Chinese Chemical Letters Vol. 14, No. 6, pp 623 – 626, 2003
http://www.imm.ac.cn/journal/ccl.html

The Performance of Rhodium Complex-diphosphine Systems in the Hydroformylation of 1-Dodecene

Xue Yuan HUANG, Rui Xiang LI, Hua CHEN, Xian Jun LI*

Department of Chemistry, Sichuan University, Chengdu 610064

Abstract: The catalytic performances of four $HRh(CO)(PPh_3)_3$-diphosphine (BISBI, BDPX, BDNA and BINAP) systems in 1-dodecene hydroformylation were investigated and compared with $HRh(CO)(PPh_3)_3$-PPh_3 system. The catalyst system $HRh(CO)(PPh_3)_3$- BISBI exhibited very high regioselectivity for the formation of linear aldehyde.

Keywords: Hydroformylation, 1-dodecene, diphosphine, rhodium complex.

Olefin hydroformylation catalyzed by rhodium complexes is a typical atom economical reaction[1]. The control of the reactivity in transition metal catalysts by the use of chelating diphosphine ligands is well documented[2]. Casey *et al.*[3,4] have developed the natural bite angle model, which is a useful tool for correlating the selectivity produced by rhodium-diphosphine catalysts with the geometry of the ligands. Although the progress has been made in the field of the olefin hydroformylation catalyzed by rhodium diphosphine complexes, the diphosphine ligands, which were studied up to date in the reaction, are still very limited. Therefore it is necessary to explore extensively the relation between the structure and the function of different diphosphines. Here we report the effect of four different diphosphines (**Scheme 1**) on the behaviors of rhodium catalyst in 1-dodecene hydroformylation and compare them with that of triphenylphosphine.

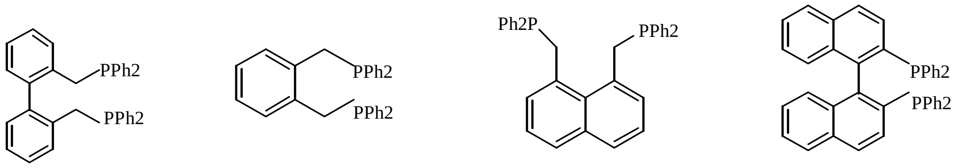
Three diphosphine ligands were synthesized according to the literature[5]: 2, 2′- bis (diphenylphosphinomethyl) -1, 1′- biphenyl (BISBI), 1, 2 - bis (diphenylphosphino methyl) benzene (BDPX), 1,8-bis(diphenylphosphinomethyl) naphthalene(BDNA). 2, 2′ -bis(diphenylphosphino)- 1, 1′-binaphthyl (BINAP) and triphenylphosphine (PPh_3) were commercial. The rhodium complexes $HRh(CO)(PPh_3)_3$ and $Rh(acac)(CO)_2$ were prepared by the literature method[6, 7]. The hydroformylation of 1-dodecene was carried out in a stainless steel autoclave with magnetic stirrer. After the rhodium catalyst, phosphine, 1-dodecene and solvent were added into the reactor it was flushed with the syngas (H_2/CO =1/1) for three times, then the syngas was introduced into the reactor. The products were determined on GC 9790 with FID and capillary column SE-30 (30m x

---

*E-mail: scuulixj@mail.sc.cninfo.net

0.25 mm) at 170°C.

Scheme 1



BISBI BDPX BDNA BINAP

$HRhCO(PPh_3)_3$ and $Rh(acac)(CO)_2$ were used as catalyst precursor in 1-dodecene hydroformylation. Their catalytic activities were investigated at the molar ratio [BDPX]/[Rh]=2.5/1 and 100°C under the pressure 2.0 MPa (total initial pressure) with the syngas (H_2/CO=1/1) for 2 h, the conversions of 1-dodecene were 92.0% and 67.1% for $HRhCO(PPh_3)_3$ and $Rh(acac)(CO)_2$, respectively. It was possible that when $Rh(acac)(CO)_2$ was used as catalyst precursor, there was an induction period in the formation process of the catalytic active species HRh(CO)(BDPX), in which the activation of hydrogen and the ligand exchange between acac and BDPX occurred, thereby the active catalyst HRh(CO)(BDPX) was produced, therefore, the activity of Rh(acac) $(CO)_2$ was lower than that of $HRhCO(PPh_3)_3$ under the same reaction conditions.

Table 1 Effect of temperature

Entry	T(°C)	Conversion (%)	L/B
1	80	72.5	5.5
2	90	86.4	3.5
3	100	92.2	3.0
4	110	90.0	2.9
5	120	84.8	2.8

$HRhCO(PPh_3)_3$ 0.0089 mmol, [BDPX]/[Rh] = 4:1, 1-dodecene 9.0 mmol, hexane 4.0 mL, 2.0 MPa (initial pressure), H_2:CO =1:1, 2 h.

