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Asymmetric hydrogenations of ketones catalyzed by Ru–achiral phosphine-enantiopure diamine complexes

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Abstract

Five novel ruthenium complexes, $RuCl_2(MOTPP)_2$[(*S*,*S*)-DPEN] [MOTPP = tris(4-methoxyphenyl)phosphine] (**1**), $RuCl_2(TFTPP)_2$[(*S*,*S*)-DPEN] [TFTPP = tris(4-trifluoromethylphenyl)phosphine] (**2**), $RuCl_2(PPh_3)_2$[(*S*,*S*)-DPEN] (**3**), $RuCl_2$(BDPX)[(*S*,*S*)-DPEN] [BDPX = 1,2-bis(diphenylphosphinomethyl)benzene] (**4**), $RuCl_2$(BISBI)[(*S*,*S*)-DPEN][BISBI = 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl]] (**5**) were synthesized and used for the hydrogenation of aromatic ketones. The complexes showed high catalytic activities, especially that the catalytic activity of complex **5** containing the diphosphine with large bite angle and complex **1** containing triarylphosphine with electron-donating group were higher than the other three complexes. The enantioselectivities of products were almost not influenced by the electron factors of phosphine.

Keywords: Ruthenium complex; Phosphine; Asymmetric hydrogenation; Diamine; Aromatic ketone

1. Introduction

Noyori and co-workers discovered that the catalyst system of Ru/chiral-diphosphine/chiral-diamine/inorganic (organic) base exhibited high efficiency and enantioselectivity for the asymmetric hydrogenation of various ketones [1–4]. The corresponding mechanisms have been suggested by Noyori and Morris et al. [5–8]. A great number of ruthenium(II) complexes containing various chiral diphosphines and chiral diamines were synthesized for the asymmetric hydrogenation of ketones in recent years [9–17]. Some of these phosphines usually contained various substitute groups, for example 4-4′-substituted BINAP [12] or xyl-BINAP [13]. There is another trend to prepare novel phosphine ligand with a large backbone in order to improve the enantioselectivity [11,17]. In general, the designing and optimizing of new catalysts rely on chemists' intuition [18]. To our knowledge, the studies on the relationship between the catalytic properties and the electron factors of phosphine ligands are rare [19,20]. In Noyori's work, $RuCl_2(PAr_3)_3$ complexes and ethylenediamine were used as catalysts in situ for the diastereoselective hydrogenation of simple ketones and exhibited a excellent activity. The ratio of *syn:anti* alcohol produced in the diastereoselective hydrogenation of 3-phenyl-2-butanone was greatly improved if ruthenium complex contained electron-donating triarylphosphine ligand [19]. According to Xiao's report [20], the diphosphine ligands in ruthenium–diphosphine–diamine complexes had significant effect on both the activity and enantioselectivity in the asymmetric hydrogenation of ketones. When the complexes contained the same diamine, the stronger basicity the phosphine was, the lower activity its ruthenium complex was.

Because Xiao and co-workers compared only the basicity of phosphine ligands with the different backbones and did not synthesize the phosphine containing the electron-donating

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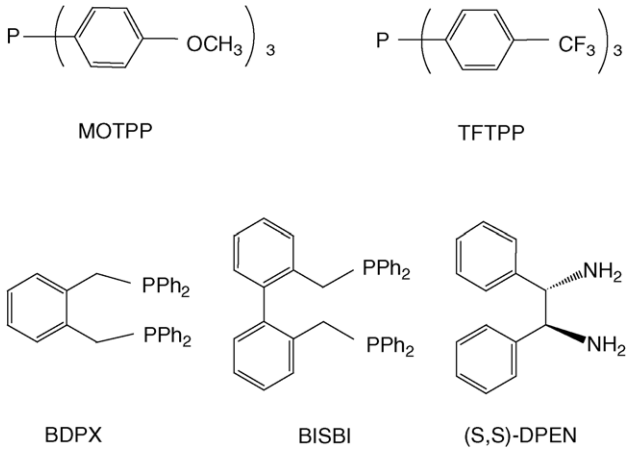


