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New chiral cationic rhodium–aminophosphine complexes for asymmetric transfer hydrogenation of aromatic ketones

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Abstract

The new chiral ligands (*S*,*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]1,2-diiminocyclohexane, [(*S*,*S*)-**1**] and (*S*,*S*)-*N*,*N*′-bis[*o*-diphenylphosphino]benzyl-1,2-diaminocyclohexane, [(*S*,*S*)-**2**] have been prepared. The interaction of [(*S*,*S*)-**1**] and [(*S*,*S*)-**2**] with $[Rh(COD)Cl]_2$ afforded the corresponding cationic rhodium complexes [(*S*,*S*)-**3**][X] and [(*S*,*S*)-**4**][X] ($X = PF_6^-$, BF_4^- or ClO_4^-), respectively. [(*S*,*S*)-**1**], [(*S*,*S*)-**2**], [(*S*,*S*)-**3**][X] and [(*S*,*S*)-**4**][X] have been fully characterized by elemental analyses and spectroscopic methods. These chiral cationic rhodium complexes serve as catalytst precursors for the asymmetric transfer hydrogenation of acetophenone derivatives in 2-propanol and [(*S*,*S*)-**4**][PF_6] acts as an excellent catalyst in the reduction of *m*-chloroacetophenone, giving the corresponding optical alcohols in 99% yield and up to 94% ee. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The bidentate and polydentate phosphines are important ligands in coordination chemistry and homogeneous catalysis. Optically active phosphine ligands, such as DIOP, CHIRAPHOS and BINAP, play a crucial role in asymmetric catalysis [1]. Recently, optically active nitrogen compounds were proved to be efficient ligands in enantioselective catalysis [2–4] and some chiral Ir, Rh and Ru complexes bearing nitrogen donor atoms have been developed with great successes for asymmetric transfer hydrogenation [5–12]. The importance and application of chiral phosphine ligands and nitrogen ligands have been further extented by combining phosphorus centers and nitrogen donor atoms in PN [13], NPN [14], PNP [15,16] or PNNP type ligands [17–19]. In the past few years, we have been interested in the synthesis of well-designed PNNP type ligands possessing two 'soft' phosphorus atoms and two 'hard' nitrogen atoms as chelating reagents for preparation of mono- and bi-metallic center complexes [20–23]. We previously reported that *trans*-$RuCl_2$ complex with a chiral tetradentate aminophosphine ligand is an excellent catalyst precursor for asymmetric transfer reduction of aromatic ketone [24]. As an extension of the ongoing research program, we would like to describe the synthesis and characterization of some new cationic rhodium–aminophosphine complexes and their application in the asymmetric hydrogen transfer reduction of aromatic ketones in this paper.

2. Experimental

2.1. General

All experiments were carried out in a nitrogen atomsphere with Schlenk and syringe techniques. All solvents were dried and purified according to standard methods before use. IR spectra were recorded on a

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PE-Spectroy 2000 spectrophotometer. NMR spectra were recorded on a Varian Unity-500 spectrometer. ^{1}H-NMR chemical shifts are reported in ppm relative to TMS. ^{31}P spectra were referenced to 85% H_3PO_4 as an external standard. The element analyses were carried out on a Fisons EA 1110. All melting points were measured in sealed tubes and were not corrected.

