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Review

Recent developments in the chemistry of azaferrocenes

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Contents

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ABSTRACT

The simplest heteroferrocene, azaferrocene, was first described in 1964, and until recently, the chemistry of these compounds has remained largely unexplored. This review will focus on recent advances in the chemistry of azaferrocenes including methods of azaferrocene synthesis and functionalization. The electrochemical behavior of azaferrocenes and their applications in catalysis and biology will also be emphasized here.

1. Introduction

For almost 60 years, the chemistry of ferrocene **1** [1,2] and its derivatives has remained a leading topic in organometallic chemistry. That privileged position was associated with the availability and stability of ferrocenes along with their rich synthetic chemistry and applications in asymmetric synthesis, materials science, and biology [3–5]. In contrast, the chemistry of the heterocyclic analogues of ferrocenes ('heteroferrocenes') has been less well established. Of the heteroferrocenes, the phosphaferrocenes have been most widely studied [6–10].

Abbreviations: Ac, acetyl; BAF, tetrakis[3,5-bis(trifluoromethyl)phenyl] borate; *n*-BuLi, *n*-butyllithium; *sec*-BuLi, *sec*- butyllithium; *tert*-BuLi, *tert*-butyllithium; BHT, butylated hydroxytoluene; Cy, cyclohexyl; DIPA, diisopropylamine; DMAP, 4-*N*,*N*-dimethylaminopyridine; DME, 1,2-dimethoxyethane; DCM, dichloromethane; EDOT, 3,4-ethylenedioxythiophene; DMF, *N*,*N*-dimethylformamide; Fc, ferrocenyl; TBS (or TBDMS), *tert*-butyldimethylsilyl; TBDPS, *tert*-butyldiphenylsilyl; TES, triethylsilyl; Tf, trifluoromethanesulfonate; THF, tetrahydrofuran; TMEDA, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; TMS, trimethylsilyl; $Pd_2(dba)_3$, tris(dibenzylideneacetone)dipalladium.

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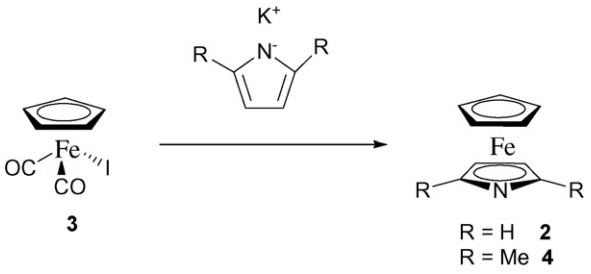
Fig. 1. The structures of ferrocene **1** and azaferrocene **2**.



Scheme 1.

Far less attention has been devoted to azaferrocenes. Azaferrocene **2**, which can be constructed by the replacement of one cyclopentadienyl methylene CH group in ferrocene by a N atom, is the simplest representative of the azaferrocene family (Fig. 1).

There is a lack of review articles dealing with azaferrocene chemistry with the exception of one paper published in 1995 which focused exclusively on the coordination of **2** to transition metal macrocyclic complexes [11]. Other reports have covered the more general field of azacyclopentadienyl–metal complex chemistry [12–14] and their applications in asymmetric catalysis [15,68]. The present review, examine the progress in azaferrocene coordination and organic chemistry, which we have been witnessed over the last years. This review covers the literature up to 2009.

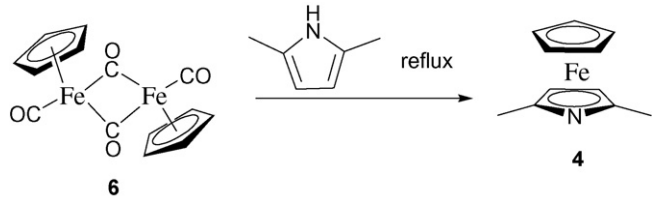
2. Synthesis of simple azaferrocenes

Azaferrocene **2** was first reported in 1964 by two independent research groups. Pauson and co-workers obtained **2** by reaction of cyclopentadienyl iron (II) dicarbonyl iodide **3** with pyrrolyl potassium in 22% yield [16]. By the same approach, the more stable 2,5-dimethylazaferrocene **4** was obtained in 32% yield (Scheme 1).

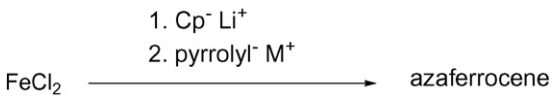
King and Bisnette also published a synthesis of **2** [17]. More recently Zakrzewski and Giannotti reported the simple and efficient synthesis of both azaferrocene **2** [18] and 2,5-dimethylazaferrocene **4** [19]. The former method was based on the photochemical reaction of cyclopentadienyl iron (II) dicarbonyl iodide **3** and pyrrole in the presence of diisopropylamine leading to the η^1-pyrrolyl complex **5**. Thermal decarbonylation of **5** gave **2** in 65% yield (Scheme 2).

In the latter method, **4** was prepared by heating of the cyclopentadienyl iron (II) dicarbonyl dimer **6** with 2,5-dimethylpyrrole (Scheme 3).

In terms of a general synthetic strategy, azaferrocenes can be prepared by reaction of the cyclopentadienyl anion, a Fe(II) containing precursor, and the corresponding pyrrolyl anion (Scheme 4).



Scheme 3.



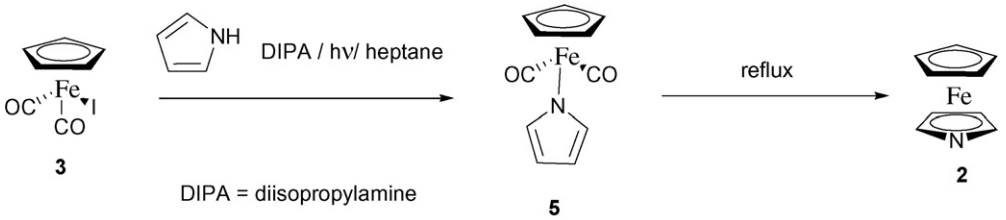
Scheme 4.

