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Synthesis of New *N*-Pyrrolylphosphane and Its Application in Hydroformylation of 1-Octene

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A new bidentate *N*-pyrrolylphosphane (**1**) which possessing strong π-acceptor property has been synthesized and applied in homogeneous rhodium-catalyzed hydroformylation of 1-octene. The effects of ligand/metal ratio, temperature, pressure and substrate/rhodium ratio on regioselectivity and activity were evaluated. The influence of the ligands (**1** and **2**) steric property on regioselectivity and activity in the hydroformylation of 1-octene was discussed. It was found that ligand **1** possess stronger chelating ability with rhodium than ligand **2** and always afforded higher regioselectivity and activity.

Keywords: Homogeneous catalysis, Hydroformylation, *N*-Pyrrolylphosphane, Rhodium catalyst, π-Acceptor.

INTRODUCTION

Rhodium-catalyzed hydroformylation of olefins to corresponding aldehydes has already been developed into one of the most important industrial processes at present. The corresponding aldehydes are mostly used for bulk chemicals, plasticizers, surfactants and applicated in pharmaceutical and fine chemical synthesis. Production volumes obtained by using this process are estimated to be over nine million tons every year[1,2]. The most important industrial hydroformylation processes use highly reactive rhodium catalysts that are modified with either *mono*- or *bis*phosphorus ligands. In recent years, much effort has been made to enhance the activity and regioselectivity of the hydroformylation of terminal olefins in order to make more desirable linear aldehydes. Phosphane-, phosphite- and diphosphoramidite- based systems have been reported, such as bisbi[3], xantphos[4], naphos[5], biphephos[6], pyXant[7], pySPAN[8] and pyrrole-based *bis*phosphoramidite[9,10]. Generally these ligands that are good electron acceptors have been found to be effective in hydroformylation. Recently, some researches have been made in this area using Beller's electron-withdrawing Naphos-type ligands[5], Ralf Jackstell's pyrrolyl-, indolyl- and carbazolyl monodentate phosphane ligands[11] and van Leeuwen's monodentate and bidentate phosphorus amidite and phosphinite ligands[9]. The results show that high regioselectivity was obtained with ligands possessing strong π-acceptor, compared with arylphosphines and arylphosphites ligands. van Leeuwen *et al.* found that pyrrolyl substituents on the phosphorus atom lead to highly π-acidic phosphorus ligands which could result in a higher active catalyst for non-functional alkenes. Building on the interest in good electron accepted ligands, we had designed and synthesized a *bis*phosphane ligand **2**[12] (**Scheme-I**). Unfortunately, when coordinated with rhodium, the ten-membered ring chelation of the ligand **2** is weak and does not afford good regioselectivity and activity in hydro-formylation of 1-octene. In order to address the issue of chelating ability, we have synthesized a new ligand **1** based on a heterocyclic amine backbone. Then we investigated some features of hydroformylation of 1-octene using $Rh(acac)(CO)_2$ as catalyst precursor and the ligand **1** as promoter (Fig. 1). As expected, the catalytic system modified by **1** provided better regioselectivity and higher activity in hydroformylation of 1-octene than ligand **2** and the good L/B ratios of about 6.6 and high activity (TOF: 3465 h^{-1}) were obtained.

EXPERIMENTAL

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. Solvents were dried with standard procedures. $Rh(acac)(CO)_2$ was prepared according to the literature[13]. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker ARX 400 NMR instrument. Mass spectra was recorded with an AMD 40223 (Interambulacra) spectrometer. The hydroformylation products were analyzed by GC-6890 with a FID detector and a capillary column (φ 0.25 m × 30 mm, SE-30).

Synthesis of 1,1'-*bis*(dipyrrolylphosphano)-2,2'-biindolyl (1): To a solution of chlorodipyrrolylphosphine (4.4 mmol, 0.87 g) in THF (10 mL) was added dropwise triethyl-

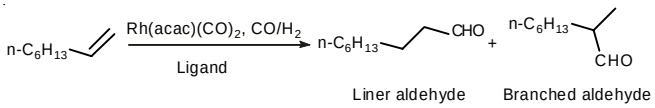
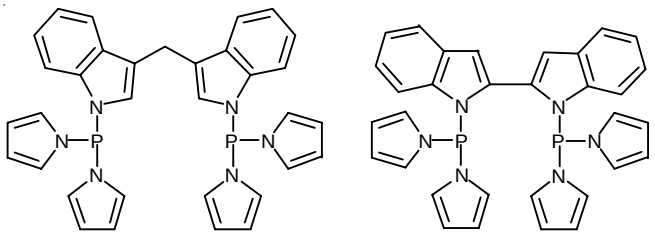


