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A Novel Chiral Phosphinediamine Ligand and Asymmetric Hydrogenation of Acrylic Acid Derivatives

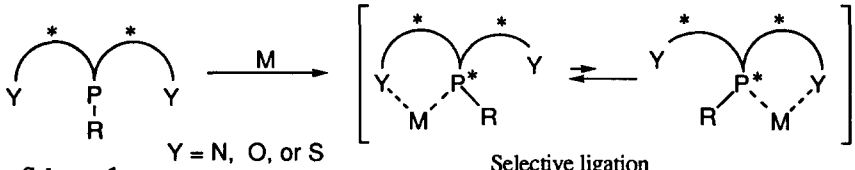
Issaku Yamada, Motowo Yamaguchi, and Takamichi Yamagishi*

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Metropolitan University,

1-1 Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

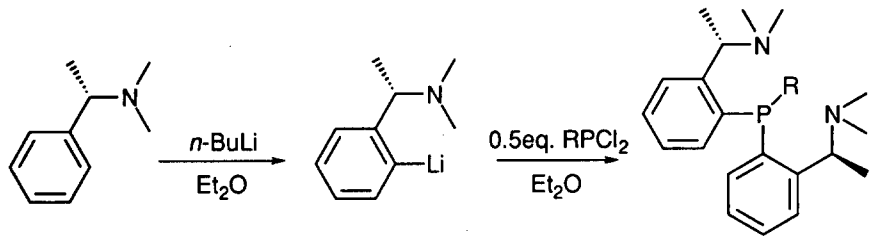
Abstract: A novel chiral phosphinediamine ligand (PN_2) was prepared from (*S*)-1-phenylethylamine and dichloroisopropylphosphine. The rhodium-PN_2 catalyst utilizing selective ligation of the amino unit and electrostatic interaction between the ligand and a substrate gave high enantioselectivities up to 92% ee in asymmetric hydrogenations of acrylic acid derivatives.

A variety of chiral phosphorus ligands were reported and applied to the asymmetric catalytic reactions. Many of them have chiral carbon(s) in their molecular structures in order to provide a chiral field. [1] Chiral phosphine ligands having chiral phosphorus atom(s)[2] are effective for induction of asymmetry in the metal-catalyzed asymmetric reactions because the stereogenic center exists near the reaction site. These ligands, however, have a drawback in the difficulties of their synthesis. Monophosphine ligands having two such substituents which have a site, such as N, O or S, capable of coordinating to metal can be prepared easily. If one of two coordination sites of these ligands ligates to the metal selectively in addition to the ligation of phosphorus atom, the phosphorus atom will become stereogenic to afford an effective chiral field (Scheme 1). The monophosphine ligands designed with such a concept has not been reported to our knowledge.[3] We have designed a novel chiral monophosphine ligand having two 2-(1-*N*,*N*-dimethylaminoethyl)phenyl units: (*S*,*S*)-alkylbis[2-(1-*N*,*N*-dimethylaminoethyl)phenyl]phosphine, PN_2 ligand. Upon selective ligation of the amino unit, free amino moiety would serve to have a secondary interaction with the substrate, for example an electrostatic interaction with the carboxyl unit of substrate.



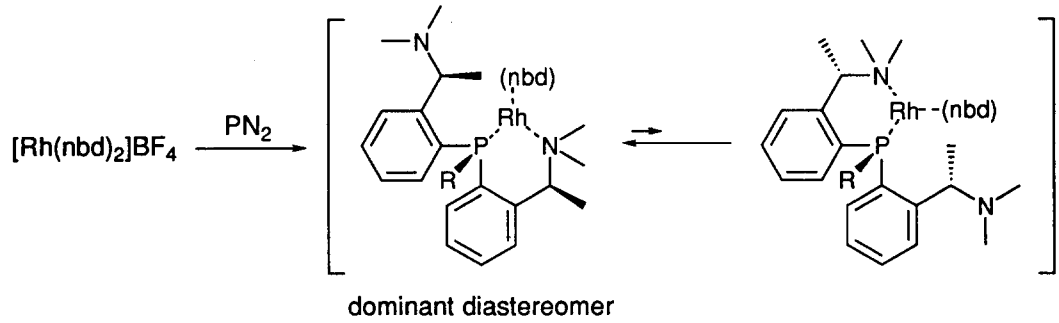
Scheme 1

The PN_2 ligands[4] were easily prepared by two-steps reaction; *ortho*-lithiation of (*S*)-*N*,*N*-dimethyl-1-phenylethylamine,[5] followed by the reaction with alkyl- or aryldichlorophosphine (Scheme 2).



Scheme 2

The rhodium-PN_2-olefin complex was formed *in situ* from PN_2 and $[Rh(nbd)_2]BF_4$. $^{31}P\{^1H\}$ NMR spectra of the complex in methanol-d_1 solution showed the presence of two diastereomers with a ratio of >9 : 1 indicating the nearly selective ligation of the amino group in the PN_2 ligand. ^1H NMR spectra supported this selective ligation of the amino group: Methyl protons of two amino units appeared with different chemical shifts. The signal of two methyl groups of the lower-field amino unit was split at 0 °C while the signal of the upper-field amino unit remained as singlet with the same chemical shift as that of free PN_2 ligand.[6] The free amino unit would serve as a unit to interact with a functional group, such as carboxyl group, of the substrates.