Scheme 1. Structures of ligands.

or electron-withdrawing group in the same backbone, the difference of the catalytic activities of the different complexes could result from the changes of ligand structures as well as the basicity of phosphines. In order to get some exact informations about how the structures and electron factors of phosphines affect the catalytic properties of ruthenium complexes, five complexes bearing phosphines with the different backbones and the different substitute groups (Scheme 1) were synthesized and their catalytic behaviors in the asymmetric hydrogenations of aromatic ketones were investigated. The results showed that the structures and electron properties of phosphines affected only the catalytic activity, and had no obvious effects on the enantioselectivity.

2. Experimental

2.1. Materials

All synthetic processes were performed with standard Schlenk technique and under argon atmosphere. Solvents were generally dried over appropriate drying agents and distilled under argon prior to use. Reagent-grade PPh_3 (Aldrich), and (*S*,*S*)-DPEN (Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences), and $RuCl_3{\cdot}xH_2O$ (Institute of Kunming Noble Metals, China) were used as received. Other materials MOTPP [21], TFTPP [22], BDPX [23], BISBI [24], $RuCl_2$(BDPX)(PPh_3) and $RuCl_2$(BISBI)(PPh_3) [25–27], $RuCl_2$(MOTPP)$_3$ [28], $RuCl_2$(TFTPP)$_3$ [28] were prepared according to the literature methods.

2.2. Analytical methods

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker ARX 300 spectrometer at room temperature, 300.13 MHz for ^1H and 121.49 MHz for ^{31}P. The chemical shifts of ^{31}P NMR were relative to 85% H_3PO_4 as external standard, ^1H relative to TMS as internal standard, with downfield shifts as positive. Elemental analyses were performed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Table 1
Crystal data for complex **5**

Empirical formula	$C_{52}H_{44}Cl_2N_2P_2Ru$
Formula weight	934.87
Temperature	294(2) K
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	$a = 10.965(2)$ Å, $\alpha = 95.38(3)^\circ$ $b = 14.026(3)$ Å, $\beta = 97.95(3)^\circ$ $c = 16.019(3)$ Å, $\gamma = 110.67(3)^\circ$
Volume *Z*	2255.7(8) Å^3
Density (calculated)	1.370 Mg m^{-3}
Absorption coefficient	0.575 mm^{-1}
F(0 0 0)	956
Crystal size (mm)	0.40 × 0.32 × 0.28
θ range for data collection	2.05–26.36°
Limiting indices	$-13 \le h \le 13$, $-10 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	13966
Independent reflections	9088 [R(int) = 0.0434]
Absorption correction	Multi scans
Max. and min. transmission	0.8557 and 0.8027
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9088/0/530
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0648$, $wR2 = 0.1402$
R indices (all data)	$R1 = 0.1144$, $wR2 = 0.1542$
Largest diff. peak and hole	0.951 and −0.981 e Å^{-3}

2.3. Catalytic hydrogenation

Appropriate amount of catalyst and substrate were introduced into a stainless steel autoclave (60 ml) equipped with a stirrer. The autoclave was evacuated and flushed consecutively with high purity hydrogen five times, then filled with the hydrogen to the desired pressure. After the reaction mixture was heated to the desired temperature, the reaction time was accounted. The hydrogenation products were analyzed by GC-960 with FID detector and β-DEX^{TM}120 capillary column (30 m × 0.25 mm, 0.25 μm film) at 115 °C.

