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# Highly Regioselective and Active Rhodium/Bisphosphite Catalytic System for Isomerization–Hydroformylation of 2-Butene

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**Abstract** The formation of linear aldehyde from isomerization–hydroformylation of 2-butene represents an important subject and current task in industry. Both high activity and excellent regioselectivity were achieved in the rhodium-catalyzed 2-butene isomerization–hydroformylation with 2,2′-bis(dipyrrolylphosphinooxy)-1,1′-(±)-binaphthyl (**1**) as ligand. Bulky phosphite with electron-withdrawing pyrrol groups dramatically improved the selectivity of linear product, and a good yield of 90.5% aldehydes was obtained with an excellent linear aldehyde regioselectivity of 95.3% under optimized condition.

**Keywords** Isomerization–hydroformylation · Homogeneous catalysis · 2-Butene · Rhodium complex

## 1 Introduction

Hydroformylation of olefins is among the most important industrial homogeneous catalytic processes for the preparation of aldehydes and corresponding alcohols which are important precursors for various pharmaceuticals, agrochemicals, and plasticizers [1–3]. As internal olefins are much cheaper and more readily available feedstock than terminal olefins, recently, researches are focused on the internal olefins hydroformylation to produce linear aldehydes. The development of highly active and selective isomerization–hydroformylation catalysts for internal olefins is of great importance from economic and environmental points of view. However, only a few progresses have been reported [4–8]. "Ligand effect", which represents on both steric and electronic properties of ligand, can drastically influence the rate and regioselectivity of the hydroformylation reaction. The steric effect of bisphosphine ligand is determined by the natural bite angle in combination with rhodium [9, 10]. Casey et al. showed experimentally that a rhodium–bisphosphine complex with a wide bite angle can easily form ee configuration (phosphine atoms occupy two equatorial positions of a trigonal bipyramid) that played a key role in the high regioselectivity of hydroformylation [11, 12] (Scheme 1). Later, the same group found that large bite angled rhodium–bisphosphine complexes with electron-withdrawing group would further improve the regioselectivity of internal olefin hydroformylation [13]. Likewise, Leeuwen and Zhang have proved the above conclusions [14–17]. Since 2-PH (2-propylheptanol), the product of condensation and hydrogenation of aldehyde that was obtained by hydroformylation of 2-butene, is superior to the standard 2-EH (2-ethylhexanol) on physical aspects due to environmental consideration and its potential value with the attractive advantage of competition [18], therefore we focused on the isomerization–hydroformylation of 2-butene to *n*-pentanal. In this study, we screened 2,2′-bis(dipyrrolylphosphinooxy)-1,1′-(±)-binaphthyl (**1**) [19, 20], 2,2′-bis(dipyrrolylphosphinooxy)-1,1′-(±)-biphenyl (**2**) [15], and 2,2′-bis(diphenylphosphino)methyl)-1,1′-biphenyl (BISBI **3**) [21] (Fig. 1) which have different electronic and steric effects to investigate how the reaction conditions as well as the differences of ligand structure influence the 2-butene hydroformylation catalytic behavior.

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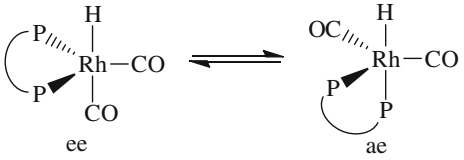



