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ARTICLE

An Iron Variant of the Noyori Hydrogenation Catalyst for the Asymmetric Transfer Hydrogenation of Ketones

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We report the design of new iron catalysts for the asymmetric transfer hydrogenation of ketones. This type of iron catalyst combines the structural characteristics of the Noyori hydrogenation catalyst (an axially chiral 2,2′-bis(phosphino)-1,1′-binaphthyl fragment and the metal-ligand bifunctional motif) and an ene(amido) group that can activate the iron center. After activation by 8 equivalents of potassium *tert*-butoxide, (S_A,R_P,*SS*)-**7a** and (S_A,R_P,*SS*)-**7b** are active but nonenantioselective catalysts for the transfer hydrogenation of acetophenone and α,β-unsaturated aldehydes at room temperature in isopropanol. A maximum turnover number of 14480 were observed for (S_A,R_P,*SS*)-**7a** in the reduction of acetophenone. The right combination of stereochemistry of the axially chiral 2,2′-bis(phosphino)-1,1′-binaphthyl group and the carbon-centered chiral amine-imine moiety in (S_A,R_P,*RR*)-**7b'** afforded a enantioselective catalyst for the preparation of chiral alcohols with moderate to good yields and broad functional group tolerance.

Introduction

Chiral alcohols are important feedstocks in fields such as the pharmaceutical, fragrance, and agrochemical industries. Asymmetric reduction, including hydrogenation, transfer hydrogenation and hydrosilylation of ketones catalyzed by homogeneous catalysts that are mainly based on precious metals, is currently a powerful tool for accessing these important chiral compounds.[1, 2] However, their limited availability and toxicity as well as the difficulty in removing these species from the final product have hampered the wide implementation of precious metal catalysts in industry. Iron could be an inexpensive and environmentally friendly substituent because iron is earth-abundant, nontoxic and essential to various biological processed.[3-32]

Therefore, many iron catalysts are currently being developed for asymmetric, high pressure and transfer hydrogenations as well as hydrosilylations.[33-35] Gao's group reported the *in situ* generation of chiral and heterogeneous iron catalysts from trinuclear iron carbonyl clusters with either tetradentate open-chain or macrocyclic multidentate P,N ligands for both asymmetric hydrogenation and transfer hydrogenation of a series of ketonic substrates with enantioselectivities approaching or exceeding those obtained by precious metal catalysts.[36-38] Morris et al. reported the first asymmetric hydrogenation and transfer hydrogenation with structurally defined iron complexes bearing tetradentate diiminodiphosphine and diaminodiphosphine ligands.[39, 40] Later, additional analogues of the tetradentate P-N-N-P iron complex catalysts were developed by the same group.[41, 42] Casey and others reported the use of structurally well-defined achiral or chiral Knölker's iron complexes in the high pressure hydrogenation and transfer hydrogenation of a series of carbonyl derivatives by mimicking the metal-ligand bifunctional pathway that occurs across the metal center and the hydroxyl group in the cyclopentadiene ligand.[43, 44] Mezzetti et al. reported a series of macrocyclic iron(II)/$(NH)_2P_2$ complexes that were sterically and electronically tuned by *bis*(isonitrile) ligands for the highly enantioselective transfer hydrogenation of aryl-alkyl ketones in isopropanol at elevated temperature (40 – 75 °C); these catalysts offered both outstanding enantioselectivities (up to 99% ee) and good catalytic activities (up to 9430 h^{-1}).[45-49] Hydrido carbonyl iron complexes bearing pyridine-based pincer ligands that are capable of metal-ligand cooperation *via* aromatization/dearomatization were reported by Milstein et al. for the hydrogenation of ketone and aldehydes under mild conditions with good reactivity and turnover numbers.[50-52]

Despite the significant advances made in the development of iron catalysts for carbonyl reduction,[37, 41, 48, 53-71] there is still need for the development of new, reactive and stereoselective catalysts. For the reduction of polar carbonyl groups, in addition to aromatization/dearomatization pathways,[50-52] the most widely used approach to iron catalyst design is the involvement of a metal-ligand bifunctional mechanism that involves cooperation between the metal and the active sites of the ligand.[2, 72] In addition, strong field ligands, such as phosphine, CO and isonitriles, are frequently introduced to keep the iron center in a low spin state to avoid the spin crossover-related reaction barriers that would otherwise occur.[5, 73] We have reported amido-ene(amido) diphosphine carbonyl iron catalysts (**A** and **B, Fig. 1**)[74] that possess carbon-centered chirality derived from the S,S-1,2-diphenyl-1,2-ethanediamine (S,S-dpen) skeleton for the efficient transfer hydrogenation of a series of prochiral ketones and activated imines. The turnover frequency was found to be as high as 242 s^{-1}.

