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Review

Timothy Noël* and Johan Van der Eycken*

Ferrocene-derived P,N ligands: synthesis and application in enantioselective catalysis

Abstract: Due to their unique steric and electronic properties, air-stability and modular structure, chiral hybrid P,N-ferrocenyl ligands play a prominent role in the field of asymmetric catalysis. This report aims to give a concise introduction to the syntheses of chiral hybrid P,N-ferrocenyl ligands and presents an overview of their application in enantioselective catalysis. This review is of special interest to chemists working on ligand design and asymmetric catalysis, as well as to the broader organic and inorganic community.

Keywords: enantioselective catalysis; ferrocene; P,N ligands.

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1 Introduction

Since its serendipitous discovery in 1951, [1–4] research towards ferrocene-containing compounds has received a lot of attention [2–7]. The general structure of ferrocene consists of two cyclopentadienyl rings which are bound on opposite sides of a central iron atom in a η^5-fashion. As a result, a so called sandwich complex is formed.

For various reasons, hybrid P,N-ferrocenyl ligands have found widespread use in asymmetric catalysis. First, ferrocenyl phosphanes are extremely stable towards oxidation and therefore are easy to handle. Second, 1,2-disubstituted ferrocene ligands can be obtained in two enantiomeric forms (Figure 1). These enantiomers possess planar chirality and are specified by the stereodescriptors S_p and R_p following the rules introduced by Schlögl [8]. The substituted cyclopentadienyl ring is monitored from the opposite site of the iron atom. The priority of the substituents is then attributed according to the Cahn-Ingold-Prelog rules. A clockwise or anticlockwise sequence of the groups results in, respectively, an R_p or S_p configuration. There exists also a second procedure to assign the enantiomers leading to the opposite planar chiral descriptors [9]. Throughout this review, we will use the first nomenclature. Third, it is also possible to put substituents on two different cyclopentadienyl rings, a so-called 1,1′-disubstitution (Figure 2). In this case, the ligand possesses no planar chirality. However, upon complexation of the ligand with a metal, axial chirality is obtained due to a restricted rotation of the two cyclopentadienyl rings. Fourth, the combination of a soft phosphorous atom and a hard nitrogen atom leads, in many cases, to very efficient ligands [10, 11].

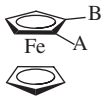
Numerous reviews have highlighted the synthesis and applications of ferrocene-based ligands in the past [12–17]. With this review, we wish to give a focused and up-to-date summary of the synthetic routes towards chiral hybrid P,N-ferrocenyl ligands and an overview of the applications of these ligands in enantioselective catalysis.

Enantioselective catalysis can be considered as "Green" since it allows the introduction of a chiral stereocenter in large amounts of prochiral substrates, by utilizing only a limited amount of valuable catalyst [18, 19]. As such, classical stoichiometric methodologies which create a lot of waste are circumvented, e.g., the use of chiral auxiliaries or the separation of two enantiomers via a resolution step.

2 General synthetic routes

2.1 Synthetic routes towards chiral 1,1′-disubstituted P,N-ferrocenes

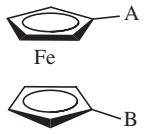
The synthesis of 1,1′-disubstituted P,N-ferrocenyl ligands is less common, because it is difficult to avoid both competing 1,2-substitutions and symmetrical substitutions.



1,2-disubstituted ferrocenes

if A>B (counterclockwise rotation): S_p
if A<B (clockwise rotation): R_p

Figure 1 1,2-Disubstituted ferrocenes possessing planar chirality.



1,1'-disubstituted ferrocenes

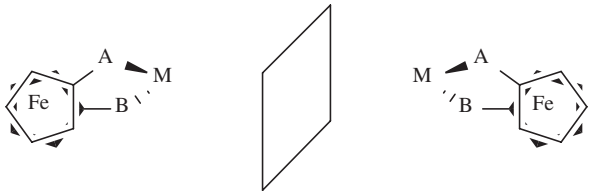


Figure 2 1,1′-Disubstituted ferrocenes possessing axial chirality upon complexation.

However, several methods have been developed to obtain these 1,1′ unsymmetrically disubstituted ferrocenes.

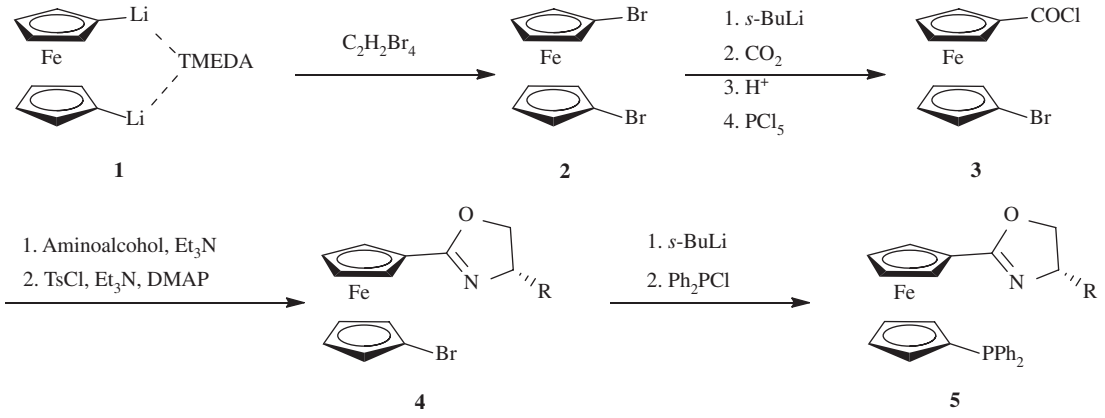
The synthesis of chiral 1-oxazolinyl-1′-(diphenylphosphino)ferrocenes **5** starts from a controlled 1,1′-dilithiation of ferrocene by *n*-BuLi in the presence of the chelating tetramethylethylenediamine (TMEDA) (Scheme 1) [20, 21]. This product **1** is transformed into the corresponding 1,1′-dibromoferrocene **2**. Via a selective lithium-halogen exchange, only one of the two bromines is lithiated and hence differentiation is possible, leading eventually to 1-bromo-1′-(2-oxazolinyl)-ferrocene **4.** A second lithium-halogen exchange, followed by a reaction with chlorodiphenylphosphane leads to the corresponding chiral hybrid oxazolinyl-ferrocenylphosphane ligand **5.**

Another specific approach, is the ring opening with phenyllithium of the strained 1-phenyl-1-phospha-[1]-ferrocenophane **6,** which can be obtained from the corresponding 1,1′-dilithiated ferrocene **1** (Scheme 2) [22–25]. When this compound is now reacted with *N,N*-dimethylformamide, the corresponding phosphane ferrocenecarbaldehyde **8** is formed. Subsequently, this compound can be condensed with a chiral hydrazine, for example (*S*)-1-amino-2-(methoxymethyl)-pyrrolidine (SAMP) **9** leading to chiral hybrid phosphane, hydrazone ligand **10** [26].