2.4. Crystallography

The single crystal was grown from solvent mixtures of CH_2Cl_2 and Et_2O. It was covered with a thin layer of paraffin oil as a precaution against the possible decomposition in air, and mounted on a Rigaku RAXIS IIC imaging-plate diffractometer. Intensity data were collected using graphite-monochromatized Mo Kα (λ = 0.71073 Å) radiation from a rotating-anode generator operating at 50 kV and 90 mA. All calculations were performed with Siemens SHELXTL PLUS (PC Version) system. The crystal data and data refinements for complexes **5** were listed in Table 1.

3. Preparation of complexes

3.1. $RuCl_2(MOTPP)_2[(S,S)$-DPEN] **1**

$RuCl_2(MOTPP)_3$ (0.123 g, 0.1 mmol) and (*S*,*S*)-DPEN (0.023 g, 0.11 mmol) were dissolved in 10 ml CH_2Cl_2. The solution was stirred under argon for 3 h at room temperature and its color changed gradually from brown to yellow. At the end of the reaction, a trace amount of precipitate was removed by filtration. The filtrate was concentrated to about 2 ml, then 10 ml diethyl-ether (or *n*-hexane) was introduced into it and some orange crystals formed. The product was filtrated, washed two times with diethyl ether, and dried under vacuum to obtain $RuCl_2(MOTPP)_2[(S,S)$-DPEN] as orange crystals (0.077 g, 71% yield). mp 215 °C (Decp.). ^{1}H NMR (C_6D_6): δ 3.2 (s, 18H, C*H*$_3$O); 3.7 (m, 2H, N*H*H); 4.1 (m, 2H, 2C*H*); 4.7 (m, 2H, NH*H*); 6.6–7.9 (m, 34H, Ph*H*); ^{31}P NMR (C_6D_6): δ 42.5 (s). Anal. calc. for $C_{56}H_{58}Cl_2N_2O_6P_2Ru$ (%): C, 61.76; H, 5.33; N, 2.57. Found: C, 61.58; H, 5.31; N, 2.62.

3.2. $RuCl_2(TFTPP)_2[(S,S)$-DPEN] **2**

Orange crystals were obtained (0.089 g, 68% yield) by reaction of $RuCl_2(TFTPP)_3$ (0.157 g, 0.1 mmol) with (*S*,*S*)-DPEN (0.023 g, 0.11 mmol) according to the same method described above. mp 226 °C (Decp.). ^{1}H NMR (C_6D_6): δ 3.3 (m, 2H, N*H*H); 3.6 (m, 2H, 2C*H*); 4.5 (m, 2H, NH*H*); 6.7–7.6 (m, 34H, Ph*H*). ^{31}P NMR (C_6D_6): δ 45.7 (s). Anal. calc. for $C_{56}H_{40}Cl_2F_{18}N_2P_2Ru$ (%): C, 51.06; H, 3.04; N, 2.13. Found: C, 50.80; H, 3.06; N, 2.07.

3.3. $RuCl_2(PPh_3)_2[(S,S)$-DPEN] **3**

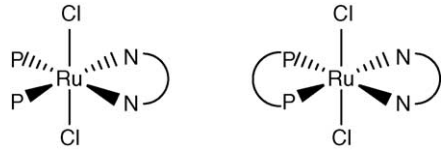
Orange crystals were obtained (0.048 g, 53% yield) by reaction of $RuCl_2(PPh_3)_3$ (0.096 g, 0.1 mmol) and (*S*,*S*)-DPEN (0.023 g, 0.11 mmol). m. p. 212 °C (Decp.). ^{1}H NMR ($CDCl_3$): δ 4.3 (m, 2H; C*H*); 3.7 (m, 2H; N*H*H); 3.3 (m, 2H; NH*H*); 6.8–7.9 (m, 40H; Ph*H*). ^{31}P NMR ($CDCl_3$): δ 44.5 (s). Anal. calc. for $C_{50}H_{46}N_2P_2Cl_2Ru$ (%): C, 66.08; H, 5.07; N, 3.08. Found: C, 66.23; H, 5.06; N, 3.10.