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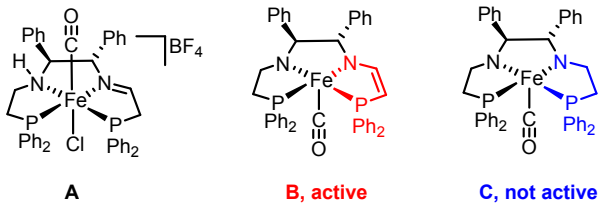

Fig. 1 Previously reported active iron catalysts with chiral ligands with C-centered chirality. **A**, the amine(imine)diphosphine iron complex precatalyst; **B**, the active amido-ene(amido) iron catalyst; and **C**, the inactive bis(amido) iron complex.[75]

The mechanistic study revealed the important role of the ene(amido) group in enabling the high catalytic reactivity, as the *bis*(amido) analogue (**C, Fig. 1**), produced by the reduction of the ene(amido) group with isopropanol in the absence of an additional base, is totally inactive.[75] A recent study on the electronic structures of the amido-ene(amido) diphosphine carbonyl iron complexes revealed the presence of π-backdonation between the iron and the ene(amido) group. This covalent metal-ligand bonding facilitates a flexible electron density transfer between the iron center and the ligands in the catalytic intermediates. Therefore, these reactive species are stabilized against deactivation.

However, one shortcoming that prevents the previous iron catalysts (**A**)[74] from being practically useful is their relatively low asymmetric induction capabilities. 2,2′-bis(phosphino)-1,1′-binaphthyl ligands have exhibited excellent asymmetric induction

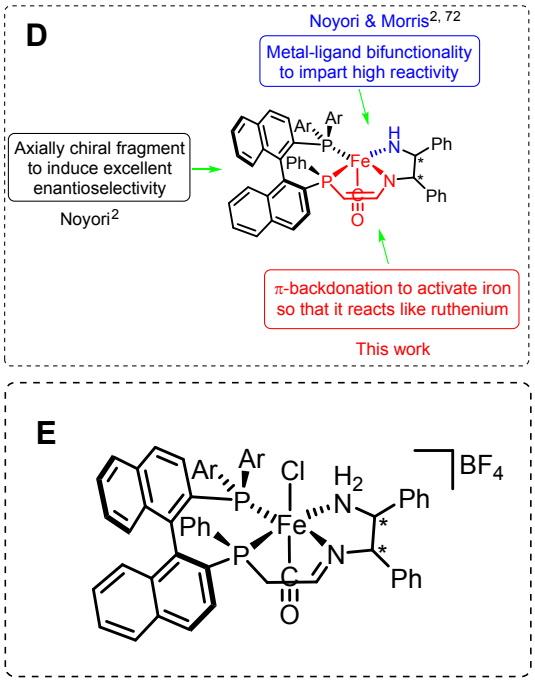

Fig. 2 The structure of the Noyori hydrogenation catalyst-type iron catalyst (**D**) and the precatalyst (**E**).

capabilities in various transition metal-catalyzed reactions. We speculated that the combination of the 2,2′-bis(phosphino)-1,1′-binaphthyl skeleton, the ene(amido) group and the metal-ligand bifunctional structural motif may lead to the development of reactive as well as enantioselective iron catalysts for asymmetric transfer hydrogenations. We report here that when combined with the highly stereo-inductive 2,2′-*bis*(phosphino)-1,1′-binaphthyl fragment, the ene(amido) group, together with a carbonyl ligand, is able to activate the iron center to achieve both reactivity and good enantioselectivity in the asymmetric transfer hydrogenation of a series of ketone substrates. The structure of this Noyori hydrogenation catalyst-type iron catalyst is shown in **Fig. 2**.

Results and discussion

The synthesis and characterization of the iron complexes

As shown in **Scheme 1**, the target iron complexes were synthesized *via* a template reaction between the 2-phosphino substituted acetaldehyde and chiral dpen in the presence of an iron cation, forming the *bis*(acetonitrile) cationic iron(II) complex. This was followed by a ligand substituent reaction between acetonitrile and CO and a chloride anion. The key step is to obtain the 2-phosphino-substituted acetaldehyde, which combines both the axial chirality of the 1,1′-binaphthyl skeleton and a P-chirogenic[76-84] moiety. This includes two challenges: (1) the diastereoselective and clean introduction of the P-chiral phosphino group into the axially chiral binaphthyl scaffold with a high yield and (2) the introduction of an aldehyde group in the presence of reactive phosphino groups. We developed a new strategy to diastereoselectively and cleanly install the P-chirogenic substituent into the 1,1′-binaphthyl scaffolds to prepare new 2,2′-bis(phosphino)-1,1′-binaphthyl analogues that possess both axial chirality and P-centered chirality. The proposed mechanism is shown in the Electronic Supporting Information (**Scheme S1**). We also developed a strategy that utilized a Sn^nBu_3 group as the precursor of a lithium salt for the subsequent introduction of an aldehyde group. This synthetic method has an acceptable overall yield.