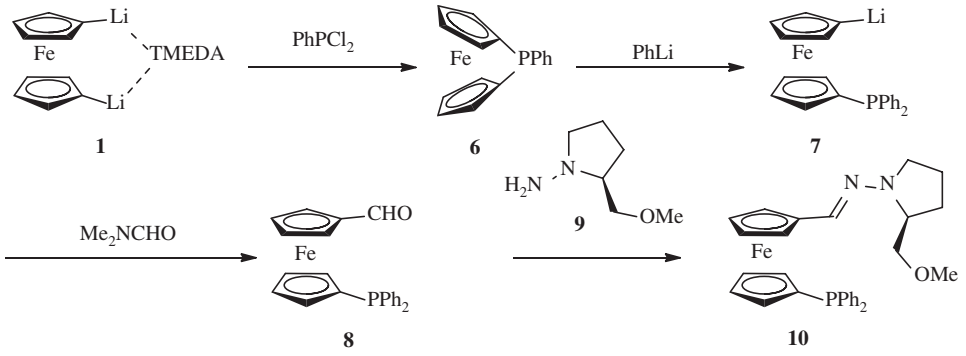
Finally, the use of *N*-methylpiperazine as a directing group leads to selective lithiation of the 1′-position (Scheme 3) [27]. Hereby, ferrocenecarbaldehyde **11** is reacted with the lithium salt of *N*-methylpiperazine, to give an aminal as a temporary protecting and directing group. Subsequent treatment with *t*-BuLi results in selective lithiation of the 1′-position. A similar directed lithiation of the 1′-position has also been observed with a Boc-protected 1-ferrocenylethylamine [28].

2.2 Synthetic routes towards chiral 1,2-disubstituted P,N-ferrocenes

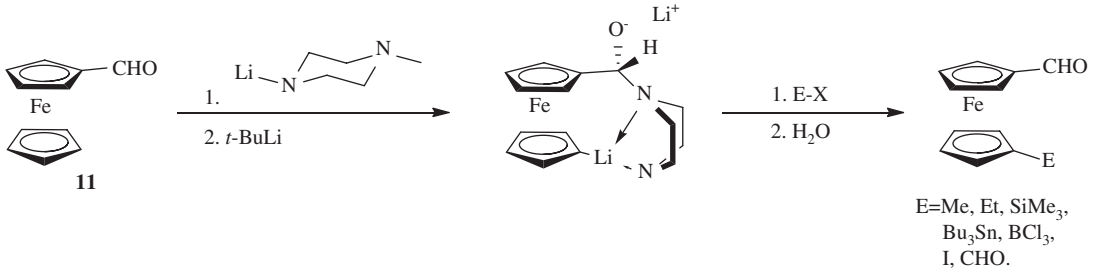
The preparation of chiral 1,2-disubstituted P,N-ferrocenes is typically achieved via diastereoselective *ortho*-lithiation, followed by quenching with an appropriate electrophile. This method was first demonstrated by Ugi with the lithiation of chiral [1-(N,N-dimethylamino)ethyl]



Scheme 1 Synthesis of chiral 1-(2-oxazolinyl)-1′-(diphenylphosphino)ferrocenes **5** via selective lithium-halogen exchange.



Scheme 2 Synthesis of chiral hybrid phosphane, hydrazone ligand **10** via a ring opening with phenyllithium of the strained 1-phenyl-1-phospha-[1]-ferrocenophane **6.**

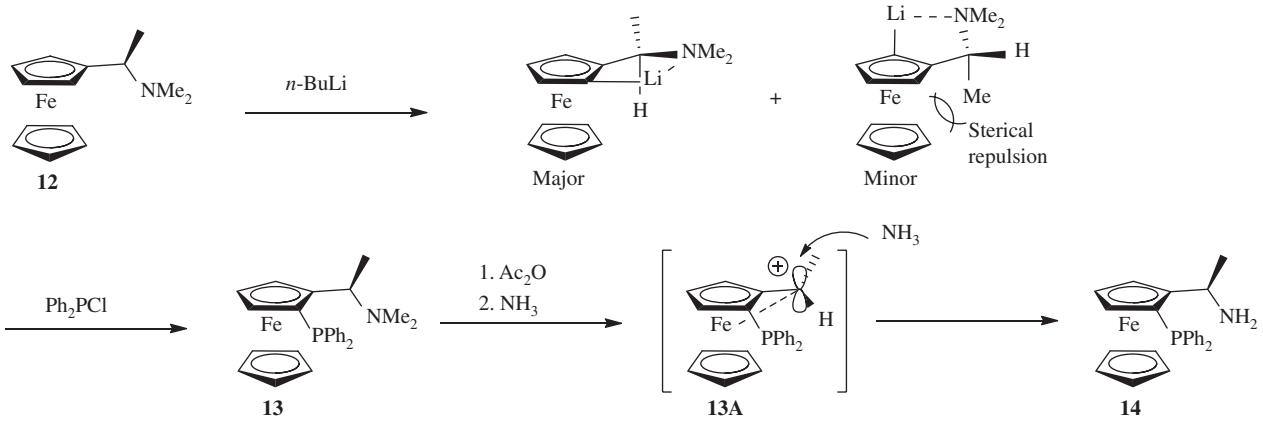


Scheme 3 Selective lithiation of the 1′-position.

ferrocene (**12**), also called Ugi's amine [29]. High diastereoselectivity is provided as a result of the sterical repulsion between the methyl substituent and the ferrocene moiety in the unfavored diastereomer (Scheme 4).

Another remarkable feature is that nucleophilic displacement reactions at the α-position proceed with complete retention of configuration [30]. This is due to the stabilization of the carbenium ion via an overlap with an iron lone pair (**13A**). Consequently, free rotation around the bond between the ferrocenyl group and the side chain is prohibited, and the nucleophile attacks from the less hindered face. This leads to a conservation of the stereochemistry at the α-center.

Since the original work of Ugi, several other chiral *ortho*-directing groups have been developed, such as sulfoxides [31], acetals [32, 33], sulfoximines [34], hydrazones [35, 36], pyrrolidines [37], imidazolines [38], azepines [39], *O*-methylephedrine derivatives [40], alcohols [41], phosphine oxides [42] and oxazophospholidines [43]. In addition, oxazolines have been shown by various groups to be excellent *ortho*-directing groups [44–47]. The origin of diastereoselection is shown in Figure 3. Due to



Scheme 4 Synthesis of 1,2-disubstituted P,N-ferrocenes via a diastereoselective *ortho*-lithiation.

steric hindrance from the ferrocene moiety, *n*-BuLi has to approach from the upper side of the ferrocene. This implies that the substituent on the oxazoline moiety has to point downwards in order to avoid sterical repulsion with the incoming *n*-BuLi molecule. Access towards the other diastereomer with opposite planar chirality is provided via introduction of a temporary protecting group, followed by lithiation and functionalization of the less favored position (Scheme 5) [46].

