The Use of Phosphite-Type Ligands in the Ir-Catalyzed Asymmetric Hydrogenation of Heterocyclic Compounds

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ABSTRACT A series of chiral phosphite-type ligands was tested in asymmetric Ir-catalyzed hydrogenation of quinolines and 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j*,*k*)carbazole. Hydrogenation of quinaldine hydrochloride provided superior enantioselectivity up to 65% *ee* compared to quinaldine free base. The ligands were tested for the first time in the asymmetric Ir-Ircatalyzed hydrogenation of 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j*,*k*)carbazole yielding the antidepressant drug, pirlindole. *Chirality 26:56–60, 2013.* © 2013 Wiley Periodicals, Inc.

KEY WORDS: asymmetric hydrogenation; phosphites; quinaldine hydrochloride; pirlindole

INTRODUCTION

Synthesis of enantioenriched heterocyclic compounds has attracted increasing interest due to its significance for preparation of a variety of biologically active compounds in pharmaceutical, agrochemical, and the fine chemical industries.[1] However, use of the traditional achiral direct cyclization reactions combined with diastereomeric resolution strategies is not efficient for preparation of these compounds in enantiomerically pure form.[2] Direct catalytic asymmetric hydrogenation of readily available heteroaromatic precursors can constitute the most convenient route to enantiomerically pure chiral heterocyclic compounds.[3] However, in comparison with asymmetric hydrogenation of unsaturated olefins, ketones, and imines, enantioselective hydrogenation of heterocyclic compounds remains a challenging task.[4,5] There are several reasons why heterocyclic compounds are difficult substrates for the hydrogenation: first, the high stability of these compounds requires harsh conditions to destroy their aromaticity; second, the hydrogenated product contains nitrogen atoms and may deactivate the chiral catalysts due to competitive coordination; third, the lack of secondary coordinating group in simple aromatic precursors may be responsible for their insufficient involvement into coordination needed for achieving high activity and/or enantioselectivity.[3,6] Several promising attempts in the metallocomplex asymmetric hydrogenation of heterocyclic compounds using expensive biphosphine ligands have been reported, providing acceptable results in terms of enantioselectivity and activity of catalysts.[3,7–11] Besides chiral bisphosphine-type ligands, other types of diphosphorus ligands including phosphine-phosphinites, phosphine-phosphites, diphosphinites, and diphosphonites have also been found to work well in iridium-catalyzed asymmetric hydrogenation of heterocyclic compounds.[12–16] Recently, Feringa and co-workers[17] employed the less expensive monodentate BINOL-derived phosphoramidite (*S*)-PipPhos ligand to the iridium-catalyzed enantioselective hydrogenation of quinolines. A very good enantioselectivity was obtained using the catalytic system that combined both piperidine hydrochloride and tri-*ortho*-tolylphosphine. The $[Ir(COD)Cl]_2$/(*S*)-PipPhos catalyst was tested in the enantioselective hydrogenation of 2- and 2,6-substituted quinoxalines. In the presence of piperidine hydrochloride as additive, full conversions and very good enantioselectivities have been obtained.[18] A series of spirophosphoramidite ligands were used in the Ir-catalyzed asymmetric hydrogenation of 1-alkyl 3,4-dihydroisoquinolines.[19] Excellent enantioselectivities (85 – 99% *ee*) were obtained using KI as the additive. Here we report application of phosphite-type ligands in the Ir-catalyzed asymmetric hydrogenation of quinaldine, 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j*,*k*) carbazole and their hydrochlorides using different Ir-precursors, solvents, and additives.

