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Enantioselective Reductions Promoted by (Cyclopentadienone)iron Complexes

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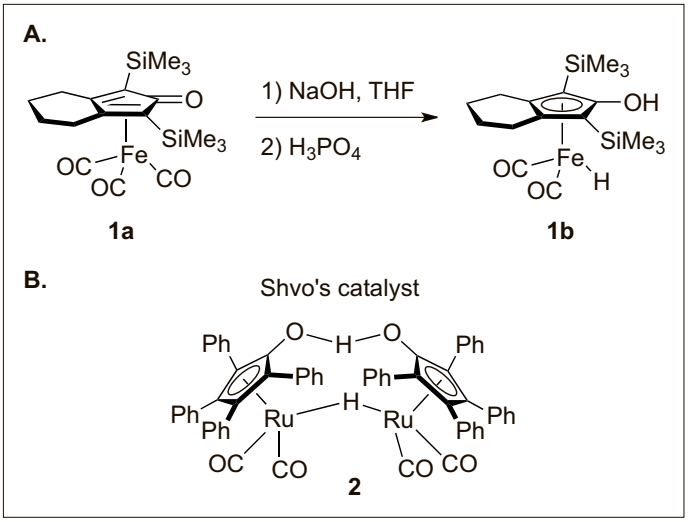
Abstract: (Cyclopentadienone)iron complexes have recently gained widespread interest as cheap metal-based pre-catalysts for the reduction of carbonyl compounds and imines, thanks to their air- and moisture-stability and easy synthesis/purification. In this account, several approaches are presented to achieve enantioselective C=O and C=N bond reduction using this class of iron complexes. Most of the examples, used in the asymmetric reduction of ketones, rely on chiral (cyclopentadienone)iron complexes, featuring a chiral cyclopentadienone backbone and/or a chiral monophosphoramidite ligand, introduced by replacement of a CO ligand. The enantiomeric excesses achieved so far with this strategy are at best moderate. Better *ee*s could be obtained with an alternative approach, used in the enantioselective reduction of C=N bonds, which consists in combining an achiral (hydroxycyclopentadienyl)iron complex (*i.e.* the activated form of a (cyclopentadienone)iron complex) with a chiral phosphoric acid.

Keywords: Asymmetric hydrogenation · Chiral (cyclopentadienone)iron complexes · Imines · Iron catalysis · Ketones

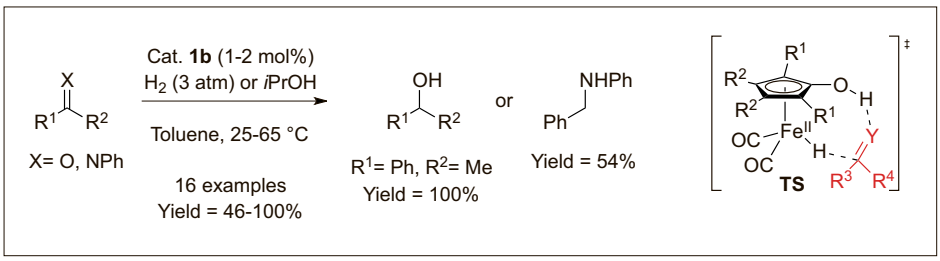
1. Introduction

(Cyclopentadienone)iron tricarbonyl complexes such as **1a** (Scheme 1) were first reported by Reppe and Vetter in 1953,[1] with the particularity of being easily synthesized and purified due to their stability to air, moisture and column chromatography on silica gel. Perhaps surprisingly, it was not before 40 more years that Knölker[2] and Pearson[3] investigated their reactivity in depth: in 1999, Knölker and co-workers synthesized and isolated the first (hydroxycyclopentadienyl)iron hydridedicarbonyl complex **1b** from the stable (cyclopentadienone)iron tricarbonyl complex **1a** using a Hieber-base reaction (Scheme 1A).[4] However, the potential use of the active hydride **1b** in catalysis remained concealed until 2007, when Casey and Guan reported its activity for the chemoselective hydrogenation of aldehydes, ketones and imines under mild conditions.[5] Complex **1b** showed similar properties to the structurally related Shvo catalyst **2** (Scheme 1B), a dinuclear ruthenium hydride, known since 1985,[6] in which the hydride ligand bridges the two ruthenium metal centers.[7]

Casey and Guan demonstrated that hydride **1b** is a highly efficient catalyst for the chemoselective hydrogenation of aldehydes, ketones and imines under mild conditions (Scheme 2) according to a concerted outer-sphere mechanism in which the ligand is involved with its OH group.[5] A large number of functional groups were tolerated under these reaction conditions, such as isolated carbon–carbon double or triple bonds, halides, nitro groups, epoxides and esters. Hydride **1b** has also been



Scheme 1. A. Conversion of (cyclopentadienone)iron complex **1a** into the corresponding (hydroxycyclopentadienyl)iron complex **1b**, as originally reported by Knölker and co-workers. B. Shvo's catalyst (**2**).