3.4. $RuCl_2(BDPX)[(S,S)$-DPEN] **4**

Yellow crystals were obtained (0.065 g, 76% yield) by reaction of $RuCl_2(BDPX)(PPh_3)$ (0.091 g, 0.1 mmol) and (*S*,*S*)-DPEN (0.023 g, 0.11 mmol). mp 196 °C (Decp.). ^{1}H NMR ($CDCl_3$): δ 2.6 (s, 4H; 2P-C*H*$_2$); 3.6 (m, 2H; N*H*H); 3.7 (m, 2H; NH*H*); 4.0 (m, 2H; 2C*H*); 6.4–8.1 (m, 34H; Ph*H*). ^{31}P NMR ($CDCl_3$): δ 39.7 (s). Anal. calc. for $C_{46}H_{44}N_2P_2Cl_2Ru$ (%): C, 64.34; H, 5.13; N, 3.26. Found: C, 64.88; H, 5.12; N, 3.12.

3.5. $RuCl_2(BISBI)[(S,S)$-DPEN] **5**

Orange crystals were obtained (0.066 g, 70% yield) by reaction of $RuCl_2(BISBI)(PPh_3)$ (0.098 g, 0.1 mmol) and (*S*,*S*)-DPEN (0.023 g, 0.11 mmol). mp 235 °C (Decp.). ^{1}H NMR ($CDCl_3$): δ 2.8 (s, 4H; 2P-C*H*$_2$); 3.6 (m, 2H; N*H*H); 3.7 (m, 2H; NH*H*); 4.0 (m, H; C*H*), 4.2 (m, H; C*H*); 6.4–7.6 (m, 38H; Ph*H*). ^{31}P NMR ($CDCl_3$): δ 45.0 (s). Anal. calc. for $C_{52}H_{48}N_2P_2Cl_2Ru$ (%): C, 66.81; H, 5.18; N, 3.00. Found: C, 66.44; H, 5.33; N, 3.17.



Scheme 2. Structure of complexes.

4. Results and discussion

4.1. Structures of the complexes **1**–**5**

All of the Ru complexes were stable to air in solid state. They were air sensitive in solution, and the solution would turn green or purple if it was exposed to air for a short time.

A singlet was observed in the ^{31}P{^{1}H} NMR spectra of all the complexes. It indicated the two phosphorus atoms were in the same chemical environment in complexes, and it was agreement with the *trans* arrangement of two Cl atoms and the *cis* arrangement of the two phosphorus atoms and two nitrogen atoms as showing in Scheme 2. The ratios of phosphines to diamine were also confirmed by the ^{1}H NMR spectra and elemental analyses.

The results of X-ray diffraction of complex **5** are listed in Tables 1 and 2, and Fig. 1. The structure is consistent with the structural analysis by NMR spectra and elemental anal-

Table 2
Selected bond lengths and angles of complex **5**

Bond	Length (Å) or angle (°)
Ru(1)–P(1)	2.3013(11)
Ru(1)–P(2)	2.2939(10)
Ru(1)–Cl(1)	2.4191(10)
Ru(1)–Cl(2)	2.4349(9)
Ru(1)–N(1)	2.193(3)
Ru(1)–N(2)	2.174(2)
Cl(1)–Ru(1)–Cl(2)	169.13(3)
P(1)–Ru(1)–P(2)	100.52(3)
N(1)–Ru(1)–N(2)	76.62(9)
N(1)–Ru(1)–P(1)	92.01(6)
N(2)–Ru(1)–P(1)	167.47(6)
N(1)–Ru(1)–P(2)	166.44(6)
N(2)–Ru(1)–P(2)	91.32(7)
N(1)–Ru(1)–Cl(1)	81.22(7)
N(2)–Ru(1)–Cl(1)	85.22(8)
P(1)–Ru(1)–Cl(1)	98.38(5)
P(2)–Ru(1)–Cl(1)	91.74(4)
N(1)–Ru(1)–Cl(2)	96.28(7)
N(2)–Ru(1)–Cl(2)	83.91(8)
P(1)–Ru(1)–Cl(2)	92.26(4)
P(2)–Ru(1)–Cl(2)	88.47(4)

