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Enantioselective transfer hydrogenation of various ketones with novel efficient iridium(III) ferrocenyl-phosphinite catalysts

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ABSTRACT

The asymmetric reduction of prochiral ketones is a pivotal reaction for the preparation of chiral alcohols which form an extremely important class of intermediates for fine chemicals and pharmaceuticals. Especially, iridium-based asymmetric reduction of ketones to enantiomerically enriched alcohols has recently attracted important attention by a number of research groups and interest in this area is growing. Therefore, a series of novel neutral mononuclear iridium(III) ferrocenyl-phosphinite complexes have been prepared and applied in the iridium(III)-catalyzed asymmetric transfer hydrogenation (ATH) of ketones to give corresponding secondary alcohols with outstanding enantioselectivities and reactivities using 2-propanol as the hydrogen source (up to 99% ee and 99% conversion). It was seen that the substituents on the backbone of the ligands resulted in a significant effect on both the activity and % enantioselectivity. Furthermore, the structural elucidation of the complexes was carried out by elemental analysis, IR and multi-nuclear NMR spectroscopic data.

1. Introduction

The development of new asymmetric catalytic systems is still a major challenge because of its importance in synthetic organic chemistry and manufacturing fine chemicals [1,2]. An increasing number of chiral compounds and enantiomerically pure drugs are prepared through transition metal-catalyzed asymmetric reactions [3–6]. Since the reactivity and stereoselectivity of an asymmetric transformation are highly dependent on the structure of the chiral ligand coordinated to the transition metal, the design and synthesis of efficient chiral ligands are important in this area and have attracted a great deal of attention from both academia and industry [7,8]. In particular, asymmetric transfer hydrogenation of prochiral ketones to provide chiral alcohols has received a great deal of attention in the last decade or so [9,10]. For that reason, among several applications such as polymers [11] to bioorganometallic chemistry [12–14], the use of ferrocene-based chiral ligands in asymmetric synthesis is the most prominent [15,16]. The ferrocene moiety has been extensively explored as a backbone of chiral phosphine ligands due to its easy modifiability and highly electron donating property [17]. Furthermore, their distinctive structure allows one to design a variety of chiral ferrocenyl phosphine ligands, which are useful tools in metal-catalyzed asymmetric hydrogenation reactions [18,19].

In spite of the encouraging performance of many ferrocene based bidendate phosphorus-chelate ligands [20–25], the past few years have witnessed a renewed interest in the development of chiral monodendate phosphorus ligands for use in asymmetric hydrogenation reactions [26–29]. This resurgence in monodendate ligands is due to the ready accessibility of a range of diverse ligand structures, and often their lower cost compared to bidendate ones [30]. Following the studies from the groups of Pringle [31], Reetz [32], Feringa [33] and more recently Chan [34] and Zhao [35] a large number of chiral monodendate phosphonite, phosphite, and phosphoramidite ligands have been found to induce good to excellent enantioselectivities in asymmetric hydrogenation reactions, comparable to or exceeding those obtained with bidendate ligands [36,37]. Furthermore, the most important advantage of chiral phosphinite ligands over the corresponding phosphine ligands is the easiness of preparation, which leads to a substantial interest to develop highly effective chiral monodendate phosphinite ligands for asymmetric catalysis [38–41].

Lately, the synthesis and applications of efficient rhodium-based catalysts have been reported in the literature [42]. However the

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interest in iridium catalysts [43], which have been successfully used for the asymmetric transfer hydrogenation, is rapidly growing in recent years. Iridium has the advantage to be much less expensive than rhodium [44]. Since the pioneering work of Mestroni et al. on the use of iridium complexes in the transfer hydrogenation of ketones [45,], numerous iridium-based catalytic systems have been studied [46]. The different catalytic systems will be presented according to the coordination pattern of the ligands involved. One of the first reports on the iridium-based ATH of ketones was by Grazani and co-workers [47]. Dichlorobis(1,4-cyclooctadiene)diiridium was used as a precatalyst in the presence of the chiral phosphines for the asymmetric transfer reduction of ketones. In addition, contemporarily, Bakos et al. found that in-situ prepared iridium complexes of phosphinites could also catalyze the ATH of aromatic ketones [48,49]. Comparable studies were carried out by numerous P-based ligands by many researchers. Even though ferrocenyl-phosphine ligands have found widespread applications in transition metal catalyzed asymmetric transformations [50–52], the analogous phosphinites provide different chemical, electronic and structural advantages compared to phosphines. For instance, the metal-phosphorus bond is often stronger in phosphinites compared to the related phosphines due to the presence of electron-withdrawing P-OR group. In addition, the empty σ*-orbital of the phosphinite $P(OR)R_2$ is stabilized, making the phosphinite a better acceptor [53].

We have recently shown that chiral monodendate ferrocenyl-phosphinites ligands, which contain sterically and electronically different ligating fragments, are able to ensure high enantioselectivities in a variety of transition-metals [54]. Furthermore, considering the advantage of phosphinites, in recent years our research group has reported the synthesis [55–57], characterization and coordination properties of this kind of ligands [58–60]. With an aim to design the efficient catalysts for asymmetric transfer hydrogenation (ATH) of ketones, herein, we describe the synthesis and characterization of novel neutral iridium(III) ferrocenyl-phosphinite complexes. As far as we know, there are not so many reports on asymmetric transfer hydrogenation of ketones by using this kind of Iridium-complexes as catalyst. Thus, these iridium complexes have been employed successfully as catalysts in the asymmetric transfer hydrogenation of various ketones.

2. Results and discussion

2.1. Synthesis and characterization of the iridium(IIII) ferrocenyl-phosphinites complexes

We have had an ongoing interest in the synthesis and use of optically active ligands in asymmetric catalysis, especially ferrocenyl-phosphinites. The synthesis of D-, L-phenylglycinol, D-, L-phenylalaninol, D-, L-valinol, L-leucinol and L-isoleucinol were accomplished in one step from D-, L-phenylglycine, D-, L-phenylalanine, D-, L-valine, L-leucine or L-isoleucine, respectively, according to the procedures described in the literature [61,62]. The ferrocene based amino alcohols were synthesized by the condensation reaction between ferrocenecarboxaldehyde [63] and amino alcohols in the presence of the base catalyst [64]. The synthetic process for the preparation of the ferrocenyl-phosphinites [65,66] is shown in Scheme 1. Ferrocenyl-phosphinite ligands, **9**–**16** were prepared by a hydrogen abstraction from the described ferrocene based chiral amino alcohols **1**–**8**, by a base (Et_3N) and the subsequent reaction with one equivalents of Ph_2PCl, in anhydrous toluene under inert argon atmosphere (Scheme 1). The progress of this reaction was conveniently followed by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of compounds, **9**–**16** show single resonances due to phosphinite at approximately δ 115 ppm [67–71] in line with the values previously observed for similar compounds [72–75]. The structures for these ferrocene based chiral amino alcohols are consistent with the data obtained from a combination of multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis.

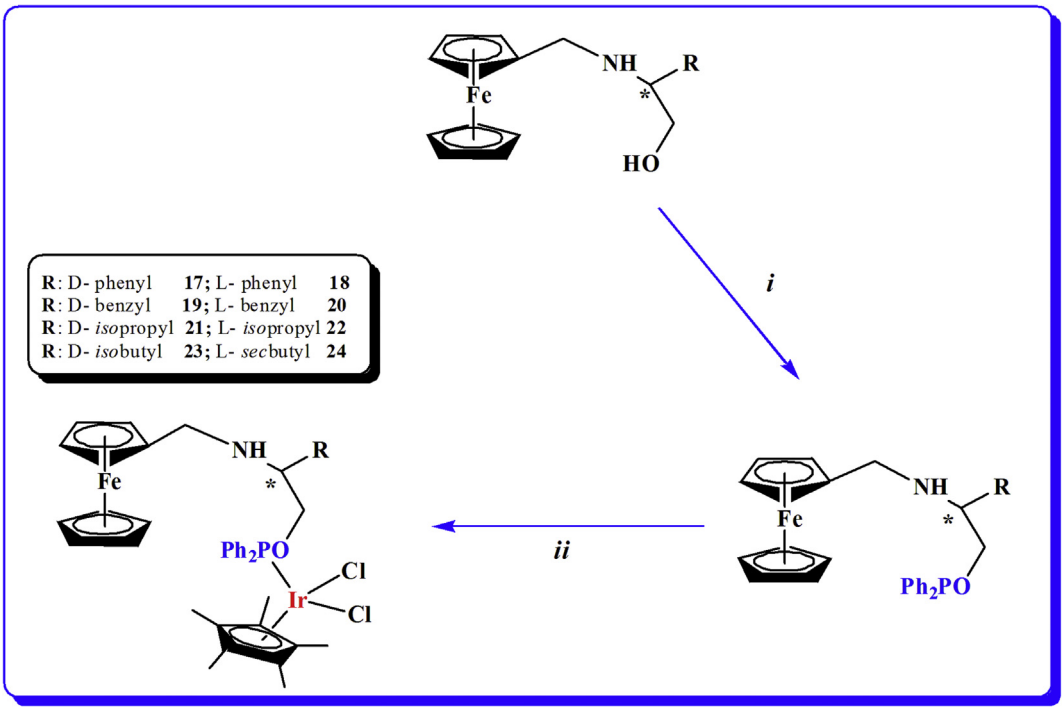
The whole reactions of $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ with ferrocenyl-phosphinite ligands, **17**–**24** are shown in Scheme 1. Treatment of $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ with ferrocenyl-phosphinites **9**–**16** in ½:1 molar ratio in CH_2Cl_2 resulted the formation of mononuclear complexes **17**–**24** as crystalline solids. All neutral iridium(III) complexes were readily synthesized in good yields, which are air stable and orange microcrystalline powders. The ferrocenyl-phosphinite ligands were expected to cleave the $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ dimer to give the corresponding complexes, **17**–**24** via monohapto coordination of the phosphinite group. All complexes were isolated as indicated by singlets in the $^{31}P\{^1H\}$ NMR spectra at approximately δ 74 ppm, with a coordination shift of approximately δ 50 ppm (see supporting information, SI) attributed to formation of the corresponding iridium(III) ferrocenyl-phosphinite complexes. The assignment of the ^1H chemical shifts was derived from 2D HH-COSY spectra and the appropriate assignment of the ^{13}C chemical shifts from DEPT and 2D HMQC spectra. Furthermore, elemental analyses of the complexes are also consistent with the suggested molecular formulas. The absorption bands corresponding to ferrocenyl-phosphinite ligands in Ir(II) complexes in the IR spectra of complexes do not exhibit significant differences with respect to those of free ligands (see Experimental section).