Scheme 2. Use of the (hydroxycyclopentadienyl)iron catalyst **1b** in the hydrogenation of aldehydes, ketones and imines.[5]

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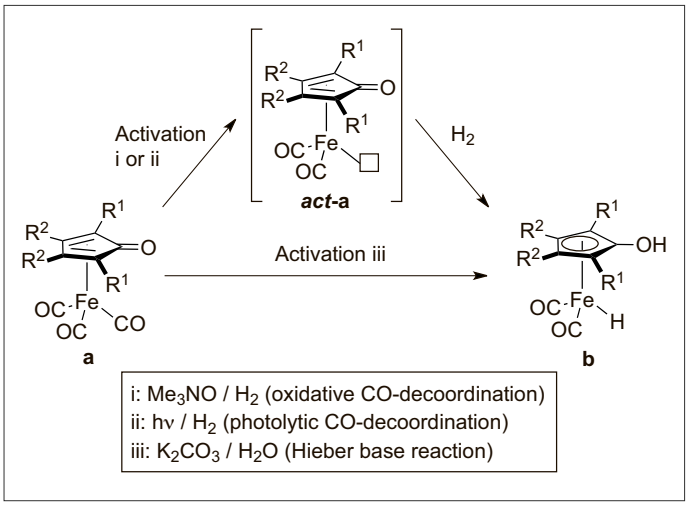


Scheme 3. Strategies for the *in situ* formation of the active complexes ***act*-a** and **b** from the stable (cyclopentadienone)iron complexes **a**.[10–12]

successfully applied in transfer hydrogenation, using isopropanol as reductant.[5,8] Sun and co-workers performed computational studies to confirm that catalyst **1b** is not able to hydrogenate olefins and alkynes at relatively low temperatures.[9]

The main drawback of the active hydride **1b** is its sensitivity to air, moisture and light,[4] which makes a glove-box necessary for its synthesis and manipulation. However, later contributions demonstrated that it is possible to use the bench-stable (cyclopentadienone)iron pre-catalysts **a** and convert them *in situ* into the corresponding active forms ***act*-a** (in the presence of Me_3NO,[10] UV light[11]) and **b** (in the presence of K_2CO_3[12]), as shown in Scheme 3.

From the point of view of ligand design, two main strategies were followed to modify the Knölker-type complex **1a** in order to improve the catalytic activity and/or achieve novel reactivity. In the first instance (Fig. 1A), the substitution pattern of the cyclopentadienone ring was modified to tune the steric and electronic properties of the complexes. This was mainly achieved by varying the cycle fused to the cyclopentadienone ring, replacing the original six-membered ring of **1a**,[13] as well as the nature of the substituents at the 2- and 5-positions of the cyclopentadienone.[13a,b,14] For example, our group recently reported the use of [bis(hexamethylene)cyclopentadienone]iron complex (**3a** in Fig. 1A) as a more active catalyst in the hydrogenation and transfer hydrogenation of carbonyl compounds.[14]

The second strategy to modulate the structure of these complexes relies on the substitution of one of the carbonyls with other ligands (Fig. 1B). Ligand exchange has been performed under oxidative conditions (Me_3NO) to replace CO with nitriles,[5c,10b,15] pyridines,[5c] amines,[3c] phosphines[3b] and, more recently, N-heterocyclic carbenes (NHCs).[16]

Both these strategies are also amenable to the introduction of stereogenic elements (stereocenters, and stereogenic axes or planes) into (cyclopentadienone)iron complexes, in order to obtain chiral pre-catalysts for enantioselective reductions such as asymmetric hydrogenation (AH) and asymmetric transfer hydrogenation (ATH). The main approaches that were followed to this end are discussed in more detail in sections 2 and 3.

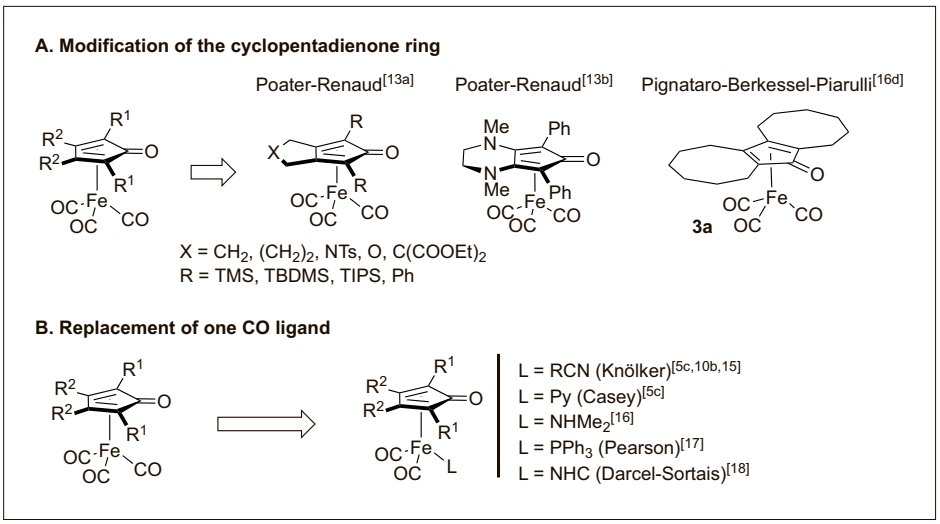


Fig. 1. Main strategies to obtain structurally modified (cyclopentadienone)iron complexes.