2.2. Synthesis of (S,S)-cyclo$C_6P_2N_2$, [(S,S)-1]

A mixture of (*S*,*S*)-1,2-diaminocyclohexane (0.35 g, 3.0 mmol), *o*-(diphenylphosphino)benzaldehyde (1.74 g, 6.0 mmol) and anhydrous Na_2SO_4 (2.56 g, 18.0 mmol) in CH_2Cl_2 (20 ml) was stirred for 24 h. A pale-orange solution was obtained. The solution was filtered, and then concentrated under reduced pressure to ca. 5 ml. To the solution was added 20 ml of ethanol and the resulting solution was cooled to −20°C to give a yellow solid, filtered and dried in vacuo (1.78 g, 90% yield). m.p. 60 ~ 62°C. IR (KBr pellet, ν (cm^{-1})): 3049 m, 2928 s, 2857 s, 1636 s, 1433 s, 1087 w, 748 vs, 697 vs, 547 w, 503 s. ^{1}H-NMR ($CDCl_3$): δ 1.26 (m, 2H, CH_2), 1.38 (d, 2H, J = 7.8 Hz, CH_2), 1.45 (m, 2H, CH_2), 1.65 (d, 2H, J = 6.0 Hz, CH_2), 3.11 (m, 2H, CH), 6.79–7.74 (m, 28H, Ar), 8.69 (d, 2H, J = 4.0 Hz, Ar–CH=N). ^{31}P-NMR ($CDCl_3$): δ −12.98. Anal. Found: C, 79.10; H, 6.39; N, 4.23. $C_{44}H_{40}N_2P_2\cdot0.5C_2H_5OH$. Calc.: C, 79.30; H, 6.31; N, 4.11%.

2.3. Synthesis of (S,S)-cyclo$C_6P_2N_2H_4$, [(S,S)-2]

A solution of compound (*S*,*S*)-**1** (1.65 g, 2.5 mmol) and $NaBH_4$ (0.57 g, 15 mmol) in absolute ethanol (30 ml) was refluxed with stirring for 24 h. The solution was cooled to room temperature and H_2O (10 ml) was added to destroy excess $NaBH_4$. The mixture solution was extracted with CH_2Cl_2 (30 ml × 3). The combined extract was washed with 10% aqueous NH_4Cl (10 ml × 2), H_2O (10 ml × 2) and the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated to ca. 5 ml. Then 15 ml of ethanol was added and cooled to −20°C to give cream-white crystals (1.34 g, 80% yield). m.p. 54 ~ 56°C. IR (KBr pellet, ν (cm^{-1})): 3051 m, 2924 s, 2852 m, 1565 w, 1433 s, 1183 m, 1114 m, 746 vs, 696 vs, 544m, 502 m. ^{1}H-NMR ($CDCl_3$): δ 0.87 (m, 2H, CH_2),1.08 (t, 2H, CH_2), 1.58 (d, 2H, J = 6.4 Hz, CH_2), 1.87 (br, 2H, NH-), 1.98 (d, 2H, J = 12.8 Hz, CH_2), 2.11 (d, 2H, J = 8.5 Hz, CH), 3.82 (d, 2H, J = 13.6 Hz, ArCH_2), 4.00 (d, 2H, J = 13.6 Hz, ArCH_2–), 6.81–7.52 (m, 28H, Ar). ^{31}P-NMR: δ −15.21. Anal. Found: C, 78.39; H, 6.78; N, 4.27. $C_{44}H_{44}N_2P_2\cdot0.5C_2H_5OH$. Calc.: C, 78.83; H, 6.86; N, 4.23%.

2.4. Synthesis of [Rh(S,S)-cyclo$C_6P_2N_2$][PF_6], [(S,S)-3][PF_6]

To a mixture of ligand [(*S*,*S*)-**1**] (0.20 g, 0.30 mmol) and $[Rh(COD)Cl]_2$ (0.074 g, 0.15 mmol) were added benzene (6 ml) and methanol (6 ml). The mixture was stirred at room temperature for 12 h. After removal of solvent, the residue was dissolved in a minimum of methanol and precipitated by addition of a solution of NH_4PF_6 (0.082 g, 0.5 mmol) in H_2O (3 ml). The precipitate was collected and washed successively with H_2O (3 ml × 3) and diethyl ether (3 ml), then dried in vacuo to afford [(*S*,*S*)-**3**][PF_6] as a yellow solid (0.20 g, 74% yield). m.p. 245°C (dec.). IR (KBr pellet, ν (cm^{-1})): 3414 m, 3055 m, 2931 m, 2857 w, 1630 m, 1555 w, 1435 s, 1177 m, 1099 s, 750 m, 696 vs, 570 w, 536 vs. ^{1}H-NMR ($CDCl_3$): δ 1.24 (m, 2H, CH_2), 1.36 (m, 2H, J = 13.5 Hz, CH_2), 1.46 (m, 2H, CH_2),1.66 (d, 2H, J = 8.0 Hz, CH_2), 3.12 (m, 2H, CH), 6.80–7.75 (m, 28H, Ar), 8.69 (d, 2H, J = 4.0 Hz, ArCH=N). ^{31}P-NMR: δ 39.60. Anal. Found: C, 56.85; H, 4.85; N, 2.87. $C_{44}H_{40}N_2F_6P_3Rh\cdot H_2O$. Calc.: C, 57.15; H, 4.59; N, 3.03%.