2.2. Asymmetric transfer hydrogenation of prochiral ketones with 2-propanol

The usage of π-arene metal complexes as catalysts for asymmetric transfer hydrogenation from an appropriate donor (usually 2-propanol or formic acid) has been a subject of ongoing research for some decades. It is well-known that hydrogen gas presents considerable safety hazards especially for large scale reactions [76,77]. The use of a solvent that can donate hydrogen overcomes these difficulties. 2-propanol is a popular reactive solvent for transfer hydrogenation reactions since it is easy to handle and relatively non-toxic, environmentally benign, and inexpensive. The volatile acetone by-product can also be easily removed to shift unfavourable equilibrium.

It was found that ferrocenyl-phosphinites demonstrate outstanding air stability and their design does not need any extreme conditions, and thus their preparation is rather easy [78]. Thus, this kind of ligands combines a number of characteristics making uniquely attractive for asymmetric catalysis [79–83]. Encouraged by our recent success in the development of new chiral and highly active catalysts [84,85, and references therein], we initiated a study of the synthesis of a series of iridium(III) ferrocenyl-phosphinite complexes in the asymmetric transfer hydrogenations.

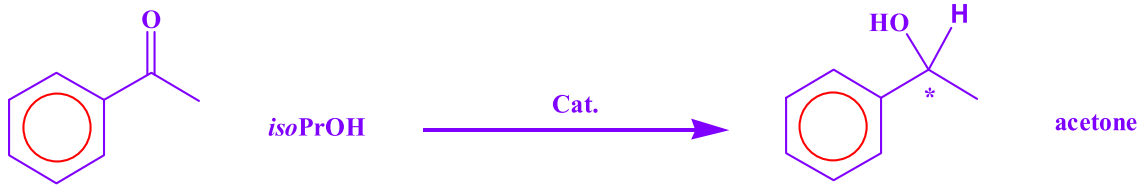
Firstly, complexes **17**–**24** were evaluated as precursors for the catalytic asymmetric transfer hydrogenation of acetophenone by 2-propanol and the results were summarized in Table 1. Catalytic experiments were carried out under argon atmosphere using standard Schlenk-line techniques. To an 2-propanol solution of Ir(III) ferrocenyl-phosphinite complex, an appropriate amount of acetophenone and KOH/2-propanol solutions were added, at room temperature. The solution was stirred, and then examined with capillary GC analysis. At room temperature, transfer hydrogenation of acetophenone occurred very slowly [86], with low conversion (up to 20%, 24 h) and moderate to high enantioselectivity (up to 92% ee) (Table 1, entries 1–8). As a result of the reversibility at room temperature prolonging the reaction time (72 h) led to a decreasing of enantioselectivity, as indicated by the catalytic results collected



Scheme 1. *Reagents and conditions (i)* 1 equiv. Ph_2PCl, 1 equiv. Et_3N, toluene for **9**–**16** (ii)1/2 equiv. $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$, CH_2Cl_2 for **17**–**24**.

with catalysts, **17**–**24** (Entries 1–4, [c]) [87,88]. Furthermore, as can be inferred from the Table 1 (Entries 9–16) the presence of base is necessary to observe appreciable conversions. It is well-known that the base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an

Table 1
Transfer hydrogenation of acetophenone with 2-propanol catalyzed by iridium(III) ferrocenyl-phosphinite complexes (**17**–**24**).



Entry	Complex	S/C/KOH	Time	Conv. (%)[d]	% ee[e]	Conf.[f]	TOF (h^{-1})[g]
1	**17**[a]	100:1:5	24 h (72 h)[c]	17 (52)[c]	86 (82)[c]	*R*	<3
2	**18**[a]	100:1:5	24 h (72 h)[c]	20 (54)[c]	92 (89)[c]	*S*	<3
3	**19**[a]	100:1:5	24 h (72 h)[c]	14 (38)[c]	78 (74)[c]	*R*	<3
4	**20**[a]	100:1:5	24 h (72 h)[c]	18 (39)[c]	83 (80)[c]	*S*	<3
5	**21**[a]	100:1:5	24 h	12	70	*R*	<3
6	**22**[a]	100:1:5	24 h	13	72	*S*	<3
7	**23**[a]	100:1:5	24 h	11	63	*S*	<3
8	**24**[a]	100:1:5	24 h	12	66	*S*	<3
9	**17**[b]	100:1	1 h	<5	–	–	–
10	**18**[b]	100:1	1 h	<5	–	–	–
11	**19**[b]	100:1	1 h	<5	–	–	–
12	**20**[b]	100:1	1 h	<5	–	–	–
13	**21**[b]	100:1	1 h	<5	–	–	–
14	**22**[b]	100:1	1 h	<5	–	–	–
15	**23**[b]	100:1	1 h	<5	–	–	–
16	**24**[b]	100:1	1 h	<5	–	–	–

Reaction conditions.
[a] At room temperature; acetophenone/Ir(III)/KOH, 100:1:5.
[b] Refluxing in 2-propanol; acetophenone/Ir(III), 100:1, in the absence of base.
[c] At room temperature; acetophenone/Ir(III)-complex/KOH, 100:1:5, (72 h).
[d] Determined by GC (three independent catalytic experiments).
[e] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column.
[f] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*S*) or (*R*) configuration was obtained in all experiments.
[g] TOF = (mol product/mol Cat.) × h^{-1}.

active species in this reaction. This is the mechanism proposed by several research groups on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [89–92]. Specifically, role of the base is to generate a more nucleophilic alkoxide ion which would rapidly attack the ruthenium complex responsible for dehydrogenation of 2-propanol.

As can be inferred from Table 2, reduction of acetophenone into (*S*)- or (*R*)-1-phenylethanol could be achieved in high yield by increasing the temperature to 82 °C (Entries 1–8). Furthermore, optimization studies of the catalytic reduction of acetophenone in 2-propanol showed that good activity was obtained with a base/ligand ratio of 5:1 (Table 2, entries 9–16). In addition, the choice of base, such as KOH and NaOH, had little influence on the conversion and enantioselectivity (Table 2, entries 1–4,[b]). It is well-known that the NH functional moiety in ligand plays an important role in catalytic system and similar tendency was reported in earlier studies [93–95]. These ferrocenyl based monodendate phosphinite ligands with amino (NH) moiety show much higher activity and enantioselectivity. Higher activity and enantioselectivity of amino containing phosphinite ligand also may be due to the fact that NH moiety can stabilize the catalytic transition state [96]. As expected, it is noteworthy that the catalytic systems, **17**–**24** display the differences in reactivity. These results indicate that the structure of the monodenate ferrocenyl-phosphinite ligands have a crucial influence on rate of the reaction. Compared to the other complexes, [(2S)-2-(ferrocenylmethylamino)-2-phenylethyldiphenyl phosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] **(18)** appears to provide a more effective chiral environment around iridium. In the context of these results, it could be reasonably argued that the absolute configuration of the product is governed by the carbon centered chirality.

As seen from Table 2, the catalytic activities in the studied hydrogen transfer reactions were generally much higher for the **17**–**18** than those for the other complexes. So, these two complexes were extensively investigated with acetophenone derivatives. The catalytic reduction of acetophenone derivatives was tested with the conditions optimized for acetophenone and the results are summarized in Table 3 which illustrates conversions of the reduction performed in a 0.1 M of 2-propanol solution containing **17**–**18** and KOH (Ketone:Cat.:KOH = 100:1:5). The results demonstrate that a range of acetophenone derivatives can be hydrogenated with good enantioselectivities. It has also been shown that the catalytic activities in the studied hydrogen transfer reactions were generally much higher for [(2S)-2-(ferrocenylmethylamino)-2-phenylethyldiphenylphosphinito(dichloro(η5-pentamethylcyclopentadienyl)iridium(III))] **(18)** than for the complex, **17**.