2. Chiral (Cyclopentadienone)-iron Complexes Featuring a Chiral Cyclopentadienone Ligand

The synthesis of (cyclopentadienone)-iron tricarbonyl complexes can be performed by two main synthetic strategies: i) complexation of the cyclopentadienone ligand using an iron carbonyl source (such as $Fe(CO)_5$ or $Fe_2(CO)_9$), or ii) cyclative carbonylation of diynes with large excesses of the same iron carbonyl complexes, which results in the formation of fused bicyclic cyclopentadienones and in the simultaneous complexation of the iron tricarbonyl moiety. Both synthetic strategies can in principle be employed for the formation of chiral (cyclopentadienone)iron complexes starting from chiral cyclopentadienone or diyne precursors. In both cases, one important issue to be considered is that, upon complexation with the iron moiety an additional stereogenic element may be formed, viz. a stereogenic plane. In this regard, Wills and co-workers synthesized a few iron complexes starting from unsymmetrical bis-propargyl ethers containing a stereocenter (Scheme 4A).[10d] During the cyclization, from each bis-propargyl ether two diastereomeric complexes (**4a/4a'**, **5a/5a'**, and **6a/6a'**) were formed in unequal quantities, which were separately tested in the ATH of acetophenone using the formic acid/triethylamine azeotrope (Scheme 4B). Both reactivity and enantioselectivity were low (*ee* ≤ 25%) and, interestingly, these results were not influenced by different hindrance of the R and Ph groups but, rather, by the proximal versus distal position of the methyl group on the stereogenic center. An interaction between the methyl and one CO ligand was invoked to explain this behavior.[10d]

Creating a stereogenic plane upon formation of the (cyclopentadienone)metal complex may be desirable, because it involves formation of chiral complexes even from simple achiral ligands and metal sources.[17] However, as can be noted in the above-discussed example by Wills and co-workers,[10d] the formation of a stereogenic plane also brings about synthetic issues linked to separation of the corresponding isomers. This problem can be circumvented by use of C_2-symmetric diynes (or cyclopentadienones) for the synthesis of the chiral complexes, leading

to formation of a single complex in which the cyclopentadienone plane is chirotopic but non-stereogenic. This approach was recently followed by our group with the introduction of a (*R*)-1,1'-bi-2-naphthyl residue in the 3,4-positions of the cyclopentadienone (Scheme 5A), reasoning that the binaphthyl backbone, with its stable and rigid framework, could efficiently shape the space around the iron atom and induce high enantioselectivity. Evaluating the structure of our catalyst we could anticipate that the binaphthyl stereoaxis would be relatively far from the reaction center, so we planned some structural modifications that in principle could improve the transfer of the stereochemical information, or allow for substrate orientation.

