Highly Regioselective and Active Rh–2,2′-Bis(dipyrrolylphosphinooxy)-1,1′-(±)-binaphthyl Catalyst for Hydroformylation of 2-Octene

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Rhodium catalyst bearing 2,2′-bis(dipyrrolyphosphinooxy)-1,1′-(±)-binaphthyl (ligand **1**) shows high regioselectivity and activity for the hydroformylation of 2-octene. The introduction of a pyrrolyl group in the ligand greatly improves the yield of the linear aldehyde. The regioselectivity is up to 97.5% under mild conditions (100 °C, 0.7 MPa H_2/CO).

The rhodium-catalyzed hydroformylation of olefins has attracted much attention as a potential tool for preparing aldehydes,[1–3] which are important precursors for synthesizing various pharmaceuticals, agrochemicals, commodity, and fine chemicals. This great demand has initiated tremendous efforts in the development of effective phosphorus ligands to achieve both high regioselectivity and activity in hydroformylation. The majority of these catalysts have been rhodium(I) complexes with chelating bis(phosphine), bis(phosphite), bis(phospholane), or mixed bis(phosphine/phosphite) ligands.[4] These ligands give reasonably high regioselectivity and conversion. After first being reported by Billig and co-workers, diphosphites were recognized as a new generation of promising ligands in rhodium-catalyzed hydroformylation of internal alkenes.[5,6] Zhang et al. used a pyrrole-based biphenyl bisphosphorus for hydroformylation of 2-octene and got better results.[7]

Many bisphosphine ligands have a natural bite angle, defined by Casey et al.[8,9] and ligand backbone chains from two to five carbons in length are reasonably accessible. Longer chains have increased natural bite angles, but are also more flexible than shorter chains. Later, Casey et al.[10–12] showed experimentally that the bite angle influences the nature of intermediate, which then influence product regioselectivity and a rhodium complex bearing a large bite angle bisphosphine gives a high n/i ratio. At the same time, it was found that the formation of an ee complex, in which biphosphine occupies two equatorial positions of a trigonal bipyramid plays a key role in the high regioselectivity. So a wide bite angle biphosphine forms easily an ee complex and promotes the formation of linear aldehydes. Casey et al. also found that introduction of electron-withdrawing groups in large bite angle biphosphines would further increase the n:i ratio.[13] NMR studies indicated that an electron-poor phosphine preferred occupying the equatorial position of metal center. The above results are also suppported by the work of van Leeuwen et al.[14]

In this contribution, we synthesized a diphosphine 2,2′-bis-(dipyrrolylphosphinooxy)-1,1′-(±)-binaphthyl with a large bite angle and electron-withdrawing pyrrolyl groups. We used a Rh^I complex bearing this ligand for the hydroformylation of 2-octene and investigated its activity and regioselectivity to linear aldehyde.

A 50-mL round-bottom flask was charged with 0.66 g (2.30 mmol) of (±)-binaphthyl, 0.82 mL (5.88 mmol) of Et_3N, and 5 mL of THF. A solution of 1.13 g (5.70 mmol) of chlorodipyrrolylphosphine in 10 mL of THF was then added dropwise with stirring over a period of 30 min at 0 °C. The reaction mixture was stirred overnight at room temperature. The Et_3N·HCl salts were then filtered off, and the solvent was removed under vacuum. The crude product was purified by recrystallization from ethanol to yield 0.90 g (64%) of ligand **1** as a white solid with a melting point of 88–90 °C.[15] ^{1}H NMR (400 Hz, $CDCl_3$): δ 7.9 (d, $J = 8.4$ Hz, 4H), 7.4 (t, $J = 7.5$ Hz, 2H), 7.3 (t, $J = 7.6$ Hz, 2H), 7.2 (d, $J = 9.9$ Hz, 2H), 7.1 (d, $J = 8.7$ Hz, 2H), 6.4 (m, 8H), 6.1 (dd, $J = 15.6$, 1.8 Hz, 8H); ^{31}P NMR (162.0 Hz, $CDCl_3$): δ 108.2 (s); ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 133.7, 130.7 (d, $J = 37.2$ Hz), 128.1, 127.1, 125.9, 125.3, 121.0 (q, $J = 37.2$ Hz), 119.2, 112.1.

A mixture of 2-octene (1.25 mmol, 0.2 mL), rhodium catalyst (0.66 mmol), ligand **1** (0.66 mmol if used) was dissolved in 1.5 mL of toluene and placed in a 100-mL autoclave with a Teflon liner and mechanical stirring. The autoclave was flushed thoroughly three times with a 1:1 syngas of H_2 to CO and pressurized to the desired pressure, and then heated to the desired temperature. The reaction was maintained under these conditions for 1 h. The autoclave was then cooled to room temperature and the gas was carefully released.

The products were identified with NMR and GC. NMR spectra were obtained on a Bruker AV-400 and AMX 360 (400 MHz for ^{1}H, 162.0 MHz for ^{31}P, and 100.6 MHz for ^{13}C). Melting points were determined with a melting point apparatus (Yanaco MP-500). Gas chromatography was performed with a Hewlett-Packard 960 instrument with an Alltech EC^{TM-1} column (30 m × 0.25 mm, 0.25-μm film).

The catalyst system showed very high activity and regioselectivity in the temperature range of 80 to 120 °C. Compared with known results, our catalytic system shows a higher regioselectivity (Table 1). At 80 °C, a conversion of 53.3% was achieved with a n/i ratio of 21.9. The n:i of 21.9 is much higher than 10.1 reported by Zhang and colleagues for the hydroformylation of 2-octene.[7] Interestingly, if the reaction temperature was increased to 100 °C, under similar conditions the n:i ratio was up to 39.5.