The key starting material for the synthesis of the chirality-hybrid compound (**2**) is (S_A)-2-bromo-2′-phosphinyl-1,1′-binaphthyl (**1**). **1** was prepared by C-P nucleophilic substitutions between chlorodiarylphosphine and (S_A)-2-lithium-2′-bromo-1,1′-binaphthyl and oxidation by H_2O_2, instead of the commonly utilized metal-catalyzed C-P cross-coupling reactions.[85-88] (S_A)-2-Lithium-2′-bromo-1,1′-binaphthyl was accessed by the reaction of (S_A)-2,2′-dibromo-1,1′-binathyl and 1.1 equivalents of *n*-butyl lithium at a low temperature (-90 °C) in THF within 5 – 15 min. Fortunately, no racemization of the axial chirality was observed during this lithium-bromide exchange or during the following C-P bond formation step, as indicated by high-performance liquid chromatography (HPLC) analysis (see the Electronic Supplementary Information for details in **Chart S1**, **Fig. S3 and Table S1**). A second lithium-bromide exchange reaction on **1** and subsequent sequential quenching reactions with

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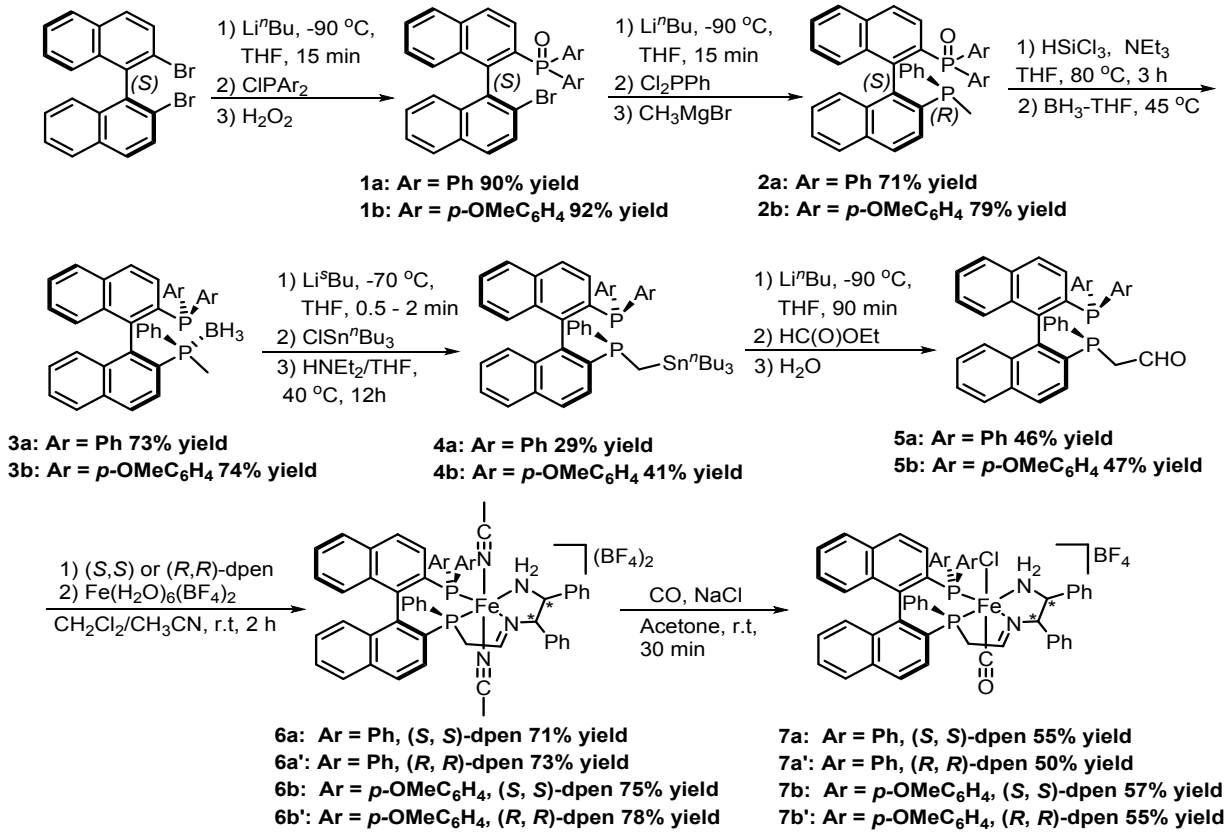

Scheme 1 The syntheses of iron complexes bearing axially chiral (S_A)-2,2'-bis(phosphino)-1,1'-binaphthyl, imine, C-centered chiral amine and carbonyl groups.