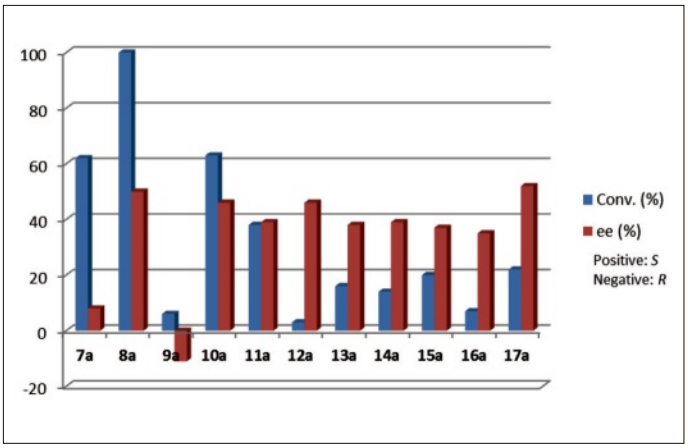
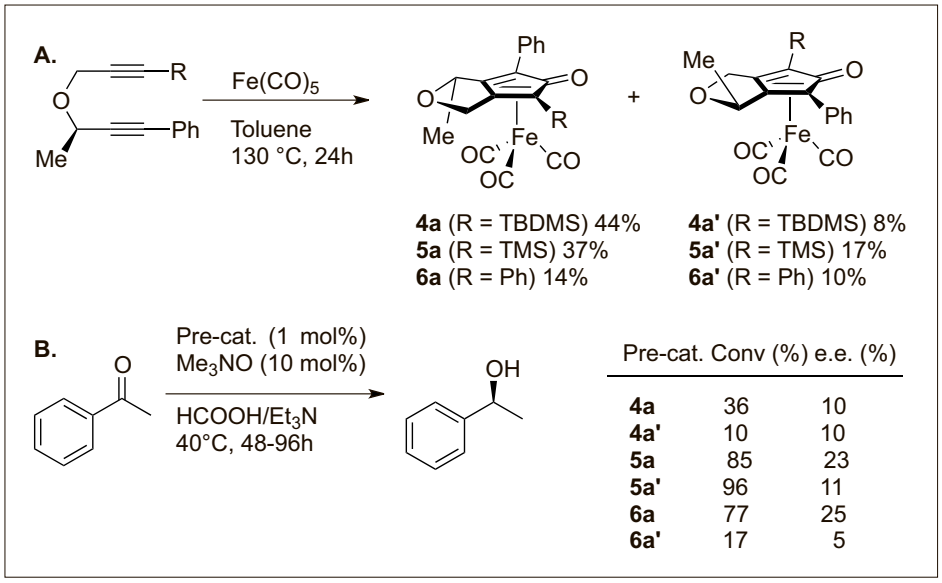
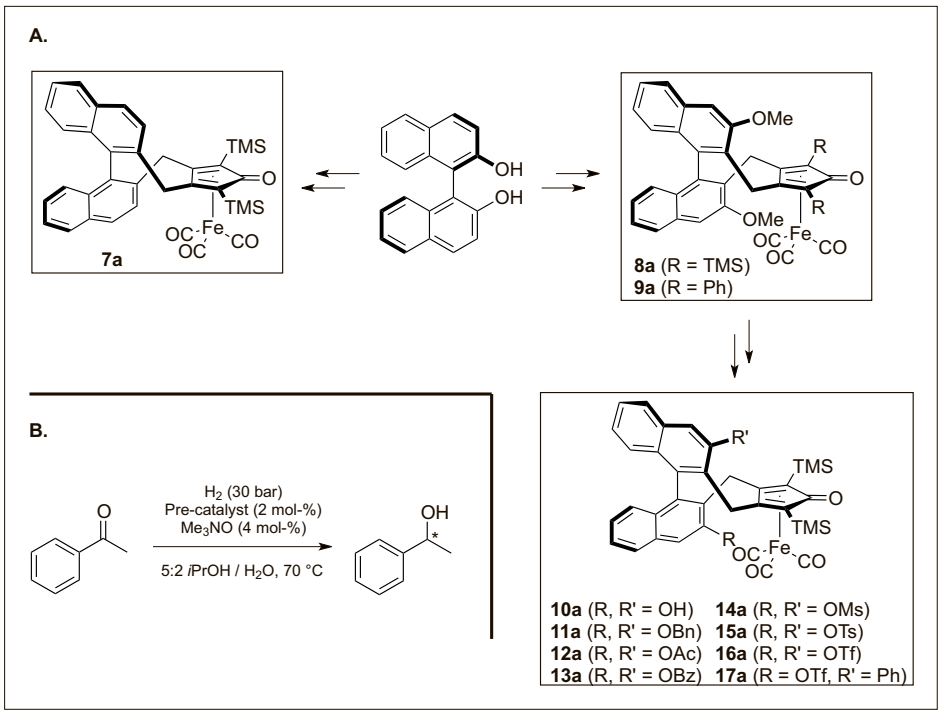


Fig. 2. Results of the screening of complexes **7a–17a** in the AH of acetophenone.



Scheme 4. A. Synthesis of chiral (cyclopentadienone)iron complexes featuring both a stereocenter and a stereogenic plane (Wills and co-workers).[10d] B. Catalytic test of complexes **4a**, **4a'**, **5a**, **5a'**, **6a** and **6a'** in the ATH of acetophenone.



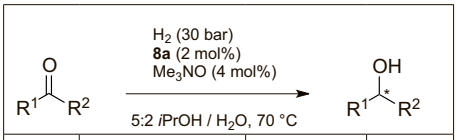
Scheme 5. A. Chiral (*R*)-BINOL-derived (cyclopentadienone)iron complexes developed by our group.[18] B. Screening of the pre-catalysts in the AH of acetophenone.

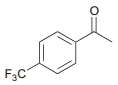
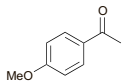
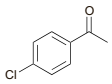
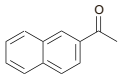
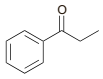
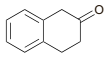
Thus, starting from (*R*)-1,1'-bi-2-naphthol (BINOL) we synthesized a small library of chiral complexes (**7a–17a** in Scheme 5A) variously substituted at the 2,5-positions and at the 3,3'-positions of the binaphthyl residue.[18] Notably, owing to the peculiar stability of (cyclopentadienone)iron complexes, the 3,3'-disubstituted compounds **10a–17a** could be prepared by modification of a common precursor (**8a**), performing functional group interconversion on the iron complexes. Compounds **7a–17a**, activated *in situ* in the presence of Me_3NO, were tested in the AH of acetophenone (Scheme 1B), giving the results shown in Fig. 2.