**Scheme 1** Equilibrium of ee–ae configurations in rhodium trigonal bipyramidal complexes

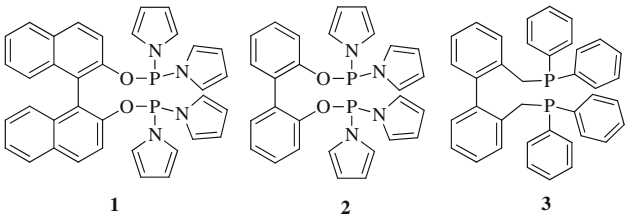



**Fig. 1** Structure of ligands **1**, **2**, and **3**

## 2 Experimental

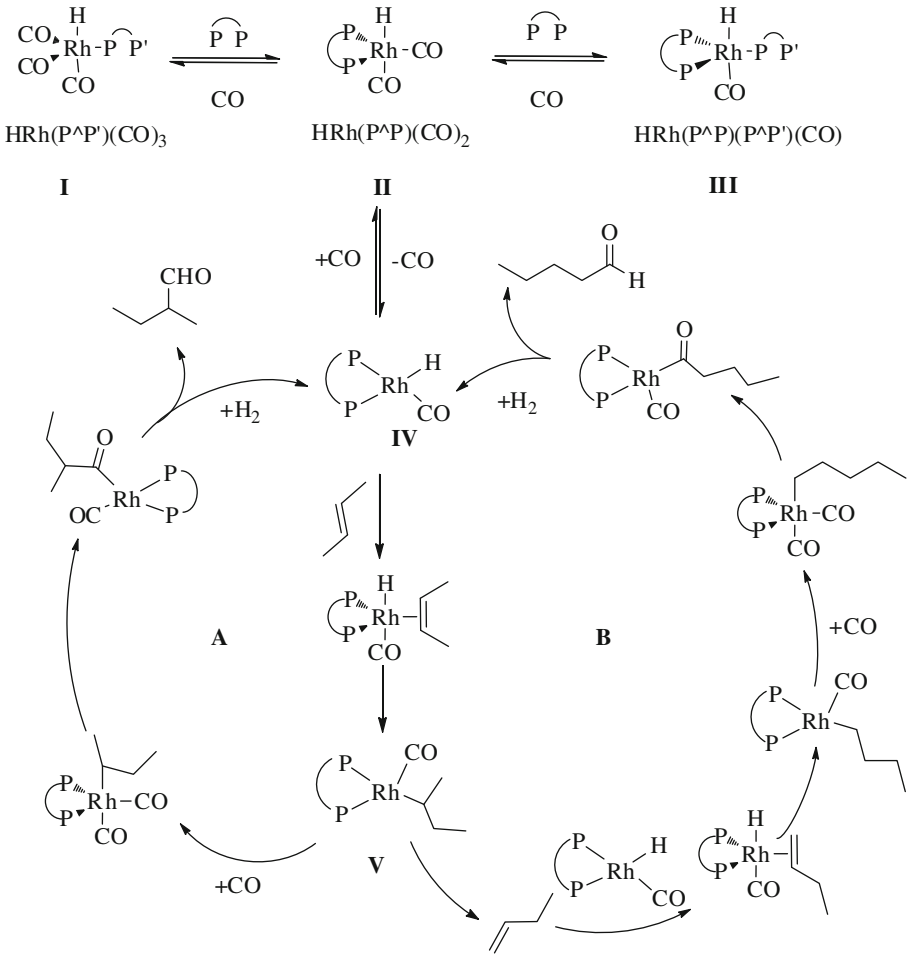
### 2.1 Reagents

The solvent toluene was purified before use. The ratio of hydrogen (99.99%) and carbon monoxide (99.9%) were 1:1. 2-Butene (97%, mixture of *trans* and *cis*), 1-butene (98%), and other reagents were of analytical grade. $Rh(acac)(CO)_2$ [22], ligand **1** [19, 20], **2** [15], and BISBI **3** [21] were prepared according to literatures and their structures were confirmed by IR and NMR spectrum.