In sharp contrast with these chiral *ortho*-directing groups, the introduction of planar chirality, with enantiomerically pure bases, is less common. Mostly, low to moderate enantioselectivities were reported [48, 49]. An interesting exception, is the use of an *n*-BuLi/(-)-sparteine adduct in the *ortho*-lithiation of ferrocenylamide **18** (Scheme 6) [50]. Excellent enantioselectivities (up to 99% ee) were obtained.

3 Catalytic applications

3.1 Enantioselective allylic substitution reactions

The enantioselective allylic substitution reaction has proven to be an excellent reaction for chiral hybrid P,N ligands. This can be attributed to the higher *trans*-effect of the phosphorus, as compared to the nitrogen, resulting in an electronic differentiation of the two allylic termini in the transition state complex. It has been shown that the attack of the nucleophile happens at the allylic terminus *trans* to phosphorus [51, 52]. It is beyond the scope of this review to cover all chiral hybrid P,N ferrocene ligands used in enantioselective allylic substitutions. We will focus our attention on the role of planar chirality in 1,1′,2′-substituted and 1,2-disubstituted P,N-ferrocenyl ligands and the influence of the nitrogen donor.

Hou et al. studied the role of planar chirality in 1,1′,2′-substituted P,N-ferrocenyl ligands (Scheme 7) [53, 54]. Ligand **22** demonstrated high enantioselectivity in the allylic substitution reaction of 1,3-diphenyl-2-propenyl acetate (**20**) with dimethyl malonate. Introduction of planar chirality into this 1,1′-disubstituted system had a very pronounced effect on the reaction outcome. Remarkably, the presence of this third substituent not only influenced greatly the enantioselectivity, but also induced a chirality switch.

Ligands lacking the central chirality on the oxazoline moiety (e.g., **25**) still provide good enantioselectivity. This indicates that planar chirality plays a decisive role in the chiral induction. Based on X-ray structures and NMR studies, an explanation for these remarkable results was provided. It was shown that planar chirality influences the ratio of the two rotamers due to sterical interactions (Scheme 8).

The role of planar chirality in 1,2-disubstituted P,N-ferrocenyl ligands was studied by Hou et al. [55] The influence of the planar chirality was less pronounced than in the case of 1,1′,2′-substituted ligands, as shown in Scheme 9. With ligand **29**, lacking the central chirality in the oxazoline moiety, a lower enantioselectivity and a chirality switch were observed. Despite the fact that the central chirality was, in this case, the most dominant parameter, it was shown that a matching of the central and planar chirality was especially crucial in allylic amination reactions.

Recently, Hou et al. reported a method where they use ketone enolates as nucleophiles for the allylic alkylation of cinnamyl *tert*-butoxycarbonyl carbonate (Scheme 10) [56–58]. As a result, two chiral centers were constructed in excellent regio-, diastereo- and enantioselectivity. Key for these results was the use of a

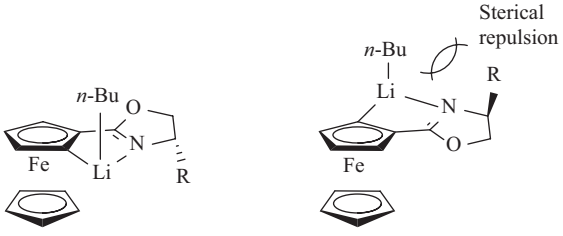
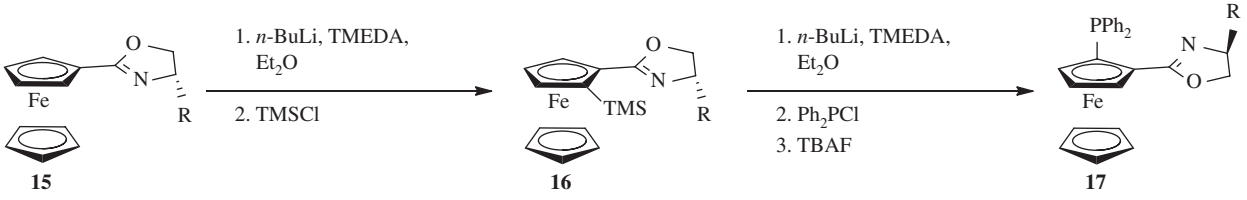
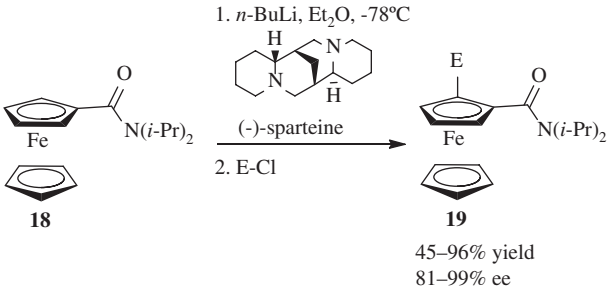


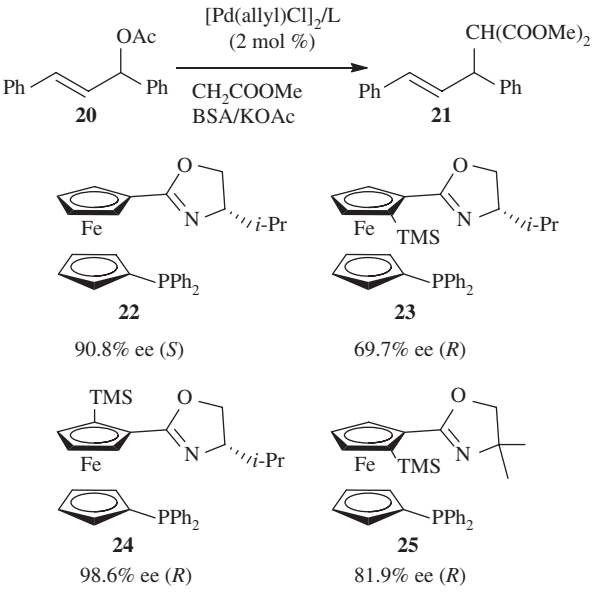
Figure 3 The origin of diastereoselection with an oxazoline as an *ortho*-directing group.



Scheme 5 Synthesis of the diastereomer with the opposite planar chirality.



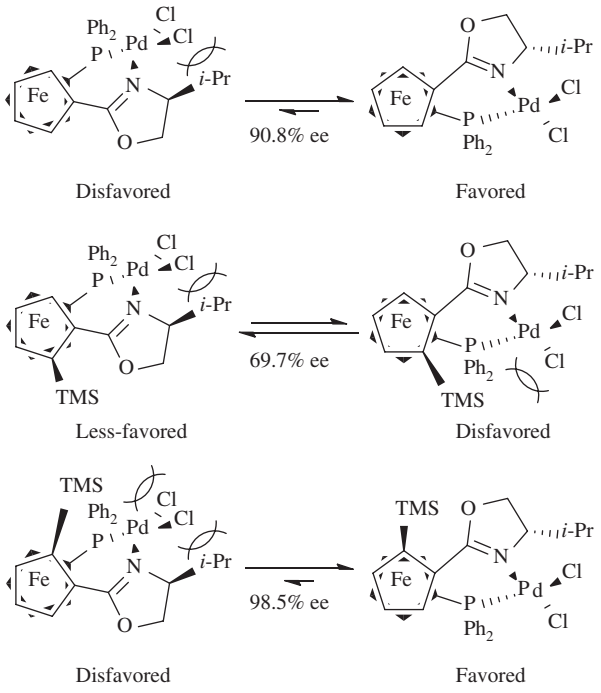
Scheme 6 Enantioselective *ortho*-lithiation.