As expected, the presence of substituents in the 3,3'-positions of the binaphthyl residue positively affected the enantioselectivity, determining a 30–40% increase of the *ee* (Fig. 2, complexes **8a** and **10a–17a** vs. complex **7a**). Remarkably, replacement of the TMS substituents at the 2,5-positions of the cyclopentadienone ring with phenyls (Fig. 2, pre-catalyst **9a**) led to reversal of the sense of stereoinduction (*R* instead of *S* enantiomer formed preferentially). Unfortunately, none of the pre-catalysts reached *ee* values higher than 52%, probably due to the insufficient size of the binaphthyl substituent pointing towards the Fe center. Indeed, introducing a bulky residue in this position turned out to be synthetically impossible for steric reasons. Finally, the substitution of the 3,3'-binaphthyl position and of the 2,5-positions of the cyclopentadienone ring strongly affected also the catalytic activity, although the observed effect is difficult to rationalize.

The best pre-catalyst (**8a**) was used in the AH of several other ketones (Table 1), showing a fairly broad scope and giving in most cases *ee* values ranging from 50% to 77%. Although these *ee* values are clearly inferior to the best literature examples of ketone AH,[19] they still represent the best results obtained so far with chiral (cyclopentadienone)iron complexes.

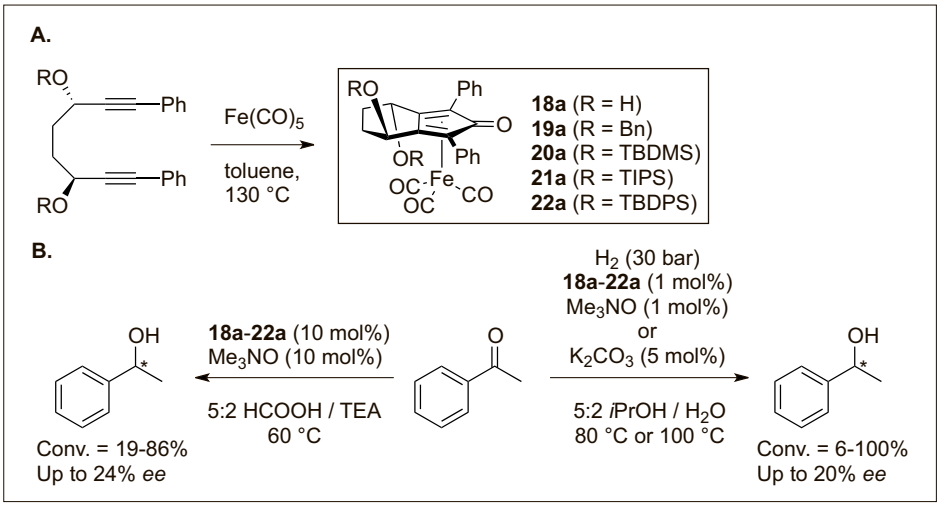
Table 1. Substrate screening for the ketone AH promoted by pre-catalyst **8a**.



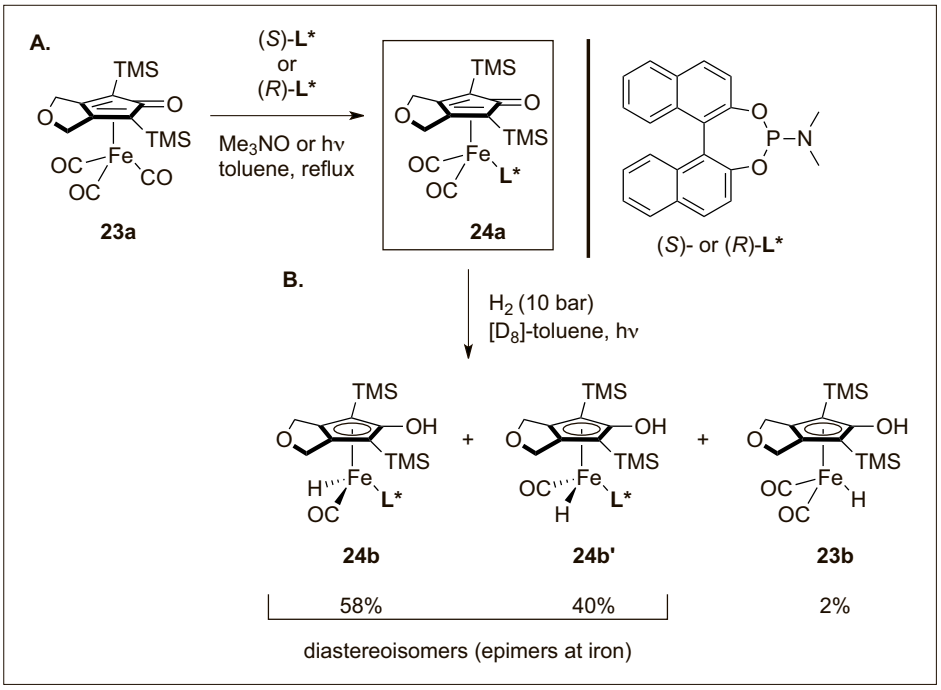
Entry	Substrate	Conversion [%][b]	*ee* [%], abs. conf.
1		100	50, *S*
2		100	46, *S*
3		64	50, *S*
4		100	51, *S*
5		43	68, *S*
6		99	51, *S*
7		35	50, *S*
8		97	57, *S*
9[a]		25	77, *S*
10		100	13, *R*
11		78	59, *R*
12		89	61, *S*
13		76	0
14		22	77, *S*