dichloroarylphosphine and methyl magnesium bromide afforded **2** in high yields, with only one diastereomer being formed. Similarly, no erosion of the axial chirality was observed. Compound **2** can be deoxygenated by either a mixture of trichlorosilane and triethyl amine in a ratio of 1:20:5 at 80 °C in THF for 3 hours or by a combination of $CeCl_3/NaBH_4/LiAlH_4$ in a ratio of 1:5:5:3 at low temperature (-90 °C) in THF.[89] Negligible racemization of the P-chirality was observed in the trichlorosilane/triethyl amine process, while the chirality of the phosphine group was unaffected when the $CeCl_3/NaBH_4/LiAlH_4$ reducing agent was employed. Deoxygenated product (S_A,R_P)-2-(methyl)(phenyl)phosphino-2'-diphenylphosphino-1,1'-binaphthyl was further reacted with one equiv. of BH_3-THF adduct in THF overnight to afford borane-phosphine adduct **3** in approximately 80% yield. The mono-phosphine protection of **3** was crucial for the following reaction, because the *bis*(boranato) adduct does not give the target product but affords unknown side products. The deprotonation of the acidic CH_3 group was facilitated by borane coordination, and the subsequent electrophilic quenching of the reactive lithium intermediate with chlorotributyltin lead to the formation of important intermediate **4** in approximately 40% yield after deboranation and purification by silica gel chromatography. The lithium-tin exchange between **4** and *n*-butyl lithium in THF at low temperature (-90 °C) led to the formation of an important lithium intermediate, which quantitatively affords the 2-phosphino-substituted acetaldehyde (**5**) after sequential quenching reactions with excess ethyl formate at -90 °C for 5 min and H_2O in THF at room temperature for 5 min. Notably, attempts to directly introduce an aldehyde group into the borane-phosphine adduct (**3**) led to reduction of the aldehyde group by the BH_3 protecting group. The aldehyde group of **5a** shows a multiplet C-H signal at δ 9.28 ppm in its ^{1}H NMR spectrum due to the coupling with both the geminal CH_2 protons and the P nuclei. The $^{31}P\{^1H\}$ NMR spectrum of **5a** exhibits two phosphorus resonances at -15.31 and -38.06 ppm with a P-P coupling of 16.2 Hz. A similar NMR spectral pattern was observed for **5b**.

Bis(acetonitrile) cationic iron(II) complex **6** was prepared by the reaction of **5**, $Fe(H_2O)_6(BF_4)_2$ and (*S*,*S*)-dpen or (*R*,*R*)-dpen in acetonitrile. Complex **6a** was obtained as a single compound in acetonitrile and showed two coupled ^{31}P signals at 52.49 and 63.34 ppm with a ^{PP}J coupling of 35.4 Hz in its $^{31}P\{^1H\}$ NMR spectrum. Complex **6a'** was obtained with two sets of phosphorus resonances in its $^{31}P\{^1H\}$ NMR spectrum (53.73, 68.49, ^{PP}J = 39.6 Hz; 52.97, 55.35,

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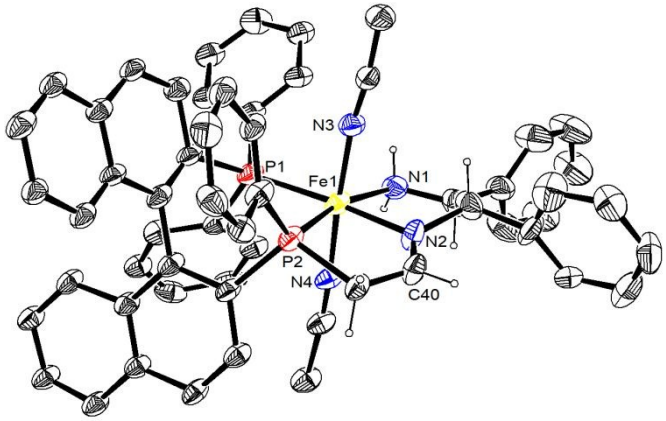

Fig. 3 The molecular structure of (S_A,R_P,*SS*)-**6a** with the thermal ellipsoids set at 10% probability. Aromatic ring protons and the two BF_4 counter anions have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Fe1–N1 2.065(7), Fe1–N2 2.005(8), Fe1–N3 1.894(8), Fe1–N4 1.858(8), Fe1–P1 2.365(3), Fe1–P2 2.235(3), C40–N2 1.313(11), P1–Fe1–P2 95.36(10), P1–Fe1–N1 98.8(3), P2–Fe1–N2 82.0(3), N1–Fe1–N2 83.6(4)

