Bulky Achiral Triarylphosphines Mimic BINAP in Ru(II)-Catalyzed Asymmetric Hydrogenation of Ketones

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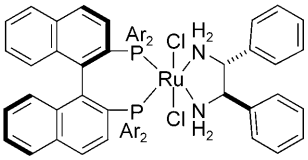
Abstract: In the present work, we report on catalysis of the enantioselective hydrogenation of ketones with Ru(II) complexes composed of cheap achiral monodentate phosphine ligands in combination with an enantiopure 1,2-diamine, affording a variety of optically active secondary alcohols with high efficiency and enantioselectivity. The steric impact of achiral monophosphine ligands in Ru complexes was found to be a critical factor for the high enantioselectivity of the reaction. This finding throws some light on a long-standing challenge, the high cost of chiral bisphosphine ligands, associated with an industrial application of the asymmetric hydrogenation of ketones.

Keywords: asymmetric catalysis; diamines; hydrogenation; ketones; monodentate phosphines; ruthenium

Enantioselective catalysis of the hydrogenation of ketones using Noyori's [$RuCl_2$\{(*R*)-BINAP\}\{(*R*,*R*)-DPEN\}] (**1**) (BINAP = 2,2′-bis(diarylphosphino)-1,1′-binaphthyl; DPEN = 1,2-diphenylethylenediamine) catalyst provides the most efficient process for the production of optically active secondary alcohols,[1,2] one of the most valuable intermediates for the manufacture of pharmaceuticals and advanced materials. In Noyori's catalyst, ruthenium is combined with a chiral diphosphane and a chiral diamine, forming an octahedral complex.[2,3] The high degree of enantioselectivity was considered to be a result of the synergistic effect of the chiral diphosphane and diamine ligands.[3] Alternatively, the use of Ru(II) complexes composed of racemic BINAP or chirally flexible diphosphane ligands in the presence of enantiopure diamine,[4] or of Ru(II) complexes of enantiopure diphosphane in combination with a cheap achiral amine[5] have also been successful in the asymmetric hydrogenation of ketones. Despite these facts, no successful use of achiral monodentate phosphine ligands has been achieved for the highly enantioselective hydrogenation of ketones, probably due to the high flexibility of monodentate phosphine ligands in Ru complexes. In the present work, we report our preliminary results on the development of highly efficient and enantioselective Ru(II) catalysts for the hydrogenation of ketones by combination of achiral monodentate phosphine ligands with chiral 1,2-diphenylethylenediamine (DPEN).



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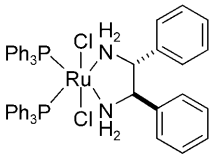

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The research was inspired by Noyori's early discovery on the use of [$RuCl_2$\{**P1**\}$_2$\{(*R*,*R*)-DPEN\}] (**2**) (**P1** = Ph_3P) complex as the catalyst for asymmetric hydrogenation of 1-acetonaphthone, affording 1-(1-naphthyl)ethanol with a moderate (75%) ee value.[2a] As an effort toward the development of truly practical catalysts for the enantioselective hydrogenation of ketones, we employed a combinatorial chemistry approach[6] for the discovery of effective achiral ligands through random screening of a variety of simple triarylphosphanes, including commercially available or easily prepared triarylphosphane derivatives. The hydrogenation of acetophenone (**5a**) was taken as the model reaction and the catalyst loading was set up at the 0.1 mol % level. As shown in Table 1, it was serendipitously found that the catalyst composed of the tri(3-tolyl)phosphine (**P2**) or tri(3,5-xylyl)phosphine (**P3**) ligand demonstrated improved enantioselectivities (77.4% and 87% ee, respectively) in comparison with that obtained with the catalyst containing triphenylphosphine (entry 1 *vs.* entries 2 and 3). A careful examination of the crystal structures of [$RuCl_2$\{**P1**\}$_2$\{(*R*,*R*)-DPEN\}] and [$RuCl_2$\{**P3**\}$_2$\{(*R*,*R*)-DPEN\}] (Figure 1a and 1b, respectively)[7] disclosed that both complexes take a distorted octahedral geometry of the Ru center like that in [$RuCl_2$\{(*R*)-tolBINAP\}\{(*R*, *R*)-DPEN\}] (Ar = 4-tolyl in **1**).[2c] The bond lengths around the Ru atoms are quite similar to those of [$RuCl_2$\{(*R*)-tolBINAP\}\{(*R*,*R*)-DPEN\}], too. The aro-