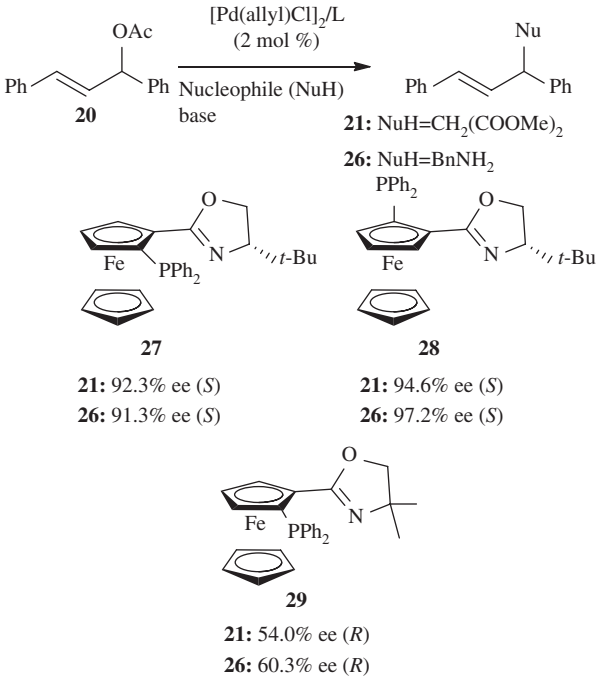
Scheme 7 The role of planar chirality in 1,1′,2′-substituted P,N-ferrocenyl ligands.

1,1′ – substituted P,N-ferrocenyl ligand (**33**) with chirality on the phosphorus.

Noël and Van der Eycken have developed the imidate/phosphane based ferrocenyl ligand **42** as a new type of P,N-ferrocenyl ligand [59, 60]. These ligands showed very high enantioselectivities in the allylic alkylation of the linear sterically hindered substrate **20,** with a wide variety of carbon nucleophiles (Scheme 11). In addition, good enantioselectivities were obtained in the allylic alkylation of linear sterically unhindered substrate **34** and cyclic substrates **36–38**, demonstrating that this catalyst system has a broad substrate scope. It was also shown that the results depended strongly on the choice of the appropriate *N,O*-bis(trimethylsilyl)acetamide (BSA)-activator. A comparison with several related nitrogen donor ligands, like **43** and **44,** revealed that the presence of the imidate nitrogen donor [61, 62] is required for both the high enantioselectivities as the broad substrate scope.

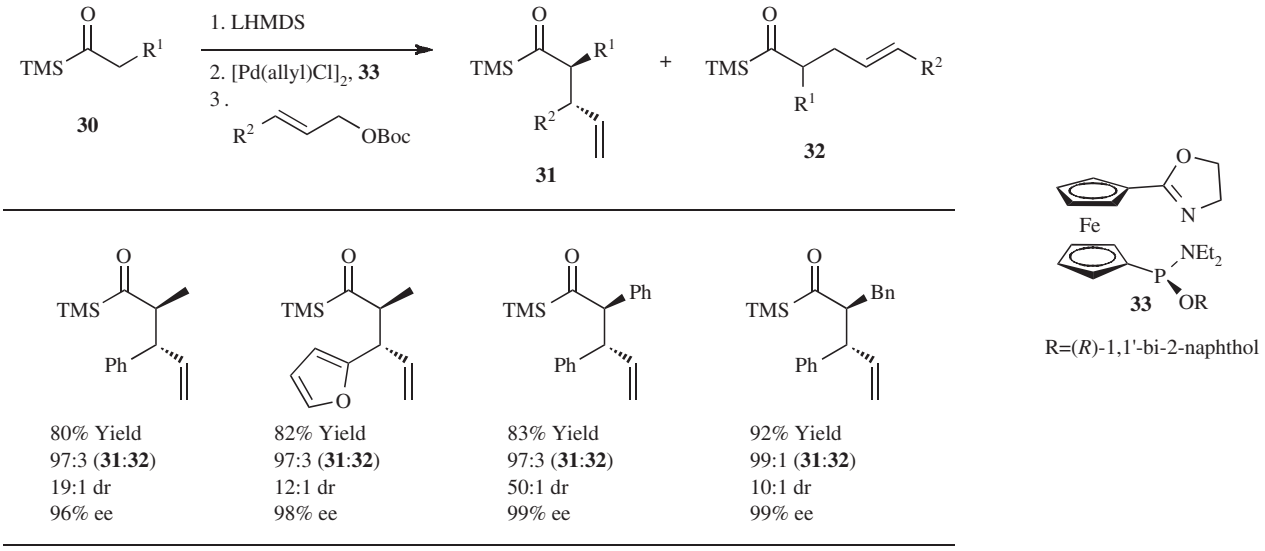


Scheme 8 Sterical interactions in 1,1′,2′-substituted P,N-ferrocenyl ligands.



Scheme 9 The role of planar chirality in 1,2-disubstituted P,N-ferrocenyl ligands.

Zheng et al. synthesized several ferrocenylphosphane-based heterocyclic ligands and examined the influence of the heterocycle moiety on the catalytic reaction



Scheme 10 Palladium-catalyzed enantioselective allylic alkylation with acyl silanes.

(Scheme 12) [63]. It was shown that the efficiency of the enantioselective allylic alkylation reaction of 1,3-diphenyl-propenyl pivalate (**45**) was strongly dependent on the number of heterocyclic nitrogen atoms. The most efficient ligand (**48**) contained a triazine moiety.

3.2 Enantioselective Heck reactions

The Heck reaction is one of the most important C-C bond forming reactions and has been used in the synthesis of several natural products [64]. Heck reactions can be performed both in an inter- as well as in an intramolecular fashion, providing many opportunities for enantioselective catalysis. Design of a ligand that can induce high enantioselectivities in both inter- and intramolecular Heck reaction is a huge challenge.

1,1′-Disubstituted oxazoline, phosphane ligand **51,** was evaluated in the intermolecular enantioselective Heck reaction of dihydrofuran **49** and phenyl triflate (Scheme 13). With these substrates, a good enantioselectivity (76.5% ee) and reactivity (80% yield in 8 h) was obtained [65]. Introduction of planar chirality led to some remarkable results. The use of ligand (*S, S*$_p$)-**52** resulted in a higher selectivity and the opposite stereochemistry. With ligand (*S, R*$_p$)-**53** an excellent enantioselectivity of 92.1% ee was obtained.