Fig. 1. Hydroformylation of 1-octene



2 **1**

Scheme-I: Bisphosphane ligand **1** *vs.* **2**

amine (1 mL) and a solution of 2,2'-biindolyl (2 mmol, 0.46 g) in THF (5 mL) at room temperature. The triethylamine HCl salts were formed immediately after the addition. The reaction mixture was stirred for 10 h at room temperature. The triethylamine HCl salts were then filtered off and the solvent was removed under vacuum. The crude product was purified by crystallized from toluene to afford the pure ligand **1** (0.83 g, 56 %), as an air-stable white solid. ^{31}P NMR (166 MHz, $CDCl_3$): δ = 73.66. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39-7.41 (d, *J* = 7.7 Hz, 2H), 7.34-7.35 (d, *J* = 7.7 Hz, 2H), 7.15-7.19 (t, *J* = 12.0 Hz, 2H), 7.04-7.07 (t, *J* = 15.4 Hz, 2H), 6.36-6.42 (d, *J* = 21.8 Hz, 8H), 6.12-6.25 (d, *J* = 52.6 Hz, 8H), 5.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 139.77-139.97 (d, J_{PC} = 20.1 Hz), 130.15, 124.58, 123.39, 122.65-122.80 (d, J_{PC} = 15.4 Hz), 122.32, 121.77, 119.96, 113.15-113.30 (d, J_{PC} = 15.4 Hz), 111.66-111.81 (d, J_{PC} = 15.4 Hz). -HRMS (ES+) calcd for $C_{32}H_{26}NaN_6P_2$ [M + Na^+] 579.1592, found 579.1618.

Hydroformylation of 1-octene: The hydroformylation of olefin was carried out in a 60 mL stainless steel autoclave equipped with a magnetic stirrer. The aqueous solution of $Rh(acac)(CO)_2$, a certain amount of ligand and olefin were introduced into the autoclave. Then it was evacuated and purged five times by syngas. The autoclave was pressurized to each desired pressure with syngas. The reaction mixture was stirred at a constant speed of 10 rps when the temperature reached the desired value. After the reaction was completed, the autoclave was quickly cooled in an ice-water bath and carefully depressurized. The reaction mixture was immediately analyzed by GC to determine the activity and regioselectivity.

RESULTS AND DISCUSSION

Synthesis of ligand: The synthesis of backbone and ligand **1** was realized as shown in Fig. 2. Following known literature procedures[14,15], oxalyl chloride was condensed with *o*-tolylamine according to the procedure of Wallace to form *N*,*N*'-*bis*(*o*-tolyl)oxamide, in quantitative yields. The Madelung cyclization was then accomplished by heating *N*,*N*'-*bis*(*o*-tolyl)oxamide with freshly prepared potassium *tert*-butoxide to 220 °C and then slowly to 300 °C. Much decomposition occurred and lots of gas released under these extreme conditions and yield of 2,2'-biindolyl was typically on the order of 50 %, though reactions at lower temperatures resulted in

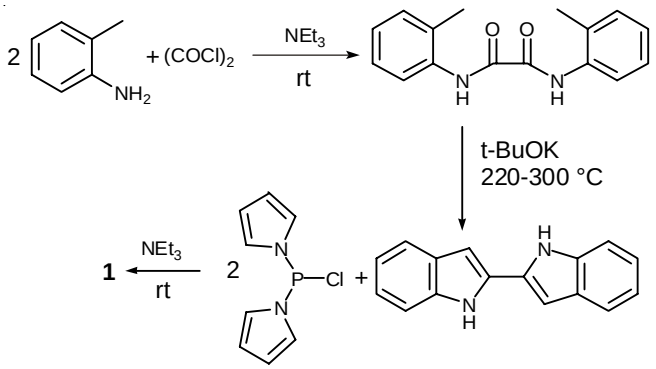


Fig. 2. Synthesis of 2,2'-biindolyl and ligand **1**

little or no product. Then reaction of chlorodipyrrolylphosphine with 2,2'-biindolyl in the presence of triethylamine afforded the desired *bis*phosphane ligand **1** in 56 % unoptimized yield. The structure of the new ligand **1** was unambiguously proven by means of ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, together with mass spectrometry.