^{PP}J = 54.6 Hz) in a 1:2 ratio. Unlike our previous synthetic procedure, which employed methanol as the solvent to accelerate the reaction, complex **6** is only stable in acetonitrile. A single crystal of **6a** suitable for X-ray diffraction was obtained by slow diffusion of diethyl ether into a dilute reaction solution. A further ligand exchange reaction of **6a** was conducted in acetone under 1 atm of carbon monoxide and in the presence of excess sodium chloride to afford complex **7a** as a single isomer. **7a** exhibited $^{31}P\{^1H\}$ resonances at 62.01 and 58.18 ppm with a ^{PP}J coupling of 55.7 Hz and showed a CO stretch at 1980 cm^{-1} in its FT-IR spectrum. Interestingly, the two sets of phosphorus resonances of **6a'** gave only one set of phosphorus resonances of **7a'** after the ligand substitution reaction. Two doublets at 58.22 and 59.14 ppm with a ^{PP}J coupling of 53.5 Hz were observed in the $^{31}P\{^1H\}$ NMR spectrum of **7a'**, and a similar CO stretching vibration at 1982 cm^{-1} was observed in the FT-IR spectrum. The structures of complexes **7a** and **7a'** were further confirmed by high-resolution mass spectrometry. The fragmentation patterns and spectroscopic data of the products of **6b**, **6b'**, **7b** and **7b'** are similar to those of **6a**, **6a'**, **7a** and **7a'**, respectively. Complex **7** was purified by crystalization in dichloromethane/diethyl ether.

The structure of the (S_A,R_P,*SS*)-*bis*(acetonitrile) complex **6a** was determined by single-crystal X-ray diffraction, and the molecular structure of the cation is shown in **Fig. 3**. This is the first example of a BINAP mononuclear iron complex and the second example of an iron complex chelating with BINAP-derived phosphorus ligands.[90] The iron is coordinated in a distorted octahedral fashion, and both the (S_A)-2,2'-bis(phosphino)-1,1'-binaphthyl and the *S*,*S*-dpen ligands were coordinated in a *δ* conformation.[91]

The catalytic results

Catalysts **7a**-**7b'** were initially evaluated for the asymmetric transfer hydrogenation of acetophenone using isopropanol as the solvent and hydrogen source (**Table 1**). Precatalysts **7a**-**7b'** were all active for the asymmetric transfer hydrogenation of acetophenone after being activated with 8 equiv. of potassium tert-butoxide. Notably, for (S_A,R_P,*SS*)-**7a**, a substrate/precatalyst ratio of 21300:1 and 42600:1 gave a maximum turnover number of 10650 and 14480 within 3 minutes, respectively. It was found that **7a** was more active than our previous active catalyst **A**[74] under the same condition, but it stayed active only for approximately 3 minutes. No further improvement on the reaction yield was observed with longer reaction time. Unfortunately, the 1-phenylethanol product was obtained as the racemate instead of a highly enantioenriched one. Similar reactivity and selectivity were observed for (S_A,R_P,*SS*)-**7b**. However, fortunately, (S_A,R_P,*RR*)-**7a'**, having the dpen skeleton with the opposite central chirality, stayed active for longer time (approximately 3 hours) and produced enantioenriched (*R*)-1-phenylethanol (82% ee), albeit with a much lower catalytic activity. Precatalyst (S_A,R_P,*RR*)-**7b'** showed much better enantioselectivity (*R*, 93%) than **7a'** but lower reactivity was seen. These results indicate that when combined with metal-ligand bifunctional chemistry, the ene(amido) group (together with a CO ligand) can activate iron to efficiently catalyze asymmetric transfer hydrogenation reactions.

The homogeneity of this iron-catalysed reaction was assumed based on several experimental observations. First, the addition of either 300 equiv. of mercury or 0.5 equiv. of trimethylphosphine[92] to the reaction mixture of **7a'** after 1 h of reaction did not affect the reaction and the analysis on the three-hour reaction showed the same yield and enantioselectivity of (*R*)-1-phenylethanol to those observed under the unmodified reactions (Table 1, entry 4). Second, the $^{31}P\{^1H\}$ NMR spectrum of the one-hour catalytic reaction on **7a'** revealed the presence of one set of doublets at *δ* 82.90, 71.64 ppm with a ^{PP}J coupling constant of 48.6 Hz, although some other unidentified signals that are derived from catalyst deactivation were also observed (see the Electronic Supplementary Information for details in **Fig. S30**). This is a typical resonance of either amido-ene(amido) iron carbonyl complex (**B**, **Fig. 1**) or the corresponding amino hydrido iron intermediate that have been observed in this type of iron-catalysed reactions.[74] The possibility of contaminations of more active metals in this transformation was ruled out by a trace metal analysis (ICP analysis) on complex **7a**, where only iron was detected (see the Electronic Supplementary Information for details in **Fig. S60**). Different from the situation of transition metal catalysis with P-chirogenic ligands,[93-102] the influence of P-chirality on the catalytic performances was indirect in the series of **7a**-**7b'**. The aim of introduction of a P-chirogenic centre in these iron complexes is to construct a planar P-N-NH-P coordination plane that is structurally reminiscent of either Noyori hydrogenation catalyst[103-107] or the previous amino(imino)diphosphine iron catalyst.[74] The preliminary results revealed that the inverse of the P-chirality in the P-N-NH-P ligand will lead to the formation of a twisted P-N-NH-P coordination plane in the new iron complex which has a *cis*-located

bis(acetonitrile)