This approach has been applied to the synthesis of 1′,2′,3′,4′,5′-pentamethylazaferrocene **7** [20], 1′,2′,3′,4′,5′-pentaphenylazaferrocene **8** [21], 1′,2′,3′,4′,5′-pentamethyl-2,5-dimethylazaferrocene **9** [22], 1′,2′,3′,4′,5′- pentamethyl-3,4-diphenylazaferrocene **10** [23] and the C_2-symmetric bisazaferrocenes **11** and **12** (Fig. 2) [24,25].

If monosubstituted, trisubstituted or non-symmetrically disubstituted pyrrolyl anions are used in the above synthetic approaches, racemic mixtures of two planar chiral azaferrocenes are formed. In some cases their separation was achieved by preparative chiral HPLC [24,25]. The preparation of new azaferrocenes critically depends on the synthetic availability of their pyrrolyl ligands. This is well illustrated by synthesis of 1′,2′,3′,4′,5′-pentamethyl-3,4-diphenylazaferrocene **10** where four steps of the overall six-step synthesis dealt with obtaining 3,4-diphenylpyrrole [23].

3. Basic properties of azaferrocenes

Azaferrocene **2** is thermally less stable than ferrocene. Its thermal degradation yielding ferrocene and metallic iron has been observed in boiling benzene and toluene solutions [26]. However 2,5-dimethylazaferrocene **4** exhibits better thermal stability. In solutions azaferrocenes are air and light sensitive, but in the solid state, they can be stored under an inert gas atmosphere at 0 °C for months without decomposition. In aqueous ethanol, the pK_a value of azaferrocene **2** is 4.5, closely resembling that of quinoline (4.65) [16]. Introduction of additional methyl groups to the pyrrolyl ring increased the pK_a value and thus the pK_a of 2,3,4,5-tetramethylazaferrocene **13** has been reported to be closely similar to alkylpyridines (pK_a = 7.2) [27]. Azaferrocenes undergo reversible protonation at the nitrogen atom. Both **2** and **4** are quite soluble in water as compared to ferrocene. Azaferrocenes **2**, **4**, and **13** easily react with methyl iodide to form the corresponding *N*-methylated derivatives **14**, **15**, and **16** [28]. The nucleophilicity of the nitrogen in 2,3,4,5-tetramethylazaferrocene **13** has been probed by its reactions with Lewis acids, yielding *N*-acetyl and *N*-BH_3 adducts **17** and **18** [27] (Fig. 3).



Scheme 2.

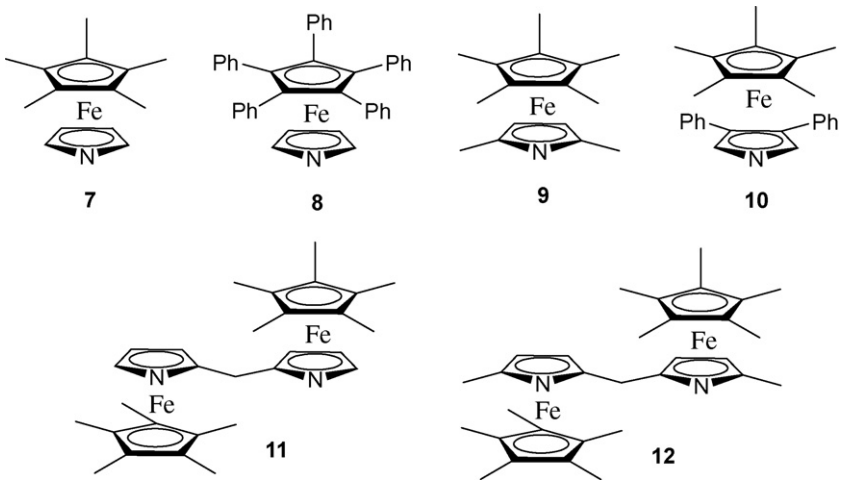


Fig. 2. The structures of azaferrocenes **7**–**12**.

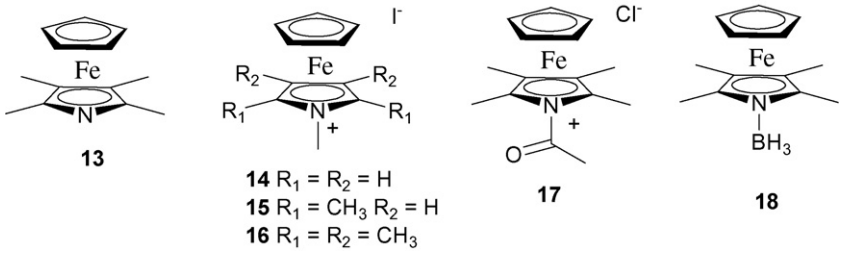


Fig. 3. The structures of azaferrocenes **13**–**18**.

Azaferrocenes **2** and **4** act as η^1-*N* ligands to form coordination complexes **19**–**22** with electron-rich Pd(II) and Pt(II) [29,30] metal centers and behave as relatively strong σ-donors and rather weak π-acceptors in complexes **23**–**26** with $M(CO)_5$ (M = W, Mo, Cr) fragments (Fig. 4) [31]. The family of azaferrocene metal–carbonyl complexes is also represented by complex **27** obtained by reaction of **13** with $Fe_2(CO)_9$ [27] and the structurally more complex orthometallated osmium carbonyl derivative **28** [32] (Fig. 4).

Azaferrocene **2** can also act as 2-electron donating axial ligand towards cobaloximes, metalloporphyrins, and phthalocyanines

