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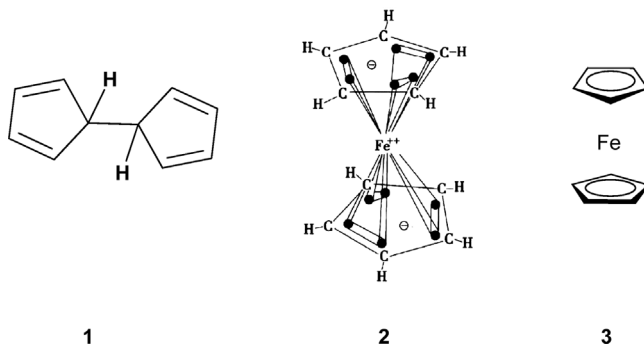
## Introduction

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### 1.1

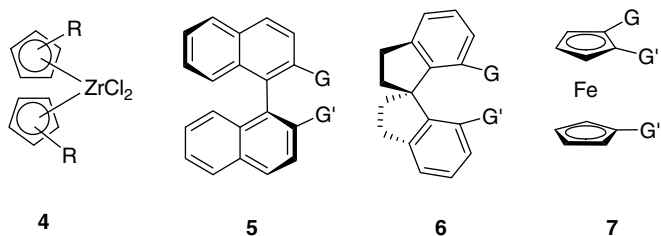
#### Foreword

The unique substance, ferrocene, was discovered in 1951 by Kealy and Pauson, [1] and Miller *et al.* [2] independently. Although the discovery was serendipitous, the impact of the discovery was huge. It opened a new era of organometallic chemistry. The unusual stability and unique properties of this new compound contradicted the expected structure **1**, the target that Pauson and Kealy aimed to synthesize, by reaction of cyclopentadienylmagnesium bromide with  $\text{FeCl}_3$ . This structural mystery soon attracted the attention of many chemists, including three prominent chemists, Geoffrey Wilkinson [3], Robert B. Woodward [4], and Emil O. Fisher [5]. Based on the unusual stability, diamagnetic nature, single C–H stretching in the IR region and nonpolar character of the substance, Wilkinson and Woodward deduced the sandwich structure and named this substance “ferrocene” with the “ene” ending implying aromaticity, following the name of benzene. The sandwich structure was later confirmed by X-ray crystallographic analysis [5–7]. The unexpected structure was disclosed in 1952 as **2**, later simplified to **3**. The carbon–metal bond of the ferrocene structure was a new concept of  $\pi$ -bonding of a carbocyclic ring to a metal atom, which was a breakthrough and a major departure from the classical Wernerian model of ligand coordination that had prevailed until that time [8]. This novel finding soon initiated the preparation of this type of compound with other metals. In just two years a vast array of sandwich compounds with other metals were prepared by Wilkinson [9] and Fischer [10]. They made bis-cyclopentadienyl-metal and cyclopentadienylmetalcarbonyl compounds of most of the transition metals. Following the name of ferrocene came the term “metallocene”.



Metallocene chemistry then became an important sub-branch of organometallic chemistry. Among numerous metallocenes prepared, an outstanding zirconocene **4** [11] has been used as a highly active, single site catalyst for olefin polymerization, which is a milestone in the field of olefin polymerization and a breakthrough in the post Ziegler–Natta era. In addition to the academic study of ferrocene, many applications of ferrocenyl derivatives have also been advanced, such as the control of the burning rate of solid propellant, fuel additives, liquid crystals, and even medicinal applications. In accord with the academic and practical significance of ferrocene, the *Journal of Organometallic Chemistry* published a special issue with 850 pages in 2001 [8], celebrating the fiftieth anniversary of the discovery of ferrocene. In addition, the IUPAC series conference on organometallic chemistry (ICOC) adopted **3** as a logo for the meeting, thus marking the significance of this unique compound, ferrocene.