The steric bulk of the R group in the ferrocenyl-ligand controls both activitity and enantioselectivity of the catalysts. That's to say, this different behavior in enantioselectivities can be clarified on the basis of aromatic moiety (phenyl) near chiral carbon center in the ligand backbone responsible for the optimization molecular rigidity. These results have also shown that enantiomeric purity of the product can be affected by electronic and steric factors of the substituents on the ligand. The examination of the results indicates clearly that with each of the tested complexes, the highest enantioselectivity was found for transfer hydrogenation of *o*-methoxyacetophenone (99% ee) when [(2*S*)-2-(ferrocenylmethylamino)-2-phenylethyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] **(18)** was used as the catalyst precursor. As already stated, electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone caused the changes in the reduction rate. Therefore, the introduction of electron withdrawing substituents to the *para* position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved giving rise to easier hydrogenation [97,98]. The introduction of electron-withdrawing substituents, such as F or NO_2, to the *para* positions of the aryl ring of the ketone, resulted in improved activity with good enantioselectivity (Table 3, entries 1–8). As expected, the lowest enantioselectivity was observed in transfer hydrogenation of *p*-methoxyacetophenone. From the results, the introduction of an electron-donating group such as methoxy group to the *p*-position decelerates the reaction, but that to the *o*-position increases the rate and improves the enantioselectivity.

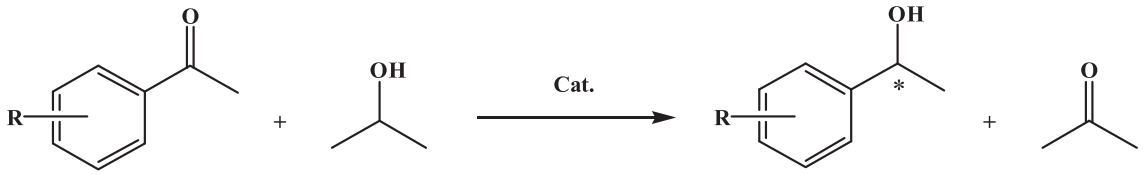
Table 4 summarizes the asymmetric transfer hydrogenation of various aryl ketones in 2-propanol at 82 °C. Other functionalized ketones could also be hydrogenated using complexes **17** and **18** as catalysts to afford the products. It was found that catalytic activity and enantioselectivity are sensitive to the structure of ketones. In

Table 2
Transfer hydrogenation of acetophenone with 2-propanol catalyzed by Ir(III) ferrocenyl based monodendate phosphinite complexes (**17**–**24**).

Entry	Catalyst	S/C/KOH	Time	Conv. (%)[c]	% ee[d]	Conf.[e]	TOF (h^{-1})[f]
1	**17**[a]	100:1:5	1/3 h (1/3 h)[b]	98 (94)	92 (87)	*R*	294 (282)
2	**18**[a]	100:1:5	1/3 h (1/3 h)[b]	99 (95)	98 (92)	*S*	297 (285)
3	**19**[a]	100:1:5	1/2 h (1/2 h)[b]	99 (96)	83 (78)	*R*	198 (192)
4	**20**[a]	100:1:5	1/2 h (1/2 h)[b]	97 (93)	88 (76)	*S*	194 (186)
5	**21**[a]	100:1:5	1/2 h	97	75	*R*	194
6	**22**[a]	100:1:5	1/2 h	98	76	*S*	196
7	**23**[a]	100:1:5	1/2 h	97	69	*S*	194
8	**24**[a]	100:1:5	1/2 h	97	72	*S*	194
9	**17**	100:1:3	1/3 h	95	85	*R*	285
10	**17**	100:1:5	1/3 h	98	92	*R*	294
11	**17**	100:1:7	1/3 h	92	88	*R*	276
12	**17**	100:1:9	1/3 h	91	84	*R*	273
13	**18**	100:1:3	1/3 h	93	91	*S*	279
14	**18**	100:1:5	1/3 h	99	98	*S*	297
15	**18**	100:1:7	1/3 h	94	90	*S*	282
16	**18**	100:1:9	1/3 h	91	89	*S*	273

Reaction conditions.
[a] Refluxing in 2-propanol; acetophenone/Ir(III)-complex/KOH, 100:1:5.
[b] Refluxing in 2-propanol; acetophenone/Ir(III)-complex/NaOH, 100:1:5.
[c] Determined by GC (three independent catalytic experiments).
[d] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column.
[e] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*S*) or (*R*) configuration was obtained in all experiments.
[f] TOF = (mol product/mol Cat.) × h^{-1}.

Table 3
Asymmetric Transfer Hydrogenation results for substituted acetophenones catalyzed by iridium(III)-ferrocenyl based monodendate phosphinite complexes, (**17**–**18**).[a]



Entry	Catalyst	Substrate	Time	Conv. (%)[b]	% ee[c]	TOF (h^{-1})[d]	Config.[e]
1	**17**	4-F	1/4 h	99	89	396	*R*
2	**18**		1/4 h	98	95	392	*S*
3	**17**	4-Cl	1/3 h	98	86	294	*R*
4	**18**		1/3 h	97	92	291	*S*
5	**17**	4-Br	1/3 h	99	83	297	*R*
6	**18**		1/3 h	98	91	294	*S*
7	**17**	4-NO_2	1/4 h	99	88	396	*R*
8	**18**		1/4 h	98	96	392	*S*
9	**17**	2-MeO	1/2 h	98	95	196	*R*
10	**18**		1/2 h	97	99	194	*S*
11	**17**	4-MeO	1 h	99	77	99	*R*
12	**18**		1 h	98	82	98	*S*

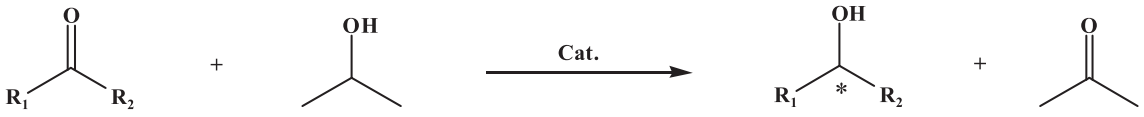
[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone.
[c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness).
[d] TOF = (mol product/mol Cat.) × h^{-1}.
[e] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values.

that case, high conversion yields (97–99%) were obtained for **17** and **18** and the highest enantioselectivity, up to 99% ee, was obtained for **18**. As seen from Table 4, the best result in terms of enantioselectivity was observed with 1-naphtyl methyl ketone (up to 99% ee, entries 9–10). The reactivity and enantioselectivity were also dependent on the bulkiness of the alkyl group (Table 4, Entries 1–8). For example, the reaction was remarkably slowed by increasing the bulkiness of the alkyl group, whereas the enantioselectivity only slightly changed. Furthermore, the hydrogenation of ketones including cyclohexyl group was very slow and the enantioselectivities were remarkable lower (Table 4, Entries 13–16).

3. Conclusions and perspectives

In summary, we designed a series of ferrocenyl-phosphinite ligands and applied them to the Ir(III)-catalyzed asymmetric transfer hydrogenation of various ketones. A wide range of ketones could be

Table 4
Asymmetric Transfer Hydrogenation results for various ketones catalyzed by Iridium(III)-ferrocenyl based monodendate phosphinite complexes, (**17**–**18**).[a]



Entry	Cat.	R_1	R_2	Time	Conv. (%)[b]	Ee (%)[c]	TOF (h^{-1})[d]	Conf.[e]
1	**17**	CH_3	CH_2CH_3	1/2 h	98	86	196	*R*
2	**18**	CH_3	C_2H_5	1/2 h	99	93	198	*S*
3	**17**	CH_3	$CH_2CH_2C_6H_5$	1 h	99	82	99	*R*
4	**18**			1 h	98	88	98	*S*
5	**17**	CH_3	$CH(CH_3)_2$	2 h	99	78	50	*R*
6	**18**			2 h	98	85	49	*S*
7	**17**	CH_3	$CH_2CH(CH_3)_2$	5/2 h	98	77	39	*R*
8	**18**			5/2 h	97	83	39	*S*
9	**17**	CH_3	1-naphthyl	1/3 h	99	93	297	*R*
10	**18**			1/3 h	99	99	297	*S*
11	**17**	CH_3	*n*-C_4H_9	3 h	98	76	33	*R*
12	**18**			3 h	99	84	33	*S*
13	**17**	CH_3	C_6H_{11}	2 h	98	65	49	*R*
14	**18**			2 h	99	73	50	*S*
15	**17**	C_6H_5	C_6H_{11}	4 h	98	71	25	*R*
16	**18**			4 h	99	78	25	*S*

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone.
[c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness).
[d] TOF = (mol product/mol Cat.) × h^{-1}.
[e] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values.

hydrogenated enantioselectively to afford the corresponding optically active alcohols in high isolated yields and with good to excellent enantioselectivity. The chirality of the carbon center in the ligand backbone is of particular importance for asymmetric induction offering an obvious target for further optimization. The simplicity and efficiency clearly make it an excellent choice of catalyst for the practical preparation of highly valued alcohols via the catalytic asymmetric transfer hydrogenation of ketones. Furthermore, the development of a practical synthesis of ferrocenyl-phosphinites and demonstration that they are competent auxiliaries for catalysis opens up a neglected vein in the rich chemistry of phosphorus ligands. Further modification of the aryl/alkyl group on ligand backbone and phosphorus atom is currently underway.