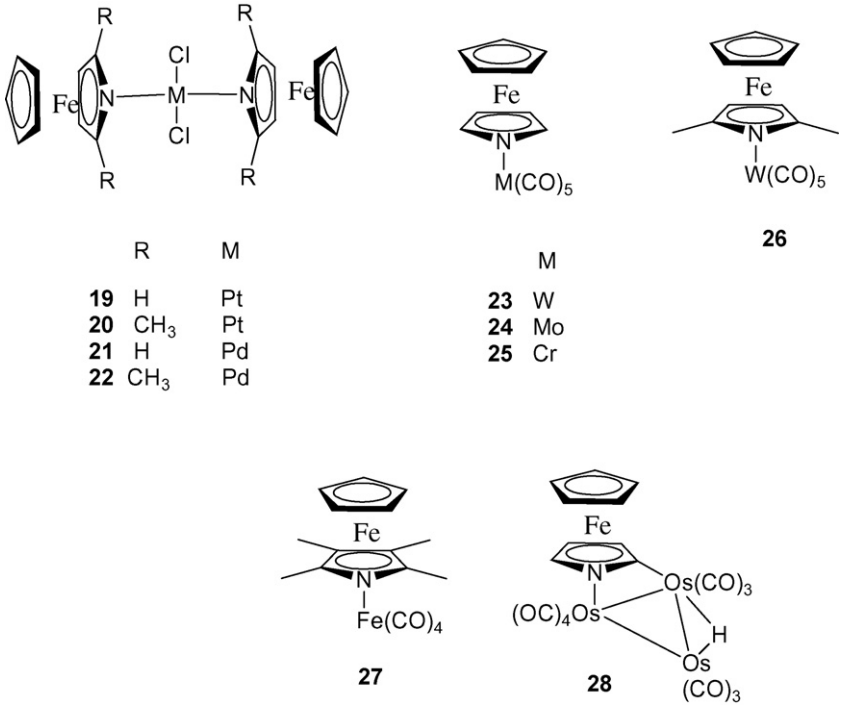


Fig. 4. The structures of azaferrocenes **19**–**28**.

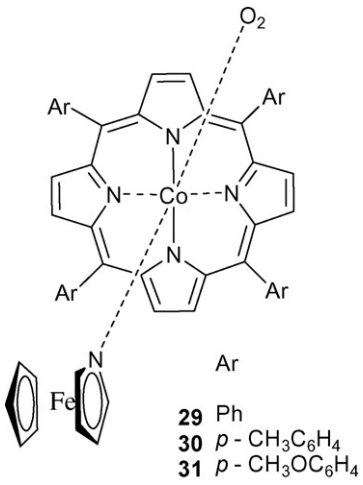


Fig. 5. The coordination of **2** to metalloporphyrins.

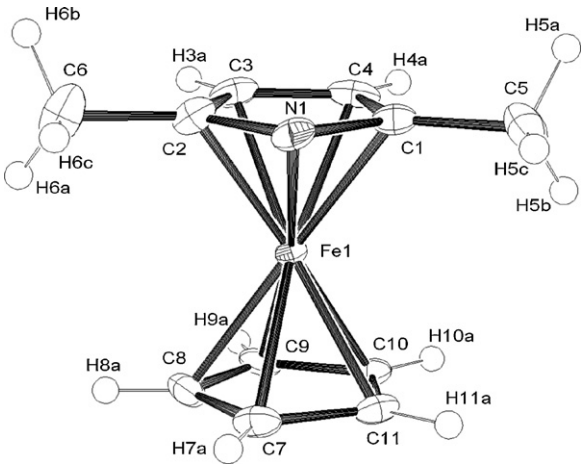


Fig. 6. ORTEP drawing of the molecular structure of azaferrocene **4** [44].

[11,33–35]. An in-depth photochemical study of these complexes showed that photoreduction of the macrocyclic ring can occur as a consequence of photoinduced electron transfer (PET) from the axially coordinated azaferrocene-donor **2**. The reversibility of that reaction, however, is strongly limited by decomposition of the unstable azaferrocenium cation. Photoactivation of cobalt porphyrin-**2**-(η^1-O_2) complexes **29**–**31** (Fig. 5) by irradiation with visible light results in the photoejection of triplet oxygen. Importantly, under the same conditions, their fully organic η^1-pyridine analogs are photostable [36]. More recently, fluorescence quenching of tetrasulfonated zinc and aluminum phthalocyanines by **2** has been reported [37,38].

The pyrrolyl ligand in **2** can undergo a $\eta^5 \rightarrow \eta^1$ haptotropic shift. The irradiation of a CO saturated cyclohexane solution of **2** at room temperature generated half-sandwich complex **5** [39] (Scheme 5.). On the other hand, a $\eta^5 \rightarrow \eta^1$-pyrrolyl rearrangement occurred in hot benzene solutions of **2** under 2.5 atm pressure of CO [26].

Azaferrocenes have been also subjected to ^{57}Fe Mössbauer spectroscopy studies [31,40–43]. The quadrupole splitting (Q.S.) values measured for azaferrocenes **2** and **4** are 2.51 mm s^{-1} and 2.48 mm s^{-1}, respectively [31]. Both of them are larger than that of 2.37 mm s^{-1} reported for ferrocene. These results suggest more electron-rich character of pyrrolyl ligand in azaferrocenes than cyclopentadienyl one in ferrocene. Mössbauer spectroscopy data showed that pyrrolyl ring in azaferrocenes acts more as electron donating than electron accepting (backbonding) ligand. The Q.S. values of metal-carbonyl azaferrocenes **23**–**26** are still similar to that of parental **2** and **4**. However either protonation or quaternisation of azaferrocene **2** effect in a lowering of Q.S. values to the same value of 2.36 mm s^{-1} [40].

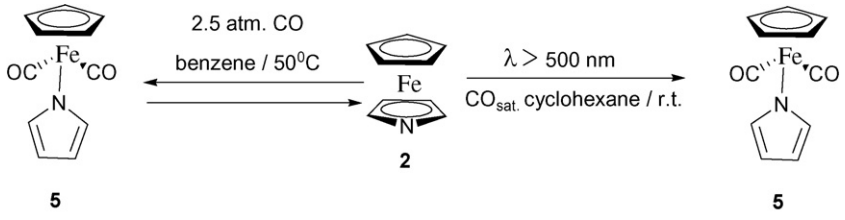
Although azaferrocene **2** has been the subject of many studies for several years, its solid-state crystal structure remains unreported. In contrast, an X-ray crystal structure of more stable 2,5-dimethylazaferrocene **4** has only been reported very recently. It revealed a sandwich structure of this heterometallocene with an iron atom positioned between a π-bonded 2,5-dimethylpyrrole and a π-bonded cyclopentadienyl ring with distances of 1.652 Å to the centroid of the pyrrole and 1.657 Å to the centroid of the cyclopentadienyl ring (Fig. 6) [44].

X-ray crystal structures of unstable *N*-methylated azaferrocenes **16** BF_4^- [45] and **15** PF_6^- have also been described [46]. Electronic structure of azaferrocenes has been also studied by quantum chemical calculations and compares to those of phosphaferrocenes and ferrocenes [52]. All of the above described rich chemistry applied to azaferrocenes has not involved their functionalization, i.e., the introduction of carbon side chains or functional groups to either the cyclopentadienyl or the pyrrolyl rings.