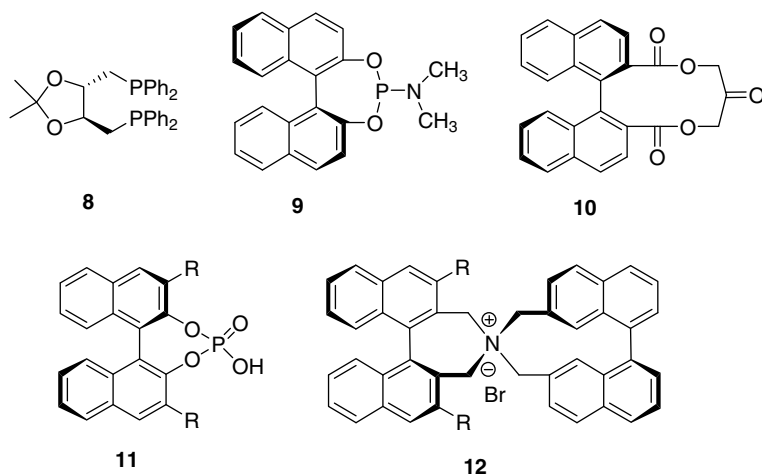
The most important application to date is the use of ferrocenyl derivatives as catalysts, especially in homogeneous asymmetric catalysis. We should point out that Togni and Hayashi reviewed the pioneering studies in this area in their famous book *Ferrocene* in 1995 [12].



For this monograph, we have concentrated on discussing the use of ferrocene as a ligand scaffold for asymmetric catalysis. The emergence of chiral technology in the past 30 years has led to a surge in the exploration of different ligands. Thousands or tens of thousands of ligands have been designed and synthesized. However, judged by the diversity of the ligands derived, the effectiveness and the stereoselectivity of the catalysts, ligands derived from three types of scaffold, the binaphthalene type **5**, the spirobiindane type **6**, and the ferrocene type **7** are the most important. In addition, there are many efficient ligands not covered by these three types. A few such ligands

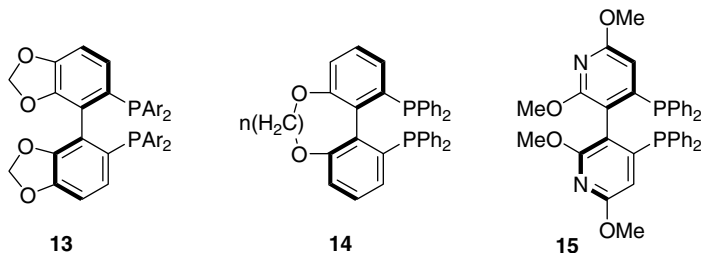
are briefly mentioned below. In the 1970s, Kagan *et al.* [13] applied a tartaric acid derived skeleton for C2-symmetric ligands such as DIOP **8**. In addition to DIOP, DIOP\* [14] and the well-known TADDOL catalysts, based on this scaffold, have also been developed [15]. Carbohydrate-based dioxiranes [16], developed by Shi, are highly efficient catalysts for the epoxidation reaction of unfunctionalized alkenes. However, only a limited number of efficient ligands derived from the carbohydrate have been developed to date. A simple benzene or cyclohexane skeleton also provides several efficient ligands. The best known are Phox [17] from benzene, and 1,2-cyclohexanediamine and its various derivatives from cyclohexane. The latter is represented by the Salen system which has been developed elegantly by Jacobsen [18] and Katsuki [19] for various catalytic enantioselective processes. A one-carbon system may be the simplest skeleton, ligands derived therefrom include, for example, miniphos [20] and Box [21].

It is true that there are many effective ligands not derived from the three above-mentioned types of skeleton, nevertheless, these three types occupy an important position in chiral ligand design. Various donor atoms such as N, P, O, and S could be introduced onto these skeletons, and a great number of ligand patterns could thus be derived. The binaphthalene 5 derived ligands enjoy a very high reputation and some of them have already found important industrial applications. BINAP (5,  $G=G'=PPh_2$ ) [22], BINOL (5,  $G=G'=OH$ ) [23], and MOP (5,  $G=OH$ ,  $G'=PPh_2$ ) [24] are some examples of this class.