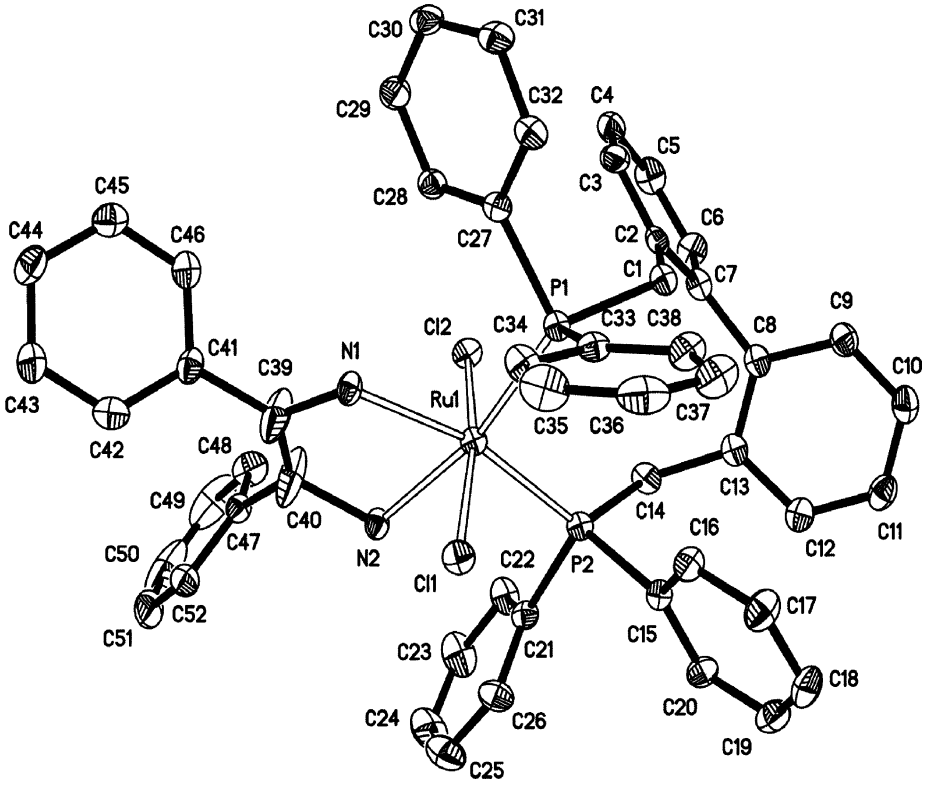


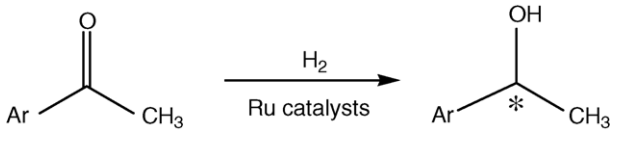
Fig. 1. The X-ray crystal structure of complex **5**.