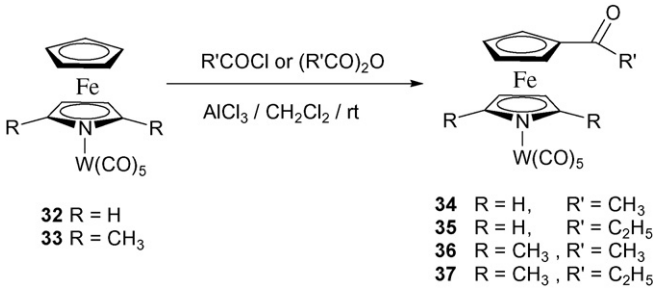
4. Functionalization of azaferrocenes

4.1. Friedel–Crafts reactions of azaferrocenes

In the early stages of azaferrocene chemistry development, Pauson and co-workers reported failure in electrophilic substitution reactions of this metallocene [16]. That lack of reactivity was in contrast to the ferrocene behavior [47]. One of the factors which demonstrated the aromatic character of ferrocene is that it can be functionalized by aromatic electrophilic substitution reactions analogously to its organic counterpart benzene [48]. Similarly to ferrocene, heterometallocenes like phosphaferrocene, 1,1′-diphosphaferrocene, arsa- and 1,1′-diarsaferrocene undergo Friedel–Crafts acylation [49–51]. The failure of azaferrocenes to undergo Friedel–Crafts acylation as well as other electrophilic substitutions reactions can be attributed to the deactivation effects of the highly electronegative pyrrolyl nitrogen atom [52]. In a well recognized analogous case, pyridine is markedly less reactive toward electrophiles than benzene. In the course of the reaction between the electrophile (or its acidic promoter) and azaferrocene, one can expect formation of an inactive cationic complex. Indeed,



Scheme 5.



Scheme 6.

compound **17** (Fig. 3) has been isolated from a reaction of **13** with acetyl chloride [27]. This result experimentally confirmed that the lone pair of nitrogen electrons strongly limited reactivity of azaferrocenes in electrophilic substitution reactions *via* formation of their unstable *N*-acyl derivatives. For over 40 years, problems with electrophilic substitutions reactions in azaferrocenes had remained unsolved. However, the first stepwise approach to the synthesis of acylazaferrocenes *via* the Friedel–Crafts reaction appeared in 2005 [53]. The key factor which allowed the reaction to succeed was coordination of the neutral $W(CO)_5$ fragment to the azaferrocenes. This trivial operation effectively eliminated the electronic influence of the lone pair of nitrogen electrons. Protected by the $W(CO)_5$ fragment, azaferrocenes **32** and **33** reacted with acetyl or propionyl chloride as well as with acetic or propionic anhydride in the presence of aluminum chloride as catalysts to afford acyl derivatives **34**–**37** (Scheme 6.).

The more electron-rich complex **33** gave higher yields (up to 50%) of acylated products **36** and **37** than did complex **32** (10–20% of isolated yield of **34** and **35**). The overall moderate yields of the reactions can be explained by decomposition of the acylated derivatives in the highly acidic reaction medium. The reaction is highly regioselective since only cyclopentadienyl-substituted products have been isolated and characterized. Selectivity is most probably determined by the steric hindrance of the $W(CO)_5$ fragment which hampered access to the pyrrolyl ligand. Additionally, coordination of the $W(CO)_5$ fragment to the azaferrocene has also the effect of decreasing the electron density of the pyrrolyl ligand. Thus, electrophilic attack is more favored to take place at the more electron-rich Cp ligand than at the electron deficient pyrrolyl one.

Very recently, a second report on electrophilic substitution reactions of azaferrocenes has been published [54]. Azaferrocene oxocarboxylic acids **38** and **39** were prepared by the $AlCl_3$ catalyzed acylation of **33** with succinic or glutaric anhydride (Scheme 7).

Similar to reactions with acyclic carboxylic acid anhydrides, cyclic carboxylic acid anhydrides also yielded exclusively cyclopentadienyl-substituted products. Apart from common spectroscopic methods, the proposed structures of the products of azaferrocene Friedel–Crafts acylations (compounds **34**, **38** and **39**) were confirmed by single crystal X-ray structure analyses [53,54].

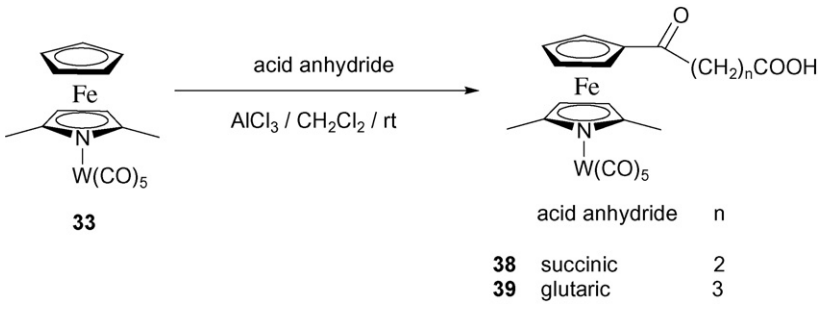
4.2. Reactions of lithiated azaferrocenes with electrophiles

Setkina and co-workers first reported the lithiation of azaferrocene **2** [55]. They examined the reaction of **2** with *n*-butyl lithium followed by addition of three types of electrophilic quenchers: methyl iodide, deuterium oxide, or trimethylsilyl chloride. Due to problems with purification the rather unstable products, their structures and mutual proportions were investigated by NMR spectroscopy. Depending on experimental conditions, different products and variations in their ratios were observed.

