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ARTICLE

Regioselective Rhodium-Diphosphine Ligand Catalyzed Hydroformylation of Vinyl Acetate

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Abstract: Rhodium-catalyzed hydroformylation of vinyl acetate with the use of diphosphine ligands was studied. A high regioselectivity (branched:linear of 99:1) and activity (TOF: 4000 h^{-1}) under optimum conditions were achieved by using a 2,2’-bis(diphenylphosphino methyl)-1,1’-biphenyl ligand. The high turnover number (9200) obtained under mild conditions and stability of the catalyst indicates that it would be useful for industrial vinyl acetate hydroformylation.

Key words: vinyl acetate; hydroformylation; regioselectivity; diphosphine ligand; 2-acetoxypropanal

Rhodium-catalyzed hydroformylation is an important reaction in academic research and industry [1]. Much effort has been devoted to the hydroformylation of functional olefins to give bifunctional products with greater added values [2−5]. For example, the hydroformylation of industrial vinyl acetate gives 1,2- and 1,3-bifunctional products with wide applications [6−8] (Scheme 1). However, due to the chelating effect of the ester carbonyl [9], there has been limited progress in this area, and there are few results with acceptable selectivity and rates. Williams et al. [10] reported that the hydroformylation of vinyl acetate in ionic liquids gave satisfactory results, but the complex procedure needed for the preparation of the ionic liquid is a limitation [11]. Recently, Dabbawala et al. [12] reported good catalytic activity with the use of a bulky phosphite, tri-1-naphthylphosphite ($P(ONp)_3$), as a ligand for the Rh-catalyzed hydroformylation of vinyl acetate, and they demonstrated that the ligand strongly influenced the catalytic performance of the rhodium complex. An important drawback of phosphite ligands is their instability, which limits their practical application [13].

We have previously reported on the hydroformylation of high added value functional olefins [14]. The results showed that bidentate phosphine ligands such as bis-3,4-diazaphospholanes gave good regio- and enantioselectivities in the asymmetric hydroformylation of vinyl acetate [15−18]. And the use of sulfonated 1,1'-bis(diphenylphosphinomethyl)-2,2'-biphenyl (BISBIS) as a ligand in Rh-catalyzed biphasic hydroformylation of high olefins gave good results [19−21], which suggested that we can use the commercially available diphosphine 1,1'-bis(diphenylphosphinomethyl)-2,2'-biphenyl (BISBI) [22] in Rh-catalyzed homogeneous hydroformylation of vinyl acetate. The satisfactory catalytic activity, excellent regioselectivity for 2-acetoxypropanal (branched aldehyde), and high turnover number (TON) that were obtained showed the practical potential of diphosphine ligands in this reaction.

1 Experimental

All hydroformylation reactions were carried out in a stainless steel autoclave of 60 ml stirred with a magnetic stirrer. A typical procedure was as follows. A toluene solution of $Rh(CO)_2(acac)$ [23], ligand, and vinyl acetate was added to the autoclave, which was subsequently evacuated and purged with synthesis gas three times. The autoclave was then pressurized with synthesis gas and stirred at the reaction conditions. After the reaction was completed, the autoclave was cooled quickly to room temperature in an ice-water bath, and then vented slowly. The reaction mixture was immediately analyzed on a HP 9710 gas chromatograph equipped with an FID detector and a capillary column (25 m × 0.53 mm) CP-SIL 5cb. The

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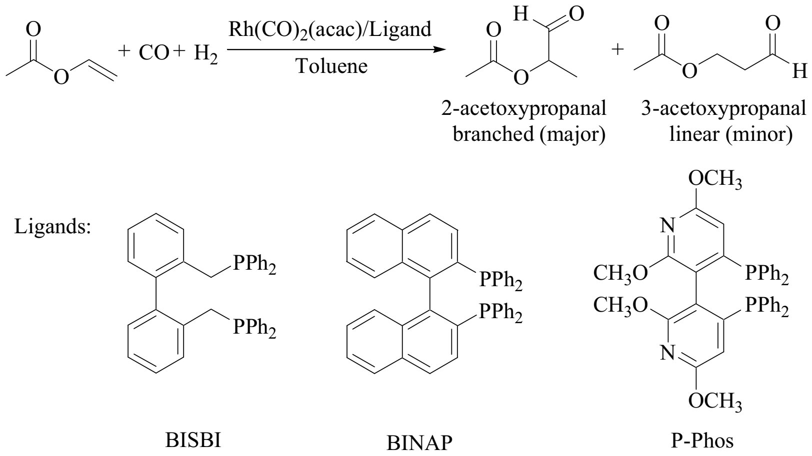