Hydroformylation experiments: Firstly, the effect of ligand 1/Rh ratio on the activity and regioselectivity of 1-octene hydroformylation was investigated and the results are summarized in Table-1. With the ligand/rhodium ratio increasing from 5 to 20, the L/B ratio of aldehyde rose from 3.4 to 4.2. The data suggested that the increase of the L/B ratio could be attributed to the high ligand concentration and the increase of ligand/rhodium ratio in a suitable concentration range could stabilize the catalytic active species[16,17]. Leeuwen *et al.*[9] concluded that the ligand/Rh ratio determined the concentration of the active species HRh(P^P)(CO) (**Scheme-II**) in solution. Under the appropriate ligand/Rh ratio, high concentration of species **II** that could transform into active species **IV** gave excellent regioselectivity. However, more excess ligand resulted in low reaction rate, as shown in Table-1 (entry 4), when the ratio was 20, the TOF value decreased to 256 h^{-1}. It could be explained that more excess ligand would form the species **III** which block the coordination site and the coordination of 1-octene with rhodiun active species **IV** would become difficult, which would cause its activity to drop[18,19].

TABLE-1
EFFECT OF MOLAR RATIO OF LIGAND (L) TO RHODIUM ON 1-OCTENE HYDROFORMYLATION

Entry	L/Rh	Aldehyde yield (%)	L/B[a]	TOF[b]
1	5	71.7	3.4	358.5
2	8	71.8	3.6	359.0
3	10	79.9	3.9	399.5
4	20	51.2	4.2	256.0

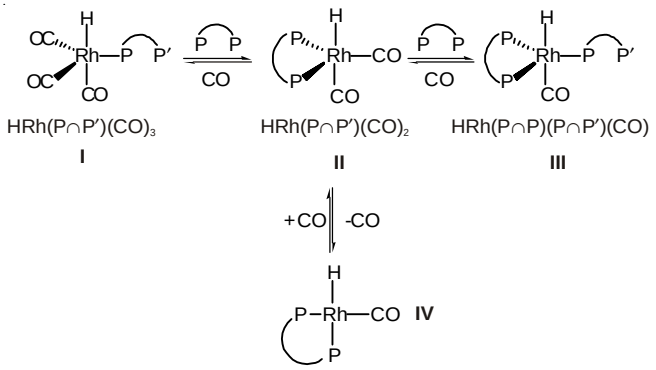
Reaction conditions: S/C-Molar ratio of substrate/catalyst = 1000. 100 °C, *p* = 2 MPa (CO/H_2 = 1), [Rh] = 1.3 × 10^{-3} mmol, 2 h, toluene 2 mL; [a]L/B-Molar ratio of linear to branched aldehyde; [b]TOF: Aldehydes (mole)/(Rh (mole) × time (h))

The effect of temperature on the behaviours of the catalyst system was also investigated and the results were listed in Table-2. The data showed that the reaction temperature also plays a key role in hydroformylation. High temperatures generally led to high reaction rates, for example, the TOF value at 60 °C was 285.0 h^{-1}, whereas this number increased to 399.0 h^{-1} at 100 °C. But the sharp change of reaction rate occurred at

TABLE-2
EFFECT OF REACTION TEMPERATURE ON 1-OCTENE HYDROFORMYLATION

Entry	Temp. (°C)	Aldehyde yield (%)	L/B	TOF
1	60	57.0	5.8	285.0
2	80	70.6	5.7	353.0
3	100	79.9	3.9	399.5
4	120	50.6	3.2	253.0

Reaction conditions: S/C = 1000, [Rh] = 1.3×10^{-3} mmol, L1/Rh = 10, p = 2 MPa (CO/H_2 = 1), 2 h, toluene 2 mL



Scheme-II: Geometry of the hydride complexes formed with the bidentate ligands

120 °C (the aldehyde yield is 50.6 %), which means that the ligand used in the reaction could not be tolerant towards high temperature. From the data, it was also found that hydroformylation of 1-octene at high temperatures resulted in high regioselectivity: the high temperature corresponds to the L/B ratio of 3.2, while the low temperature (60 °C) corresponds to the L/B ratio of 5.8. Therefore the formation of linear aldehyde was favorable at low temperature.