Guiry et al. investigated 1,2-disubstituted P,N-ferrocenyl ligand **27** in this intermolecular Heck reaction of dihydrofuran **49** and phenyl triflate [66]. Despite the fact that excellent enantioselectivities (up to 99% ee) were observed, rather poor yields (52% yield) were obtained even after 14 days of reaction.

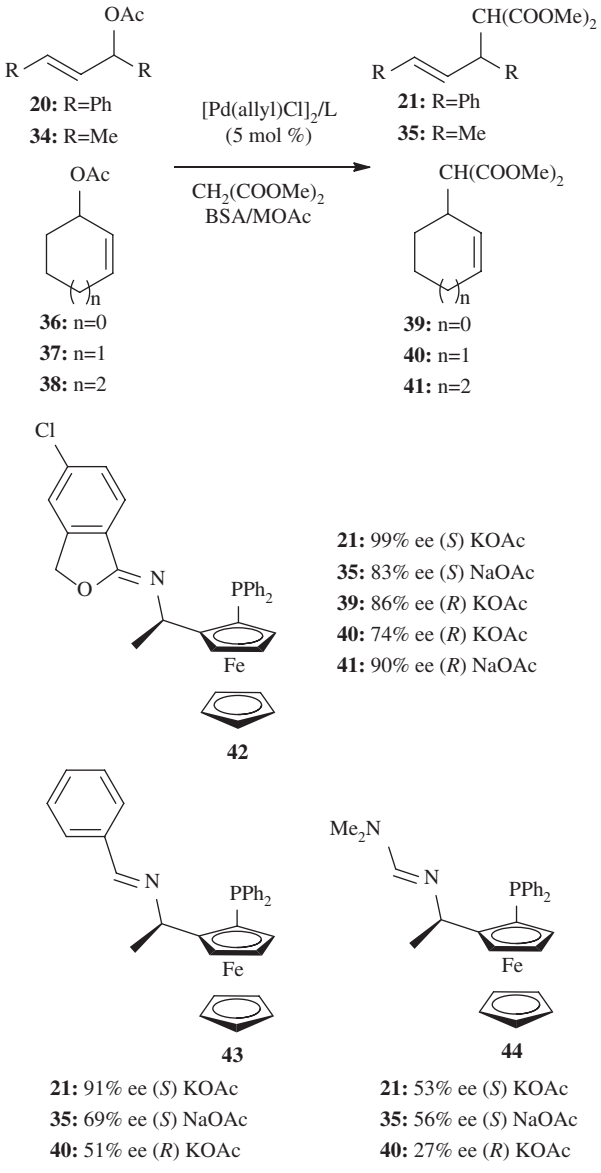
Intramolecular Heck reactions have been evaluated too. However, most of the time, moderate conversions and enantioselectivities were obtained [67, 68].

3.3 Enantioselective hydrogenation reactions

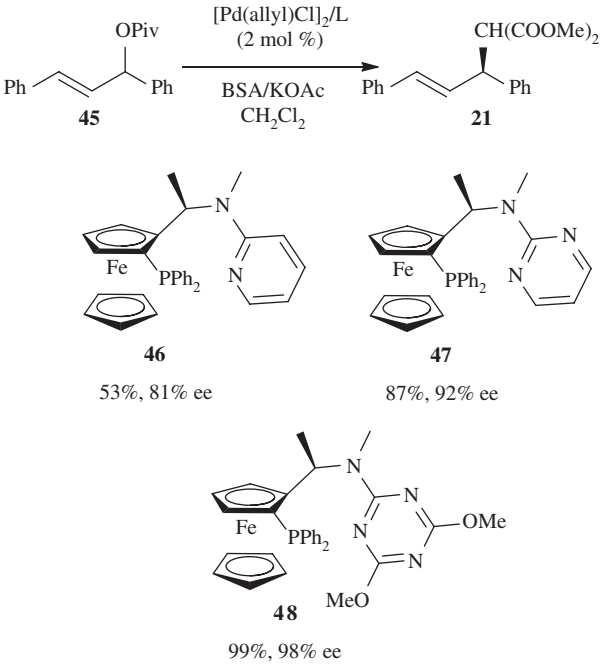
Catalytic enantioselective hydrogenation reactions of unsaturated compounds are one of the most reliable methods used to synthesize enantiopure compounds. Many research efforts are devoted to the development of new and improved hydrogenation catalyst systems. This is due to the fact, that for some substrate classes, the development of enantioselective catalyst systems is quite challenging [69].

Zhou et al. used ligands **27**, **28** and **56** in the iridium-catalyzed hydrogenation of quinolines (**54**) and studied the role of planar chirality in this reaction (Scheme 14) [70]. It was shown that the best result was obtained with ligand (*S,S*$_p$)-**27**. With ligand **56**, lacking the planar chirality, a significantly lower enantioselectivity was obtained. Since the absolute configuration of the product was in all cases *R*, it can be assumed that the steric course of the reaction is mainly controlled by the central chirality on the oxazoline ring.

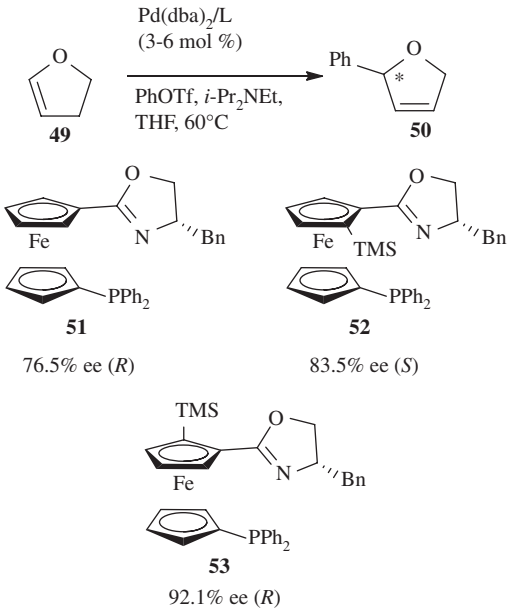
A small library of imidate/phosphane based ferrocenyl ligands was screened in the iridium(I)-catalyzed hydrogenation of unfunctionalized olefins **57** [71]. These substrates are considered as challenging substrates, since



Scheme 11 The use of imidate/phosphane based ferrocenyl ligands in enantioselective allylic alkylation reactions.



Scheme 12 The influence of the heterocyclic moiety on the catalyst performance.