4. Experimental section

4.1. Materials and methods

Unless otherwise mentioned, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. The starting materials D-, L-phenylglycine, D-, L-phenylalanine, D-, L-valine, L-leucine, L-isoleucine, PPh_2Cl and Et_3N were purchased from Fluka and used as received. Ferrocenecarboxaldehyde, [68] and $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ [99] were prepared according to the literature procedures. ^1H (at 400.1 MHz), ^{13}C (at 100.6 MHz) and $^{31}P\text{-}\{^1H\}$ NMR (at 162.0 MHz) spectra were recorded on a Bruker AV400 spectrometer, with TMS (tetramethylsilane) as an internal reference for ^1H NMR and ^{13}C NMR or 85% H_3PO_4 as external reference for $^{31}P\text{-}\{^1H\}$ NMR. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer. Specific rotations were taken on a Perkin-Elmer 341 model polarimeter. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

GC analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness). Racemic samples of alcohols were obtained by reduction of the corresponding ketones with $NaBH_4$ and used as the authentic samples for ee determination. The GC parameters for asymmetric transfer hydrogenation of ketones were as follows; initial temperature, 50 °C; initial time 1.1 min; solvent delay, 4.48 min; temperature ramp 1.3 °C/min; final temperature, 150 °C; initial time 2.2 min; temperature ramp 2.15 °C/min; final temperature, 250 °C; initial time 3.3 min; final time, 44.33 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

4.2. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of iridium complexes **17**–**24** (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed 2-propanol (5 mL) was refluxed until the reaction completed. Then, a sample of the reaction mixture is taken off, diluted with acetone and analyzed immediately by GC, conversions obtained are related to the residual unreacted ketone.

4.2.1. General procedures for synthesis of ferrocene based iridium(III) ferronenyl-phosphinites complexes (*17*–*24*)

$[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ (0.15 mmol) and ferrocene based phosphinite (0.30 mmol) were dissolved in 20 mL of CH_2Cl_2 and stirred for 30 min at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of *n*-hexane (20 mL) gave the corresponding complex as an orange microcrystalline solid. The product was collected by filtration and dried in vacuo.

4.2.2. [(2R)-2-(ferrocenylmethylamino)-2-phenylethyldiphenylphosphinito(dichloro(η5-pentamethylcyclopentadienyl)iridium(III))] (*17*)

Yield: 234 mg, 84.9%; mp:131–133 °C; $[\alpha]_D^{20} = -25.4°$(c 1, CH_2Cl_2). **^1H NMR ($CDCl_3$, ppm)**: δ 1.38 (d, 15H, $^4J = 2.4$ Hz, CH_3 of Cp* (C_5**Me$_5$**)), 3.23 (d, $J = 13.0$ Hz, 1H, CH_2NH, (a)), 3.43 (d, $J = 13.1$ Hz, 1H, CH_2NH, (b)), 3.79 (br, 1H, C*H*NH), 3.90–3.95 (m, 2H, CH_2OP), 4.09 (s, 5H, C_5H_5), 4.12 (s, 3H, C_5H_4), 4.18 (s, 1H, C_5H_4), 7.35–7.38 (m, 6H, *m*- and *p*-protons of phenyls +5H, C_6H_5), 7.92 (m, 4H, *o*-protons of phenyls); **^{13}C NMR ($CDCl_3$, ppm)**: δ 8.21 (*C*H$_3$ of Cp*(C_5**Me$_5$**)), 46.26 (*C*H$_2$NH), 62.14 (d, $^3J = 7.0$ Hz, *C*HNH), 67.65, 67.90, 68.04, 68.40, 68.75, 70.64 (C_5H_4+C_5H_5+*C*H$_2$OP), 86.06 (*i*-C_5H_4), 94.11 (d, $^2J = 3.0$ Hz, C_5Me_5), 127.75, 127.85, 127.94, (C_6H_5), 128.47 (s, carbons of phenyls), 130.95 (d, $J = 6.7$ Hz, *m*-carbons of phenyls), 133.10 (d, $J = 11.5$ Hz, *o*-carbons of phenyls), 135.75 (d, $J = 60.3$ Hz, *i*-carbons of phenyls), 139.78 (*i*-C_6H_5); **$^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, ppm)**: δ 74.08 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3054, (C=C-Cp): 1451, (P-Ph): 1436, (O–P): 1023; **Anal. Calcd for** [$C_{41}H_{45}$NOPFeIrCl$_2$] (917.76 g/mol): C, 53.66; N, 1.53; H, 4.94; Found: C, 53.29; N, 1.41; H, 4.49.

4.2.3. [(2S)-2-(ferrocenylmethylamino)-2-phenylethyldiphenylphosphinito(dichloro(η5-pentamethylcyclopentadienyl)iridium(III))] (*18*)

Yield: 237 mg, 86.0%; mp:131–133 °C; $[\alpha]_D^{20} = +25.9°$ (c 1, CH_2Cl_2). **^1H NMR ($CDCl_3$, ppm)**: δ 1.38 (d, 15H, $^4J = 2.0$ Hz, CH_3 of Cp* (C_5**Me$_5$**)), 3.25 (d, $J = 12.6$ Hz, 1H, CH_2NH, (a)), 3.46 (br, 1H, CH_2NH, (b)), 3.87 (br, 1H, C*H*NH), 3.95 (br, 2H, CH_2OP), 4.09 (s, 5H, C_5H_5), 4.13 (s, 3H, C_5H_4), 4.23 (s, 1H, C_5H_4), 7.31–7.39 (m, 6H, *m*- and *p*-protons of phenyls +5H, C_6H_5), 7.90 (d, $J = 7.5$ Hz, 4H, *o*-protons of phenyls); **^{13}C NMR ($CDCl_3$, ppm)**: δ 8.26 (*C*H$_3$ of Cp* (C_5**Me$_5$**)), 46.17 (*C*H$_2$NH), 62.06 (d, $^3J = 8.0$ Hz, *C*HNH), 67.82, 68.10, 68.12, 68.17, 68.45, 68.62 (C_5H_4+C_5H_5+*C*H$_2$OP), 86.61 (*i*-C_5H_4), 94.14 (d, $^2J = 3.0$ Hz, C_5Me_5), 127.72, 127.82, 127.93, (C_6H_5), 128.57 (s, carbons of phenyls), 131.06 (d, $J = 15.1$ Hz, *m*-carbons of phenyls), 132.95 (br, *o*-carbons of phenyls), 135.70 (d, $J = 61.4$ Hz, *i*-carbons of phenyls), 141.54 (*i*-C_6H_5); **$^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, ppm)**: δ 74.24 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3058, (C=C-Cp): 1451, (P-Ph): 1436, (O–P): 1023; **Anal. Calcd for** [$C_{41}H_{45}$NOPFeIrCl$_2$] (917.76 g/mol): C, 53.66; N, 1.53; H, 4.94; Found: C, 53.23; N, 1.40; H, 4.45.

4.2.4. [(2R)-2-(ferrocenylmethylamino)-3-phenylpropyldiphenylphosphinito(dichloro(η5-pentamethylcyclopentadienyl)iridium(III))] (*19*)

Yield: 238 mg, 85.3%; mp:125–126 °C); $[\alpha]_D^{20} = +19.6°$ (c 1, CH_2Cl_2). **^1H NMR ($CDCl_3$, ppm)**: δ 1.38 (d, 15H, $^4J = 2.1$ Hz, CH_3 of Cp* (C_5**Me$_5$**)), 2.82 (br, 1H, C$H_2C_6H_5$ (a)), 2.86 (m, 1H, C$H_2C_6H_5$ (b)), 3.03 (br, 1H, C*H*NH), 3.38 (br, 1H, CH_2NH, (a)), 3.46 (m, 1H, CH_2NH, (b)), 3.83 (br, 2H, CH_2OP), 4.01 (s, 5H, C_5H_5), 4.07 (s, 3H, C_5H_4), 4.12 (s, 1H, C_5H_4), 7.12–7.40 (m, 6H, *m*- and *p*-protons of phenyls +5H, $CH_2C_6H_5$) 7.95–8.02 (m, 4H, *o*-protons of phenyls); **^{13}C NMR ($CDCl_3$, ppm)**: δ 8.22 (*C*H$_3$ of Cp* (C_5**Me$_5$**)), 37.97 (*C*H$_2$Ph), 46.51 (*C*H$_2$NH), 58.66 (d, $^3J = 7.0$ Hz, *C*HNH), 67.84, 68.40, 68.63, 68.80, 69.07, 69.66 (C_5H_4+C_5H_5 +*C*H$_2$OP), 86.51 (*i*-C_5H_4), 94.10 (d, $^2J = 3.0$ Hz, C_5Me_5), 126.51, 128.60, 129.31, ($CH_2C_6H_5$), 127.81 (d, $J = 11.1$ Hz, *m*-carbons of phenyls), 132.61 (d, $J = 11.1$ Hz, *p*-carbons of phenyls), 133.69 (d, $J = 11.1$, *o*-carbons of phenyls), 136.17 (br, *i*-carbons of phenyls), 138.16 (*i*-$CH_2C_6H_5$); **$^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, ppm)**: δ 73.72 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3058, (C=C-Cp): 1451,

(P-Ph): 1436, (O–P): 1023; **Anal. Calcd for** [$C_{42}H_{47}NOPFeIrCl_2$] (931.78 g/mol): C, 54.14; N, 1.50; H, 5.08; Found: C, 54.00; N, 1.38; H, 5.00.