In addition, Ferringa catalyst **9** [25], Yang's chiral dioxirane **10** [26], chiral Brønsted acids **11** [27], phase transfer catalyst **12** [28], tetrahydro- and octahydro derivatives [29, 30] are further examples derived from the binaphthalene skeleton. Furthermore, on the skeleton of **5**, some supporting groups could be introduced at the 3-, 6-, or other positions to finely tune the steric and electronic properties of the ligands. Thus, it can be envisaged that the ligands derived from this binaphthalene skeleton will have very rich diversity. This type of ligand scaffold is characterized by the presence of an axial chirality and it is also manifested as an atrop-isomer. Similarly, some biphenyl and

biheteroaryl ligands, such as Segphos **13** [31], Tunaphos **14** [32], and P-Phos **15** [33], are also very efficient, and this type may also be called bi-aryl ligands.



The second type, spirobiindane **6**, is the skeleton of several new ligands which have appeared only in this millennium [34]. Although no industrial scale application has been documented, a number of very recent reports [35] show that this unique skeleton really deserves to be regarded as one of the three important scaffolds. Almost all the derivatization of the binaphthalene system can be applied to the spirobiindane system, and many of the chiral ligands derived therefrom displayed better performance, either in efficiency or in enantioselectivity. Some examples are SIPHOX **6** ( $\text{G} = \text{oxazoline}$ ,  $\text{G}' = \text{PAr}_2$ ); SDP **6** ( $\text{G} = \text{G}' = \text{PAr}_2$ ); SIPIROBOX **6** ( $\text{G} = \text{G}' = \text{oxazoline}$ ); SPINOL **6** ( $\text{G} = \text{G}' = \text{OH}$ ). The spirobiindane system is also associated with axial chirality. Fortunately, the synthesis of spirobiindanes is quite straightforward.

What makes the third type, the ferrocene skeleton, different from the other two types? The most significant feature is the planar chirality associated with this type in most cases, while the other two types are mainly associated with axial chirality. In a special design, multichiralities, central, planar and axial, could be installed in the catalyst derived from a single ferrocenyl ligand [36]. Furthermore, several ligands of this type have been used in practical applications, from kilogram to pilot plant scales and even to 10 000 ton  $\text{y}^{-1}$  production. Examples of the ferrocenyl ligands are Josiphos, Taniaphos, Walphos, Bophos, TRAP, Fc-Phox, PPFA, BPPFA, SiocPhox (see Chapter 8), and so on. Therefore, ligands derived from the ferrocene skeleton are really a class of importance, it is the aim of this book to give readers a comprehensive overview of ferrocenyl ligands in asymmetric catalysis.

In the following sections, various characteristics of the ferrocene scaffold that make it different from other types of skeleton will be discussed.

## 1.2

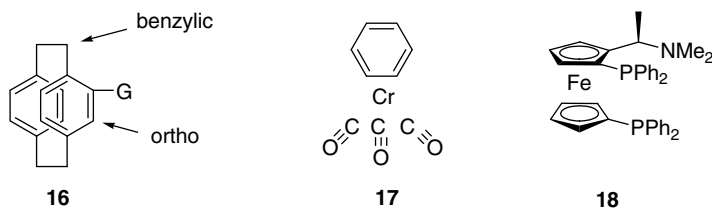
### Planar Chirality of Ferrocenyl Ligands

Since the first preparation of an optically active planar chiral ferrocene 50 years ago [37] and the diastereoselective introduction of planar chirality from Ugi's amine in 1970 [38], planar chirality has become important in ligand design for enhancing or tuning the stereoselectivity of the ligand. Now comes the question: how to introduce

the planar chirality efficiently? Chapter 2 of this book, contributed by Deng, Snieckus and Metallinos gives a thorough answer to this question. In Ugi's work, the amino-group served as a directed metalation group (DMG). Since then many DMGs have been developed, such as Kagan's chiral acetal [39], chiral oxazoline independently developed by Richards [40], Sammakia [41] and Uemura [42], methoxy DMG developed by Knochel [43], Enders' SAMP hydrazone [44], and sulfoximines developed by Bolm [45]. All of these DMGs can give a highly selective directed orthometalation (DoM) reaction, followed by trapping with an  $E^+$  to introduce the E group at a definite position, giving the system an additional planar chirality. The DoM reaction or the complex induced proximate effect (CIPE) [46], makes this protocol highly diastereoselective. Snieckus is one of the major players in this field and his chapter will give readers a good understanding of DoM. He [47] went further by using a directing reagent, sparteine, instead of a DMG. This is unarguably a significant improvement. Planar chirality can then be introduced by using optically pure sparteine or other chiral amines.