[a]Substrate/**8a**/Me_3NO = 100:5:10.

Recently, Wills and co-workers reported another class of chiral (cyclopentadienone) iron complexes possessing a C_2-symmetric cyclopentadienone ligand (Scheme 6) and differing from each other in the protection at the oxygen atoms of the fused cyclohexane ring.[20] Complexes **18a**–**22a** (Scheme 6), after activation with Me_3NO or K_2CO_3, were tested in the AH and in the ATH of acetophenone, showing moderate catalytic activity and low enantioselectivity (up to 24% *ee*). Such a poor enantiocontrol is probably due to the remarkable distance of the stereocenters from the catalytic site of complexes **18a**–**22a**, which does not allow an efficient transfer of stereochemical information.



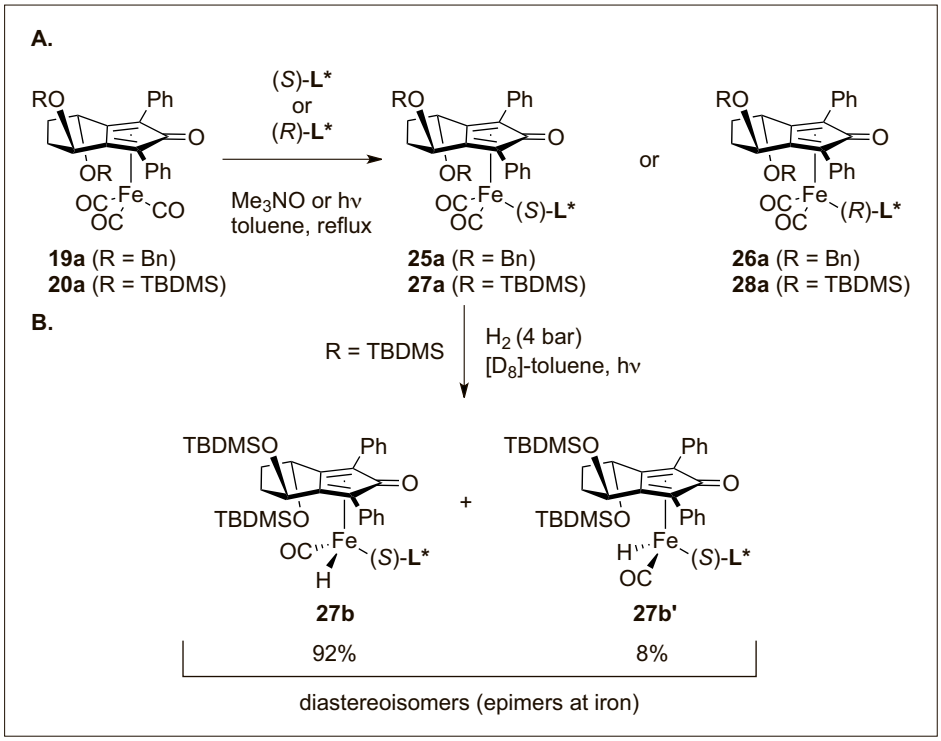
Scheme 6. A. Chiral (cyclopentadienone)iron complexes featuring a C_2-symmetric cyclopentadienone ligand developed by Wills and co-workers.[20] B. Screening of complexes **18a**–**22a** in acetophenone AH and ATH.