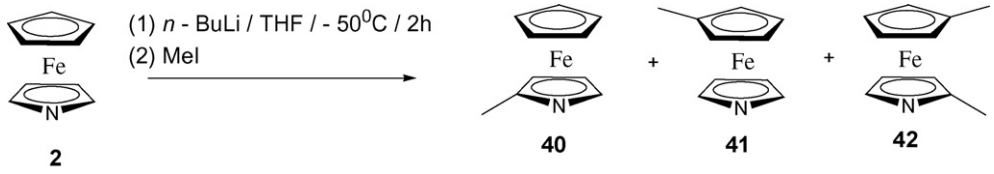
When the lithiated azaferrocene **2** was treated with *n*-butyl lithium for a period of 2 h and then quenched by MeI addition, the resulting product mixture contains 49% of an α-pyrrolyl (ortho lithiated) derivative **40**, 36% of a cyclopentadienyl-substituted derivative **41**, and 15% of a disubstituted derivative **42** (Scheme 8).

Products derived from lithiation of the β-pyrrolyl position were not detected at all. Decreasing the reaction time resulted in the generation of solely **40** and **41**, and longer reaction times favored formation of dilithiated **2**. Similar results were obtained when a reaction mixture was treated with D_2O and Me_3SiCl as quenchers.

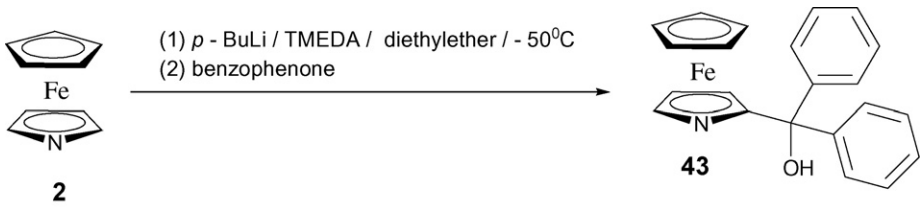
In an extension of their initial work, Setkina's group examined other conditions of the lithiation reaction with respect to solvents and electrophilic quenchers. In an attempt to obtain the 2,1′-disubstituted azaferrocene derivatives of **2**, they reacted azaferrocene **2** with *n*-butyl lithium in hexane in the presence of TMEDA at r.t. followed by an addition of benzophenone as an electrophile. Unexpectedly, these experimental conditions yielded only starting material **2** [56]. This result contrasts with the reactivity of ferrocene which under the same conditions is readily 1,1′-dilithiated and can react with various electrophiles [3]. However, replacement of *n*-hexane by diethyl ether as the solvent, decreasing the reaction temperature to −50 °C provided



Scheme 7.



Scheme 8.



Scheme 9.

2-diphenylhydroxymethylazaferrocene **43** as the sole and fully characterized regioisomer (Scheme 9) [56].

In a subsequent series of experiments, lithiated **2** was reacted with different carbonyl compounds like benzaldehyde, dibenzyl ketone, diisopropyl ketone, and cyclohexanone under the same conditions as those employed for the reaction of benzophenone [57]. Reaction with cyclohexanone led to cyclopentadienyl functionalized alcohol **44** and the other electrophiles reacted to give α-pyrrolyl derivatives **45**–**47** (Fig. 6). Products originating from 1′,2-dilithiated azaferrocene were not observed at all.

The yields of reactions were 40–55% for pyrrole-substituted azaferrocenes **45**–**47** and 25% for **44**. The isolations of the products were accompanied by partial recovery of the starting azaferrocene **2**.

The lithiation reaction with respect to 2,5-dimethylazaferrocene **4** was investigated by Kowalski and Zakrzewski [58]. In contrast to azaferrocene **2**, 2,5-dimethylazaferrocene **4** has two methyl groups at the α-pyrrolyl positions which are potentially amenable to lateral lithiation. Ferrocene chemistry has demonstrated that methyl substituted ferrocenes tend to undergo lithiation at the cyclopentadienyl rings instead of the methyl groups [59]. Such a behavior indicates stronger acidic character of the cyclopentadienyl protons as opposed to the methyl protons [60,61] along with a greater ability for the electron-rich Fc group to stabilize negative charges at the cyclopentadienyl ring than at the CH_2 group. On the other hand, the presence of the nitrogen atom causes the 2-methylpyridine to be lithiated at the methyl group more easily as is the case for toluene [62]. In that context, it was interesting to examine whether **4** would be lithiated exclusively on the cyclopentadienyl ring like the methyl substituted ferrocenes, on the methyl groups like 2-methylpyridine, or at both positions and in which ratios. In order to address that question, **4** was lithiated with *sec*-BuLi and then quenched by addition of D_2O (Scheme 10) [58].

Firstly, the completeness of the deuteration reaction was confirmed by FAB-MS measurements of deuterated and non-deuterated *N*-methyl iodide [**4**-Me]$^+$ I^- salts. The ^{2}H NMR spectrum of deuterated **4** indicated formation of three products **47** having a deuterium atom incorporated into the cyclopentadienyl ring, **48** having deuterium atom in the methyl group, and **49** having a deuterium atom in the β-pyrrolyl position. Relative ratios of products were: 54% for **47**, 38% for **48**, and 8% for **49**.

Deuteration experiments showed that competitive lithiation of the cyclopentadienyl ring, the methyl groups, and the β-pyrrolyl positions took place in **4** to different extents. Interestingly, methyl group lithiation takes place to a significant extent even in the presence of reactive cyclopentadienyl C–H bonds. Taking into account the different numbers of C–H bonds in each reaction site, the relative reactivities of a single C–H bond have been estimated as Cp:Me:β-pyrrolyl = 2.7:1.6:1.

To gain a deeper understanding of the reaction of lithiated 2,5-dimethylazaferrocene **4**, D_2O was replaced by various carbon [58,63] and heteroatom [63–65] electrophiles. Depending on the applied electrophile, mutual yields of pyrrolyl **50**–**57** and cyclopentadienyl-derived products **58**–**64** were different. In all cases, recovery of starting 2,5-dimethylazaferrocene **4** occurred, but no products derived from the lithiated β-pyrrolyl positions were isolated (Scheme 11).

Most of the products shown in Scheme 11 are air-stable orange oils. Thus, to investigate their molecular structures, selected representatives of these compounds were transformed into crystalline $W(CO)_5$-derivatives [63–65] and investigated by X-ray single crystal diffraction techniques.