Then the effect of total pressure of CO/H_2 (pressure ranging from 0.5 MPa to 3 MPa) was evaluated in Table-3. It was showed that the activity increased with increasing pressure, when the pressure increased from 0.5 to 3.0 MPa, the TOF value increased from 129.0 to 427.5 h^{-1}. However, an opposite trend of regioselectivity was observed. The highest regioselectivity (L/B ratio of 6.6) was obtained under a CO/H_2 pressure of 1.0 MPa, while the L/B ratio of 4.7 was obtained at 3.0 MPa. As previously mentioned (**Scheme-II**), 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.

The effect of the substrate/Rh ratio on hydroformylation of 1-octene was examined. As shown in Table-4, a slight decrease in the linear/branched (L/B) ratio was observed when the substrate/Rh ratio was increased from 1000 to 10000. However, the reaction rate is much faster than at low substrate/

TABLE-3
EFFECT OF REACTION PRESSURE ON 1-OCTENE HYDROFORMYLATION

Entry	P (MPa)	Aldehyde yield (%)	L/B	TOF
1	0.5	25.8	4.7	129.0
2	1.0	59.8	6.6	299.0
3	2.0	83.5	5.0	417.5
4	3.0	85.5	4.7	427.5

Reaction conditions: S/C = 1000, [Rh] = 1.3×10^{-3} mmol, L1/Rh = 10, 80 °C, 2 h, toluene 2 mL

TABLE-4
EFFECT OF SUBSTRATE/RHODIUM ON 1-OCTENE HYDROFORMYLATION

Entry	S/C	Aldehyde yield (%)	L/B	TOF
1	1000	59.8	6.6	299.0
2	5000	60.0	5.5	1500.0
3	10000	69.3	4.3	3465.0

Reaction conditions: 80 °C, [Rh] = 1.3×10^{-3} mmol, 2 h, toluene 2 mL, L1/Rh = 10, p = 2 MPa (CO/H_2 = 1)

rhodium ratios. When the substrate/rhodium ratio is 10000, the highest TOF (3465.0 h^{-1}) could be obtained.

It demonstrated that the hydroformylation of 1-octene was sensitive to the reaction conditions according to the above data. And then we subsequently investigated the effect of ligand and the results are summarized in Table-5. Ligand **1** obviously improved the selectivity of linear aldehyde and the reaction activity, while ligand **2** showed less advantage either on activity or regioselectivity. According to the comparison of ligand **1** and **2**, it is not difficult to find that the ten-membered ring chelations of the ligand **2** with rhodium is so weak that the species **II** (**Scheme-II**) could not form easily. However, the seven-membered ring chelations of the ligand **1** with rhodium addressed the issue of chelating ability, leading to high regioselectivity of linear aldehyde and activity. It indicated that, in order to achieve high regioselectivity in the hydroformylation of 1-octene, a strategy to enhance the chelating ability of ligands is needed.

Conclusion

In conclusion, a new pyrrole-based biphosphane ligand **1**, possessing strong π-acceptor, has been prepared and applied in hydroformylation of 1-octene. To the best of our knowledge, this is the first report of the new ligand. The good regioselectivity (L/B: 6.6) and high activity (TOF: 3465.0 h^{-1}) in hydroformylation of 1-octene has been achieved under the optimum conditions. Our results clearly indicate that the biphosphane ligand **1** has enhanced ability to coordinate to rhodium and thus afforded better regioselectivity in hydroformylation of 1-octene compared with the corresponding *bis*phosphane ligand **2**. Further ligand developments based on this new concept are now under investigation and will be reported in due course.

TABLE-5
COMPARISON OF BISPHOSPHANE LIGAND **1** AND LIGAND **2**

Entry	Legend	Temperature (°C)	P (MPa)	Aldehyde yield (%)	L/B	TOF
1	1	80	2.0	70.6	5.7	353.0
2	1	80	1.0	59.8	6.6	299.0
3[a]	2	120	2.0	69.4	2.7	347.0
4[a]	2	120	1.0	39.7	3.4	198.5

Reaction conditions: S/C = 1000, [Rh] = 1.3×10^{-3} mmol, L/Rh = 10, toluene (2 mL). [a]data from the literature [Ref. 12]

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