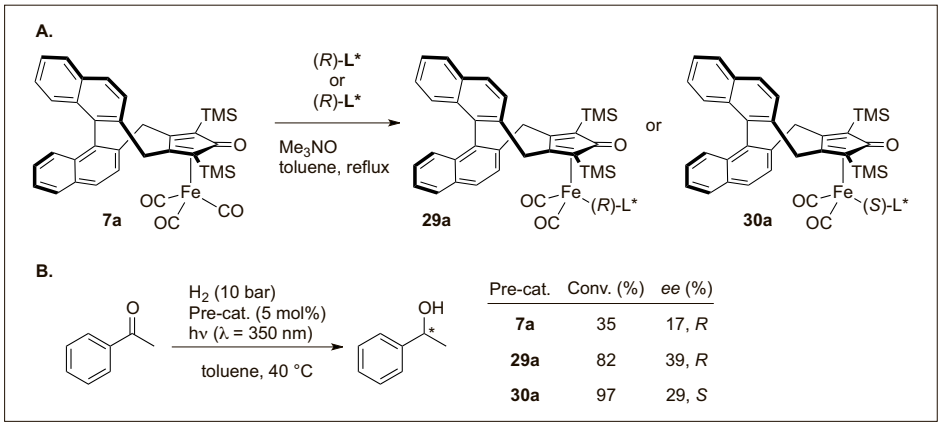
Scheme 7 A. Synthesis of chiral (cyclopentadienone)iron complexes (**24a**) by replacement of a CO with a chiral monodentate ligand (MONOPHOS). B. Formation of the diastereoisomeric (hydroxycyclopentadienyl)iron complexes (**24b** and **24b'**) possessing a stereocenter at Fe.

3. Chiral (Cyclopentadienone)iron Complexes Prepared by Exchange of a CO with a Chiral Ligand

Berkessel and co-workers proposed an alternative approach to generate chiral (cyclopentadienone)iron complexes starting from simple achiral complexes such as **1a** or **23a** (Scheme 7A).[11] Here, one of the CO groups bound to iron is simply removed – either photolytically (under UV irradiation) or oxidatively (Me_3NO) – and replaced with a chiral monodentate ligand such as MONOPHOS. When one of the two remaining CO ligands is substituted by H in the activation step (Scheme 7B), an active (hydroxycyclopentadienyl)iron complex is formed possessing a stereocenter at the iron atom, and therefore existing as a mixture of diastereoisomers (**24b** and **24b'**). NMR studies carried out under the activation conditions revealed that diastereoselectivity in the formation of **24b** and **24b'** is low (**24b**/**24b'** = 1.45:1). Moreover,



Scheme 8. A. Replacement of one CO ligand of two complexes developed by Wills and co-workers (**19a** and **20a**) with a (*R*)- or (*S*)-MONOPHOS (L*) to yield complexes **25a**–**28a**.[20] B. Formation of the activated (hydroxycyclopentadienyl)iron complexes (**27b** and **27b'**) possessing a stereocenter at Fe.[21]



Scheme 9. A. Replacement of one CO ligand of complex **7a**, developed by our group[18] with a (*R*)- or (*S*)-MONOPHOS (L*) to yield complexes **29a** and **30a**.[21] B. Screening of complexes **29a** and **30a** in the AH of acetophenone.

a small amount (2%) of the achiral (hydroxycyclopentadienyl)iron complex **23b** was also observed, deriving from removal of the chiral ligand. The poor observed selectivity in the formation of the diastereoisomeric active complexes **24b** and **24b'** is reflected by the low enantioselectivity that was obtained using pre-catalyst **23a** in the AH of acetophenone (up to 31% *ee*).

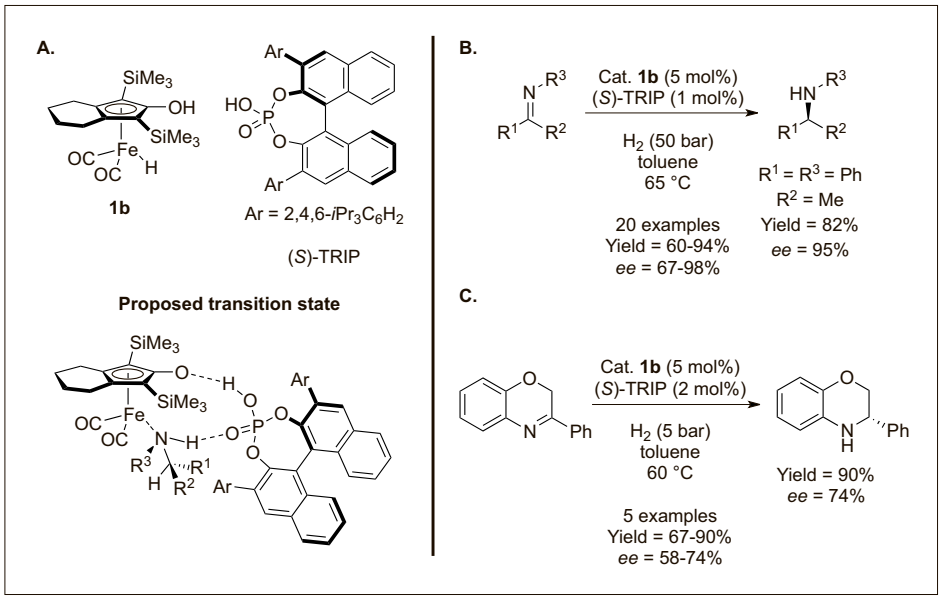
To overcome the problem of the unselective formation of a stereocenter at Fe, Wills and co-workers applied Berkessel's approach to complexes **19a** and **20a** (Scheme 6), which were subjected to exchange of a CO ligand with MONOPHOS (L* in Scheme 8).[20] In this case, since the original iron complexes (**19a** and **20a**) are chiral themselves, the use of either enantiomer (*R* or *S*) of the phosphoramidite ligand created matched and mismatched pairs (**25a**/**26a** and **27a**/**28a**). Each of these complexes was fully characterized and then tested for the enantioselective catalytic applications.