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Table 1 Precatalyst screening and reaction condition optimization for the asymmetric transfer hydrogenation of acetophenone using potassium tert-butoxide as the base.[a]

Precatalyst	Substrate /precatalyst	Time at maximum yield	Maximum yield and TON	Enantiomeric Excess at Maximum yield
7a	21300	3 min	50%, 10650	0%
A	21300	10 min	72%, 15300	60%, (R)
7a	42600	3 min	34%, 14480	0%
7a'	21300	3 h	9%, 1870	82%, (R)
7b	21300	3 min	41%, 8650	0%
7b'	21300	3 h	8%, 1620	93%, (R)

[a]General conditions: [precatalyst]= 6.02×10^{-5} M, [KO^{t}Bu] = 4.82×10^{-4} M, [isopropanol] = 11.1 M, 25 °C.

ligands.[108, 109] In this case, the stereo induction behaviour will otherwise be determined by the steric bulkiness on the chiral P-donor and the chirality on the diamine moiety, and the chirality induction capability of the binaphthyl ligand was lost.

In addition to acetophenone and similar to the case of **A**,[74] (S_A,R_P,*SS*)-**7a** can also mediate the reduction of aldehydes with high reactivity and high turnover numbers. The exclusive preferential reduction of C=O over C=C was observed in the reduction of α,β-unsaturated aldehydes (cinnamaldehyde and citral) to afford unsaturated alcohols that are important starting materials in the perfume and pharmaceutical industries.[110-112] This beneficial chemoselectivity was attributed to the known metal-ligand bifunctional mechanism that was operative in our previous processes and was not observed in related iron catalytic systems, which are mechanistically heterogeneous or undefined.[110] (S_A,R_P,*RR*)-**7b'** was found to be enantioselective for a series of substituted acetophenones, and the corresponding *R*-enriched alcohols were generally obtained with moderate to good turnover numbers and enantiomeric excess of >90%, which is significantly improved compared to the results obtained with **A**.[74] The standard conditions employed 0.023 mol% of the iron complex precursor and 8 equivalents of KO^{t}Bu with a catalyst concentration of 3.00×10^{-4} M in isopropanol at 25 °C. In general, the introduction of bulky substituents at the meta-position of the phenyl group of acetophenone led to some reactivity and good enantioselectivity, similar to what is observed with iron catalysts having *bis*(isonitrile) ligands.[113] The catalytic performances in terms of reactivity and enantioselectivity were less influenced by the electronic properties of the substituent at that position, as both electron-donating groups, such as NMe_2 and OMe, and electron-withdrawing groups, including chloride, bromide and nitrile, provided similar results. The relatively lower TON observed with 3'-CN acetophenone was due to the lower solubility of the substrate in isopropanol. Thus, 3'-methylacetophenone yield the corresponding *R*-enriched alcohol with 55% yield and an ee of 96% under the standard conditions. The tolerance of nitrile groups in the synthesis of (*R*)-1-(3'-cyanophenyl) ethanol makes the current iron-catalyzed process versatile in the preparation of a series of functionalized chiral alcohols by further functionalization of the nitrile group. With (S_A,R_P,*RR*)-**7b'**, 5-acetylindan was hydrogenated to the R-alcohol with an ee of 97%. The reduction of 2-acetyl-5,6,7,8-tetrahydronaphthalene with (S_A,R_P,*RR*)-**7b'** afforded (*R*)-5,6,7,8-tetrahydro-α-methyl-2-naphthalenemethanol with 43% yield and an ee of 94%. Subjecting 2-acetonaphthone to the same catalytic reaction conditions furnished (*R*)-1-(2-naphthyl)-1-ethanol in 93% ee, which is significantly improved compared to the results with our previous PNNP iron catalyst (**A**).[74]