*4.2.5. [(2S)-2-(ferrocenylmethylamino)-3-phenylpropyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] (**20**)*

Yield: 229 mg, 81.9%; mp:129–130 °C; $[\alpha]_D^{20} = -19.2°$ (c 1, CH_2Cl_2). **^{1}H NMR (CDCl$_3$, ppm)**: δ 1.38 (d, 15H, ^4J = 1.3 Hz, *CH*$_3$ of Cp* (C_5**Me$_5$**)), 2.77–2.82 (br, 2H *CH*$_2$C$_6$H$_5$), 3.05 (br, 1H, *CH*NH), 3.48 (br, 2H, *CH*$_2$NH), 3.84 (br, 2H, *CH*$_2$OP), 4.02 (s, 5H, C_5H_5), 4.08 (s, 3H, C_5H_4), 4.14 (s, 1H, C_5H_4), 7.11–7.40 (m, 6H, *m*- and *p*-protons of phenyls +5H, $CH_2C_6H_5$) 7.93–8.01 (m, 4H, *o*-protons of phenyls); **^{13}C NMR (CDCl$_3$, ppm)**: δ 8.23 (*CH*$_3$ of Cp* (C_5**Me**$_5$)), 38.06 (*CH*$_2$Ph), 46.53 (*CH*$_2$NH), 58.65 (d, ^3J = 6.0 Hz, *CH*NH), 67.82, (^2J = 7.0 Hz, *CH*$_2$OP), 67.91, 68.40, 68.62 68.79, 69.66 (C_5H_5+C_5H_4), 86.65 (*i*-C_5H_4), 94.10 (d, ^2J = 2.0 Hz, C_5Me_5), 126.51, 128.60, 129.31, ($CH_2C_6H_5$), 127.80 (d, *J* = 11.1 Hz, *m*-carbons of phenyls), 132.63 (d, *J* = 11.1 Hz, *p*-carbons of phenyls), 133.68 (d, *J* = 12.1, *o*-carbons of phenyls), 136.17 (br, *i*-carbons of phenyls), 138.17 (*i*-$CH_2C_6H_5$); **^{31}P-{^{1}H} NMR (CDCl$_3$, ppm)**: δ 73.85 (s, **O-P**(Ph)$_2$; **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3054, (C=C-Cp): 1449, (P-Ph): 1436, (O–P): 1023; **Anal. Calcd. for** [$C_{42}H_{47}NOPFeIrCl_2$] (931.78 g/mol): C, 54.14; N, 1.50; H, 5.08; Found: C, 53.98; N, 1.37; H, 4.99.

*4.2.6. [(2R)-2-(ferrocenylmethylamino)-3-methylbutyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] (**21**)*

Yield: 230 mg, 86.8%; mp: 138–139 °C); $[\alpha]_D^{20} = -29.5°$ (c 0.5, CH_2Cl_2). ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ: 0.81 (d, *J* = 6.6 Hz, 6H, CH(*CH*$_3$)$_2$), 1.44 (s, 15H, *CH*$_3$ of Cp* (C_5**Me$_5$**)), 1.84 (m, 1H, *CH*(CH$_3$)$_2$), 2.58 (br, 1H, *CH*NH), 3.55 (br, 2H, *CH*$_2$NH), 3.75 (br, 2H, *CH*$_2$OP), 4.12–4.22 (m, 5H, C_5H_5+4H, C_5H_4), 7.33–7.40 (m, 6H, *m*- and *p*-C_6H_5P), 7.97 (br, 4H, *o*-C_6H_5P); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ: 8.32 (*CH*$_3$ of Cp* (C_5**Me**$_5$)), 18.52 (CH(*CH*$_3$)$_2$), 28.60 (*CH*(CH$_3$)$_2$), 46.93 (*CH*$_2$NH), 62.12 (d, *J* = 7.0 Hz, *CH*NH), 67.98, 68.06, 68.52, 68.82, 68.97, 69.43(C_5H_5+C_5H_4+*CH*$_2$OP), 84.84 (*i*-C_5H_4), 94.11 (C_5Me_5), 127.75 (t, *J* = 10.6 Hz, *m*-C_6H_5P), 130.96 (s, *p*-C_6H_5P), 133.27 (d, *J* = 12.6 Hz, *o*-C_6H_5P), 135.55 (d, *J* = 23.1 Hz, *i*-C_6H_5P); **^{31}P–{^{1}H} NMR (162.0 MHz,CDCl$_3$, ppm)** δ: 74.33 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3057, (C=C-Cp): 1448, (P-Ph): 1435, (O–P): 1024; **Anal. Calc. for [C$_{38}$H$_{47}$NOPFeIrCl$_2$]** (883.74 g/mol): C 51.65, N 1.59, H 5.36; found: C 51.51, N 1.48, H 5.21%.

*4.2.7. [(2S)-2-(ferrocenylmethylamino)-3-methylbutyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] (**22**)*

Yield: 227 mg, 85.7%; mp: 132–134 °C); $[\alpha]_D^{20} = +29.2°$ (c 0.5, CH_2Cl_2). **^{1}H NMR (400.1 MHz, CDCl$_3$, ppm)** δ: 0.81–0.89 (m, 6H, CH(*CH*$_3$)$_2$), 1.44 (s, *CH*$_3$ of Cp* (C_5**Me$_5$**)), 1.84 (br, 1H, *CH*(CH$_3$)$_2$), 2.57 (br, 1H, *CH*NH), 3.54 (br, 2H, *CH*$_2$NH), 3.75 (br, 1H, *CH*$_2$OP), 4.12–4.21 (m, 5H, C_5H_5+4H,C_5H_4), 7.33–7.40 (m, 6H, *m*- and *p*-C_6H_5P), 7.97 (br, 4H, *o*-C_6H_5P); **^{13}C NMR (100.6 MHz, CDCl$_3$, ppm)** δ: 8.31 (*CH*$_3$ of Cp* (C_5**Me**$_5$)), 18.53 (CH(*CH*$_3$)$_2$), 28.50 (*CH*(CH$_3$)$_2$), 46.95 (*CH*$_2$NH), 62.15 (d, *J* = 5.0 Hz, *CH*NH), 67.91, 68.02, 68.13, 68.50, 68.77, 68.89 (C_5H_5+C_5H_4+*CH*$_2$OP), 84.57 (*i*-C_5H_4), 94.10 (d, *J* = 1.8 Hz, C_5Me_5), 127.75 (t, *J* = 9.6 Hz, *m*-C_6H_5P), 130.98 (s, *p*-C_6H_5P), 133.19 (d, *J* = 22.1 Hz, *o*-C_6H_5P), 135.58 (d, *J* = 28.2 Hz, *i*-C_6H_5P); **^{31}P–{^{1}H} NMR (162.0 MHz, CDCl$_3$, ppm)** δ: 73.72 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3057, (C=C-Cp): 1448, (P-Ph): 1436, (O–P): 1024; **Anal. Calc. for** [$C_{38}H_{47}NOPFeIrCl_2$] (883.74 g/mol): C 51.65, N 1.59, H 5.36; found: C 51.53, N 1.43, H 5.24%.

*4.2.8. [(2S)-2-(ferrocenylmethylamino)-4-methylpentyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))] (**23**)*

(Yield: 229 mg, 85.1%; mp: 140–141 °C); $[\alpha]_D^{20} = +37.5°$ (c 0.5, CH_2Cl_2). **^{1}H NMR (400.1 MHz, CDCl$_3$, ppm)** δ: 0.87 (d, *J* = 4.8 Hz, 6H, CH(*CH*$_3$)$_2$), 1.27–1.36 (m, 15H,*CH*$_3$ of Cp* (C_5**Me$_5$**)+2H,*CH*$_2$CH+1H, *CH*(CH$_3$)$_2$), 2.89 (br, 1H, *CH*NH), 3.67 (br, 2H, *CH*$_2$NH), 3.78 (br, 2H, *CH*$_2$OP), 4.07–4.31 (m, 5H, C_5H_5+4H, C_5H_4), 7.41–7.44 (m, 6H, *m*- and *p*-C_6H_5P), 7.87–7.96 (m, 4H, *o*-C_6H_5P); **^{13}C NMR (100.6 MHz, CDCl$_3$, ppm)** δ: 8.32 (*CH*$_3$ of Cp* (C_5**Me**$_5$)), 22.19, 22.98 (CH(*CH*$_3$)$_2$), 24.57 (*CH*(CH$_3$)$_2$), 39.31 (*CH*$_2$CH), 45.88 (*CH*$_2$NH), 55.08 (d, *J* = 6.0 Hz, *CH*NH), 65.48, 68.64, 68.85, 69.06, 69.32, 69.73 (C_5H_5+C_5H_4+ *CH*$_2$OP), 84.62 (*i*-C_5H_4), 94.16 (d, *J* = 3.0 Hz, C_5Me_5), 127.89 (t, *J* = 9.1 Hz, *m*-C_6H_5P), 130.83 (s, *p*-C_6H_5P), 133.67 (d, *J* = 12.1 Hz, *o*-C_6H_5P); 135.74 (d, *J* = 17.1 Hz, *i*-C_6H_5P); **^{31}P–{^{1}H} NMR (162.0 MHz, CDCl$_3$, ppm)** δ: 72.13 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3057, (P-Ph): 1436, (C C-Cp): 1449, (O P): 1026; **Anal. Calc. for** [$C_{39}H_{49}NOPFeIrCl_2$] (897.77 g/mol): C 52.18, N 1.56, H 5.50; found: C 52.00, N 1.26, H 5.24%.