ysis. It was a distorted octahedron and with two Cl atoms in *trans* position, just the same configuration as other analogous complexes reported [2]. The two phenyl rings of BISBI backbone are not in a same face and they show a similar chirality as Biphep (Biphep = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl) after two P atoms coordinate to ruthenium [29]. At room temperature, $^{31}P\{^{1}H\}$ NMR spectra of complex **5** show a broaden singlet which could result from the dissociation and coordination of BISBI and the formation of diastereomers in complex **5**. The big nine-membered chelating ring formed by the coordination of BISBI gives a bigger P–Ru–P angle (100.52°) in this complex than its analogous seven-membered chelating ring $RuCl_2$[(*R*)-tolbinap] [(*S*,*S*)-DPEN] (91.50°) [2]. As a result, the N–Ru–N bit angle (76.62°) is smaller than that in $RuCl_2$[(*R*)-tolbinap] [(*S*,*S*)-DPEN] (78.0°). The bond lengths of Ru(1)–P(1) 2.3013 Å and Ru(1)–P(2) 2.2939 Å are little longer than that of Ru(1)–P(1) 2.276(2) Å and Ru(1)–P(2) 2.296(2) Å, but Ru(1)–N(1) 2.193(3) Å and Ru(1)–N(2) 2.174(2) Å are close to Ru(1)–N(1) 2.141(5) Å Ru(1)–N(2) 2.189(6) Å in $RuCl_2$[(*R*)-tolbinap] [(*S*,*S*)-DPEN].

*4.2. Hydrogenation of aromatic ketones catalyzed by Ru complexes **1**–**5***

The catalytic activities of five ruthenium complexes in the asymmetric hydrogenation of various aromatic ketones were investigated (Scheme 3). As showed in Table 3, the electronic factors of the phosphine ligands have obvious influence on the catalytic activity in the hydrogenation of acetophenone. The activity of complex **2** decreased sharply when electron-withdrawing group $-CF_3$ was introduced into phenyl rings of triphenylphosphine (Table 3, entry 2). The complex **1** gave the highest conversion (Table 3, entry 1) among the five complexes owing to electron-donating group $-OCH_3$, which was introduced into phenyl ring of triphenylphosphine. For the hydrogenations of other aromatic ketones, complex **1** also showed much higher activities than that of complex **2** (Table 4, entry 2–6).

Besides the electronic factor, the changes of backbone of phosphine ligand also obviously affected the catalytic activities in the same experimental conditions (Table 3, entry 3–5). The bite angles of P–Ru–P in ruthenium complexes were **5** > **3** > **4**, the catalytic activities of the ruthenium complexes for the hydrogenation of acetophenone also decreased according to the above order. For example, the bite angle of P–Ru–P in complex **5** was the largest (100.52°), and thus its activity was the highest. These results were in agreement with the conclusion obtained by Xiao and co-workers [20].



Scheme 3. Hydrogenation reaction of ketone.

Table 3
Results of asymmetric hydrogenation of acetophenone (Ar = C_6H_6) by complexes **1**–**5**

Entry	Catalyst	Conv. (%)	P–Ru–P (°)	e.e.	Config.
1	$RuCl_2$(MOTPP)$_2$[(*S*,*S*)-DPEN] (**1**)	99 (>99)		66	*R*
2	$RuCl_2$(TFTPP)$_2$[(*S*,*S*)-DPEN] (**2**)	– (46)		68	*R*
3	$RuCl_2(PPh_3)_2$[(*S*,*S*)-DPEN] (**3**)	54 (>99)	98.10[a]	68	*R*
4	$RuCl_2$(BDPX)[(*S*,*S*)-DPEN] (**4**)	28 (>99)	95.27	65	*R*
5	$RuCl_2$(BISBI)[(*S*,*S*)-DPEN] (**5**)	92 (>99)	100.52	72	*R*