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MATERIALS AND METHODS

Ligands **L1–L4**, $[Ir(COD)Cl]_2$, $[Ir(COD)_2]$BARF (BARF – {tetrakis [3,5-bis(trifluoromethyl)phenyl]borate} and 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j*,*k*)carbazole were prepared as published.[20–26] Hydrochlorides **1a, 3a-c**, and **5a** were prepared analogously to the known procedure.[27]

Hydrogenation Procedure for Substrates 1, 1a, and 3a-c

The hydrogenation experiments were carried out in a 10-mL stainless-steel high-pressure reactor. The reactor was charged with $[Ir(COD)Cl]_2$ (2 mg, 0.003 mmol) or $[Ir(COD)_2]$BARF (7 mg, 0.006 mmol), ligand (0.006 mmol or 0.012 mmol), and CH_2Cl_2 (0.4 mL). After the mixture was stirred at room temperature for 5 min, in several cases (see Tables) an additive (0.06 mmol) was placed in the reactor and the solution was stirred additionally for 10 min, before removing the solvent in vacuo. Substrates **1** or **1a** (0.6 mmol) and the corresponding solvent (2 mL) or solvent mixture (V/V = 1/1) were added to the catalyst and the reactor was pressurized with hydrogen (55 atm). Hydrogenation was performed at 20 or 50 °C for the indicated period of time. After stirring, the vessel was depressurized. In the case of substrate **1** the catalyst was removed via a short silica gel column. The filtrate was concentrated in vacuo. In the case of substrates **1a** and **3a-c** the reaction mixture was fully evaporated, toluene (3 mL) and 30% aqueous solution of NaOH (3 mL) were added and the mixture was stirred for 1 h at room temperature. The phases were separated. The organic phase was dried with Na_2SO_4 and concentrated in vacuo to afford the target product. The conversion of **1**

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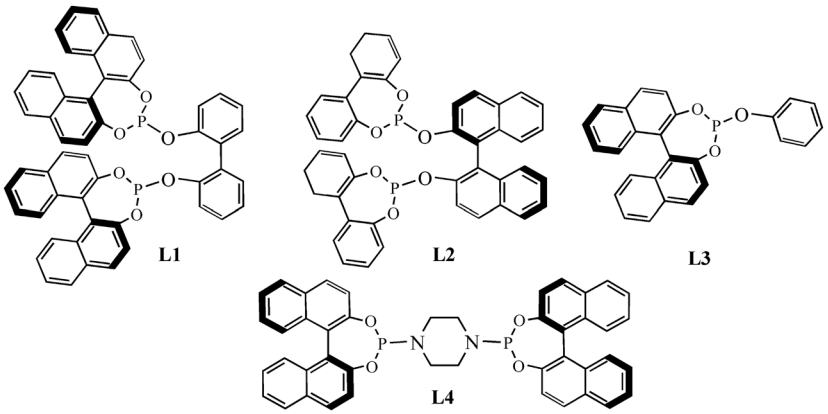


Scheme 1. Phosphite-type ligands.

and **1a** was determined according to integration of the corresponding peaks in ^{1}H NMR. Enantioselectivity of hydrogenation reactions was determined by chiral high-performance liquid chromatography (HPLC) according to literature procedures.[8,28]

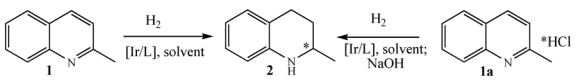
Hydrogenation Procedure of Substrates 5 and 5a

Hydrogenation of the substrates **5** and **5a** was performed analogously to **1** and **1a** using 2% mol of the corresponding catalyst. The conversion of **5** and **5a** was determined according to ^{1}H nuclear magnetic resonance (NMR). Enantiomeric excess (*ee*) of pirlindole **6** was determined using a Chiralcel OD-H column (0.46 × 25 cm); eluent: isocratic, hexane/i-PrOH/diethylamine – 95/5/0.1; flow rate: 0.9 mL/min; temperature: 25 °C; UV detection: 260 nm. Substrate **5** eluted at 10.8 min; (+)-**6** enantiomer at 14.5 min and (–)-**6** enantiomer at 16 min.

RESULTS AND DISCUSSION

Readily available chiral phosphite-type ligands **L1–L4** (Scheme 1), all prepared from (*S*)-BINOL, were first screened in the asymmetric hydrogenation of quinaldine **1** (Scheme 2) as the model compound.