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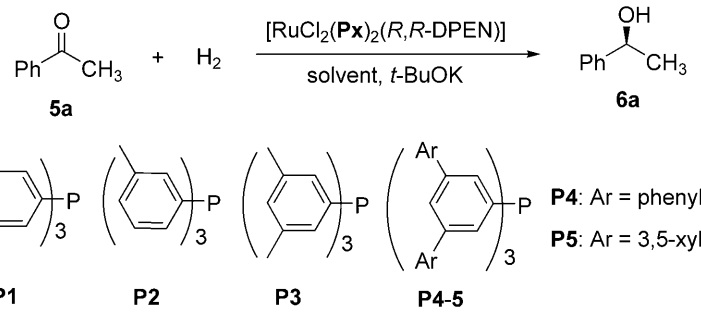
Table 1. The influence of monodentate phosphine ligands (**Px**) and reaction solvents on the enantioselective catalysis of hydrogenation of acetophenone (**5a**) using (**Px**)$_2$/Ru(II)/(*R,R*)-DPEN.[a]



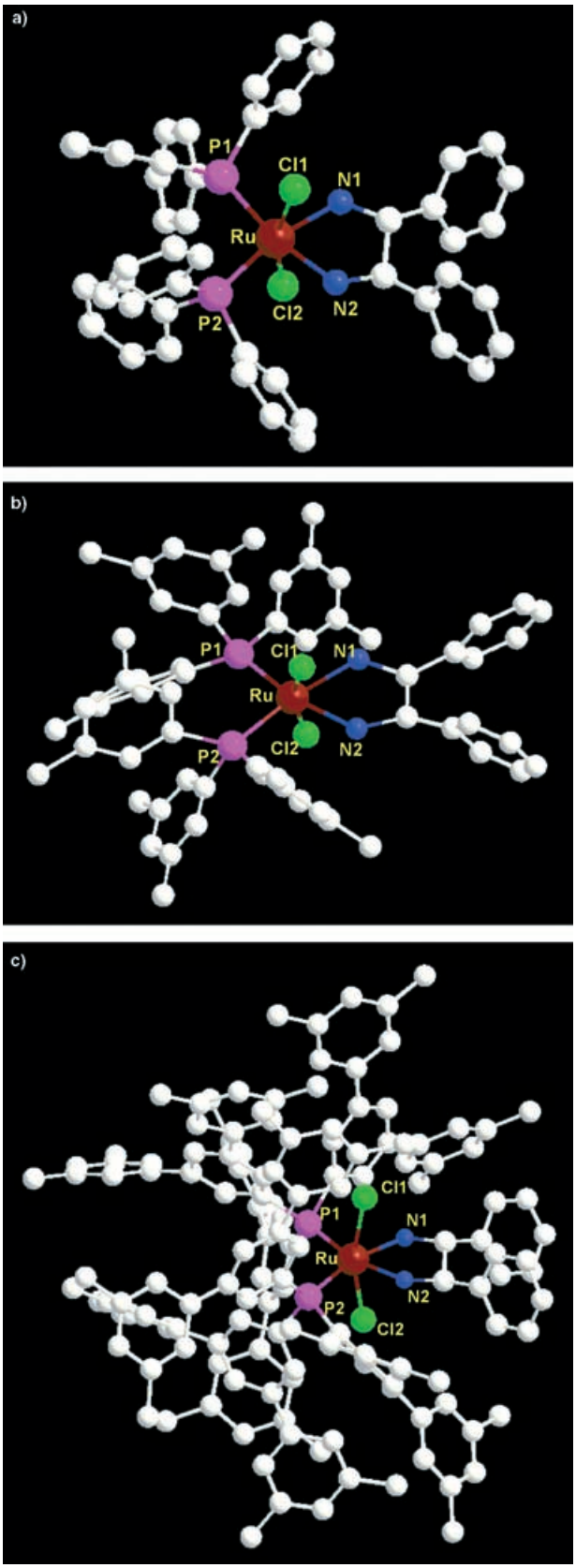
Entry	**Px**	Solvent	Conversion [%][b]	*ee* [%][c]	Configuration[d]
1	**P1**	*i*-PrOH	>99	76.7	*S*
2	**P2**	*i*-PrOH	96	77.4	*S*
3	**P3**	*i*-PrOH	>99	87.0	*S*
4	**P4**	*i*-PrOH	>99	88.8	*S*
5	**P5**	*i*-PrOH	>99	89.0	*S*
6	**P5**	MeOH	98	62.8	*S*
7	**P5**	EtOH	>99	90.0	*S*
8	**P5**	*n*-PrOH	>99	95.5	*S*
9	**P5**	*n*-BuOH	>99	94.9	*S*
10	**P5**	*n*-Pentanol	>99	94.7	*S*