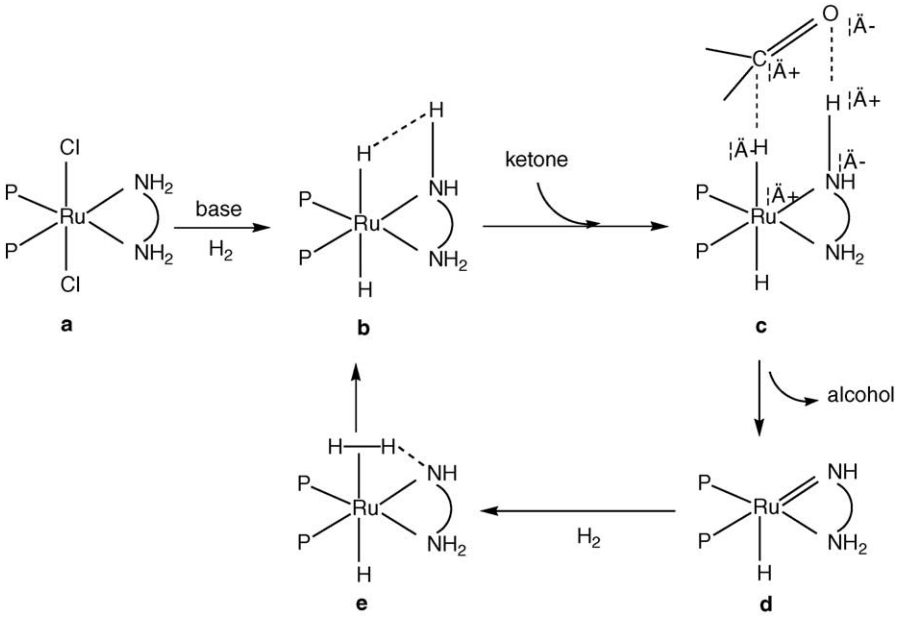
Reaction conditions: temperature = 30 °C, time = 2.0 h, *P* = 3.0 MPa, *i*-PrOH as solvent (6 mL), acetophenone concentration = 4.15 mol/L, S/C/KOH (molar ratio) = 5000:1:400.
In parentheses, acetophenone concentration = 0.83 mol/L, S/C/KOH (molar ratio) = 1000:1:100.
[a] Be not published crystal data in my research group.

Table 4
Results of asymmetric hydrogenation of aromatic ketones by complexes **1**–**5**

Ar	Conv.(%), e.e. (%)										Config.
	Complex **1**		Complex **2**		Complex **3**		Complex **4**		Complex **5**		
C_6H_5	>99	66	46	68	>99	68	>99	65	>99	72	*R*
o-FC_6H_4	>99	36	9	36	>99	40	>99	43	>99	41	*R*
o-ClC_6H_4	>99	60	52	59	>99	62	>99	48	>99	45	*R*
o-BrC_6H_4	>99	67	24	64	>99	66	>99	58	>99	54	*R*
p-$CF_3C_6H_4$	>99	56	93	59	>99	58	>99	45	>99	63	*R*
p-$OCH_3C_6H_4$	>99	68	96	69	>99	69	>99	65	>99	66	*R*

Reaction conditions: *T* = 30 °C, time = 2.0 h, *P* = 3.0 MPa, *i*-PrOH as solvent (6 mL), aromatic ketones concentration = 0.83 mol/L, S/C/KOH (molar ratio) = 1000:1:100.

According to the metal–ligand difunctional catalysis mechanism given by Noyori and Morris [1,6,8], the catalytic species could be the dihydride diamine and hydrido amido–amine complexes as showed in Scheme 4. The dihydride species **b** reacted directly with ketones to form alcohols and it could be regenerated by the reaction of the hydrido amido–amine complex **d** with hydrogen gas. The heterolytic splitting of a η^2-dihydrogen ligand, which was weakly coordinated to ruthenium, was the turnover limited step in this catalytic cycle [8]. The electron-withdrawing ligand like TFTPP would lead to the decrease of the electron density on the Ru center, so that the Ru=N bond in the hydrido amido–amine complex **d** would be strengthened, which was a disadvantage to regenerate the dihydrides. As a result, it gave the lowest conversion in the hydrogenation of acetophenone catalyzed by complex **2** (Table 1, entry 2). On the contrary, the electron-donating phosphine MOTPP had a promoting effect on the catalytic activity and complex **1** bearing MOTPP showed a higher activity than TFTPP and PPh_3 analogues (Table 3, entry 1, 3).



Scheme 4. .