To optimize reaction conditions, we examined the effect of syngas pressures and found that the syngas pressure of 0.7 MPa gave the best results with conversion of 85.0% and n/i ratio of 39.5. van Leeuwen[16] and his co-workers concluded that the concentrations of HRh(P^P)(P^P′)(CO) and HRh(P^P)$(CO)_2$ in solution depend on the ratio of ligand to rhodium as well as the carbon monoxide pressure (Figure 1). For ligand **1** a higher ligand-to-rhodium ratio than 1 is required to reach complete

Table 1. Hydroformylation of 2-octene with ligand **1**[a]

p/MPa	T/°C	P/Rh	n/i[b]	Conversion /%[c]	Regioselectivity /%[d]
0.7	80	1.5	21.9	53.3	95.6
0.7	90	1.5	23.0	67.3	98.5
0.7	100	1.5	39.5	85.0	97.5
0.7	100	2.0	18.5	53.1	94.9
0.7	100	1.0	12.4	45.6	92.5
0.7	110	1.5	16.2	20.2	94.1
0.5	100	1.5	25.5	47.0	96.2
1.0	100	1.5	22.1	29.0	95.7

[a]Condition: [Rh] = 0.66 mM, P:Rh:2-octene = 5:1:1325, toluene (1.0 mL) as solvent, time: 1 h. [b]Linear/branched ratio, determined on the basis of GC analysis. [c]Percentage of linear and branched aldehydes in all aldehydes. [d]Percentage of linear aldehyde in linear and branched aldehydes.

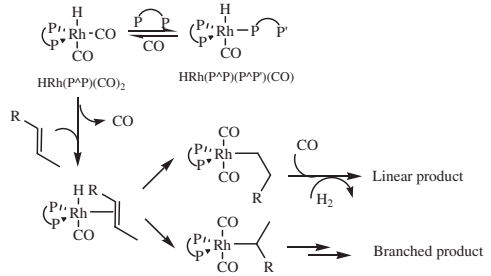

Figure 1. Catalytic procedure for hydroformylation of 2-octene.

conversion to the rhodium–hydride complex [HRh(P^P)$(CO)_2$] and L/Rh = 1.5 gives the best results. When the syngas pressure is high in the case of L/Rh > 1.5, the rhodium–hydride complex HRh(P^P)$(CO)_2$ is converted to hydride complex HRh(P^P)-(P^P′)(CO). One of the bidentate ligands, denoted P^P′, coordinates in a monodentate fashion.[17] It was reported that linear Rh–alkyl intermediate forms faster than the branched isomer intermediate.[18] At 100 °C and 0.7 MPa, linear rhodium–alkyl complex undergoes carbon monoxide insertion to form linear aldehydes.[16]

The hydroformylation of 2-octene was also studied by varying the rhodium precursors in toluene (Table 2). Rh(acac)$(CO)_2$ shows a high conversion of 85.0% with a n/i ratio of 39.5. According to reported results, the active intermediate $RhH(L)_2(CO)$ is easily formed in a system composed of Rh(acac)$(CO)_2$ and the diphosphine even at low temperature[19] and gives a high n/i ratio. When HRh(CO)$(PPh_3)_3$ was used as a catalyst precursor, it gave a conversion of 44.9% with a regioselectivity of 97.0%, which is lower than Rh(acac)$(CO)_2$. The probable reason is the stronger base PPh_3 in the rhodium precursor is not easily substituted by the weak base ligand **1**, so that the partial existence of PPh_3 in active intermediate does not efficiently stabilize the ee coordination model active species that can give high n/i ratio aldehyde. Similarly, RhCl(CO)$(PPh_3)_2$ as the catalytic precursor gave a close regioselectivity to RhH(CO)$(PPh_3)_3$, but a lower activity was obtained as the transformation of of RhCl(CO)$(PPh_3)_2$ into the active species under the reaction conditions is slower than RhH(CO)$(PPh_3)_3$.[20] For precursor $[Rh(COD)Cl]_2$, COD is probably difficult to hydrogenate and dissociates from the metal center under low syngas pressure, so it gave the lowest activity and selectivity.

Table 2. Effect of different rhodium-precursors on hydroformylation with ligand **1**[a]

Rhodium precursors	n/i[b]	Conversion /%[c]	Regioselectivity/%[d]
RhCl(CO)$(PPh_3)_2$	25.8	20.5	96.3
Rh(acac)$(CO)_2$	39.5	85.0	97.5
$[Rh(COD)Cl]_2$	6.9	11.3	87.3
HRh(CO)$(PPh_3)_3$	31.8	44.9	97.0

[a]Condition: [Rh] = 0.66 mM, P:Rh:2-octene = 5:1:1325, toluene (1.0 mL) as solvent, time: 1 h. [b]Linear/branched ratio, determined on the basis of GC analysis. [c]Percentage of linear and branched aldehydes in all aldehydes. [d]Percentage of linear aldehyde in linear and branched aldehydes.

In summary, compound **1** with a bulky binaphthyl backbone and electron-withdrawing pyrrolyl groups is an excellent ligand for the hydroformylation of 2-octene. A low ligand to Rh molar ratio of 1.5/1 gave the highest n/i ratio of 39.5 with an olefin conversion of 85.0%.

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