[a] All of the reactions were carried out at 25 °C under 300 psi pressure of H_2 at a substrate/catalyst/*t*-BuOK ratio of 1000/1/20 for 10 h.
[b] Determined by ^{1}H NMR.
[c] Determined by GC on a Supelco BETA-DEX120 column.
[d] Determined by sign of optical rotation.

matic rings of the triarylphosphine ligands in the complexes adopt a propeller arrangement with the same screw direction in the solid state. The introduction of 3,5-dimethyl groups in the triphenylphosphine ligand allows the *P*-aryl rings to approach the (*R,R*)-DPEN moiety more closely because of steric repulsion between the two monophosphine ligands. Meanwhile, the P–Ru–P angle in the complexes is increased with the enlargement of the *P*-aryl rings. Such a structural change in the catalyst precursor will inevitably increase the impact of monophosphine ligands on the asymmetric induction of its Ru(I) complexes in the hydrogenation on the basis of Noyori's non-classical six-membered pericyclic mechanism.[3a]

Based on an understanding of the impact of steric hindrance on the enantioselection of the hydrogenation mentioned above, we then designed the sterically more bulky achiral monophosphine ligands **P4** and **P5** for the construction of Ru catalysts in combination with (*R,R*)-DPEN in order to further improve the enantioselectivity of the reaction. As expected, the complexes generated with **P4** and **P5** indeed showed enhanced enantioselectivities in the model reaction under the same experimental conditions, affording 88.8% and 89.0% ee of product **6a**, respectively. Based on the leading results mentioned above, we then investigated the solvent effect on the enantioselectivity of the reaction. As shown in Table 1, *n*-PrOH was the best choice of the solvent among several alcohols examined (entries 5–10) and up to 95.5% ee of the product **6a** could be attained with >99% conversion. According to the traditional belief, an excellent enantioselectivity of the catalysis is usually associated with a strongly chelating chiral bidentate phosphine ligand which is able to reduce the rotational freedom around the donor-metal bond in the chelating ring. Therefore, this result is indeed unprecedented in terms of using achiral monophosphine ligands.