2.5. Synthesis of [Rh(S,S)-cyclo$C_6P_2N_2H_4$][PF_6], [(S,S)-4][PF_6]

In a similar fashion as described for [(*S*,*S*)-**3**][PF_6], using ligand [(*S*,*S*)-**2**] instead of [(*S*,*S*)-**1**], [(*S*,*S*)-**4**][PF_6] as a yellow solid was obtained (0.19 g, 70% yield). m.p. 238°C (dec.). IR (KBr pellet, ν (cm^{-1})): 3414 m, 3056 m, 2857 w, 1591 w, 1482 w, 1436 s, 1167 m, 1098 s, 750 m, 723 m, 697 vs, 541 vs, 464 w. ^{1}H-NMR ($CDCl_3$): δ 1.21 (m, 4H, CH_2), 1.77 (d, 2H, J = 28.5 Hz, CH_2), 2.17 (br, 2H, NH), 3.19 (s, 2H, CH_2), 4.01 (d, 2H, J = 10 Hz, CH), 4.36 (m, 2H, ArCH_2), 4.86 (m, 2H, ArCH_2), 6.52–7.82 (m, 28H, Ar). ^{31}P-NMR ($CDCl_3$): δ 33.03. Anal. Found: C, 55.83; H, 5.11; N, 2.96. $C_{44}H_{44}N_2F_6P_3Rh\cdot2H_2O$. Calc.: C, 55.84; H, 5.28; N, 2.91%.

2.6. Synthesis of [Rh(S,S)-cyclo$C_6P_2N_2H_4$]BF_4, [(S,S)-4][BF_4]

In an analogous manner and using $NaBF_4$ instead of NH_4PF_4, [(*S*,*S*)-**4**][BF_4] as a yellow solid was isolated (0.20 g, 77% yield). m.p. 194°C (dec.). IR (KBr pellet, ν (cm^{-1})): 3405 m, 3232 m, 2932 m, 2862 w, 1589 w, 1436 s, 1170 m, 1095 vs, 751 m, 697 s, 539 s, 466 w. ^{1}H-NMR ($CDCl_3$): δ 0.87 (m, 2H, CH_2), 1.08 (m, 2H, CH_2), 1.59 (d, 2H, J = 7.5 Hz, CH_2), 1.98 (m, 4H, CH_2), 2.13 (m, 2H, NH), 3.83 (d, 2H, J = 13.5 Hz, ArCH_2), 4.00 (d, 2H, J = 13.5 Hz, ArCH_2), 6.82–7.52 (m, 28H, ArCH_2). ^{31}P-NMR ($CDCl_3$): δ 32.56. Anal. Found: C, 59.33; H, 5.74; N, 3.04. $C_{44}H_{44}N_2BF_4P_2Rh$. Calc.: C, 59.47; H, 5.46; N, 3.15%.