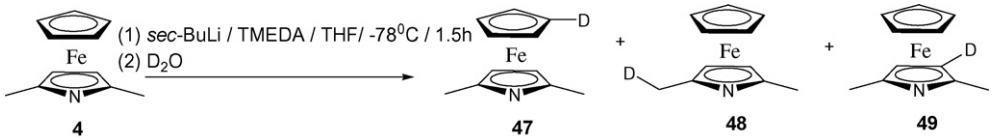
As indicated by ^{31}P and ^{1}H NMR spectroscopy, phosphines **54** and **61** underwent oxidations to the corresponding P-oxides [63]. The yields were moderate, but undoubtedly the lithiation procedure was the first technique which provided easy access to numerous stable and structurally diverse 2,5-dimethylazaferrocene derivatives.

4.3. Synthesis of chiral azaferrocenes via lithiation approach

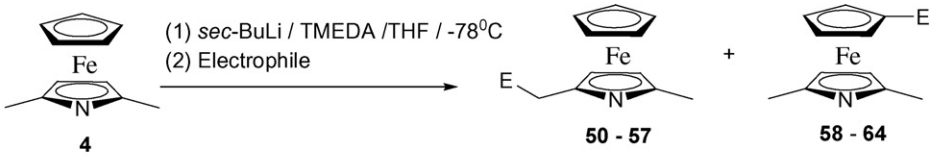
Planar chiral 1,2-disubstituted ferrocenes continue to attract substantial interest due to their applications in catalysis [3,4,66,67]. Similar to ferrocenes, planar chiral heteroferrocenes like phospha- and 1,1′-diphosphaferrocenes are also of great interest due to their application as planar chiral ligands for enantioselective catalysis [8,68] and as molecules for non-linear optical (NLO) materials [69]. As with phosphaferrocenes, planar chirality in azaferrocenes is induced by replacing the hydrogen atoms in either of the two enantiotropic α- or β-positions of the pyrrolyl ligand by another substituent (Fig. 7).

The first preparation of an optically active azaferrrocene, (−)-(2R)-methylazaferrocene, was reported by Schlögl and co-workers in 1969 [70]. His strategy relied on the separation of diastereomeric salts formed by (−)-6,6′-dinitrodiphenic acid with racemic 2-methylazaferrocene. Recently, great efforts have been devoted to the synthesis of enantiomerically pure planar chiral azaferrocenes. In the search for new catalytically active heterometallocenes, Fu and co-workers succeeded in the preparative HPLC isolation of single enantiomers from racemic mixtures of azaferrocenes **11**, **12**, **65** and **66** (Fig. 8) [15,20,71].

Other approaches to access enantiomerically pure or enriched azaferrocenes have included the generation of their planar chiral anions [72,21], direct lithiation of azaferrocenes



Scheme 10.



4 → **50 - 57** + **58 - 64**

Electrophile	E	**lateral product**, yield %	**Cp-product**, yield %
$PhCH_2Cl$	$PhCH_2$	**50**, 35 %	Not observed
p-(MeO)PhCHO	CHOH-*p*-(MeO)Ph	**51**, 30%	Not observed
$(p\text{-(MeO)Ph})_2CO$	$COH((p\text{-(MeO)Ph})_2$	**52**, 21 %	**58**, 25 %
p-(MeO)PhCOMe	CMeOH-*p*-(MeO)Ph	**53**, 13 %	**59**, 24%
DMF	CHO	Not observed	**60**, 22%
$ClPPh_2$	PPh_2	**54**, 13 %	**61**, 25 %
$(PhSe)_2$	SePh	**55**, 26 %	**62**, 10 %
$ClPO(OEt)_2$	$PO(OEt)_2$	**56**, 21 %	**63**, 25 %
$(SMe)_2$	SMe	**57**, 30 %	**64**, 14 %

Scheme 11.

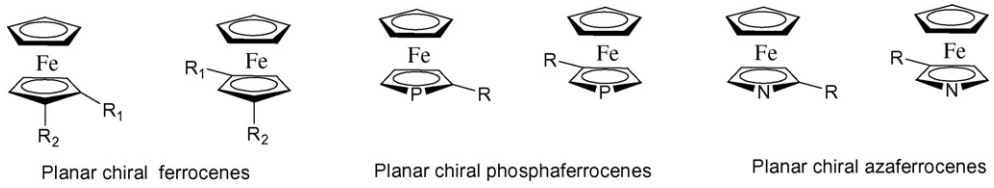


Fig. 7. The general examples of planar chiral metallocenes.

in the presence of chiral bases [23,21], or kinetic resolution [75]. In elegant work, Johannsen and co-workers reported the general and simple synthetic route leading to optically pure planar chiral azaferrocenes **71**–**82** [72,21]. The key step of their strategy involved synthesis and chromatographic separation of diastereoisomeric (S_s,S_p)- and (S_s,R_p)-2-*p*-tolylsulfinyl-1′,2′,3′,4′,5′-pentamethylazaferrocenes **67** and **68** obtained by reaction of lithiated **7** with (−)-(1R,2S,5R)-menthyl-(S)-*p*-toluenesulfinate (Scheme 12). The absolute configurations of **67** and **68** were determined by X-ray crystal structure analysis [72].