Under the optimized conditions, a variety of aromatic and heteroaromatic ketones was submitted to the hydrogenation under the catalysis of [$RuCl_2${**P5**}$_2${(*R,R*)-DPEN}], 87.3–96.3% ee of the secondary alcohols could be obtained with quantitative conversion of the ketones (Table 2). The present catalyst system is particularly effective for the asymmetric hydrogenation of β-amino ketone **5t**, affording the corresponding β-amino alcohol **6t**, an important chiral drug intermediate,[8] with 96.7% ee (entry 20). This result is comparable to that obtained by using Noyori's [$RuCl_2${xylBINAP}$_2$ {DAIPEN}] [DAIPEN = 1,1-di(4-anisyl)-2-isopropyl-1,2-ethylenediamine] catalyst (97.5% ee).[2e] When the catalyst loading was reduced to 0.01 mol %, the hydro-



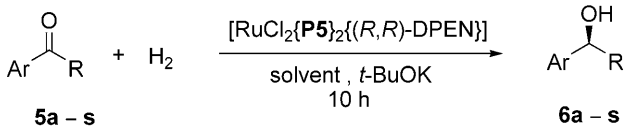
genation of **5a** proceeded smoothly without loss of enantioselectivity (entry 21 *vs.* 1), demonstrating the high activity of the present catalyst system.

It should be noticed that the preparation of the monodentate achiral triarylphosphine ligands was quite simple. The Suzuki coupling of arylboric acids with very cheap 1,3,5-tribromobenzene, an industrial product, gave the corresponding 3,5-diarylphenyl bromide in 50–55% yield. Treatment of the 3,5-diarylphenyl bromide with *n*-BuLi followed by addition of PCl_3 to the resultant aryllithium solution at $-78\,^{\circ}C$ afforded **P4** and **P5** in 58% and 53% yields, respectively. The facile preparation of **P4** and **P5** again demonstrated the practicality of the present catalyst system.

As an effort to probing the origin of the high enantioselectivity of the present catalyst system, the simulated structure of the catalyst precursor $[RuCl_2\{\mathbf{P5}\}_2\{(R,R)\text{-DPEN}\}]$ was created using a molecular mechanics method (Universal Force Field implemented in GAUSSIAN '98) based on the structural information of $[RuCl_2\{\mathbf{P1}\}_2\{(R,R)\text{-DPEN}\}]$ because of the difficulty for getting a crystal of suitable quality X-ray diffraction. As shown in Figure 1c, the maximum diameter of the ligand **P5** is 1.73 nanometer and two 3,5-di(3,5-xylyl)-phenyl groups extend to the (*R,R*)-DPEN moiety equatorially in the complex. This structural feature might induce the helix chirality of the achiral phosphine ligands through steric communication around the Ru(II) center because of a sufficiently close proximity between the *P*-aryl group and the phenyl group of (*R,R*)-DPEN (the closest atom distance is 1.73 Å). Moreover, the crowded environment of the ligands will inevitably hinder the rotation around the *P*-aryl bonds, and hence the induced chiral conformation of the achiral phosphine ligands might be frozen to some extent. This could be observed from the changes of the CD spectra of complex $[RuCl_2\{\mathbf{P5}\}_2\{(R,R)\text{-DPEN}\}]$ with different temperatures. Other axial *P*-aryl groups build up a bulky aromatic fence in the axial orientation of the complex, which allows the prochiral ketone to approach the catalyst surface in such a way as to minimize the non-bonded repulsion between the *P*-aryl group and the aromatic ring of

Figure 1. Molecular structures of $[RuCl_2\{\mathbf{P1}\}_2\{(R,R)\text{-DPEN}\}]$ (**a**) and $[RuCl_2\{\mathbf{P3}\}_2\{(R,R)\text{-DPEN}\}]$ (**b**) (H atoms were omitted for clarity). Selected interatomic distances [Å], and angles [°] for $[RuCl_2\{\mathbf{P1}\}_2\{(R,R)\text{-DPEN}\}]$: Ru–N(1) 2.133(3), Ru–N(2) 2.139(3), Ru–P(1) 2.317(8), Ru–P(2) 2.311(8), Ru–Cl(1) 2.429(8), Ru–Cl(2) 2.430(8), Cl(1)–Ru–Cl(2) 162.71(3), P(1)–Ru–P(2) 98.02(3), N(1)–Ru–N(2) 77.40(11). Selected interatomic distances [Å], and angles [°] for $[RuCl_2\{\mathbf{P3}\}_2\{(R,R)\text{-DPEN}\}]$: Ru–N(1) 2.101(13), Ru–N(2) 2.204(14), Ru–P(1) 2.308(6), Ru–P(2) 2.336(5), Ru–Cl(1) 2.418(5), Ru–Cl(2) 2.430(5), Cl(1)–Ru–Cl(2) 164.4(2), P(1)–Ru–P(2) 100.9(2), N(1)–Ru–N(2) 75.9(5). Ball and stick presentation of the energy-minimized structure of complex $[RuCl_2\{\mathbf{P5}\}_2\{(R,R)\text{-DPEN}\}]$ (**c**).