2.7. Synthesis of [Rh(R,R)-cycloC$_6$P$_2$N$_2$H$_4$][ClO$_4$], [(R,R)-4][ClO$_4$]

[(*R*,*R*)-**4**][ClO$_4$] was prepared by means of the above similar procedures. The product was contaminated somewhat with $NaClO_4$ and was further purified by washing with H_2O and extracting with CH_2Cl_2. The solvent was removed in vacuo. The resulting residue was recrystallized from CH_2Cl_2/hexane to afford an analytical sample (0.18 g, 70% yield). m.p. 116°C (dec.). IR (KBr pellet, ν (cm^{-1})): 4324 m, 3056 m, 2933 m, 2858 w, 1590 w, 1436 m, 1159 m, 1094 vs, 751m, 697 s, 629 w, 524 s, 467 w. ^{1}H-NMR ($CDCl_3$): δ 0.89 (m, 2H, CH_2), 1.10 (m, 2H, CH_2), 1.60 (d, 2H, $J = 8.5$ Hz, CH_2), 2.02 (m, 2H, NH), 2.15 (d, 2H, $J = 8.5$ Hz, CH), 3.83 (d, 2H, $J = 13.5$ Hz, CH_2), 3.89(m, 2H, ArCH_2), 4.00 (m, 2H, ArCH_2), 6.82–7.62 (m, 28H, Ar). ^{31}P-NMR ($CDCl_3$): δ 32.81. Anal. Found: C, 63.66; H, 5.72; N, 2.75. $C_{44}H_{44}N_2O_4ClP_2Rh \cdot C_6H_{14}$ Calc.: C, 63.12; H, 6.16; N, 2.95%.

2.8. Typical procedure for asymmetric transfer hydrogenation of ketones

The catalyst precursor (0.01 mmol) was added to a Schlenk tube and 2-propanol (20 ml), *iso*-PrOK/*iso*-PrOH solution (0.1 M, 0.1 ml) were introduced under nitrogen. The mixture was stirred for 10 min, acetophenone was added and the solution was stirred for the required reaction time. At the end of the experiment, the reaction products were analyzed by capillary gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization of (S,S)-1 and (S,S)-2

(*S*,*S*)-**1** was prepared by Schiff base condensation of *o*-(diphenyl-diphosphino)benzylaldehyde (2 equivalents) and (*S*,*S*)-1,2-diamino-cyclohexane in dicholomethane with anhydrous Na_2SO_4 as dehydrating agent. A pale-yellow solid (*S*,*S*)-*N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]-cyclohexane-1,2-diamine[(*S*,*S*)-**1**] was obtained in 87–90% yield (Scheme 1). The IR spectrum of (*S*,*S*)-**1** exhibits a strong C=N stretch at 1636 cm^{-1}. The ^{1}H-NMR spectrum exhibits a doublet ($J = 4.5$ Hz) at δ 8.69 for the imino protons. The ^{31}P-NMR spectrum presents a singlet at δ −12.98. These spectroscopic data and results of elemental analysis indicate that (*S*,*S*)-**1** contains diimino and the two diphosphino groups are equivalent.

Reduction of the diiminodiphosphine (*S*,*S*)-**1** with excess $NaBH_4$ was carried out in refluxing ethanol to afford the corresponding (*S*,*S*)-*N*,*N*′-bis[*o*-(diphenyl-diphosphino)benzyl]cyclohexane-1,2-diamine (*S*,*S*)-**2** in 75–81% yield. In the ^{1}H-NMR spectrum the presence of (*S*,*S*)-**2** at δ 1.87 for the –NH– protons and the disappearance of infrared band at 1636 cm^{-1} indicate that the two imino groups were reduced to the corresponding diamino groups. The ^{31}P-NMR spectra present a singlet at δ −15.21 in accord with two equivalent phosphino groups.

In an analogous procedure the ligands (*R*,*R*)-**1** or (*R*,*R*)-**2** were also prepared.