There are some other systems in addition to ferrocene that may offer planar chirality. Cyclophane is one such system of interest. Although Pyne has developed a highly selective hydrogenation catalyst with a chiral cyclophane skeleton [48], the introduction of planar chirality with a DMG on a cyclophane system is sometimes problematic. It has been reported [49] that the DoM reaction of **16** (G = oxazoline) gave a mixture of ortho- and benzylic substituted products, which are not easily separable. The difficulty in making a selective and distinct product has somewhat limited the using of cyclophane as a viable skeleton.

$\pi$ -Arene chromium tricarbonyl is another system that may provide planar chirality, however, the derivatization is also tedious with limited variations. Thus, ferrocene is now the most appropriate scaffold to provide planar chirality for various ligand patterns. Chapter 2 not only describes the preparation of ligands with planar chirality, but also discusses the role of planar chirality in asymmetric catalysis.



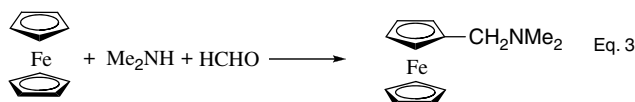
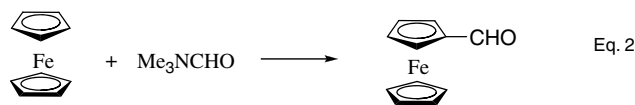
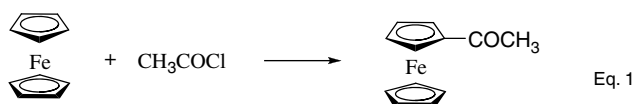
How to denote the absolute configuration is clearly described in Chapter 2. There are several symbols or methods used to designate the absolute configuration of planar chirality in the literature. Some authors use a subscript Fc to symbolize the planar chirality of ferrocene. For instance, compound **18** is denoted as (*R*,  $S_{Fc}$ ) where the central chirality is *R* in absolute configuration and the planar chirality is *S*. Other authors give no additional signs but list the absolute configurations by an order of priority for the elements of chirality, that is: central > axial > planar. Thus **18** is described as (*R*, *S*), the *R* listed first for central chirality and the *S* listed second for planar chirality. In many cases, a subscript italic letter P (planar) is used with the

absolute configuration *R* or *S*. Then **18** is described as (*R*, *S<sub>p</sub>*) where *S<sub>p</sub>* means the planar chirality with *S* configuration. Similar to this, some authors prefer to put the letter *P* before the letter indicating the absolute configuration, as (*R*, *<sub>p</sub>S*). For unification of this whole book, (*R*, *S<sub>p</sub>*) for **18** and this symbol are used throughout. If a phosphorus chiral center exists, *R<sub>p</sub>hos* or *S<sub>p</sub>hos* is used for the P-central chirality.

### 1.3

#### Derivatization of the Ferrocene Scaffold

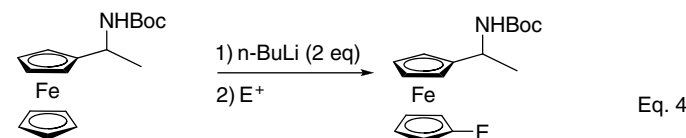
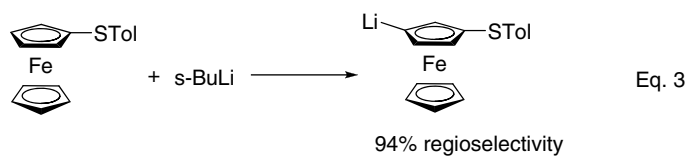
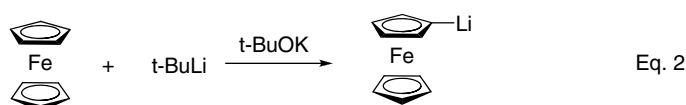
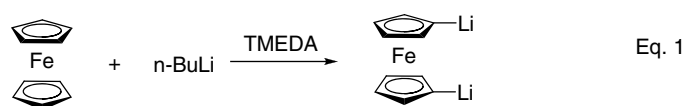
During the study of the unusual structure of ferrocene, Woodward *et al.* [4] demonstrated the remarkable similarity between the reactivity of ferrocene and that of a benzene ring. Ferrocene undergoes typical aromatic electrophilic substitution reactions such as the Friedel–Crafts acylation reaction (Scheme 1.1, Eq. 1). For a comparison of the reactivity, when one molecule of ferrocene and ten molecules of anisole were allowed to react with a limited amount of acetyl chloride–aluminum chloride complex in chloroform solution, acetyl-ferrocene was formed exclusively, without any detectable amount of methoxy acetophenone. This is attributed to the fact that the electronic density of the cyclopentadienyl ring is much higher than that of a benzene ring. The  $\pi$ -back donation of the d-orbital of iron may even strengthen the electron negativity of the Cp ring. The reactivity of the Friedel–Crafts reaction of ferrocene is  $10^6$  times higher than that of a benzene ring. The same trend is evident for other electrophilic substitution reactions, like the Vilsmeier reaction for introducing a formyl group (Scheme 1.1, Eq. 2) and the Mannich reaction for introducing a dimethylaminomethyl group (Scheme 1.1, Eq. 3). These reliable transformations allow ready access to useful intermediates such as Ugi's amine and ferrocenyl