### 2.2 General Procedure of Hydroformylation Experiments

The hydroformylation reaction was carried out in a 60 mL stainless steel autoclave with magnetic stirring. Ligand and $Rh(acac)(CO)_2$ were dissolved in toluene at certain ratio, and 2-butene was transferred into autoclave using Schlenk-technique at low temperature. After filling with syngas to

**Scheme 2** Proposed mechanism for the isomerization–hydroformylation of internal olefin to linear aldehyde




(A) hydroformylation of internal olefin, (B) isomerization-hydroformylation ofinternal olefin

desired pressure, the autoclave was heated to the reaction temperature and vigorously stirred. At the end of the reaction, the vessel was cooled before excess syngas was carefully released. Using *n*-heptane as internal standard, the products were analyzed on Agilent 6890N gas chromatography with a capillary column SE-30 (30 m × 0.25 mm).

## 3 Results and Discussion

A goal of ligand screening is to achieve high activity and regioselectivity in the isomerization–hydroformylation of internal olefins. The catalyst must perform higher isomerization rate of internal olefin to terminal olefin (Scheme 2, **B**) than direct hydroformylation rate of internal olefin (Scheme 2, **A**), so that the system can maintain a small amount of terminal olefin in the olefin mixture under the thermodynamic equilibrium, as a result of which, once terminal olefin was formed, it would be immediately transformed to aldehyde in the presence of syngas due to the more quick hydroformylation rate of terminal olefin. Meanwhile, if only the activity and regioselectivity for the hydroformylation of the terminal olefin are high enough, the linear aldehyde would be the main product [1, 16, 18].

The isomerization–hydroformylation of 2-butene was first investigated using $Rh(acac)(CO)_2$/**1** as catalyst, and the effects of temperature and molar ratio of ligand to rhodium were summarized in Table 1. The temperature played a key role in the reaction. At low temperature, though high regioselectivity was observed, the activity was unsatisfactory. High temperature (120 °C) that could accelerate the isomerization of 2-butene to 1-butene was more active for the isomerization–hydroformylation of 2-butene, and a good yield of 63.2% aldehydes was achieved with an excellent regioselectivity of 96% (Table 1, entries 1–4). And the results excelled the previous report (yield of 27.3% aldehydes with regioselectivity of 86.3% for the hydroformylation of 2-butene using 2,2′-bis(diindolylphosphinooxy)-1,1′-(±)-biphenyl as ligand) [23]. Further increasing the temperature the thermodynamic equilibrium between *β*-hydride elimination of branched rhodium–alkyl complex (Scheme 2, **V**) to 1-butene and 2-butene was broken (2-butene is more stable than 1-butene on thermodynamics), resulting in lower activity and regioselectivity (Table 1, entry 5). Compared with isomerization–hydroformylation of 2-butene under high temperature (120 °C), hydroformylation of 1-butene was carried out at 60 °C, giving excellent activity and regioselectivity (Table 1, entry 6). The results indicated that high temperature at certain range benefits isomerization process.

**Table 1** Isomerization–hydroformylation of 2-butene with ligand **1** under different conditions[a]

| Entry | L/Rh | *T* (°C) | *n*:*i*[b] | Linear (%)[c] | Yield (%)[d] |
|---|---|---|---|---|---|
| 1 | 5 | 90 | 38.0 | 97.4 | 24.8 |
| 2 | 5 | 100 | 28.1 | 96.6 | 50.2 |
| 3 | 5 | 110 | 27.1 | 96.4 | 59.4 |
| 4 | 5 | 120 | 23.9 | 96.0 | 63.2 |
| 5 | 5 | 130 | 12.9 | 92.8 | 57.1 |
| 6[e] | 5 | 60 | 128.0 | 99.3 | 63.8 |
| 7 | 1 | 120 | 7.9 | 88.8 | 37.8 |
| 8 | 3 | 120 | 18.3 | 94.8 | 57.8 |
| 9 | 8 | 120 | 26.2 | 96.3 | 46.5 |

[a] [Rh] = $6.0 \times 10^{-3}$ mmol, 2-butene (2.4 g), S/C = 7,143, $p$ = 2.5 MPa, $t$ = 2 h, toluene (2.0 mL) as solvent, heptanes as internal standard