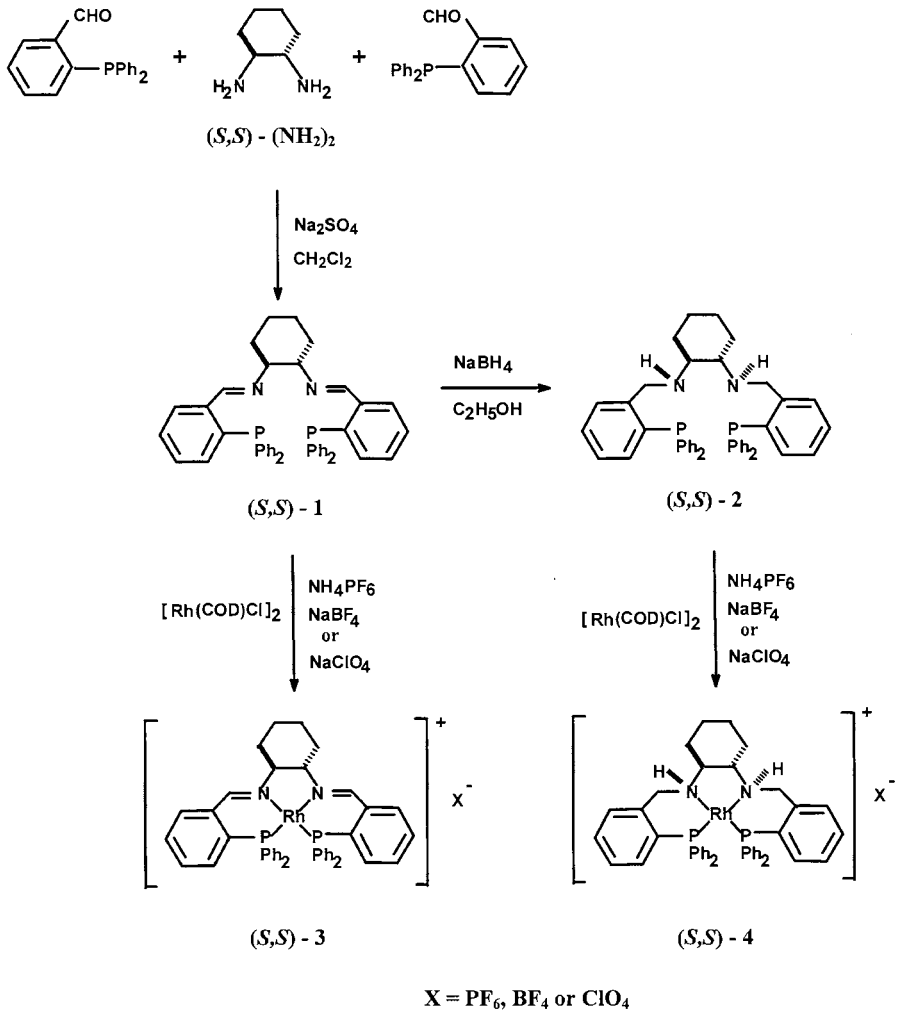
3.2. Synthesis and characterization of cationic rhodium–aminophosphine complexes

Treatment of [Rh(COD)Cl]$_2$ with (*S*,*S*)-cycloC$_6$P$_2$N$_2$ [(*S*,*S*)-**1**] in an 1:1 mixture of methanol–benzene and then precipitation by the addition of a solution of NH_4PF_6 in water afforded a yellow solid of cationic rhodium complex (*S*,*S*)-**3** in 74% yield. The ^{31}P-NMR spectrum of (*S*,*S*)-**3** exhibited a singlet at 39.60 indicating that the two phosphino groups of the (*S*,*S*)-**1** ligand were coordinated and equivalent (Scheme 2). Complexes [(*S*,*S*)-**4**][PF$_6$], [(*S*,*S*)-**4**][BF$_4$] and [(*S*,*S*)-**4**][ClO$_4$] were also prepared by a similar procedure and by the addition of a solution of NH_4PF_4, $NaBF_4$ or $NaClO_4$, respectively (Scheme 1). While using (*R*,*R*)-**1** or (*R*,*R*)-**2** instead of (*S*,*S*)-**1**, the corresponding complexes (*R*,*R*)-**3** and (*R*,*R*)-**4** were also isolated. All these complexes have been fully characterized by elemental analyses and IR and NMR spectroscopic methods.