**Scheme 1.1** Typical electrophilic reactions of ferrocene in the early days.

carboxylic acid. In addition to the electrophilic reaction, a nucleophilic reaction could also be carried out easily for the derivatization of ferrocene. For example, treatment of bromoferrocene with BuLi could lead to various ferrocenyl compounds upon quenching with different electrophiles. Notably, Nesmeyanov's [50] and Benkeser's groups [51] were pioneers in studying the metalation reaction by using *n*-butyl lithium.

The lithioferrocene can react further to deliver many useful intermediates. Reaction with CO<sub>2</sub> leads to carboxylic acid and then to oxazolines on treating with amino alcohols. Reaction with PPh<sub>2</sub>Cl could install a diphenylphosphino group on the Cp ring. The metalation reaction is even more powerful than the Friedel–Crafts reaction, given the recent reported selective metalation reactions. For example, *n*-butyl lithium converts ferrocene into 1,1'-dilithioferrocene in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) [52] (Scheme 1.2, Eq. 1) while the direct lithiation of ferrocene by *tert*-butyl lithium is a practical method for mono-lithioferrocene (in the presence of excess ferrocene). An improved method using *tert*-butyl lithium and super base (potassium *tert*-butoxide) provides the mono-lithio ferrocene in 90% yield (Scheme 1.2, Eq. 2) [53]. The metalation reaction is the most useful method for substituted ferrocenes. However, compared to the methods for preparing 1,2-disubstituted ferrocene, the preparation of 1,3-disubstituted ferrocene is less studied. Brown [54] developed a method for preparing 1,3-disubstituted ferrocene as shown in Scheme 1.2, Eq. 3. The 1,1'-disubstituted ferrocene could



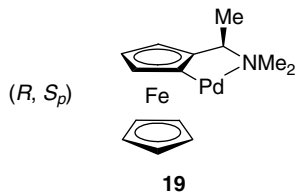
**Scheme 1.2** Metalation reaction of ferrocene.

also be prepared by selective lithiation of a Boc-protected ferrocenylalkylamine [55] (Scheme 1.2, Eq. 4) or a ferrocenyl carbaldehyde [56].

With the availability of these efficient methods, partially represented by the above examples, it is very easy to introduce various donor groups or supporting groups onto the skeleton of ferrocene. Ferrocenes with different substitution patterns, such as di-, tri- or multi- substituted, and ferrocenes bearing groups with different electronic or steric properties could thus be synthesized easily in order to study the relationship between the structure and catalytic activity of the catalyst [57].