The effect of temperature was studied with the composite catalyst system ($HRhCO(PPh_3)_3$-BDPX). The results (**Table1**) showed that when temperature was over 100°C, the conversion of olefin decreased, and the L/B ratio of aldehyde, which indicated the regioselectivity of olefin hydroformylation, dropped with increasing temperature.

The effect of [phosphine]/[Rh] ratios of different ligands on the catalytic activities and regioselectivities was studied using $HRhCO(PPh_3)_3$ as the catalyst precursor. The results were listed in **Table 2**.

The data showed that the conversions of olefin did not change obviously with increasing [phosphine]/[Rh] ratio, but the variation of L/B value was large with different diphosphine. When the molar ratio of BINAP, BDPX and BDNA to rhodium complex increased the L/B value rose slightly, but they all were low (1.4 ~3.2). However when the molar ratio of BISBI to rhodium complex increased from 3:1 to 7:1, the L/B value jumped from 3.5 to 21.8. Moreover, the L/B value rose further to 32.4, when the molar ratio of [BISBI]/[Rh] was 10:1. The phenomena suggested that the introduction of four diphosphine ligands could form the different coordination circumstance, due to their different natural bite angle[4, 5] (the bite angles of BISBI, BDNA, BDPX and BINAP are 120°, 104°, 90° and 85°, respectively.). BISBI has a large bite angle and suitable flexibility, when the ratio of [BISBI]/[Rh] is in a certain range, it may create a diequatorial steric configuration (ee type) of Rh-diphosphine complex, which was favourable for the formation of linear alkyl-Rh intermediate[4], thus high regioselectivity of 1-dodecene hydroformylation can be reached. BINAP, BDPX and BDNA did not exhibit diphosphine stereoselective effect, this was connected with their small bite angles and flexibilities. The lower conversion of olefin in the presence of diphosphine than that of PPh_3 could be attributed to the stabilization of rhodium complex by chelation of diphosphine ligand.

Table 2 Effect of [phosphine]/[Rh] ratio (mol/mol)

Entry	phosphine	[phosphine]/[Rh] ratio (mol/mol)	Conversion (%)	L/B
1	BINAP	3:1	84.8	2.3
2	BINAP	4:1	86.0	2.4
3	BINAP	5:1	86.6	2.5
4	BINAP	6:1	86.8	2.5
5	BINAP	7:1	87.0	2.5
6	BISBI	3:1	77.5	3.5
7	BISBI	5:1	85.6	4.7
8	BISBI	7:1	80.0	21.8
9	BISBI	10:1	79.6	32.4
10[a]	BDPX	1:1	89.9	2.0
11[a]	BDPX	1.5:1	91.9	2.4
12[a]	BDPX	2.5:1	92.0	2.5
13[a]	BDPX	3:1	92.1	3.0
14[a]	BDPX	5:1	92.5	3.1
15[a]	BDPX	6:1	91.8	3.2
16[a]	BDPX	7:1	91.0	3.2
17	BDNA	5:1	82.8	1.4
18	BDNA	7:1	83.0	1.6
19	PPh_3	10:1	95.7	2.4

$HRhCO(PPh_3)_3$ 0.00118 mmol, 1-dodecene 9.0 mmol, hexane 4.0 mL, 2.0 MPa (initial pressure), H_2:CO = 1:1, 100℃, 2 h, [a] $HRhCO(PPh_3)_3$ 0.0089 mmol.

Acknowledgments

We thank the National Basic Research Project of China (G2000048008) for the financial support.

References

1. G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, 2nd Ed, John Wiley & sons, New York, **1992**, pp. 106.
2. C. D. Frohning, C. W. Kohlpaintner, *Applied Homogeneous Catalysis with Organo -metallic*

Compounds, Ed. by B. Cornils and W. A. Herrmann, VCH, New York, **1996**, pp. 85.
3. C. P. Casey, G. T Whiteker, *Isr. J. Chem*., **1990**, *30*, 299.
4. P. W. N. M. Van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.,* **2000**, *100*, 2741.
5. R. X. Li, X. J. Li, N. B. Wong, K. C. Tin, Z. Y. Zhou, T. C. W. Mak, *J. Mol. Catal. A. Chem.,* **2002**, *178*, 181.
6. N. Ahmad, J. J. Levison, S. D. Robinson, *Inorg. Synth.,* **1974**, *15,* 59.
7. G. Wilkinson, *J. Chem. Soc.*, **1964**, 3156.

Received 4 November, 2002