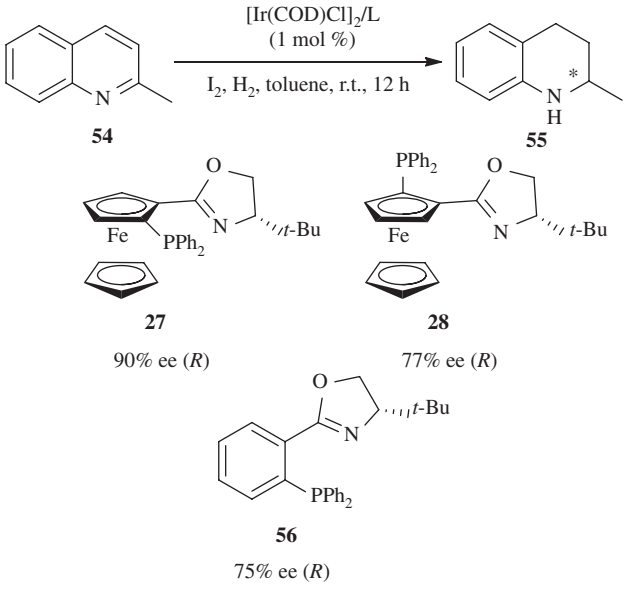


Scheme 13 The role of planar chirality in the enantioselective Heck reaction with 1,1′,2′-substituted P,N-ferrocenyl ligands.

they do not have a polar coordinating group which can coordinate to the complex to provide high enantioselectivities [72, 73]. The best results were obtained with ligand **59;** up to 99% for substrate **57b** (Scheme 15).

Ligand **27** also proved to be effective in the ruthenium-catalyzed hydrogenation of aryl ketones. High enantioselectivities (up to 99% ee) were obtained with excellent turnover numbers (TON, up to 50,000) [74, 75]. In sharp contrast with the catalyst system of Noyori, [76] these complexes contain no N-H group, suggesting a mechanism with a classical C=O coordination-insertion of H_2.

Ligand **27** was found to be the ligand of choice in the iridium-catalyzed enantioselective hydrogenation of α,β-unsaturated amides, furnishing amides with an α-chiral center in excellent enantioselectivities (up to 98% ee) [77]. The authors concluded that the presence of a hydrogen on the amide nitrogen was required for obtaining high selectivities.



Scheme 14 Enantioselective hydrogenation of 2-methylquinoline.

Also in ruthenium-catalyzed transfer hydrogenations of aryl ketones, oxazolinyl-ferrocenylphosphane ligands proved to be effective. Enantioselectivities of >95% ee were usually obtained using *i*-PrOH as a hydrogen donor [78–82].

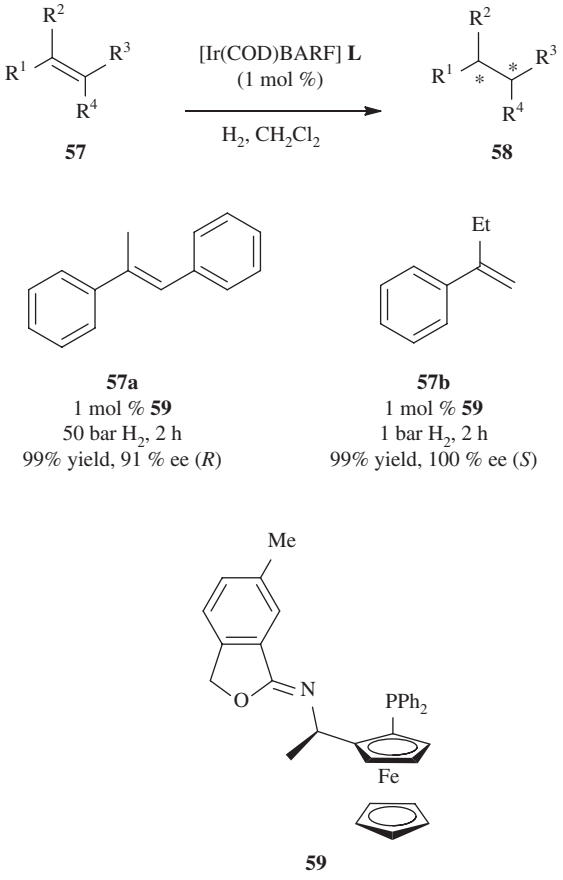
3.4 Enantioselective hydrosilylation reactions

The rhodium-catalyzed hydrosilylation followed by hydrolysis of the silyl ether, is a practical alternative for the enantioselective hydrogenation of ketones. Hayashi et al. reported the use of mixed imino/phosphane ferrocenyl ligands in enantioselective rhodium-catalyzed asymmetric hydrosilylation of ketones with diphenylsilane [83]. Enantioselectivities of up to 90% ee were obtained.

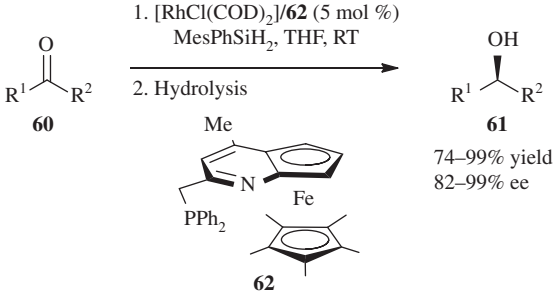
Excellent enantioselectivities for this transformation were reported by Fu et al. using planar chiral ligand **62** (Scheme 16) [84]. It was shown that the enantioselectivity is highly dependent on the proper choice of the silane. Enantioselectivities up to 98% ee were obtained with $MesPhSiH_2$ for acetophenone as a model substrate. Several other aryl alkyl ketones and dialkyl ketones were subjected to the enantioselective hydrosilylation and, in almost all cases, enantioselectivities of >99% ee were obtained.

3.5 Enantioselective [3+2] cycloadditions

1,3-Dipolar cycloadditions are useful reactions for synthesizing five-membered heterocycles. Fu et al. demonstrated



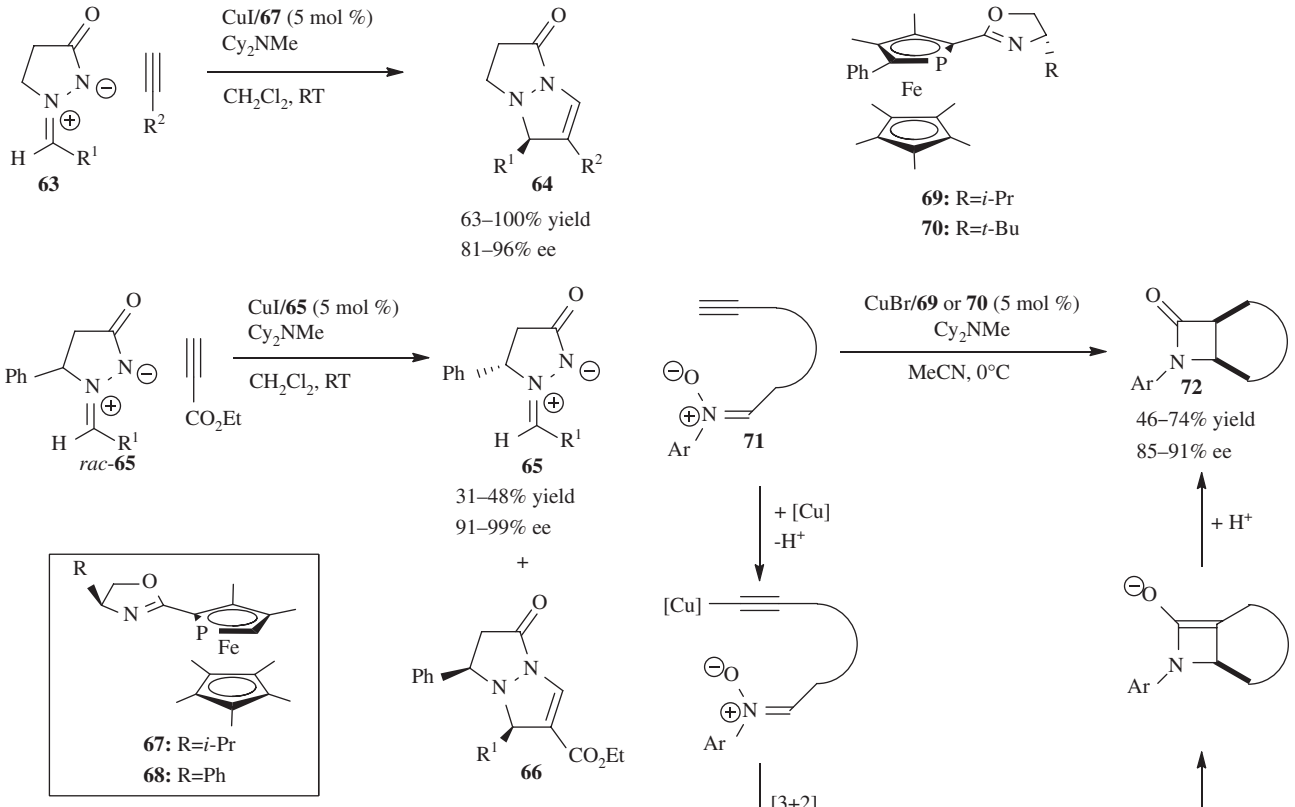
Scheme 15 Enantioselective hydrogenation of unfunctionalized olefines.