Hence, thousands of ferrocenyl ligands have been designed and prepared. In this book, the ferrocenyl ligands are discussed according to their substitution patterns. In Chapter 3, Tim Jamison of MIT and You, Xia of SIOC discuss the monodentate chiral ligands, mainly Jamison's work on the P-chiral phosphine ligand. Chapter 4 on bidentate 1,2-ferrocenyl diphosphine ligands is contributed by Blaser and Lotz of Solvias AG. They pay much attention to the industrial application of ferrocenyl ligands. Although the industrial application of asymmetric catalysis has recently been documented in two books [58], the authors of this chapter provide us with many up to date references. We trust that the industrial application of the ferrocenyl ligands will be highly interesting to the readers. Chapter 5, contributed by Zhou and Hou, deals with 1,2-*N,P*-bidentate ferrocenyl ligands. The ferrocene derivatized ligands are not limited to *N*- and *P*- donors, the *N,O*-bidentate ligands are also an important class. Carsten Bolm of Aachen and his group have contributed greatly to this subject and summarize the progress in this area in Chapter 6. The subsequent two chapters deal with 1,1'-bidentate ligands. The symmetrical 1,1'-bidentate ligands are discussed by Zhang and Liu of Jiaotong University of Shanghai, in Chapter 7, and the unsymmetrical 1,1'-bidentate ligands are discussed by You of SIOC in Chapter 8. In addition, the donor atoms could be further extended to S and Se, as discussed by Carretero, Adrio and Rivero in Chapter 9. Some of their ligands, such as Fesulphos, showed excellent performance. Since the appearance of DIOP 5 in the 1970s  $C_2$ -symmetry has become one of major importance in ligand design. The biferrocene ligands discussed in Chapter 10 are the incorporation of this strategy into the ferrocene system. Kuwano describes this type of ligand explicitly and TRAP is a representative of this type. The last two chapters describe special types of derivatization. In addition to changing the groups on the Cp-ring, the Cp-ring itself could be modified. In Chapter 11, Greg Fu of MIT tells us the story of aza- or phospho-ferrocene, in which one CH unit of the Cp ring is replaced by an N-atom or a P-atom. These unique systems and also the pyridino-Cp ring system delivered many very interesting results and showed us how vast the imagination is. In the last chapter, Christopher Richards of UEA (University of East Anglia) discusses metallocyclic ferrocenyl ligands, in which the complexing metal is bonded to an  $sp^2$  carbon atom and becomes a direct component of the element of planar chirality, as illustrated in the example below. These palladacyclic ligands showed excellent selectivity in the asymmetric Overman rearrangement. Finally, an appendix has been added to help the readers access easily most of the significant ligands and reactions.





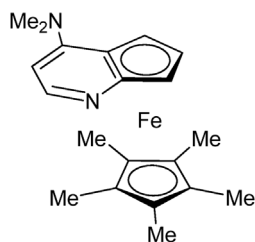
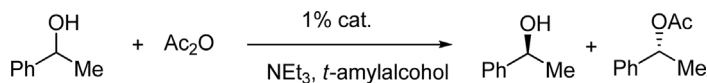
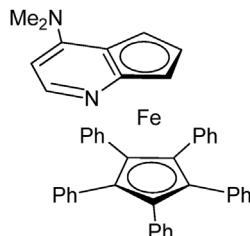
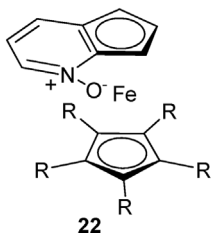
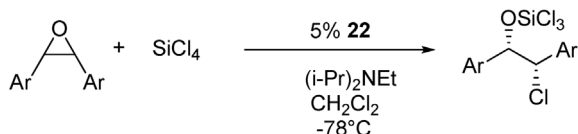
#### 1.4

#### Stability, Rigidity and Bulkiness of the Ferrocene Scaffold

Ferrocene is a highly thermal stable compound. It volatilizes without decomposition into a monomeric undissociated vapor which obeys the perfect-gas law, even at 400 °C [59]. Ferrocene is resistant to pyrolysis at 470 °C in a N<sub>2</sub> atmosphere. It also has great chemical stability, which is important for its use as a ligand.

For a chiral ligand, the skeleton should not be too flexible so as to provide an appropriate chiral environment. Therefore, ring compounds with a certain rigidity are usually required for a ligand framework. In Section 1.1, the three types of good ligand skeleton, binaphthalene, spiroindane and ferrocene are all ring compounds with adequate rigidity. On the other hand, the skeleton should not be too rigid so as to allow complexation with a metal and the approach of the reactants. All these three types of skeleton have a certain limited degree of freedom of rotation or tilting. In the case of ferrocene, although the two cyclopentadienyl rings are parallel to each other, they can tilt to some extent if the stereo-environment requires it.