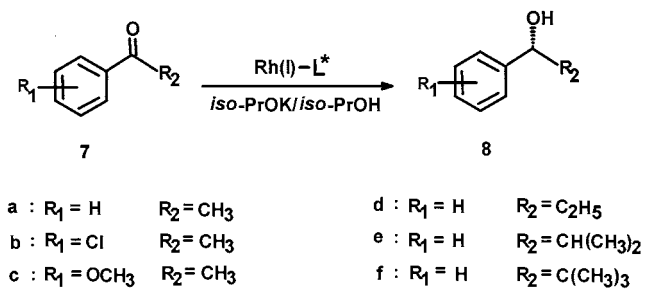
3.3. Asymmetric transfer hydrogenation of aromatic ketones with cationic rhodium(I) complexes as catalysts

In the studies of asymmetric transfer hydrogenation of aromatic ketones, the 2-propanol/potassium 2-propoxide system has been used as a source of hydrogen. New cationic rhodium(I) complexes as catalyst precursors for the reduction of acetophenone have been examined (Scheme 2) and typical results are summarized in Table 1.

A mixture system from [Rh(COD)Cl]$_2$ and ligand (*R*,*R*)-**2** as catalyst precursor only gave low conversion and enantioselectivity (Table 1, Run 1). When cationic rhodium(I) complex with diiminodiphosphine ligand (*R*,*R*)-**3** was used, the activity and ee were still low (Table 1, Run 2). However, when cationic rhodium(I) complexes containing diaminodiphosphine ligands were employed as catalysts, high conversion and ee were obtained (Table 1, Runs 3–11). These results are similar to that of earlier studies [24–26], indicating that the NH functions in the ligands are responsible for the high activity and the NH linkage possibly can stabilize a catalytic transition state [11,27]. The cationic rhodium(I) complex [(*S*,*S*)-**4**][PF$_6$] has been proved to be a



Scheme 1.



Scheme 2.

good catalyst, giving (*R*)-1-phenylethanol in 97% yield and 91% ee after reaction for 7 h at 82°C (Table 1, Run 3). Although the yields gradually decreased on increasing the mole ratios of [acetophenone]/[Rh] from 100:1 to 400:1, the enantioselectivity was still high (Table 1, Runs 3–6). Comparing the cationic rhodium(I) complexes with various anions PF_6^-, BF_4^- and ClO_4^- (Table 1, Runs 4, 9 and 10), [(*S*,*S*)-**4**][PF_6] gave better yield and ee, but [(*S*,*S*)-**4**][BF_4] exhibited very high reactivity with some loss of the enantiometric purity of the product. The addition of ligand (*R*,*R*)-**2** decreased the reaction rate, but the highest enantioselectivity (96%) was obtained (Table 1, Runs 8 and 11).

With the cationic rhodium(I) complex [(*R*,*R*)-**4**][PF_6], a variety of alkyl arylketones were transformed to the corresponding secondary alcohols (Table 2). The reactivity and enantioselectivity were very dependent on the position of the ring substituent and the bulkiness of the alkyl group. The introduction of both an electron-withdrawing group such as chloro and an electron-releasing group such as methoxyl to the *meta* position accelerated the reaction with a high enantioselectivity (Table 2, Runs 3 and 5), while the chloro or methoxyl group to the *para* position tended to lower the rate and the stereoselectivity (Table 2, Runs 4 and 6). The reaction rate was remarkably decreased by increasing the bulkiness of the alkyl group (Table 2, Runs 7–9), but the enantioselectivity was not significantly influenced.