*4.2.9. [(2S-3S)-2-(ferrocenylmethylamino)-3-methylpentyldiphenylphosphinito(dichloro(η^5-pentamethylcyclopentadienyl)iridium(III))], (**24**)*

(Yield: 234 mg, 86.8%; mp: 131–132 °C); $[\alpha]_D^{20} = +34.0°$ (c 0.5, CH_2Cl_2). **^{1}H NMR (400.1 MHz, CDCl$_3$, ppm)** δ 0.69 (br, 3H, CH_2CH_3), 0.83 (d, *J* = 6.6, 3H,CH(*CH*$_3$)), 1.01 (m, 2H, CHC*H*$_2$(CH$_3$)), 1.14 (m, 1H, *CH*CH$_2$(CH$_3$)), 1.43 (s, 15H, *CH*$_3$ of Cp* (C_5**Me$_5$**)), 2.79 (br, 1H, *CH*NH), 4.84 (br, 2H, *CH*$_2$NH+2H,*CH*$_2$OP), 4.17–4.33 (m, 5H, C_5H_5+4H, C_5H_4), 7.31–7.45 (m, 6H, *m*- and *p*-C_6H_5P), 7.86–7.97 (m, 4H, *o*-C_6H_5P); **^{13}C NMR (100.6 MHz, CDCl$_3$, ppm)** δ: 8.33 (*CH*$_3$ of Cp* (C_5**Me**$_5$)), 11.68 (CH_2CH_3), 14.59 (CH*CH*$_3$), 25.84 (*CH*CH$_2$CH$_3$), 34.47 (CH*CH*$_2$CH$_3$), 45.96 (*CH*$_2$NH), 60.31 (d, *J* = 9.1 Hz, *CH*NH), 68.51, 68.74, 68.93, 69.09, 69.16 (C_5H_5+C_5H_4+*CH*$_2$OP), 84.62 (*i*-C_5H_4), 94.24 (C_5Me_5), 127.82 (t, *J* = 10.1, *m*-C_6H_5P), 130.82 (s, *p*-C_6H_5P), 133.02 (d, *J* = 23.7, *o*-C_6H_5P), 135.78 (d, *J* = 30.3 Hz, *i*-C_6H_5P); **^{31}P–{^{1}H} NMR (162.0 MHz, CDCl$_3$, ppm)** δ: 72.89 (s, **O-P**(Ph)$_2$); **IR (KBr pellet in cm^{-1})** υ: (C-Cp): 3056, (C=C-Cp): 1451, (P-Ph): 1435, (O–P): 1026; **Anal. Calc. for** [$C_{39}H_{49}NOPFeIrCl_2$] (897.77 g/mol): C 52.18, N 1.56, H 5.50; found: C 51.97, N 1.28, H 5.22.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.06.002.

References

[1] Ads E.N. Jacobsen, A. Pfaltz, H. Yamamoto, Asymmetric Catalysis in Organic Synthesis, Vol. 1–3, Springer, Berlin, 1999.
[2] G.-Q. Lin, Y.-M. Li, A.S.C. Chan, Principles and Applications of Asymmetric Synthesis, 8, Wiley-Blackwell, New York, 2001.
[3] R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994.
[4] H. Takaya, T. Ohta, R. Noyori, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH Publishers, inc, New York, 1993 (Chapter 3) pp.1.
[5] W. Tang, X. Zhang, New chiral phosphorus ligands for enantioselective hydrogenation, Chem Rev 103 (2003) 3029–3069.
[6] H. Shimizu, I. Nagasaki, K. Matsumura, N. Sayo, T. Saıto, Developments in asymmetric hydrogenation from an industrial perspective, Acc Chem Res 40 (2007) 1385–1393.
[7] R.A. Sheldon, Chirotechonology, Marcel Dekker, New York, 1993.
[8] T. Ohkuma, M. Kitamura, R. Noyori, Catalytic Asymmetric Synthesis, second ed., Wiley, New York, 2000.
[9] H.-U. Blaser, The chiral switch of (S)-Metolachlor: a personal account of an industrial odyssey in asymmetric catalysis, Adv Synth Catal 344 (1) (2002)