Hydrogenation experiments were performed in CH_2Cl_2 at 55 atm of hydrogen pressure and 20 °C using catalyst prepared in situ from 0.5 mol% of $[Ir(COD)Cl]_2$ and



Scheme 2. Asymmetric hydrogenation of quinaldine and its hydrochloride.

corresponding chiral ligand. After 20 hours full conversion was obtained only with monodentate ligand **L3** (Table 1, entries 1–4). Moreover, the asymmetric hydrogenation of **1** resulted in very low *ee* in all cases. Considering the remarkable impact of the additive on catalytic activity and enantioselectivity in the asymmetric hydrogenation of heterocyclic compounds,[3] we then examined the additive effect. Addition of iodine (10 mol%) had a positive effect on the enantioselectivity (Table 1, entries 5–8). Remarkably, product **2** was obtained in the opposite absolute configuration in all these cases, probably because of oxidation of Ir(I) catalysts to Ir(III) species, which changes the hydrogenation pathway.[29] Recently, the superiority of a Brønsted acid or the corresponding salt as an additive has been demonstrated in asymmetric hydrogenation.[17,18] The addition of 10 mol% piperidine hydrochloride increased the *ee* in the case of **L1**; however, the reaction was slowed down (Table 1, see entries 1, 5, and 9). The ligands **L2–L4** showed low conversion and enantioselectivity (Table 1, entries 10–12). We also tested hydrogenation of **1** using $[Ir(COD)_2]$BARF/**L1** as the catalyst with addition of 10 mol% piperidine hydrochloride, but again low conversion and *ee* were obtained (Table 1, entry 13).

Recently, a novel observation for the Ir-catalyzed hydrogenation of heterocyclic compounds using phosphine ligands was described. It have been found that the use of prochiral 3,4-dihydroisoquinoline and isoquinoline hydrochlorides as the substrates produce increased enantioselectivity

TABLE 1. Asymmetric Ir-catalyzed hydrogenation of quinaldine (P H_2 = 55 atm, 20 h)

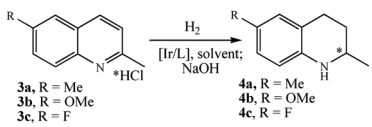
Entry	Catalyst	Solvent	Additive	T, °C	Conversion (%)	ee (%)
1	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2	—	20	38	11 (*S*)
2	$[Ir(COD)Cl]_2$/2**L2**	CH_2Cl_2	—	20	18	8 (*S*)
3	$[Ir(COD)Cl]_2$/4**L3**	CH_2Cl_2	—	20	100	0
4	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2	—	20	56	2 (*S*)
5	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2	I_2	20	85	35 (*R*)
6	$[Ir(COD)Cl]_2$/2**L2**	CH_2Cl_2	I_2	20	68	15 (*R*)
7	$[Ir(COD)Cl]_2$/4**L3**	CH_2Cl_2	I_2	20	54	4 (*R*)
8	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2	I_2	20	100	20 (*R*)
9	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2	$C_5H_{10}N$*HCl	20	15	**39** (*S*)
10	$[Ir(COD)Cl]_2$/2**L2**	CH_2Cl_2	$C_5H_{10}N$*HCl	20	10	27 (*S*)
11	$[Ir(COD)Cl]_2$/4**L3**	CH_2Cl_2	$C_5H_{10}N$*HCl	20	42	0
12	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2	$C_5H_{10}N$*HCl	20	1	—
13	$[Ir(COD)]_2$BARF/**L1**	CH_2Cl_2	$C_5H_{10}N$*HCl	20	18	10 (*S*)

TABLE 2. Asymmetric Ir-catalyzed hydrogenation of quinaldine hydrochloride 1a (P H_2 = 55 atm)

Entry	Catalyst	Solvent	T, °C	t, h	Conversion (%)	ee, (%)
1	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2	20	20	0	-
2	$[Ir(COD)Cl]_2$/2**L1**	MeOH	20	20	18	5 (*S*)
3	$[Ir(COD)Cl]_2$/2**L1**	EtOH	20	20	22	12 (*S*)
4	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2/EtOH	20	20	40	16 (*S*)
5	$[Ir(COD)Cl]_2$/2**L1**	CH_2Cl_2/EtOH	50	6	53	22 (*S*)
6	$[Ir(COD)Cl]_2$/2**L2**	CH_2Cl_2/EtOH	50	6	42	31 (*S*)
7	$[Ir(COD)Cl]_2$/4**L3**	CH_2Cl_2/EtOH	50	6	60	60 (*S*)
8	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2/EtOH	50	6	75	62 (*S*)
9	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2/MeOH	50	6	46	41 (*S*)
10	$[Ir(COD)Cl]_2$/2**L4**	CH_2Cl_2/*i*PrOH	50	6	44	30 (*S*)
11	$[Ir(COD)_2]$BARF/2**L3**	CH_2Cl_2/EtOH	50	6	72	**65** (*S*)
12	$[Ir(COD)_2]$BARF/**L4**	CH_2Cl_2/EtOH	50	6	86	50 (*S*)
13	$[Ir(COD)_2]$BARF/2**L3**	CH_2Cl_2/EtOH	50	12	100	64 (*S*)