Table 2. Enantioselective hydrogenation of ketones **5a**–**t** under the catalysis of $[RuCl_2\{\mathbf{P5}\}_2\{(R,R)\text{-DPEN}\}]$.[a]



5a – s **6a – s**

Entry	Ar and R in ketone	ee [%][b]	*ee* [%] using Noyori's catalyst[c]
1	Ar = Ph, R = Me (**5a**)	95.5 (*S*)	87–99
2	Ar = 2′-MeC_6H_4, R = Me (**5b**)	95.1 (*S*)	95–99
3	Ar = 4′-MeC_6H_4, R = Me (**5c**)	93.7 (*S*)	84–98
4	Ar = 2′-$MeOC_6H_4$, R = Me (**5d**)	93.7 (*S*)	82–92
5	Ar = 4′-$MeOC_6H_4$, R = Me (**5e**)	89.9 (*S*)	86–100
6	Ar = 2′-BrC_6H_4, R = Me (**5f**)	96.1 (*S*)	96–98
7	Ar = 3′-BrC_6H_4, R = Me (**5g**)	93.3 (*S*)	77–99.5
8[d]	Ar = 2′-ClC_6H_4, R = Me (**5h**)	96.3 (*S*)	94–98
9	Ar = 3′-ClC_6H_4, R = Me (**5i**)	95.3 (*S*)	–
10	Ar = 2′-FC_6H_4, R = Me (**5j**)	95.1 (*S*)	82–97
11	Ar = 4′-F C_6H_4, R = Me (**5k**)	91.5 (*S*)	73–97
12	Ar = 2′-$CF_3C_6H_4$, R = Me (**5l**)	96.5 (*S*)	99
13	Ar = 3′,5′-$(CF_3)_2C_6H_3$, R = Me (**5m**)	90.9 (*S*)	–
14[d]	Ar = 1-naphthyl, R = Me (**5n**)	94.7 (*S*)	97–99
15[d]	Ar = 2-naphthyl, R = Me (**5o**)	90.5 (*S*)	98
16	Ar = ferrocenyl, R = Me (**5p**)	87.3 (*S*)	87
17	Ar = 2-furyl, R = Me (**5q**)	89.5 (*S*)	99
18	Ar = 2-thienyl, R = Me (**5r**)	95.9 (*S*)	99
19	Ar = Ph, R = Et (**5 s**)	96.3 (*S*)	92–99
20[e]	Ar = Ph, R = $Me_2NCH_2CH_2$ (**5 t**)	96.7 (*S*)	97.5
21[f]	Ar = Ph, R = Me (**5a**)	95.1 (*S*)	87–99

[a] All of the reactions were carried out at 25 °C under 300 psi pressure of H_2 at a substrate/catalyst/*t*-BuOK ratio of 1000/1/20 for 10 h. The conversion of the substrates was determined by ^1H NMR to be >99%.
[b] Determined by HPLC on a Chiralcel OD or AS column and GC on a Supelco BETA-DEX120 column. Absolute configurations were determined by the sign of optical rotations.
[c] The data taken from ref.[1c]
[d] The reaction was carried out in *n*-BuOH.
[e] The reaction was carried out at a substrate/catalyst/*t*-BuOK ratio of 1000/1/10.
[f] At 0.01 mol % of catalyst loading and 24 h of reaction time.

the ketone, leading to a more favored transition state which mimics that of Noyori's $[RuCl_2\{(BINAP)(DPEN)\}]$ (**1**) catalysts[3a] and resulting in a high level of enantioselectivity of the catalysis.