17–31.
[10] C. Saluzzo, R. ter Halle, F. Tauchard, F. Fache, E. Schulz, M. Lemarie, Recent progress in asymmetric heterogeneous catalysis: use of polymer-supported catalysts, J Organomet Chem 603 (2000) 30–39.
[11] A.S. Abd-El-Aziz, E.K. Todd, Organoiron polymers, Coord Chem Rev 246 (2003) 3–52.
[12] U. Schatzschneider, N. Metzher-Nolte, New principles in medicinal organometallic chemistry, Angew Chem Int Ed Engl 45 (2006) 1504–1507.
[13] D.R. van Staveren, N. Metzher-Nolte, Bioorganometallic chemistry of ferrocene, Chem Rev 104 (2004) 5931–5985.
[14] E. Hillard, A. Vessieres, L. Thouin, G. Jaouen, C. Amatore, Ferrocene-Mediated proton- coupled electron transfer in a series of ferrocifen-type Breast-Cancer drug candidates, Angew Chem Int Ed Engl. 45 (2006) 285–290.
[15] J. Holz, M. Quirmbach, A. Börner, Strategies for the synthesis of chiral hydroxy phosphines-a class of versatile ligands and ligand precursors for asymmetric catalysis, Synthesis (1997) 983–1006.
[16] L.–X. Dai, T. Tu, S.–L. You, W.–P. Deng, X.–L. Hou, Asymmetric catalysis with chiral ferrocene ligands, Acc Chem Res 36 (2003) 659–667.
[17] D. Liu, W. Li, X. Zhang, A novel chiral ferrocenyl phosphine ligand from Sugar: applications in Rh-Catalyzed asymmetric hydrogenation reactions, Org Lett 4 (25) (2002) 4471–4474.
[18] S. ichi, H. Fukuzawa, M. Oki, J. Hosaka, S. Sugasawa, Kikuchi, ClickFerrophos: new chiral ferrocenyl phosphine ligands synthesized by click chemistry and the use of their metal complexes as catalysts for asymmetric hydrogenation and allylic substitution, Org Lett 9 (26) (2007) 5557–5560.
[19] U. Işık, M. Aydemir, N. Meriç, F. Durap, C. Kayan, H. Temel, A. Baysal, Tunable ferrocenyl-phosphinite ligands for the ruthenium(II)-catalyzed asymmetric transfer hydrogenation of ketones, J Mol Catal A Chem 379 (2013) 225–233.
[20] A. Patti, G. Nicolosi, Preparation of chiral C2-symmetrical 1,1′-disubstituted ferrocenes, Tetrahedron Asymmetry 11 (2000) 3687–3692.
[21] M. Watanabe, Asymmetric synthesis of 1,1′-bis(1-hydroxyalkyl)metallocenes and their derivatization to the novel chiral metallocenes with C_2 symmetry, Tetrahedron Lett 36 (1995) 8991–8994.
[22] G. İftime, J.–C. Daran, E. Manoury, G.G.A. Balavoine, Highly enantioselective one-pot synthesis of chiral tri- and tetrasubstituted ferrocenes from 1,1′-ferrocenedicarbaldehyde, Angew Chem Int Ed Eng 37 (1998) 1698–1701.
[23] N. Taniguchi, M. Uemura, Planar chiral C_2-symmetric bisferrocenes: stereoselective pinacol coupling of α-substituted ferrocenecarboxaldehydes, Tetrahedron Lett 39 (1998) 5385–5388.
[24] X. Li, Q. Li, X. Wu, Y. Gao, D. Xu, L. Kong, Enantioselective hydrogenation of olefins with planar chiral iridium ferrocenyloxazolinylphosphine complexes, Tetrahedron Asymmetry 18 (2007) 629–634.
[25] A. Tarraga, P. Molina, D. Curiel, D. Bautista, Asymmetric synthesis of ferrocenylazido alcohols and their derivatization to novel chiral ferrocenyl-thiazoline ligands with C2- symmetry, Tetrahedron Asymmetry 13 (2002) 1621–1628.
[26] K. Taguchi, H. Nakagawa, T. Hirabayashi, S. Sakaguchi, Y. Ishii, An efficient direct α-alkylation of ketones with primary alcohols catalyzed by $[Ir(cod)Cl]_2$/PPh_3/KOH system without solvent, J Am Chem Soc 126 (2004) 72–73.
[27] G. Onodera, Y. Nishibayashi, S. Uemura, Ir- and Ru-Catalyzed sequential reactions: asymmetric α-alkylative reduction of ketones with alcohols, Angew Chem Int Ed Eng 45 (2006) 3819–3822.
[28] S.E. Clapham, A. Hadzovic, R.H. Morris, Mechanisms of the H_2-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes, Coord Chem Rev 248 (2004) 2201–2237.
[29] Y.-M. Zhang, P. Liu, H.-L. Zhang, The application of chiral diferrocenylphosphine- diimines ligands in the asymmetric transfer hydrogenation of ketones, Synth React Inorg Metal-Org Nano-met Chem 38 (2008) 778–780.
[30] Q.-H. Zeng, X.-P. Hu, Z.-C. Duan, X.-M. Liang, Z. Zheng, Unsymmetrical ferrocenylethylamine-derived Monophosphoramidites: highly efficient chiral ligands for Rh-Catalyzed enantioselective hydrogenation of enamides and α-dehydroamino acid derivatives, J Org Chem 71 (2006) 393–396.
[31] C. Claver, F. Fernandez, A. Gillion, K. Heslop, D. Hylett, A. Martoreli, A.G. Orpen, P.G. Pringle, Biarylphosphonites: a class of monodentatephosphorus(III) ligands that outperform their chelatinganalogues in asymmetric hydrogenation catalysis, Chem Commun (2000) 961–962.
[32] M.T. Reetz, G. Mehler, Highly enantioselective Rh-Catalyzed hydrogenation reactions based on chiral monophosphite ligands, Angew Chem Int Ed Eng 39 (2000) 3889–3890.
[33] M. van den Berg, A.J. Minnaard, E.P. Schudde, J. van Esch, A.H.M. de Vries, J.G. de Vries, B.L. Feringa, Highly enantioselective rhodium-catalyzed hydrogenation with monodentate ligands, J Am Chem Soc 122 (2000) 11539–11540.
[34] X. Jia, X. Li, L. Xu, Q. Shi, X. Yao, A.S.C. Chan, Highly efficient rhodium/monodentate phosphoramidite catalyst and its application in then enantioselective hydrogenation of enamides and α-dehydroamino acid derivatives, J Org Chem 68 (2003) 4539–4541.
[35] A.–G. Hu, Y. Fu, J.–H. Xie, H. Zhou, L.–X. Wang, Q.–L. Zhou, Monodentate chiral spiro phosphoramidites: efficient ligands for rhodium-catalyzed enantioselective hydrogenation of enamides, Angew Chem Int Ed Eng 41 (2002) 2348–2350.
[36] Y. Fu, X.-X. Guo, S.-F. Zhu, A.-G. Hu, J.-H. Xie, Q.-L. Zhou, Rhodium-catalyzed asymmetric hydrogenation of functionalized olefins using monodentate spiro phosphoramidite ligands, J Org Chem 69 (14) (2004) 4648–4655.
[37] D. Pena, A.J. Minnaard, J.G. de Vries, B.L. Feringa, Highly enantioselective rhodium- catalyzed hydrogenation of β-dehydroamino acid derivatives using monodentate phosphoramidites, J Am Chem Soc 124 (49) (2002) 14552–14553.
[38] R. Guo, X. Chen, C. Elphelt, D. Song, R.H. Morris, Applications of ruthenium hydride borohydride complexes containing phosphinite and diamine ligands to asymmetric catalytic reactions, Org Lett 7 (2005) 1757–1759.
[39] M. Aydemir, N. Meric, A. Baysal, B. Gümgüm, M. Toğrul, Y. Turgut, A modular design of ruthenium(II) catalysts with chiral C2-symmetric phosphinite ligands for effective asymmetric transfer hydrogenation of aromatic ketones, Tetrahedron Asymmetry 21 (2010) 703–710.
[40] T. Ohta, H. Takaya, R. Noyori, Bis(diarylphosphino)-1,1 binaphthyl (BINAP)-ruthenium(II) dicarboxylate complexes: new, highly efficient catalysts for asymmetric hydrogenations, Inorg Chem 27 (1988) 566–569.
[41] R.H. Grubbs, R.A. DeVries, Asymmetric hydrogenation by an atropisomeric diphosphinite rhodium complex, Tetrahedron Lett. 18 (1977) 1879–1880.
[42] K. Murata, T. Ikariya, New chiral rhodium and iridium complexes with chiral diamine ligands for asymmetric transfer hydrogenation of aromatic ketones, J Org Chem 64 (1999) 2186–2187.
[43] S.J. Roseblade, A. Pfaltz, Iridium-catalyzed asymmetric hydrogenation of olefins, Acc Chem Res 40 (2007) 1402–1411.
[44] Values based on www.platinum.matthey.com. (Accessed 09.03.2016).
[45] G. Mestroni, G. Zassinovich, A. Camus, F. Martinelli, Transfer of hydrogen from alcohols to ketones catalyzed by iridium complexes with 2,2′-bipyridine, 1,10-phenanthroline, and their derivatives, J Organomet Chem 198 (1980) 87–96.
[46] F. Martinelli, G. Mestroni, A. Camus, G. Zassinovich, $[Ir(3,4,7,8\text{-}Me_4phen)(CH_2{=}CH_2)_2Cl]$: a very active catalyst precursor for hydrogen transfer from alcohols to unsaturated organic substrates, J Organomet Chem 220 (1981) 383–392.
[47] R. Spogliarich, G. Zassinovich, J. Kaspar, M. Graziani, Asymmetric transfer hydrogenation of ketones catalyzed by iridium(I) complexes, J Mol Catal 16 (1982) 359–361.
[48] P. Kvintovichs, J. Bakos, B. Heil, Asymmetric transfer hydrogenation of ketones catalyzed by iridium(I) and rhodium(I) complexes, J Mol Catal 32 (1985) 111–114.
[49] M. Aydemir, A. Baysal, S. Özkar, L.T. Yıldırım, trans- and cis-Ru(II) aminophosphine complexes: syntheses, X-ray structures and catalytic activity in transfer hydrogenation of acetophenone derivatives, Inorg Chim Acta 367 (1) (2011) 166–172.
[50] A. Patti, S. Pedotti, Screening of chiral ferrocenyl amino alcohols as ligands for ruthenium-catalysed transfer hydrogenation of ketones, Tetrahedron Asymmetry 14 (2003) 597–602.
[51] T. Sammakia, E.L. Stangeland, Transfer hydrogenation with ruthenium complexes of chiral (Phosphinoferrocenyl)oxazolines, J Org Chem 62 (1997) 6104–6105.
[52] L. Schwink, T. Ireland, K. Püntener, P. Knockel, New C2-symmetrical ferrocenyl diamines as ligands for ruthenium catalyzed transfer hydrogenation, Tetrahedron Asymmetry 9 (1998) 1143–1163.
[53] P.W. Galka, H.-B. Kraatz, Synthesis and study of amino acid based phosphinite ligands, J Organomet Chem 674 (2003) 24–31.
[54] M. Aydemir, A. Baysal, E. Şahin, B. Gümgüm, S. Özkar, Aminophosphine–palladium(II) complexes: synthsesis, structure and applications in Suzuki and Heck cross-coupling reactions, Inorg Chim Acta 378 (2011) 10–18.
[55] M. Aydemir, A. Baysal, N. Meric, B. Gümgüm, New active ruthenium(II) complexes based N3,N3′-bis(diphenylphosphino)-2,20-bipyridine-3,3′-diamine and P,P'- diphenylphosphinous acid-P,P′-[2,2'-bipyridine]-3,3'-diyl ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol, J Organomet Chem 694 (2009) 2488–2492.
[56] D. Elma, F. Durap, M. Aydemir, A. Baysal, N. Meriç, B. Ak, Y. Turgut, B. Gümgüm, Screening of C_2-symmetric chiral phosphinites as ligands for ruthenium(II)-catalyzed asymmetric transfer hydrogenation of prochiral aromatic ketones, J Organomet Chem 729 (2013) 46–52.
[57] M. Aydemir, N. Meric, A. Baysal, B. Gümgüm, M. Toğrul, Y. Turgut, A modular design of ruthenium(II) catalysts with chiral C2-symmetric phosphinite ligands for effective asymmetric transfer hydrogenation of aromatic ketones, Tetrahedron Asymmetry. 21 (2010) 703–710.
[58] M. Aydemir, N. Meric, A. Baysal, C. Kayan, M. Toğrul, B. Gümgüm, New chiral phosphinite ligands with C_2-symmetric axis and their possible applications in Ru-catalyzed asymmetric transfer hydrogenation, Appl Organomet Chem 24 (2010) 215–221.
[59] M. Aydemir, N. Meric, F. Durap, A. Baysal, M. Toğrul, Asymmetric transfer hydrogenation of aromatic ketones with the ruthenium(II) catalyst derived from C_2 symmetric N,N0- bis[(1S)-1-benzyl-2-O-(diphenylphosphinite)ethyl] ethanediamide, J Organomet Chem 695 (2010) 1392–1398.
[60] M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldağ, B. Gümgüm, S. Özkar, L.T. Yıldırım, Novel neutral phosphinite bridged dinuclear ruthenium(II) arene complexes and their catalytic use in transfer hydrogenation of aromatic ketones: X-ray structure of a new Schiff base, N3,N3-di-2-hydroxybenzylidene-[2,2]bipyridinyl-3,3-diamine, J Mol Catal A Chem 326 (2010) 75–81.
[61] M.J. McKennon, A.I. Meyers, K. Drauz, M. Schwarm, A convenient reduction of amino acids and their derivatives, J Org Chem 58 (1993) 3568–3571.
[62] Y. Turgut, H. Hoşgören, Synthesis of chiral monoaza-15-crown-5 ethers from l-valinol and the enantiomeric recognition of chiral amines and their perchlorates salts, Tetrahedron Asymmetry 14 (2003) 3815–3818.
[63] J.-H. Jia, X.-M. Tao, Y.-J. Li, W.-J. Sheng, L. Han, J.-R. Gao, Y.-F. Zheng, Synthesis and third-order optical nonlinearities of ferrocenyl Schiff base, Chem Phys