A series of industrially and synthetically useful chiral alcohols can be prepared with good enantiopurities using our iron-catalyzed process. For example, (*R*)-1-(1-Napthyl)ethanol, which can be used for the synthesis of (+)-compactin and 1233A, was obtained in an ee of 96%.[114-116] Furthermore, (*R*)-1-[3'-(trifluoromethyl)phenyl]ethanol and (*R*)-1-[3',5'-bis(trifluoromethyl)phenyl]ethanol, which are the staring materials for the industrial synthesis of fungicides[117, 118] and NK1 antagonists,[119] could be produced with 97% and 97% ee, respectively. Chiral β-amino alcohols are important building blocks in industrial scale syntheses of physiologically active compounds[120] and are widely used as chiral auxiliaries.[121] This catalytic system is also compatible with a dimethylamino group at the 2-position of 2-(dimethylamino)acetophenone and gave (*R*)-2-(dimethylamino)-1-phenylethanol in an ee of 87% with a TON up to 500. Importantly, under similar conditions (S_A,R_P,*SS*)-**7a** allows the smooth transfer hydrogenation of an α-keto acetal (2,2-dimethoxyacetophenone) to give a chiral α-hydroxyl acetal [(*R*)-2-(dimethoxy)-1-phenylethanol] in a moderate optical purity of 54% ee. Despite the relatively low enantioselectivity, this is the first example of the preparation of this highly value-added chiral alcohol by an iron-catalyzed process. After initial hydrolysis of the acetal group, this versatile α-hydroxyl acetal synthon could be transformed into a variety of highly value-added chiral products, including 1,2-diols, α-hydroxyl acids, and β-amino alcohols, which are useful chiral building blocks for the synthesis of biologically active natural products, pharmaceutically important molecules, chiral ligands and fine chemicals.[122-125] Higher optical purities have been reported with heterogeneous Pt catalysts[126] modified with chiral cinchonidine ligands or by biocatalytic process.[127] Homogeneous catalytic precedents with enantioselectivity were mediated by ruthenium catalysts ligated by pyrrolidinebisphosphine ligands.[128] Interestingly, an excellent

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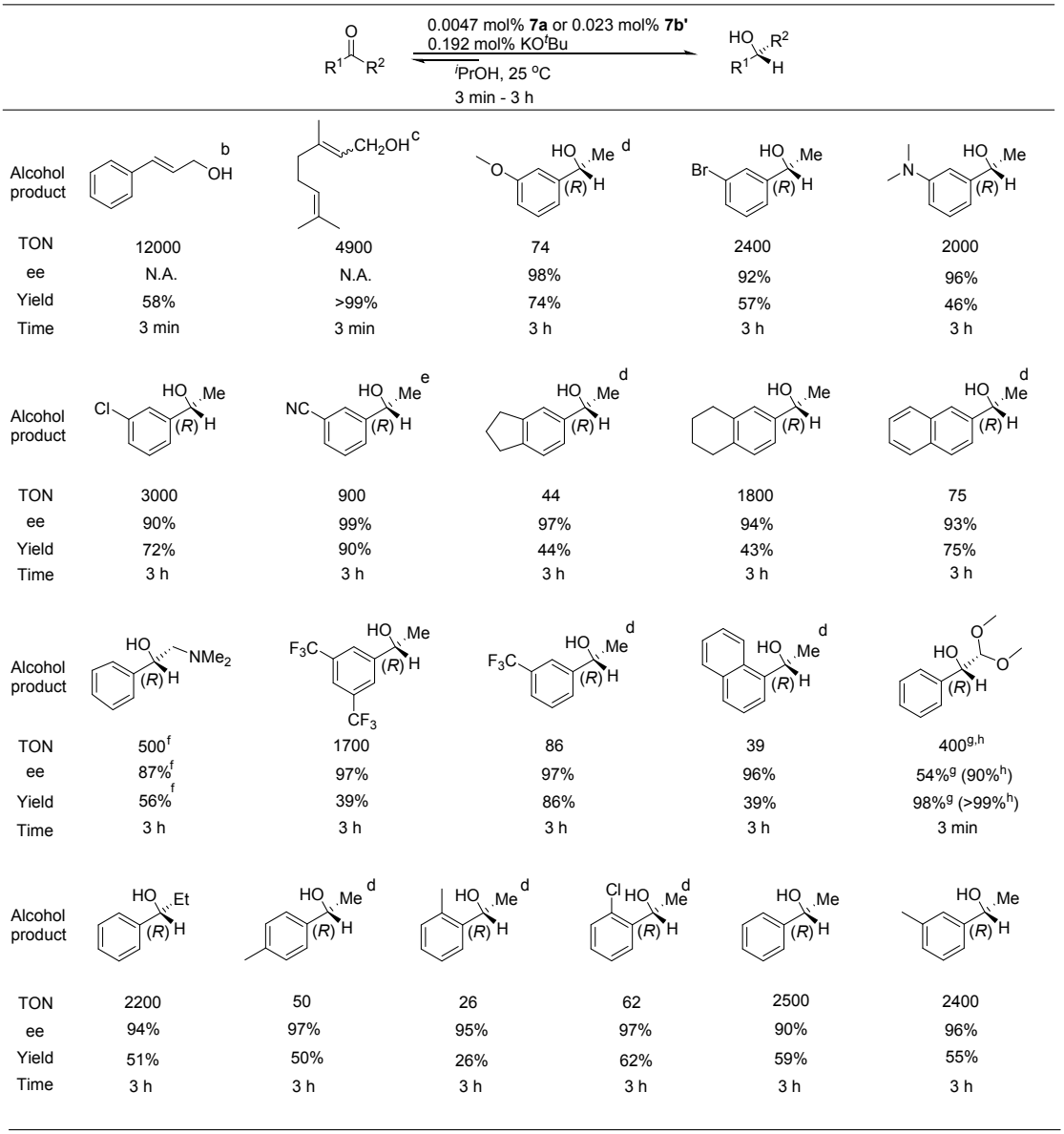
Table 2 Transfer hydrogenation of ketones and aldehydes catalyzed by complexes (S_A,R_P,*RR*)-**7b'** and (S_A,R_P,*SS*)-**7a**. [a]General conditions for (S_A,R_P,*RR*)-**7b'**: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25 °C. The absolute configurations were determined by gas chromatography or HPLC by comparison to known standards.