Table 5
Results of asymmetric hydrogenation of acetophenone (Ar = C_6H_6) by complexes **1**, **4**, **5**

Entry	Catalyst	30 °C, e.e. (%)	20 °C, e.e. (%)	5 °C[a], e.e. (%)	Config.
1	$RuCl_2$(MOTPP)$_2$[(*S*,*S*)-DPEN] (**1**)	66	68	72	*R*
2	$RuCl_2$(BDPX)[(*S*,*S*)-DPEN] (**4**)	65	67	69	*R*
3	$RuCl_2$(BISBI)[(*S*,*S*)-DPEN] (**5**)	72	82	87	*R*

Reaction conditions: time = 2.0 h, *P* = 3.0 MPa, *i*-PrOH as solvent (6 mL), acetophenone concentration = 0.83 mol/L, S/C/KOH (molar ratio) = 1000:1:100.
[a] Time = 12 h.

According to reference [20], the phosphines with the small bite angle could lead to a more electron rich on ruthenium, which decreased the acidity of Ru–H_2 and suppressed the rate of H_2 heterolysis. These factors caused the fall of the catalytic activities of the complexes with the small bite angles of P–Ru–P. However, our results did not support the above conclusion, because the coordination of MOTPP increased the electron density on ruthenium and promoted the hydrogenation reaction. We prefer to think that the change of a bite angle or ligand backbone mainly results in a steric effect rather than electron effect.

It was interesting that the hydrogenations catalyzed by complexes bearing the different triarylphosphines showed nearly the same e.e. in the same conditions. It seemed that the e.e. value relied mainly on the structures of the substrates and was not remarkably influenced by the electron factor (Table 4, complexes **1**–**3**).

The use of an enantiopure ligand (L^*) in combination with achiral or *meso* ligands (L) in a catalyst M(L)L^* was a different approach to asymmetric catalysis because achiral or *meso* ligands were more easily prepared than enantiopure ligands and were inexpensive in general [18]. Here we used five achiral phosphines (L) and an enantiopure diamine *S*,*S*-DPEN (L^*) to prepare ruthenium complex catalysts. The studies on their catalytic performances in the asymmetric hydrogenation of acetophenone showed that an e.e. of 87% could be obtained by using $RuCl_2$(BISBI)[(*S*,*S*)-DPEN] (**5**) as catalyst at 5 °C (Table 5, entry 3). When BISBI coordinated to metal center, two diastereomers of $RuCl_2$(BISBI)[(*S*,*S*)-DPEN] (**5**) similar to the complex $RuCl_2$(Biphep)[(*S*,*S*)-DPEN] of Biphep or $RuCl_2$(Dm-biphep)[(*S*,*S*)-DPEN] of Dm-Biphep (Dm-biphep = 2,2′-[(3,5-dimethylphenyl)-phosphanyl]biphenyl) reported by Mikami et al. [29,30] could form. If the configuration of a diastereomer in ruthenium complex containing BISBI and *S*,*S*-DPEN was matching each other, the diastereomer would showed higher catalytic activity and enantioselectivity than another one according to the results reported by Noyori and Mikami et al. [29,30]. The reaction temperature would influence the equilibrium between two diastereomers, the decrease of temperature would be favourable for the stabilization of the structural matching isomer. Therefore, when the reaction temperature was decreased to 5 °C, the enantioselectivity was obviously improved and the e.e. value rose to 87%. The broadened peak at ^{31}P NMR spectrum demonstrated the above opinion. Compared with complexes **5**, the complexes **1** and **4** could not form diastereomers, so the e.e. values were not obviously improved when temperature was decreased (Table 5, entry 1, 2).

5. Conclusion

Five new complexes were synthesized and characterized. Their hydrogenation results indicated that a phosphine ligand which was of a large bite angle or an electron-donated group could improve the catalytic activity in the hydrogenation of carbonyl group. The electron factors of triarylphosphine had no remarkable effects on the e.e. value.

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