Scheme 16 Enantioselective hydrosilylation of ketones.

that P,N-phosphaferrocenyl ligands **67** and **68** are excellent ligands for the copper-catalyzed [3+2] cycloaddition of azomethine imines **63** and alkynes (Scheme 17) [85]. Enantioselectivities up to 96% ee were obtained. Using a ligand with the opposite planar chirality resulted in a significant decrease in ee.

In an extension of this method, it has been shown that the same catalyst system is also effective in the kinetic resolution of racemic azomethine imines *rac*-**65** (Scheme 17) [86]. As a result, a wide variety of enantioenriched



Scheme 17 Cu-catalyzed [3+2] asymmetric cycloadditions of terminal alkynes with azomethine imines.

Scheme 18 Catalytic enantioselective synthesis of β-lactams through an intramolecular Kinugasa reaction.

1,3-dipoles **65** could be isolated. Subsequent reaction with dipolarophiles provides functionalized pyrazolidinones.

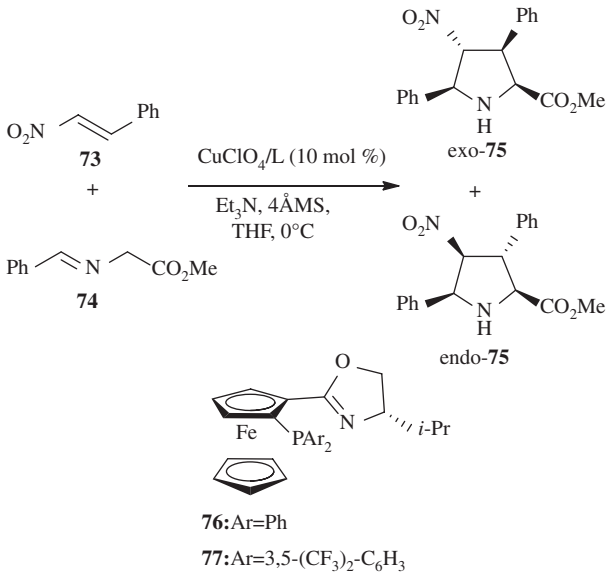
The Cu(I)-catalyzed reaction of nitrones with terminal alkynes results in the formation of β-lactams. This reaction is also called the Kinugasa reaction [87]. The first step involves a 1,3-dipolar cycloaddition with an *in situ* generated copper(I) acetylide. Hence, a five-membered ring intermediate is formed. Subsequent rearrangement results in the formation of the β-lactam. Fu et al. developed an enantioselective intramolecular version of this Kinugasa reaction [88]. With planar chiral phosphaferrocenyl-oxazoline ligands **69** and **70**, good to excellent enantioselectivities (85–91% ee) were obtained (Scheme 18).

A chiral oxazolinyl-ferrocenylphosphane complex with AgOAc catalyzed the enantioselective cycloaddition of an N-metalated azomethine ylide with electron-deficient alkenes, leading to *endo*-pyrrolidines in excellent enantioselectivities (88–98% ee) [89]. Interestingly, when copper(I) complexes of chiral oxazolinyl-ferrocenylphosphane ligands were used, the pyrrolidine products were obtained with a high *exo*-selectivity and excellent enantioselectivity (84–98% ee) [90].

Using the same copper source and a similar ligand, Hou et al. developed a 1,3-dipolar cycloaddition of nitroalkenes **73** with N-metalated azomethine ylides derived from **74** (Scheme 19) [91]. Variations on the nature of the aryl group on the phosphorus atom resulted in a dramatic change of the *endo*/*exo* selectivity: electron-rich phosphanes (**76**) promoted the formation of the *exo*-adduct as the sole product, while electron poor phosphanes (**77**) afforded mainly the *endo*-adduct.

3.6 Miscellaneous reactions

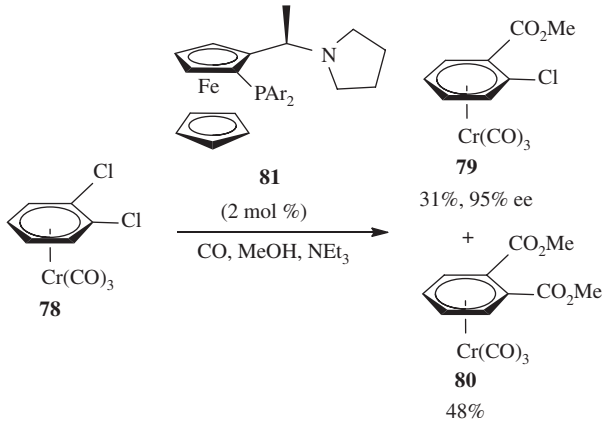
Schmalz et al. introduced planar chirality in *meso*-(arene) chromium complexes via an enantioselective methoxycarbonylation (Scheme 20) [92–94]. Although low to moderate yields of **79** were obtained, the induced enantioselectivity was up to 95% ee with a chiral pyrrolidinoethyl-ferrocenylphosphane ligand **81**.



Entry	Ligand	Yield [%]	exo/endo	ee [%] (exo/endo)
1	**76**	58	only exo	97/n.d.
2	**77**	62	18:82	88/97

Scheme 19 Cu-catalyzed asymmetric 1,3-dipolar cycloaddition of azomethine ylides: influence of the nature of the P-aryl substituent on the phosphorus atom.