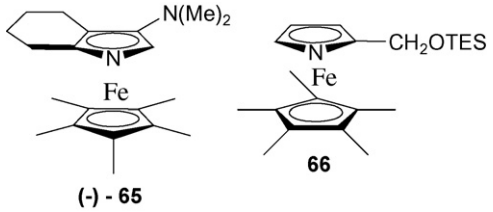
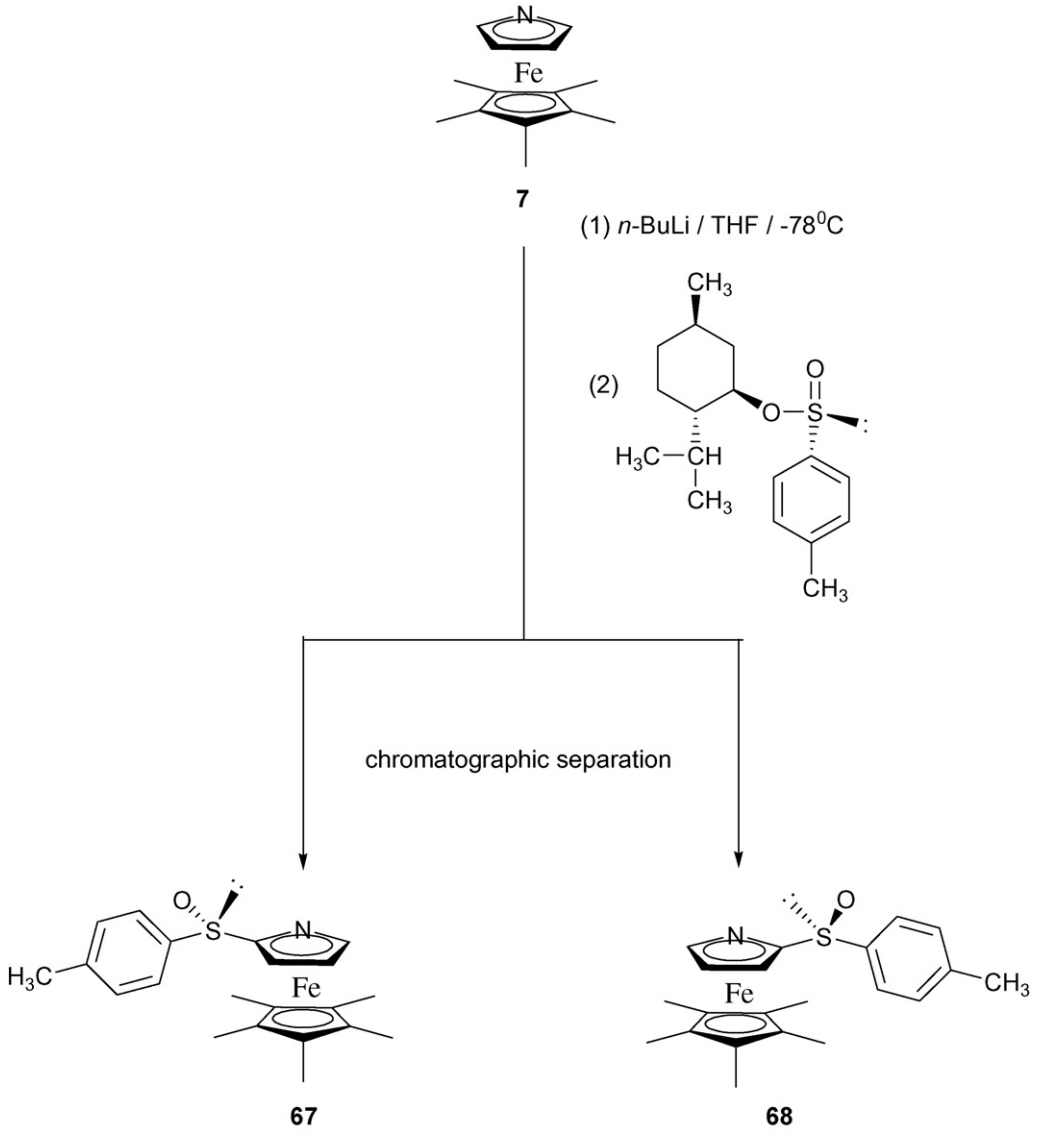


Fig. 8. The structures of azaferrocenes **65** and **66**.

In next step, optically pure azaferrocenyl anions **69** or **70** were generated by reaction of **67** or **68** with *tert*-BuLi and allowed to react with a desired electophile (Scheme 13). Complexes (S_p)-**71**–**76** and (R_p)-**77**–**82** obtained by this approach had ee values higher than 99% (Scheme 13).

Another synthetic strategy leading to optically active planar chiral azaferrocenes has been described by the Iwao group [22,23]. They investigated both ortho- and lateral lithiations of azaferrocenes **7**, **9** and **10** in the presence of chiral ligands like (−)-sparteine **83**, *N*,*N*,*N*′,*N*′-tetramethyl-(1R,2R)-1,2-diaminocyclohexane **84**, *S*-valine-derived bis(oxazoline) **85**,



Scheme 12.

N,*N*,*N*′,*N*′-tetramethyl-(1R,2R)-1,2-diphenylethylenediamine **86** and *S*-proline-derived ligands **87** and **88** (Fig. 9).

(−)-Sparteine **83** was the best chiral inducer in enantioselective ortho-lithiation reactions of **7** with *sec*-BuLi in Et_2O at −78 °C followed by addition of selected electrophiles (Scheme 14).

The configurations of **89**–**91** were S_p in chiroptical comparisons with the data reported by Johannsen and co-workers [72,21]. Screening experiments designed to select the best chiral inducers for enantioselective lateral lithiation of **9** indicated that *S*-valine-derived bis(oxazoline) **85** was the superior ligand. Careful control of the reaction temperature at −55 °C allowed the conversion of **85** to azaferrocenes **92**–**95** in excellent ee of mostly 99% (Scheme 15) [22].

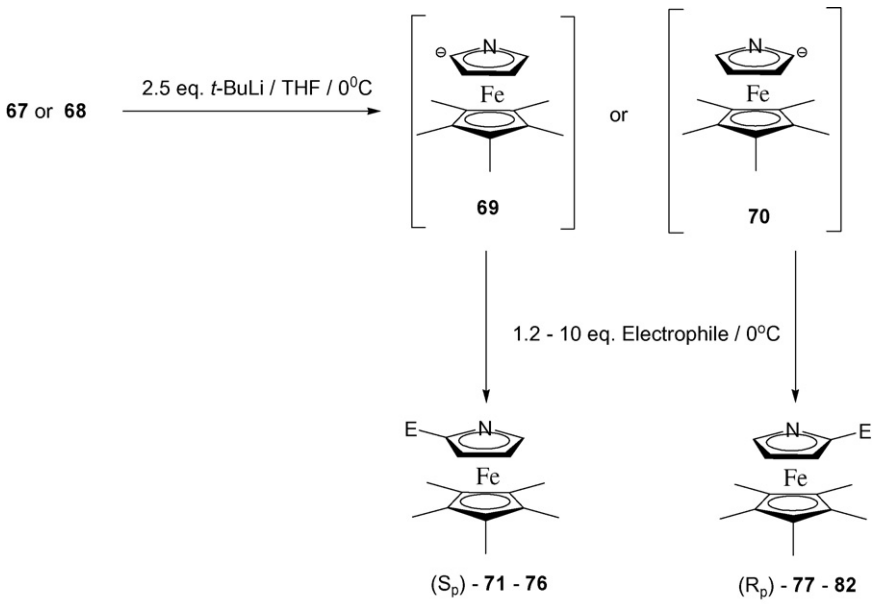
Iwao and co-workers determined the absolute configurations of complex **93** as R_p with indications that **92**, **94**, and **95** have the same configurations. Due to the low thermal and chemical stability of azaferrocenes **89**–**95**, Iwao's group undertook the synthesis of new more stable 1′,2′,3′,4′,5′-pentamethyl-3,4-diphenylazaferrocene **10** and studied its enantioselective ortho-lithiation in the presence of chiral inductors **83**–**88** [23]. As in the case of previous experiments with **7**, lithiation of **10** proceeded most effectively when (−)-sparteine **83** was employed (Scheme 16).