compared to a 3,4-dihydroisoquinolines and isoquinolines as a free base.[27,30] We chose to run a set of experiments using quinaldine hydrochloride **1a** (Scheme 2) as the substrate. Using the catalyst prepared in situ from 0.5 mol% of $[Ir(COD)Cl]_2$ and **L1** in CH_2Cl_2 showed no conversion (Table 2, entry 1). In protic solvents such as MeOH and EtOH better conversions in 20 h were obtained, but low (5–12% *ee*) enantiomeric excess of the product **2** was observed (Table 2, entries 2,3). A significant increase in the reaction rate was obtained when the reaction was performed in the mixture of CH_2Cl_2/EtOH (Table 2, entry 4). To evaluate the effect of temperature and to increase the reaction rate the temperature was raised from 20 to 50 °C. In that case, 53% conversion was reached in 6 h and superior enantioselectivity was observed (Table 2, entry 5). Following these exploratory experiments, the improved protocol was applied to ligands **L2–L4** (Table 2, entries 6–8). With the use of ligand **L2** moderate conversion and 31% *ee* was obtained (Table 2, entry 6). Furthermore, monodentate phosphite ligand **L3** and diamidophosphite **L4** demonstrated a very good conversion in 6 h while providing 60% and 62% *ee*, respectively (Table 2, entries 7 and 8). Using diamidophosphite **L4**, which gave the best result, we also tested MeOH and *i*PrOH as cosolvents yet lower *ee*'s and conversion were obtained (Table 2, entries 9 and 10). We also checked the hydrogenation of hydrochloride **1a** using ligands **L3**, **L4**, and $[Ir(COD)_2]$BARF as a cationic iridium precursor. $[Ir(COD)_2]$BARF was found to give a better conversion, compared to $[Ir(COD)Cl]_2$, and very good enantioselectivities were observed (Table 2, entries 7, 8 and 11, 12). With increasing reaction time from 6 to 12 h a complete conversion and 64% *ee* were obtained using $[Ir(COD)_2]$BARF/2 **L3** as the catalyst (Table 2, entry 13).

The asymmetric hydrogenation of other quinaldine hydrochloride derivatives (Scheme 3) using $[Ir(COD)_2]$BARF/2 **L3** catalyst was also carried out in the CH_2Cl_2/EtOH



Scheme 3. Asymmetric hydrogenation of quinaldine hydrochloride derivatives with ligand **L3**.

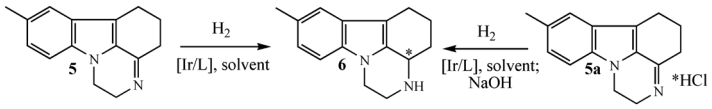
mixture and the results are summarized in Table 3. Good enantioselectivities and conversion were achieved in the hydrogenation of hydrochlorides **3 a–c**. It should be noted that the hydrochloride **3c** with an electron-withdrawing group gave lower enantioselectivity compared to substrates **1a** and **3a,b**.