Lett 514 (2011) 114–118.
[64] S. Bastin, F. Agbossou-Niederncorn, J. Brocard, L. Pelinski, Enantioselective alkylation of benzaldehyde with diethylzinc catalyzed by 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols, Tetrahedron Asymmetry 12 (2001) 2399–2408.
[65] B. Ak, D. Elma, N. Meriç, C. Kayan, U. Işık, M. Aydemir, F. Durap, A. Baysal, New chiral ruthenium(II)-phosphinite complexes containing a ferrocenyl group in enantioselective transfer hydrogenation of aromatic ketones, Tetrahedron Asymmetry 24 (2013) 1257–1264.
[66] B. Ak, M. Aydemir, Y.S. Ocak, F. Durap, C. Kayan, A. Baysal, H. Temel, Readily available ferrocenyl-phosphinite ligands for Ru(II)-catalyzed enantioselective transfer hydrogenation of ketones and fabrication of hybrid heterojunctions, Inorg Chim Acta 409 (2014) 244–253.
[67] A. Baysal, M. Aydemir, F. Durap, B. Gümgüm, S. Özkar, L.T. Yildırım, Synthesis and characterizations of 3,3′-bis(diphenylphosphinoamine)-2,2′-bipyridine and 3,3'bis(diphenylphosphinite)-2,2'-bipyridine and their chalcogenides, Polyhedron 26 (2007) 3373–3378.
[68] M.S. Balakrishna, R. McDonald, Synthesis, spectroscopic study and X-ray crystal structure of unsymmetrical bis(phosphine)-platinum complex, $[PtCl_2\{\eta^2$- $Ph_2POCH_2CH_2N(CH_3)PPh_2]$, Inorg Chem Commun 5 (2002) 782–786.
[69] P. Bergamini, V. Bertolasi, M. Cattabriga, V. Ferretti, U. Loprieno, N. Mantovani, L. Marvelli, Template synthesis of chiral vicinal diphosphinites as their Pt^{II} and Pd^{II} complexes, Eur J Inorg Chem (2003) 918–925.
[70] I.D. Kostas, Synthesis of new nitrogen-containing phosphinite and phosphine– phosphinite ligands. Application to rhodium-catalyzed hydroformylation of styrene, Inorg Chim Acta 355 (2003) 424–427.
[71] G. Esquius, J. Pons, R. Yanez, J. Ros, Organometallic rhodium (I) complexes with 1- alkylaminopyrazole ligands, J Organomet Chem 619 (2001) 14–23.
[72] E. Hauptman, R. Shapiro, W. Marshall, Synthesis of chiral bis(phosphinite) ligands with a tetrahydrothiophene Backbone: use in asymmetric hydrogenation, Organometallics 17 (1998) 4976–4982.
[73] K. Ruhlan, P. Gigler, E. Herdtweck, Some phosphinite complexes of Rh and Ir, theirintramolecular reactivity and DFT calculations about their application in biphenylmetathesis, J Organomet Chem 693 (2008) 874–893.
[74] E.A. Broger, W. Burkart, M. Hennig, M. Scalone, R. Schmid, New amidophosphine-phosphinites (tLANOPs) as chiral ligands for asymmetric hydrogenation reactions, Tetrahedron Asymmetry 9 (1998) 4043–4054.
[75] G. Esquius, J. Pons, R. Yanez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugan, Synthesis of a new potentially hemilabile ligand: 1-[2-(Diphenylphosphanyl) ethyl]-3,5-dimethylpyrazole, and comparison of its bonding properties with the related 1-[2-(Ethylamino)ethyl]-3,5-dimethylpyrazole ligand toward Rh^{I}, Eur J Inorg Chem (2002) 2999–3006.
[76] G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts, Chem Rev 92 (1992) 1051–1069.
[77] R. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, Acc Chem Res 30 (1997) 97–102.
[78] D. Liu, W. Li, X. Zhang, A novel chiral ferrocenyl phosphine ligand from Sugar: applications in Rh-Catalyzed asymmetric hydrogenation reactions, Org Lett 4 (25) (2002) 4471–4474.
[79] N.W. Boaz, J.A. Ponasic Jr., S.E. Large, A versatile synthesis of phosphine–aminophosphine ligands for asymmetric catalysis, Tetrahedron Asymmetry 16 (2005) 2063–2066.
[80] J.-H. Xie, Q.-L. Zhou, Chiral diphosphine and monodentate phosphorus ligands on a spiro scaffold for transition-metal-catalyzed asymmetric reactions, Acc Chem Res 41 (2008) 581–593.
[81] V. Turcry, C. Pasquier, F. Agbossou-Niedercorn, Aminophosphine phosphinite (AMPP) and enantioselective hydrogenation of ketones: further developments, C R Chim 6 (2003) 179–184.
[82] M. Alvarez, N. Lugan, R. Mathieu, Synthesis and evaluation of the bonding properties of a potentially tridentate ligand: 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane, J Chem Soc Dalton Trans (1994) 2755–2760.
[83] G. Venkatachalam, R. Ramesh, Ruthenium(III) Schiff base complexes of [ONNO]-type mediated transfer hydrogenation of ketones, Inorg Chem Commun 8 (2005) 1009–1013.
[84] M. Aydemir, F. Durap, C. Kayan, A. Baysal, Y. Turgut, Bis(phosphinite) with C_2-Symmetric Axis; effects on the ruthenium(II)- catalyzed asymmetric transfer hydrogenation of acetophenone derivatives, Synlett 23 (2012) 2777–2784.
[85] F. Durap, M. Aydemir, D. Elma, A. Baysal, Y. Turgut, New C2-symmetric chiral phosphinite ligands based on amino alcohol scaffolds and their use in the ruthenium- catalysed asymmetric transfer hydrogenation of aromatic ketones, C R Chim 16 (2013) 363–371.
[86] J. Takehara, S. Hashiguchi, A. Fujii, S.-ichi. Inoue, T. Ikariya, R. Noyori, Amino alcohol effects on the ruthenium(II)-catalysed asymmetric transfer hydrogenation of ketones in propan-2-ol, J Chem Soc Chem Commun (1996) 233–234.
[87] S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya, R. Noyori, Kinetic resolution of racemic secondary alcohols by Ru^{II}-catalyzed hydrogen transfer, Angew Chem Int Ed Engl 36 (1997) 288–290.
[88] T. Ikariya, A.J. Blacker, Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts, Acc Chem Res 40 (2007) 1300–1308.
[89] H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, F.A. England, T. Ikariya, R. Noyori, trans-[RuCl2(phosphane)2(1,2-diamine)] and chiral trans-[RuCl2(diphosphane)(1,2-diamine)]: shelf-stable precatalysts for the rapid, productive, and stereoselective hydrogenation of ketones, Angew Chem Int Ed Engl 37 (1998) 1703–1707.
[90] E.P. Kelson, P.P. Phengsy, Synthesis and structure of a ruthenium(II) complex incorporating κN bound 2-pyridonato ligands; a new catalytic system for transfer hydrogenation of ketones, J Chem Soc Dalton Trans (2000) 4023–4024.
[91] J.-S. Chen, Y.-Y. Li, Z.-R. Dong, B.-Z. Li, J.-X. Gao, Asymmetric transfer hydrogenation of aromatic ketones catalyzed by the iridium hydride complex under ambient conditions, Tetrahedron Lett 45 (2004) 8415–8418.
[92] J. Hannedouche, G.J. Clarkson, M. Wills, A new class of “tethered” ruthenium(II) catalyst for asymmetric transfer hydrogenation reactions, J Am Chem Soc 126 (2004) 986–987.
[93] J.-X. Gao, t. Ikariya, R. Noyori, A ruthenium(II) complex with a C_2-Symmetric diphosphine/diamine tetradentate ligand for asymmetric transfer hydrogenation of aromatic ketones, Organometallics 15 (1996) 1087–1089.
[94] P. Gamez, F. Fache, M. Lemaire, Asymmetric catalytic reduction of carbonyl compounds using C_2 symmetric diamines as chiral ligands, Tetrahedron Asymmetry 6 (1995) 705–718.
[95] Y. Jiang, Q. Jiang, X. Zhang, A new chiral bis(oxazolinylmethyl)amine ligand for Ru- catalyzed asymmetric transfer hydrogenation of ketones, J Am Chem Soc 120 (1998) 3817–3818.
[96] K.–J. Haack, S. Hashiguchi, A. Fuji, T. Ikariya, R. Noyori, The catalyst precursor, catalyst, and intermediate in the Ru^{II}-promoted asymmetric hydrogen transfer between alcohols and ketones, Angew Chem Ed Engl 36 (1997) 285–288.
[97] J.W. Faller, A.R. Lavoie, Catalysts for the asymmetric transfer hydrogenation of ketones derived from l-prolinamide and $(p\text{-}CymeneRuCl_2)_2$ or $(Cp^*RhCl_2)_2$, Organometallics 20 (2001) 5245–5247.
[98] İ. Özdemir, S. Yaşar, B. Çetinkaya, Ruthenium(II) N-heterocyclic carbene complexes in the transfer hydrogenation of ketones, Trans Met Chem 30 (2005) 831–835.
[99] C. White, A. Yates, P.M. Maitlis, M. Heinekey, (η5-Pentamethylcyclopentadienyl) rhodium and -iridium compounds, Inorg Synth 29 (1992) 228–234.