In conclusion, a highly efficient and enantioselective Ru(II) catalyst composed of achiral monophosphine ligands and a chiral diamine has been developed for the hydrogenation of ketones. The steric hindrance of achiral monophosphine ligands in Ru(II) complexes was found to be a critical impact factor for the high enantioselectivity of the catalysis. Although the enantioselectivies of the reactions using the present catalyst system have not yet been optimized to the perfect stage, e.g. >99% ee, the results gained from this work will definitely stimulate further research to develop practical catalysts for the enantioselective hydrogenation of ketones using simple and cheap achiral monodentate phosphine ligands. This is particularly important for industrial applications of asymmetric catalysis that are currently hindered due to the expense chiral diphosphine ligands.[2,9]

Experimental Section

General Procedure for Asymmetric Hydrogenation

To a test tube containing a stirring bar, the precatalyst $[RuCl_2\{P5\}_2\{(R,R)\text{-DPEN}\}]$ (0.002 mmol), and *t*-BuOK (4.5 mg, 0.04 mmol) was added *n*-PrOH (2.0 mL) under argon and the resultant mixture was stirred at room temperature for 20 min before the aromatic ketone 5 (2.0 mmol) was introduced. The test tube was transferred to a stainless steel autoclave and then sealed. After purging with hydrogen for 5 times, the final H_2 pressure was adjusted to 300 psi. After stirring at

room temperature for 10 hours, the reaction was stopped. The solvent was removed under reduced pressure and the residue was submitted to ^{1}H NMR analysis to assess the conversion of the starting materials. The enantiomeric excess of the product was determined by chiral GC or HPLC.

Crystal Data for $RuCl_2(P1)_2$(*R,R*)-DPEN

$C_{50}H_{46}N_2Cl_2P_2Ru$, $M_r = 908.80$, orthorhombic, space group $P2_12_12_1$, $a = 13.0457(7)$, $b = 16.5901(10)$, $c = 20.0597(12)$ Å; $V = 4341.5(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.390$ g·cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å), crystal dimensions $0.752 \times 0.653 \times 0.608$ mm^3. A total of 26,682 reflections were collected on a Bruker Smart CCD area detector at 293(2)K, of which 10027 were independent and 8,908 were greater than $2\sigma(I)$. The structure was solved by direct methods and refined with using full-matrix least-squares on F^2 using the SHELXTL (version 6.10) software package. Final residuals, $R1 = 0.0392$, $wR2 = 0.0817$ (all data), P_{max}, $P_{min} = 0.670$, -0.617 Å^{-3}.

Crystal Data for $[RuCl_2\{P3\}_2\{(R,R)$-DPEN$\}]$

$C_{62}H_{70}N_2Cl_2P_2Ru$, $M_r = 1077.11$, monoclinic, space group $P2_1$, $a = 19.4269(19)$, $b = 12.9634(13)$, $c = 23.563(2)$ Å, $\beta = 109.372(2)^\circ$, $V = 5598.2(10)$ Å^3, $Z = 4$, $\rho_{calc} = 1.278$ g·cm^{-3}, Mo-Kα radiation ($\lambda = 0.71073$ Å), crystal dimensions $0.495 \times 0.210 \times 0.071$ mm^3. A total of 32,727 reflections were collected on a Bruker Smart CCD area detector at 293(2)K, of which 21118 were independent and 7212 were greater than $2\sigma(I)$. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using the SHELXTL (version 6.10) software package. Final residuals, $R1 = 0.0666$, $wR2 = 0.1435$ (all data), P_{max}, $P_{min} = 0.892$, -0.912 Å^{-3}.

CCDC-260521 and CCDC-260522 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdec.cam.ac.uk).

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