catalyst might be due to the exchange of **L2-OCOPh** by CO ligands in $[\text{RhH}(\text{CO})_{4-n}\text{L}_n]$ type complexes, leading to different Rh(I) catalytic species in solution, under hydroformylation conditions. To gain some insight into the catalytic species, we used **L4-OCOPhCl** as a model monophosphite ligand to perform a deeper inspection into the possibility of the formation of Rh(I)/phosphite species. Different amounts of monophosphite ligands were added to $\text{Rh}(\text{acac})(\text{CO})_2$ dissolved in CDCl_3 under a N_2 atmosphere, and the mixture was stirred at room temperature for 5–30 min. As shown in Fig. 3, the ^{31}P NMR spectra of the resulting solutions were registered, and the spectra revealed that in all cases, a doublet peak in the range $\delta = 114\text{--}116\text{ ppm}$ with $J(^{103}\text{Rh}, ^{31}\text{P}) = 295\text{ Hz}$ corresponding to a single phosphorus species was observed. When a twofold excess amount of ligand was used, the ^{31}P NMR spectra revealed a 1:1 ratio between the same signal and a singlet at $\delta = 132\text{ ppm}$, which is typical of the non-coordinated phosphite ligand (Fig. 3(3)). These results indicate that only one bulky ligand can coordinate to the rhodium precursor.

4. Conclusions

In conclusion, the catalytic systems which were readily constituted from a catalytic precursor $\text{Rh}(\text{acac})(\text{CO})_2$ and tris- H_8 -binaphthyl monophosphite ligands **L1–L4**, were successfully developed for the Rh-catalyzed hydroformylation of DCPD to TCDDA. The results demonstrate that high selectivity of TCDDA could be obtained using ligand **L4** under relatively mild reaction conditions (120 °C, 6 MPa). Moreover, such catalytic systems can be tuned through the structural modulation of the ester substituents at the 2'- H_8 -binaphthyl positions of the bulky phosphites.

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Graphical Abstract

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Highly efficient Rh(I)/tris-*H*₈-binaphthyl monophosphite catalysts for hydroformylation of dicyclopentadiene to dialdehydes

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Catalytic systems for Rh(I)-catalyzed hydroformylation of dicyclopentadiene have been developed using tris-*H*₈-binaphthyl monophosphite as ligands. The catalyst exhibited high catalytic activity ($S/C = 4000$, $TON = 3286$) and good to excellent selectivity to dialdehydes. The Rh(I) complex bearing the ligands with chlorophenyl ester substituents led to 99.9% conversion and 98.7% selectivity to dialdehydes under relatively mild condition (6 MPa, 120 °C).

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铑 (I)/三-*H*₈-联萘单齿亚磷酸酯高效催化双环戊二烯氢甲酰化制备双醛田 密^{a,b,†}, 李海峰^{a,†}, 王来来^{a,c,*}^a中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室, 甘肃兰州730000^b中国科学院大学, 北京100049^c广州理文科技有限公司, 广东广州511458

摘要: 双环戊二烯(DCPD)是石脑油和燃料油裂解蒸汽的C₅馏分中最重要的组分之一。DCPD经氢甲酰化反应可转化为具有广泛应用前景的三环癸烷不饱和单甲醛(TCDMA)和三环癸烷二甲醛(TCDDA),并可通过还原或胺化进一步转化为相

应的醇和胺类化合物,用于农药、医药、润滑油和香料等的合成。但是,由于其分子结构中含有 3,4-位和 8,9-位两种不同活性的不饱和双键,因此DCPD 氢甲酰化反应的产物通常非常复杂。过去数十年,研究者们为此相继开发了高转化率和高选择性的催化体系。但是反应条件相对都比较苛刻,尤其是对于双醛TCDDA的合成,通常需要较高的反应温度和反应压力以及大量的催化剂。

本文以 2'-联萘位置含有不同酯取代基(OCOMe, OCOPh, OCOAdamantyl 和 OCOPhCl)的三-H8-联萘单齿亚磷酸酯 **L1**–**L4** 为配体,以不同价态的金属铑前驱体为催化剂,开发了 Rh 催化 DCPD 氢甲酰化反应的新体系,并对亚磷酸酯配体、不同价态的金属铑催化剂前驱体、反应温度、反应时间、溶剂以及不同的底物和催化剂的S/C摩尔比对 DCPD 转化率和 TCDDA 选择性的影响进行了深入的研究。结果表明,当以金属铑前驱体 Rh(acac)(CO)₂ 和配体 **L4**-OCOPhCl 为催化体系时,在 DCPD 氢甲酰化反应中表现出很高的活性,尤其是当 S/C = 4000 时,TON 值达到 3286,并且该催化体系对于双醛 TCDDA 具有良好的选择性。值得注意的是,在相对温和的条件 (6 MPa, 120 °C)下,Rh(I) 催化剂与氯苯酯基取代的三-H₈-联萘单齿亚磷酸酯所形成的配合物在催化 DCPD 的氢甲酰化反应中,DCPD 的转化率达到 99.9%,而双醛 TCDDA 的选择性达到 98.7%。此外,我们采用 **L4**-OCOPhCl 作为模型单齿磷酸配体,在溶液中通过 NMR 对可能形成的 Rh(I)/亚磷酸酯催化物种进行了深入的考察。¹³P NMR 谱图表明,在 DCPD 的氢甲酰化反应中,催化物种[Rh(acac)(CO)(**L4**-OCOPhCl)]比 [Rh(acac)(CO)(**L2**-OCOPh)]具有更好的稳定性,而且只有体积较大的配体 **L4**-OCOPhCl 才能与铑前驱体 Rh(acac)(CO)₂ 进行很好的配位。

关键词: 氢甲酰化; 双环戊二烯; 单亚磷酸酯; 二醛; 均相催化

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