Scheme 1. Hydroformylation of vinyl acetate. BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; P-Phos: 2,2',6,6'-tetramethoxy-4,4'-bis(diphenylphosphino)-3,3'-bipyridine.

products were identified by GC-MS and ^{1}H NMR spectroscopy.

2 Results and discussion

BISBI was chosen as the ligand to investigate the effect of the reaction parameters on the Rh-catalyzed hydroformylation of vinyl acetate. The branched aldehyde was the main product, with propanal, acetic acid, and a marginal amount of 2-acetoxypropanol as side products. To our surprise, no linear aldehyde (3-acetoxypropanal) was detected in all the experiments.

2.1 Effect of reaction temperature

Previous studies on the kinetics demonstrated that the temperature plays a key role in the hydroformylation of vinyl acetate [24], thus the influence of temperature on the activity and selectivity of the Rh/BISBI catalyzed vinyl acetate hydroformylation was first investigated in the range of 80−120 °C. As shown in Table 1, the reaction rate was low at 80 °C although a high regioselectivity was observed. The increase in temperature from 80 to 120 °C led to a large increase in reaction rate. However, the chemoselectivity decreased from 95% to 81%, with propanal as the main byproduct. This was explained by that a high temperature favored the direct reaction of vinyl acetate with the rhodium hydride complex to ethylene and acetic acid [9], and ethylene was converted to propanal under the hydroformylation conditions.

Table 1 Effect of temperature on Rh-catalyzed hydroformylation of vinyl acetate with BISBI as ligand

Entry	Temperature (°C)	Conversion[a] (%)	Chemoselectivity[b] (%)	Regioselectivity[c]
1	80	25	95	> 99
2	90	52	92	> 99
3	100	76	90	> 99
4	110	96	90	> 99
5	120	96	81	> 99

Reaction conditions: vinyl acetate = 5.4 mmol, [Rh] = 1.4 mmol/L, S:C = 2000, 30 min, 4 MPa (CO:H_2 = 1), [BISBI]:[Rh] = 1.

[a] Conversion of vinyl acetate. [b] Selectivity for 2-acetoxypropanal and 3-acetoxypropanal. [c] Molar ratio of branched to linear aldehyde.

To have a high reaction rate and acceptable chemoselectivity, 110 °C was chosen as the reaction temperature for the following experiments.

2.2 Effect of pressure

The total pressure of CO/H_2 is also a key element in the hydroformylation of vinyl acetate. As shown in Table 2, under low pressure, both reaction rate and chemoselectivity were low. Increasing the pressure from 2 to 6 MPa greatly improved the reaction rate (no substrate was detected at 6 MPa), and increased the chemoselectivity. The carbonyl group of vinyl acetate hindered the insertion of CO into the Rh–R bond of the rhodium complex to give the active intermediate Rh–COR, which slowed down the reaction rate. A higher pressure weakens the hindrance to CO insertion and improves the reaction rate. In addition, more CO and H_2 inhibited the direct reaction of vinyl acetate with the rhodium complex to produce ethylene, and suppressed the formation of the propanal by-

Table 2 Effect of pressure on Rh-catalyzed hydroformylation of vinyl acetate with BISBI as ligand

Entry	Pressure (MPa)	Conversion (%)	Chemoselectivity (%)	Regioselectivity
1	2	72	80	> 99
2	3	90	87	> 99
3	4	96	90	> 99
4	5	99	91	> 99
5	6	100	93	> 99

Reaction conditions: vinyl acetate = 5.4 mmol, [Rh] = 1.4 mmol/L, S:C = 2000, 30 min, 110 °C, [BISBI]:[Rh] = 1.