[b] Molar ratio of linear to branched aldehydes, determined on the basis of GC

[c] Percentage of linear aldehyde in all aldehydes

[d] The yield of all aldehydes, determined on the basis of GC

[e] Hydroformylation of 1-butene, [Rh] = $4.0 \times 10^{-3}$ mmol, 1-butene (2.4 g), S/C = 10,714, $p$ = 2.5 MPa, $t$ = 1 h, toluene (2.0 mL) as solvent, heptanes as internal standard

The ligand/[Rh] molar ratio has a dramatic effect on the isomerization–hydroformylation (Table 1, entries 4, 7–9). At low ratios, low regioselectivity was obtained. Ligand/[Rh] ratio of five is essential to give the best result. Further increasing the ligand/[Rh] ratio does not significantly influence the regioselectivity, however, resulted in lower activity. In contrast to the data (Table 1, entry 4), ligand/[Rh] ratio of 1.5 gave the best result in hydroformylation of 2-octene in our previous work (Rh: 2-octene = 1:1325, $T$ = 100 °C, $p$ = 0.7 MPa) [20]. Due to the different concentrations of catalyst in both systems, the best results might be obtained under respective L/[Rh] ratios. Leeuwen et al. [15] concluded that the ligand/[Rh] ratio as well as the CO pressure determined the concentration of the active species HRh(P^P)(CO) (Scheme 2, **IV**) in solution. Under the appropriate ligand/[Rh] ratio, high concentration of species **II** that could transform into active species **IV** gave excellent regioselectivity.

Due to the rapid pressure–dropping during the reaction, the effect of pressure was investigated at constant pressure range from 1.5 to 3.5 MPa (Table 2). The increasing of pressure benefitted the activity of 2-butene hydroformylation. However, the regioselectivity of linear aldehyde improved to 95.7% at 2.5 MPa then decreased later with the increasing of the pressure, especially at 3.5 MPa the regioselectivity dropped to 84.4%. As previously mentioned (Scheme 2), regardless of high or low pressure, the concentration of **II** decreased, followed by the reduction of active species **IV**, leading to low regioselectivity of linear aldehyde.

**Table 2** Isomerization–hydroformylation of 2-butene with ligand **1** under constant pressure[a]

| Entry | *p*/MPa | *n*:*i*[b] | Linear (%)[c] | Yield (%)[d] |
|---|---|---|---|---|
| 1 | 1.5 | 14.3 | 93.5 | 63.5 |
| 2 | 2.0 | 19.5 | 95.1 | 71.4 |
| 3 | 2.5 | 22.7 | 95.7 | 73.2 |
| 4 | 3.0 | 20.4 | 95.3 | 76.0 |
| 5 | 3.5 | 5.4 | 84.4 | 79.8 |

[a] [Rh] = $6.0 \times 10^{-3}$ mmol, 2-butene (2.4 g), S/C = 7,143, L/[Rh] ratio = 5, $T$ = 120 °C, $t$ = 2 h, toluene (2.0 mL) as solvent, heptanes as internal standard, maintain constant pressure during the reaction

[b–d] see Table 1

**Table 3** Comparison of different ligands in isomerization–hydroformylation of 2-butene[a]

| Entry | L | *t* (h) | *n*:*i*[b] | Linear (%)[c] | Yield (%)[d] |
|---|---|---|---|---|---|
| 1 | None | 2 | 0.8 | 44.4 | 17.9 |
| 2 | 1 | 0.5 | 27.4 | 96.5 | 35.7 |
| 3 | 1 | 1 | 22.9 | 95.8 | 53.0 |
| 4 | 1 | 6 | 20.3 | 95.3 | 90.5 |
| 5 | 2 | 1 | 9.0 | 90.0 | 46.7 |
| 6 | 2 | 6 | 3.3 | 76.7 | 85.7 |
| 7 | 3 | 1 | 3.7 | 78.7 | 24.2 |
| 8 | 3 | 6 | 0.9 | 47.4 | 59.8 |