In an experiment similar to the one described by Berkessel (see above), the activation of complex **27a** was studied by NMR. Perhaps owing to the presence of an additional chiral ligand compared to **24a**, this time the activated (hydroxycyclopentadienyl)iron complexes **27b** and **27b'** were obtained in *ca.* 12:1 ratio (Scheme 8B). However, despite this highly diastereoselective activation, use of pre-catalysts **25a**–**28a** led to very low activity and enantioselectivity in both AH and ATH of acetophenone (both conv. and *ee* < 20%).[20]

A similar approach was also followed by our group making use of the binaphthyl-derived chiral cyclopentadienone complex **7a** (see above) combined with MONOPHOS (L*).[21] The two air-stable diastereomeric complexes **29a** and **30a**, containing either (*R*)- or (*S*)-MONOPHOS, were prepared and screened in the hydrogenation of acetophenone (Scheme 9). Yields were satisfactory (>80%) with both pre-catalysts, which showed better enantioselectivity than the parent complex **7a**. Complex **29a** represents the matched combination, forming (*R*)-1-phenylethanol with 39% *ee*, whereas **30a** is the mismatched combination, affording (*S*)-1-phenylethanol in 29% *ee*.

4. Dual Catalysis Approach to AH Involving Achiral (Hydroxycyclopentadienyl)iron Complexes

A completely different approach to achieve enantioselectivity in the reductions promoted by (cyclopentadienone)/(hydroxycyclopentadienyl)iron complexes was described in 2011 by Beller and co-workers, who developed a procedure for the AH of *N*-aryl ketoimines (Scheme 10B) using the achiral (hydroxycyclopentadienyl)iron catalyst **1b** in combination with a chiral phosphoric acid, (*S*)-TRIP.[22] According to the proposed mechanism[23] (displayed in Scheme 10A), the Brønsted acid acts as a chiral template, forming hydrogen bonds simultaneously with the catalyst and with the substrate. A wide variety of different *N*-aryl ketoimines were hydrogenated with high yields and excellent *ee*. Employing the same system it was also possible to hydrogenate quinoxalines to tetrahydroquinoxalines and 2*H*-1,4-benzoxazines to dihydro-2*H*-benzoxazines (Scheme 10B), with high yields and excellent *ee* values.[24] Furthermore, Beller and co-workers applied the same concept also to the asymmetric reductive amination of ketones with anilines, once more with good yields and excellent *ee* values.[25] Although this methodology allowed to achieve better enantioselectivity than those relying on chiral (cyclopentadienone)iron complexes (see sections 2 and 3), it has the limitation of employing the sensitive complex **1b**, whose synthesis and handling must be performed in glovebox. Moreover, the cost of the chiral phosphoric acid co-catalyst, whose synthesis is not trivial, should be taken into consideration.



Scheme 10. Combined use of the (hydroxycyclopentadienyl)iron complex **1b** and a chiral phosphoric acid [(*S*)-TRIP] to achieve the AH of ketoimines[22] (A) and quinoxalines[24] (B).

5. Conclusions

(Cyclopentadienone)iron tricarbonyl complexes have recently attracted a lot of interest as reduction pre-catalysts thanks to their straightforward synthesis, air- and moisture-stability and easy purification by chromatography on silica gel. Numerous reports have shown that these stable complexes can be converted *in situ* into highly efficient catalysts for the chemoselective reduction of aldehydes, ketones and imines. In this account, we have described several approaches to achieve enantioselective C=O and C=N reductions relying either on chiral (cyclopentadienone) iron complexes – obtained by modification of the cyclopentadienone backbone and/or replacement of a CO with a chiral ligand – or on combination of achiral iron complexes with chiral co-catalysts. These approaches were aimed at bringing the stereogenic elements capable to create the enantiodiscrimination as close as possible to the reactive site and induce an efficient stereocontrol. Although all the examples shown suffer from serious limitations (low *ee*s in the case of the chiral complexes, poor practicality in the case of the dual catalysis approach), this represents a highly challenging field of research which is being actively investigated and will bring new perspectives to the development of enantioselective base metal-derived catalysts.

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