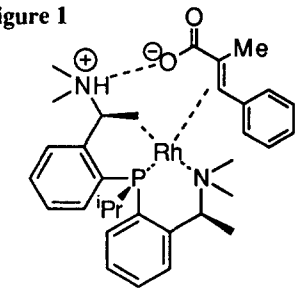


Scheme 3

We have applied this PN_2 ligands to the asymmetric hydrogenation of acrylic acid derivatives with rhodium catalyst. The rhodium-phosphine catalysts, except a few examples,[7] gave only low enantioselectivities for the hydrogenation of unsaturated carboxylic acids without another functional group,[8] for example, the hydrogenation of 2-methylcinnamic acid by rhodium-DIOP catalyst gave 62% ee.[8a] In the

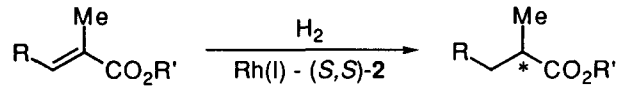
asymmetric hydrogenation of 2-methylcinnamic acid by rhodium-PN_2 systems, rhodium-(*S*,*S*)-**2** effectively catalyzed the hydrogenation while with rhodium-(*S*,*S*)-**1** the substrate was recovered intact. This suggests that an increase of electron density on the phosphorus atom of PN_2 ligand accelerates the hydrogenation reaction. The rhodium-(*S*,*S*)-**2** gave high enantiomeric excess (92% ee) under 40 atm of hydrogen using neutral rhodium precursor at the ligand/rhodium ratio of 1.5 (Table 1, entry 4). For methyl 2-methylcinnamate, the reaction was extremely slow and the enantioselectivity was low. This difference may be ascribed to the participation of the electrostatic interaction between PN_2 ligand and 2-methylcinnamic acid for incorporation of substrate and asymmetric induction. For tiglic acid, good selectivity (75% ee) was obtained at 20 atm of hydrogen.

Figure 1



The application of this PN_2 ligand to other asymmetric reactions utilizing secondary interaction is under way.

Table 1. Asymmetric hydrogenation of acrylic acid derivatives by rhodium - **2** catalyst[a]



Entry	R	R'	PH_2 (atm)	Ligand/Rh	Time (h)	Conversion[b] (%)	% ee[c]
1	Ph	H	20	1.1	57	75	63 (*R*)
2	Ph	H	20	1.5	120	100	84 (*R*)
3	Ph	H	20	2.0	156	100	77 (*R*)
4	Ph	H	40	1.5	86	100	92 (*R*)
5	Ph	Me	20	1.5	120	< 6	—
6	Ph	H	80	1.5	43	100	59 (*R*)[d]
7	Ph	Me	80	1.5	88	17	42 (*R*)[d]
8	Me	H	20	1.5	94	100	75 (*S*)

[a] Hydrogenation was carried out at 25 °C in methanol with 1 mmol of substrate in the presence of 2 mol % of catalyst, catalyst precursor being $[RhCl(nbd)]_2$. [b] Conversion was determined by ^1H NMR. [c] Enantiomeric excess was determined by ^{13}C NMR integrating diastereotopic signals of the 2-methyl group of 2-methyl-3-phenylpropionic acid or 2-methylbutyric acid in the presence of (*R*)-1-phenylethylamine. See ref. 9. For the methyl ester, % ee was determined from the optical rotation. For the 2-methylbutyric acid, absolute configuration was determined by ^{13}C NMR of diastereomer salts with (*R*)-1-phenylethylamine. See ref. 9. Absolute configuration of 2-methyl-3-phenylpropionic acid was determined based on the sign of the optical rotation. See ref. 10. [d] Reaction temperature was 40 °C.

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4. The NMR spectra for **1** and **2** are as follows: **1** : ^{1}H NMR (270MHz, $CDCl_3$, TMS) δ 1.04 (d, 3H), 1.16 (d, 3H), 2.14 (s, 12H), 3.98 (m, 1H), 4.11 (m, 1H), 6.80-7.62 (m, 13H). $^{31}P\{^{1}H\}$NMR (109MHz, $CDCl_3$, 85% H_3PO_4) δ -28.9. FAB-MAS (*m*-nitrobenzyl alcohol matrix) 405. **2**: ^{1}H NMR (270MHz, $CDCl_3$, TMS) δ 0.89 (d, 3H), 1.00 (dd, 3H), 1.13 (dd, 3H), 1.35 (d, 3H), 2.15 (s, 6H), 2.24 (s, 6H), 2.40 (m, 1H), 4.16 (m, 1H), 4.26 (m, 1H), 7.06-7.60 (m, 8H). $^{31}P\{^{1}H\}$NMR (109MHz, $CDCl_3$, 85% H_3PO_4) δ -29.0. FAB-MAS (*m*-nitrobenzyl alcohol) 371.
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6. The NMR spectra for the *N*-methyl groups are as follows: Rh-**1**: ^{1}H NMR (270MHz, $CDCl_3$, TMS, 273 K) δ 2.02 (s, 6H), 2.59 (br-s, 3H), 2.69 (br-s, 3H). Rh-**2**: ^{1}H NMR (270MHz, $CDCl_3$, TMS, 273 K) δ 1.96 (s, 6H), 2.55 (br-s, 3H), 2.65 (br-s, 3H). The dominant rhodium-PN_2-olefin complex was supposed to have the structure *left* in Scheme 3 by NOE measurement of the proton signals in ^{1}H NMR.
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