The above-mentioned approach was further extended to asymmetric Ir-catalyzed hydrogenation of 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j,k*)carbazole **5** (Scheme 4). The reaction constitutes a new one-step approach to enantiomerically enriched form of the antidepressant drug pirlindole (8-methyl-2,3,3a,4,5,6-hexahydro-Hl-pyrazino[3,2,1-j,k]carbazole (**6**)).[2,31]

Ir-catalyzed asymmetric hydrogenation of carbazole **5** in the presence of ligands **L2** and **L4** showed complete conversion in 20 h using $[Ir(COD)Cl]_2$ (1 mol%) as a precatalyst, while phosphites **L1** and **L3** were less effective (Table 4, entries 1–4). In all these cases enantioselectivities were low. When $[Ir(COD)_2]$BARF was used as the metal precursor, complete conversion in 20 h was obtained in the case of **L3** as well as **L4** (Table 4, entries 5–8). Interestingly, monodentate phosphite **L3** showed a good *ee*. The ligand **L3** was also tested in the hydrogenation of hydrochloride **5a** (Scheme 4). Good conversion was observed in both the neat EtOH and CH_2Cl_2/EtOH mixture; in CH_2Cl_2 substrate **5a** was found to have limited solubility (Table 4, entries 9–11). It should be noted that the phosphite **L3** gave lower enantioselectivity in the hydrogenation of **5a**, compared to that obtained with the free base **5**. The use of

TABLE 3. Asymmetric Ir-catalyzed hydrogenation of 3a-c (P H_2 = 55 atm)

Entry	Substrate	Solvent	T, °C	t, h	Conversion (%)	ee (%)
1	**3a**	CH_2Cl_2/EtOH	50	6	75	64 (*S*)
2	**3b**	CH_2Cl_2/EtOH	50	6	71	65 (*S*)
3	**3c**	CH_2Cl_2/EtOH	50	6	80	58 (*S*)



Scheme 4. Ir-catalyzed asymmetric hydrogenation of **5** and its hydrochloride.

TABLE 4. Asymmetric Ir-catalyzed hydrogenation of carbazole 5 and its hydrochloride 5a in the presence of ligands L1-L4(P H_2 = 55 atm, 20 h, 20°C)

Entry	Catalyst	Substrate	Solvent	Conversion (%)	ee (%)
1	$[Ir(COD)Cl]_2$/2**L1**	**5**	CH_2Cl_2	15	17 (–)
2	$[Ir(COD)Cl]_2$/2**L2**	**5**	CH_2Cl_2	100	15 (–)
3	$[Ir(COD)Cl]_2$/4**L3**	**5**	CH_2Cl_2	68	5 (–)
4	$[Ir(COD)Cl]_2$/2**L4**	**5**	CH_2Cl_2	100	5 (–)
5	$[Ir(COD)]_2$BARF/**L1**	**5**	CH_2Cl_2	25	10 (–)
6	$[Ir(COD)_2]$BARF/**L2**	**5**	CH_2Cl_2	53	15 (–)
7	$[Ir(COD)_2]$BARF/2**L3**	**5**	CH_2Cl_2	100	**42** (–)
8	$[Ir(COD)_2]$BARF/**L4**	**5**	CH_2Cl_2	100	13 (–)
9	$[Ir(COD)_2]$BARF/2**L3**	**5a**	CH_2Cl_2	8	3 (–)
10	$[Ir(COD)_2]$BARF/2**L3**	**5a**	EtOH	55	4 (–)
11	$[Ir(COD)_2]$BARF/2**L3**	**5a**	CH_2Cl_2/EtOH	86	10 (–)
12	$[Ir(COD)_2]$BARF/**L4**	**5a**	CH_2Cl_2/EtOH	100	21 (–)

diamidophosphite **L4** in the hydrogenation of **5a** in CH_2Cl_2/EtOH mixture showed complete conversion and 21% *ee* (Table 4, entry 12).

CONCLUSION

The Ir-catalyzed asymmetric hydrogenation of quinaldine as a free base and quinaldine hydrochloride was examined in the presence of phosphite-type ligands. We found that the use of the hydrochloride salt as the substrate gave increased enantioselectivity, compared to the usual approach to the hydrogenation of quinaldine by using iodine or piperidine hydrochloride as additives. Moreover, mixture of CH_2Cl_2/EtOH as a solvent gave better enantioselectivity and conversion in the hydrogenation of quinaldine hydrochloride, compared to neat solvents. The ligands were tested for the first time in the asymmetric Ir-catalyzed hydrogenation of 2,4,5,6-tetrahydro-1H-pyrazino(3,2,1-*j*,*k*)carbazole yielding an antidepressant drug, pirlindole.

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