In addition, chiral hybrid P,N-ferrocenyl ligands also effectively introduce axial chirality. In the presence of *N,N*-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]ethylamine (**13**, ppfa) as a ligand, a C_2-symmetrical binaphthalene was obtained in very good enantioselectivity (up to 85% ee) via an enantioselective Suzuki cross-coupling [95, 96].



Scheme 20 Introduction of planar chirality via a catalytic enantioselective methoxycarbonylation.

The $Cu(OTf)_2$-catalyzed addition of diethylzinc to imines in the presence of ppfa **13** as chiral ligand, resulted in good enantioselectivities (86–92% ee) [97].

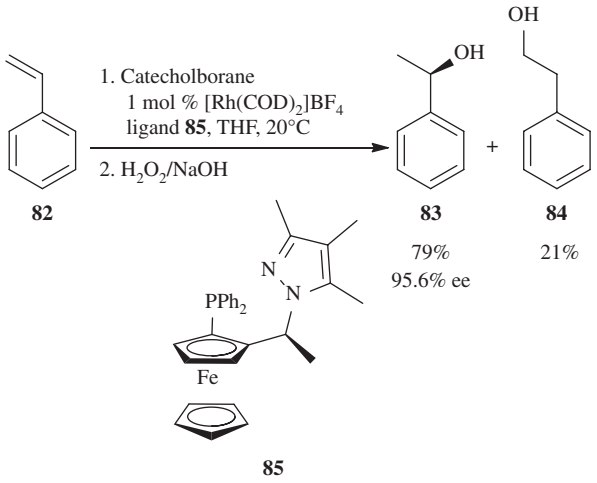
Togni et al. demonstrated that pyrazolylethylferrocenylphosphane ligands **85** were effective in rhodium-catalyzed hydroboration reactions (Scheme 21) [98]. A maximum of 95.6% ee was obtained, albeit with a moderate regioselectivity (branched **83** /linear **84**, 79:21). Similar results were obtained by Knochel et al. with a (2-quinolyl)-ferrocenylmethylphosphane ligand [99].

A chiral oxazolinyl-ferrocenylphosphane ligand (*ent*–**76**) was used in a nickel-catalyzed enantioselective intramolecular arylcyanation reaction (Scheme 22) [100, 101]. The intermediate product **87** had an enantioselectivity of 96% ee and was further used in the synthesis of (-)-esermethole **88**.

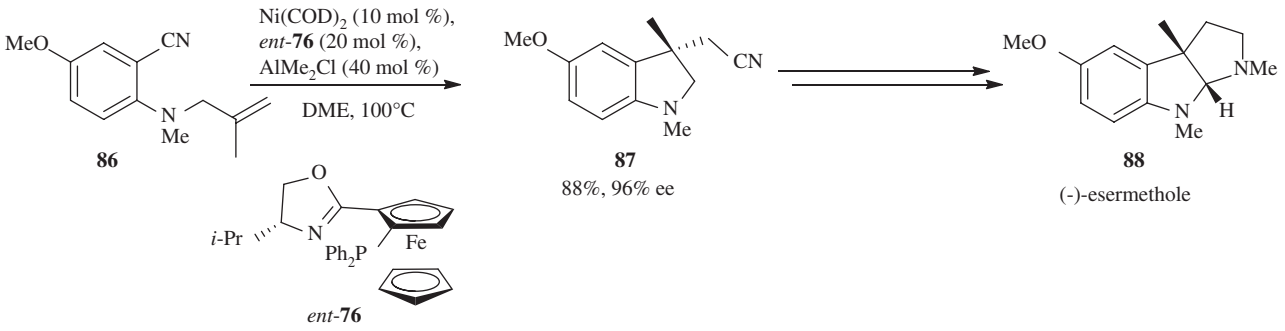
The same ligand proved to be excellent in a nickel-catalyzed enantioselective annulation reaction of *N*-aryl-1,2,3-benzotriazin-4(3*H*)-ones **89** with allenes **90** (Scheme 23) [102]. The chiral oxazolinyl-ferrocenylphosphane ligand (**76**) gave both excellent regio- and enantioselectivities (87–97% ee). The same catalyst system appeared to be also useful for the enantioselective [2+2+2] cycloaddition of isocyanates and allenes [103].

4 Conclusions

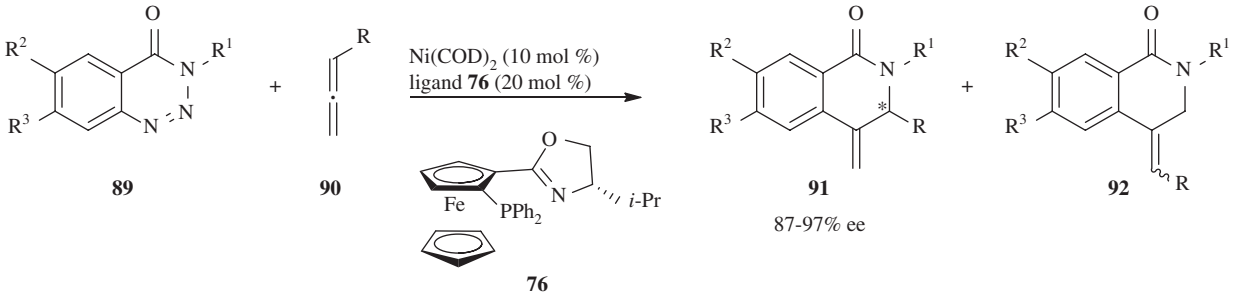
In this review, we presented an introduction to the synthesis of ferrocene-derived P,N-ligands and compiled a selection of the most important enantioselective transformations in which these ligands were used.



Scheme 21 Catalytic enantioselective hydroboration of styrene with catecholborane.



Scheme 22 Catalytic enantioselective intramolecular arylcyanation and its application in the synthesis or (-)-esermethole.



Scheme 23 Catalytic enantioselective annulation reaction of *N*-aryl-1,2,3-benzotriazin-4(3*H*)-ones **89** with allenes **90**.

Due to their unique steric and electronic properties, air stability and modular structure, chiral hybrid P,N-ferrocenyl ligands have evolved in recent years as exceptional ligands, capable of addressing a wide range of enantioselective reactions. We believe that these ligands should be part of each chiral ligand kit for the initial screening of ligands for any new enantioselective reaction. Recently, continuous-flow microreactors have received a significant amount of interest to facilitate rapid screening of chiral catalysts [104, 105].

Although, a significant amount of research has been done, progress is not without challenges. Much time has been devoted to the synthesis of this valuable ligand class. Due to its modular structure, a rapid diversification of the ligand is possible, and consequently, many P,N ligands bearing the ferrocene moiety have been synthesized. This gives the impression that for almost every enantioselective reaction, a good ligand is available. In fact, this is not the case. Reactions that generate chiral centers are constantly appearing in the literature and the demand for new and improved chiral catalysts with new reactivities increases. We are convinced that chiral hybrid P,N-ferrocenyl ligands will play further a central role in the discovery of new enantioselective reactions.

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