[a] [Rh] = $6.0 \times 10^{-3}$ mmol, 2-butene (2.4 g), S/C = 7,143, $p$ = 2.5 MPa, L/[Rh] ratio = 5, $T$ = 120 °C, toluene (2.0 mL) as solvent, heptanes as internal standard, maintain constant pressure during the reaction

[b–d] see Table 1

It demonstrated that the isomerization–hydroformylation of 2-butene was sensitive to the reaction conditions according to the data above. And then we subsequently investigated the effect of ligand and the results were summarized in Table 3. Being free of ligand, neither activity of catalyst nor regioselectivity of linear product was satisfactory (Table 3, entry 1); it is essential for the existence of ligand in isomerization–hydroformylation of 2-butene. In addition, the nature of ligands also influences the isomerization–hydroformylation of 2-butene. Ligand **1** with a bulky binaphthyl backbone and electron-withdrawing pyrrol groups obviously improves the selectivity of linear aldehyde (Table 3, entries 2–4), while ligand **2** and **3** showed less advantage either on activity or regioselectivity (Table 3, entries 5–8). According to the comparison of ligand **2** and **3**, both of which have similar backbone, ligand **2** showed better activity and regioselectivity than ligand **3**, and electronic effect played a decisive role.

To evaluate the stability of the catalytic system, the hydroformylation of 2-butene was performed by prolonging the reaction time as well as recycling the use of catalyst.

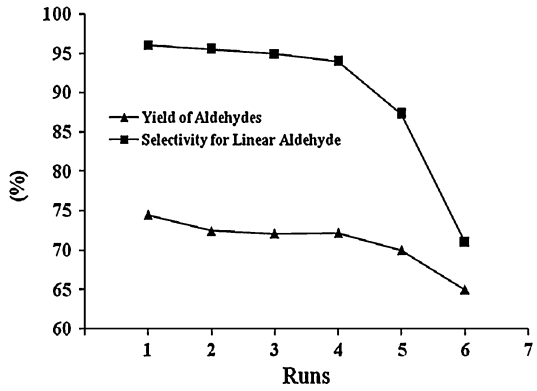



**Fig. 2** Recycle of Rh/**1** catalytic system for 2-butene isomerization–hydroformylation [Rh] = $5.0 \times 10^{-2}$ mmol, 2-butene (20 g), S/C = 7,143, L/[Rh] ratio = 5, $T$ = 120 °C, $t$ = 2 h, toluene (20 mL) as solvent, heptanes as internal standard, maintain constant pressure (2.5 MPa) during the reaction

Under optimized reaction condition (120 °C, $p$ = 2.5 MPa, ligand/[Rh] ratio = 5), high regioselectivity have been achieved with ligand **1** (96.5% of linear aldehyde in all aldehyde products after 0.5 h) (Table 3, entry 2). Though elongating the reaction time to 6 h resulted in slightly lower *n*/*i* ratio, and the linear aldehyde percentage remained high up to 95.3% with a high yield of 90.5% aldehyde (Table 3, entry 4). We then recycled the Rh/**1** catalytic system; it maintained excellent activity and regioselectivity until the fifth run of the catalyst (Fig. 2). As for ligand **2** and **3**, the regioselectivity decreased obviously when reaction time elongated (Table 3, entries 6, 8). In summary, ligand **1** showed outstanding catalytic performance and stability on isomerization–hydroformylation of 2-butene.

## 4 Conclusions

In conclusion, the bisphosphite ligand with bulky skeleton and electron-withdrawing groups can effectively promote the isomerization–hydroformylation of internal olefins regardless of the reaction activity and regioselectivity. What is different from terminal olefins is that internal olefins require higher temperature for isomerization–hydroformylation. To the best of knowledge, the catalyst system provides high activity, excellent regioselectivity, and stability in isomerization–hydroformylation of 2-butene with ligand **1**. More applications of this ligand and mechanism studies are now under further investigation and will be reported in due course.

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