Table 1
Asymmetric transfer hydrogenation of acetophenone (**7a**) catalyzed by chiral Rh(I) complexes [a]

Run	Catalyst precursor	Time (h)	Alcohol		
			Yield (%) [b]	ee (%) [c]	Configuration [d]
1	$[Rh(COD)Cl]_2$/(*R*,*R*)-**2** [h]	9	56	36	*S*
2	[(*R*,*R*)-**3**][PF_6]	7	40	40	*S*
3	[(*S*,*S*)-**4**][PF_6]	7	97	91	*R*
4	[(*S*,*S*)-**4**][PF_6] [e]	12	86	86	*R*
5	[(*S*,*S*)-**4**][PF_6] [f]	16	81	89	*R*
6	[(*S*,*S*)-**4**][PF_6] [g]	24	85	89	*R*
7	[(*R*,*R*)-**4**][PF_6]	9	86	89	*S*
8	[(*R*,*R*)-**4**][PF_6]/(*R*,*R*)-**2** [h]	24	58	96	*S*
9	[(*S*,*S*)-**4**][BF_4]	7	98	80	*R*
10	[(*R*,*R*)-**4**][ClO_4]	9	87	86	*S*
11	[(*R*,*R*)-**4**][ClO_4]/(*R*,*R*)-**2** [h]	24	73	92	*S*

[a] The reaction was carried out at refluxing temperature (82°C) using catalyst (0.01 mmol), 2-propanol (20 ml) and *iso*-PrOK/*iso*-PrOH solution (0.1 M, 0.1 ml). [Acetophenone]:[Rh(I)]:[*iso*-PrOK] = 100:1:1 in mole ratio, unless otherwise stated.
[b] Yield was determined by GLC.
[c] Determined by capillary GLC analysis using a Chiral Chrompack CP-cyclodextrin-β-236-M-19 column.
[d] Determined by comparison of the retention times of the enantiomers on the GLC traces with literature values.
[e] [acetophenone]:[Rh] = 200:1 in mole ratio.
[f] [acetophenone]:[Rh] = 300:1 in mole ratio.
[g] [acetophenone]:[Rh] = 400:1 in mole ratio.
[h] [Rh]:[(*R*,*R*)-**2**] = 1:1 in mole ratio.

Table 2
Asymmetric transfer hydrogenation of alkyl aryl ketones catalyzed by [(*R*,*R*)-**4**][PF_6] [a]

Run	Ketone	Time (h)	Alcohol		
			Yield (%) [b]	ee (%) [c]	Configuration [d]
1	**7a**	9	86	89	*S*
2	**7a** [e]	9	93	89	*S*
3	*m*-**7b**	22	99	94	*S*
4	*p*-**7b**	22	68	73	*S*
5	*m*-**7c**	22	97	90	*S*
6	*p*-**7c**	22	49	71	*S*
7	**7d**	22	91	80	*S*
8	**7e**	22	38	78	*S*
9	**7f**	22	13	76	*S*

[a] The reaction was carried out in the presence of [Rh(*R*,*R*)-cyclo$C_6P_2N_2H_4$][PF_6] (0.01 mmol) using a 0.05 M solution of ketone (1.0 mmol) in 2-propanol (20 ml) at 82°C; [ketone]:[Rh]:[*iso*-PrOK] = 100:1:1.
[b] Yield was determined by GLC analysis.
[c] Determined by capillary GLC analysis using a chiral CP-cyclodextrin-β-236-M-19 column.
[d] Determined by comparison of the retention times of the enantiomers on the GLC traces with literature values.
[e] The reaction was carried out in 2-propanol (18 ml) + THF (2 ml).

4. Conclusions

In summary, we have synthesized the new cationic rhodium(I) complexes with chiral diimino- or diaminodiphosphine tetradentate ligands and investigated their use in asymmetric transfer hydrogenation of ketone. The asymmetric catalysis attains a high efficiency using rhodium(I) complexes with diaminodiphosphine tetradentate ligands. The high catalytic activity is contrasted to the low reactivity of a structurally similar diiminodiphosphine-based complex. These results suggest that the NH moiety in the ligand is responsible for the high reactivity and enantioselectivity. To our knowledge, these are excellent enantioselective systems for the asymmetric transfer hydrogenation of ketone catalyzed by chiral rhodium complexes. In order to reveal the exact reaction mechanism, isolation and characterization of the catalytic active species is under further investigation.

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