[b]Conditions for (S_A,R_P,*SS*)-**7a**: [**7a**] = 5.95 × 10^{-5} M, [KO^{t}Bu] = 4.76 ×10^{-4} M, [ketone] = 1.27 M, [^{i}PrOH] = 11.1 M, 25°C. [c]Conditions for (S_A,R_P,*SS*)-**7a**: [**7a**] = 6.67 × 10^{-5} M, [KO^{t}Bu] = 5.34 ×10^{-4} M, [ketone] = 0.33 M, [^{i}PrOH] = 12.4 M, 25°C. [d]Conditions for (S_A,R_P,*SS*)- **7b'**: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. [e]Conditions for (S_A,R_P,*SS*)- **7b'**: [**7b'**] = 3.54 × 10^{-4} M, [KO^{t}Bu] = 2.83 ×10^{-3} M, [ketone] = 3.54 × 10^{-1} M, [^{i}PrOH] = 12.4 M, 25°C. [f]Conditions for (S_A,R_P,*RR*)-**7b'**: [**7b'**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 × 10^{-3} M, [ketone] = 0.26 M, [^{i}PrOH] = 12.4 M, 25°C. [g]Conditions for (S_A,R_P,*SS*)-**7a**: [**7a**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 ×10^{-3} M, [ketone] = 0.10 M, [^{i}PrOH] = 12.4 M, 25°C. [h]Conditions for **A**: [**A**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 ×10^{-3} M, [ketone] = 0.10 M, [^{i}PrOH] = 12.4 M, 25°C.

enantioselectivity of 90% was obtained using our previous less-enantioselective iron catalyst (**A**).[74]

When ligated with macrocyclic chiral ligands, iron catalysts, either generated *in situ* with triiron carbonyl clusters or with well-defined structures, reported by Gao[37, 38] and Mezzetti et al.,[45, 46, 49] could achieve both high reactivity (up to 9430 h^{-1}) and excellent enantioselectivity (up to 99%) in the asymmetric transfer hydrogenation of a series of aromatic ketones at elevated temperatures (40 – 75 °C). Although slightly inferior, the enantioselectivity (>90% in most cases) exhibited by (S_A,R_P,*RR*)-**7b'** is

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also good and of synthetic relevance. In addition, (S_A,R_P,*RR*)-**7a** was 2 orders of magnitude more active and chemoselectively hydrogenated α,β-unsaturated aldehydes to the corresponding unsaturated alcohols, which are important feedstocks in industry, with high turnover numbers. In addition, (S_A,R_P,*RR*)-**7b'** and our previous PNNP iron precatalyst (**A**)[74] have potential practical applicability in catalytic asymmetric transfer hydrogenations of functionalized ketonic substrates to produce a series of highly value-added chiral alcohols that are important building blocks for various industries with good to excellent enantioselectivities.

Conclusions

A new strategy to the stereoselective synthesis of chirality hybridized 2,2'-bis(phosphino)-1,1'-binaphthyl ligands was developed. Based on this, a series of new iron catalysts were designed and synthesized for the asymmetric transfer hydrogenation of ketones. These new iron catalysts contain 1,1'-binaphthyl axial chirality, P-centered chirality and C-centered chirality derived from a chiral 1,2-diphenyl-1,2-ethanediamine. For precatalysts (S_A,R_P,*SS*)-**7a** and (S_A,R_P,*SS*)-**7b**, it was found that the combination of the metal-ligand bifunctional structural motif and the ene(amido) group (as well as carbonyl) could activate the iron for the fast transfer hydrogenation of acetophenone and α,β-unsaturated aldehydes, although the catalysts decomposed rapidly and were not enantioselective. For precatalysts (S_A,R_P,*RR*)-**7a'** and (S_A,R_P,*RR*)-**7b'**, however, the right matching of the axial chirality and the carbon-centered chirality was important to confer iron catalysts good stereoselectivity. With **7b'**, a series of ketone substrates were reduced to the corresponding chiral alcohols, including some important synthetic building blocks, with good enantioselectivities.

Conflicts of interest

There are no conflicts to declare.

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A new type of iron catalyst that structurally mimics the Noyori hydrogenation catalyst can catalyze asymmetric transfer hydrogenation of ketones.