Bulkiness is another factor for consideration in designing chiral ligands. A bulkier group may shield one side from attack thus restricting the attack to only the re or si face. The bulkier groups used are usually *tert*-Bu, TMS, and mesityl. Obviously the volume demanded by a ferrocenyl group is high. Wang *et al.* applied the ferrocenyl group as a bulky substituent [60]. In Chapter 11, contributed by Greg Fu and Nicolas Marion, the elegantly designed catalysts, the azaferrocene and the planar chiral DMAP, contain a pentamethylcyclopentadienyl Cp\* moiety. The Cp\* moiety apparently enhances the shielding from attack of the lower parts, the catalyst thus becomes a highly selective and efficient one. Fu and Marion give us an insightful discussion of this novel class of catalysts. The bulky shielding effect could be further enhanced by using five phenyl groups or 3,5-dimethylphenyl groups instead of Me groups. In the kinetic resolution of a racemic secondary alcohol, we may perceive the effect of the steric demand of the ligand used. The selectivity factor on using DMAP is 2, while with a more sterically demanding ligand, C<sub>5</sub>Ph<sub>5</sub>, the selectivity factor increases dramatically to 43 [61]. (For the definition of the selectivity factor, please refer to Chapter 11). A further example is the desymmetrization of a meso-epoxide with SiCl<sub>4</sub> [62]. For this ligand, the nucleophilic site is not the N of the DMAP-derivative, but an oxygen atom of the N-oxide. As the N–O bond extends further from the pyridine ring, **22b** is not bulky enough to give good shielding while **22c** displays the best enantioselectivity.

**20** DMAP,  $S = 2$ **21**  $\text{C}_5\text{Ph}_5\text{DMAP}$   $S = 43$ 

- a,  $\text{R} = \text{Me}$ ,  $\text{ee} = 11\%$  (at  $0^\circ\text{C}$ )  
 b,  $\text{R} = \text{Ph}$ ,  $\text{ee} = 60\%$   
 c,  $\text{R} = 3,5\text{-Me}_2\text{-C}_6\text{H}_3$ ,  $\text{ee} = 92\%$

## 1.5

### Outlook

From the previous sections, the intrinsic characteristics of ferrocene as a chiral ligand in asymmetric catalysis have fully demonstrated why ferrocene is a truly important and wonderful scaffold for various chiral ligands. Since the preparation and application in asymmetric catalysis of the first chiral ferrocenyl ligands in 1974 by Kumada, Hayashi, and their coworkers, the development of chiral ferrocenyl ligands has been really fast. The use of Josiphos by Togni and Blaser in the catalytic asymmetric transfer hydrogenation of imine for the production of Metachlor still holds the record for the largest scale asymmetric catalysis, which is a really impressive achievement. We may say that the development of chiral ferrocenyl ligands has already reached a high point. When considering practical applications, the cost of the ligand has become a necessary consideration. Presently, ferrocene is a chemical in tonnage production by an electrolytic process. The price is around 65 000 RMB/ton (or 65 RMB/kg), that is around 10 US\$/kg, 6–7 €/kg. [63] The price

from Sigma-Aldrich (2009) is 1340 RMB/500 g. As described in the Introduction in Chapter 4, we may expect that new industrial applications of chiral ferrocenyl ligands will continue to appear. By checking the SciFinder explorer with “ferrocene” and “chiral” as the two keywords, 50 or more papers have appeared every year in this new millennium, thus we may also expect the development of more important chiral ferrocenyl ligands. We may be proud to say that ferrocene has played and is playing a vital role in both the academic world and in the industrial world serving mankind.

### Acknowledgments

We sincerely thank all the authors for their contributions. They are all pioneers or major players in the areas related to the corresponding chapters, which assures the maintenance of a high standard throughout the whole book.

We are indebted to Dr. Tao Tu for compiling the Appendix during his short visit to Shanghai from the University of Bonn. We are grateful to Dr Elke Maase of Wiley-VCH who initiated and motivated our interest in editing this book and to Lesley Belfit for her help during the whole editing process. We also thank Professor Shu-Li You for instructive suggestions and Miss Di Chen for the typing work.

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