In reactions using paraformaldehyde as a quencher, the replacement of *sec*- or *n*-BuLi by *tert*-BuLi resulted in different regioselectivity of the products. While *sec*- or *n*-BuLi gave exclusively product **96** having the electrophile attached at the ortho pyrrolyl position, treatment with *tert*-BuLi yielded exclusively non-chiral η^5-C_5Me_5 substituted product **101** (Scheme 17).

The ratio of products **96** *vs* **101** has been attributed to the complex-induced proximity effect (CIPE) [73,74].

Recently, Anderson et al. investigated the lithiation of 1,2,3,4,5-pentamethylazaferrocene **7** [75]. Like Iwao, they applied the *sec*-BuLi and (−)-sparteine **83** couple as a chirality-inducing system in the synthesis of planar chiral derivatives **102**–**107** (Scheme 18).

The ee along with the optical purity of the products were investigated by a combination of chiral HPLC and optical rotation measurements. It is worth noting that recrystallization markedly enriched the ee values of the solid products. The enantiopurity was also extrapolated based on the chemical transformation into respective derivatives with known absolute configurations. Furthermore, Anderson's group presented the first attempts to achieve enantiomeric enrichment of azaferrocenes *via* one pot kinetic resolution. However, due to generation of some undefined



Electrophile	E	(S_p)-**product**, yield %	(R_p)-**product**, yield %
I_2	I	**71**, 52	**77**, 68
$(CH_2O)_n$	CH_2OH	**72**, 58	**78**, 54
Ph_2CO	$C(OH)Ph_2$	**73**, 79	**79**, 55
$ClPPh_2$	PPh_2	**74**, 50	**80**, 38
n-Bu_3SnCl	*n*-Bu_3Sn	**75**, 39	**81**, 35
TMSCl	$Si(CH_3)_3$	**76**, 74	**82**, 60

Scheme 13.

reactive by-products, that methodology was only successful for the preparation of complexes **105** (80%, 99% ee) and **106** (60%, 90% ee).

4.4. Transmetallation and Pd catalyzed cross-coupling reactions of azaferrocenes

In an extension of their studies, Anderson's group developed the transmetallation of azaferrocene lithium compounds followed by Negishi-type coupling reactions (Scheme 19).

Recrystallization of C_1-symmetric complexes **110** and **111** resulted in their enantiomeric enrichment of up to >95% ee. In the same paper, enantioselective syntheses of C_2-symmetric bis(azaferrocenes) **115** and **116** *via* iron catalyzed oxidative coupling were described along with syntheses of *N*,*N*,*N*- and *P*,*N*-azaferrocene chelating systems **117** and **118**.

The analogy between the planar chiral azaferrocenes **117** and **118** and the purely organic ligands **119** and **120** is noteworthy [76–78] (Fig. 10).

Concurrently with the reports from Anderson's group, Kowalski and Winter reported the synthesis of 1′-heteroaryl-2,5-dimethylazaferrocenes **121**–**123** *via* transmetallation/palladium catalyzed cross-coupling reactions [79] (Scheme 20) and, in a later publication, the heteroaryl bridged derivatives **124**–**126** (Fig. 11) [44].

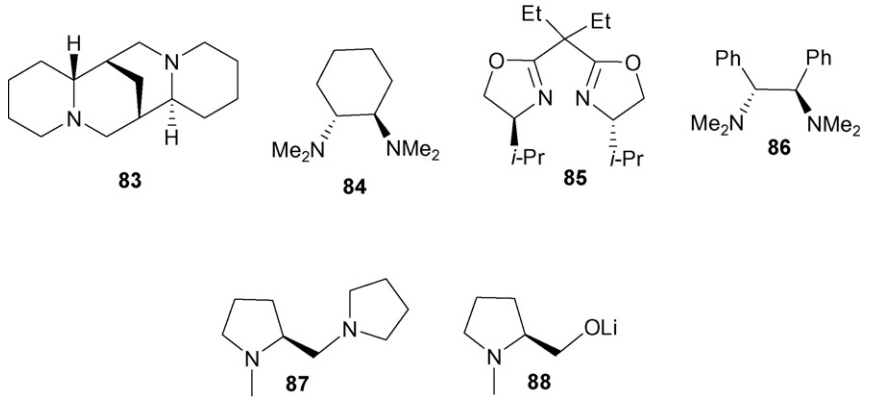
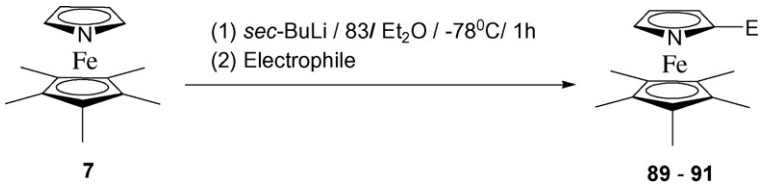


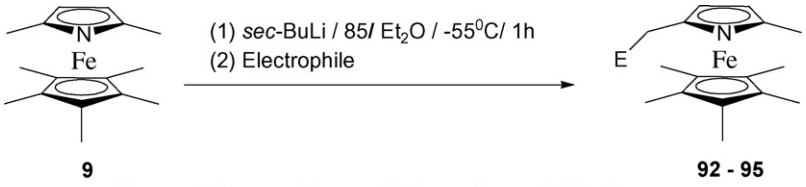
Fig. 9. The structures of chiral ligands **83**–**88**.



7 89 - 91

Electrophile	E	(S_p)-**product**, yield %	% ee
$(CH_2O)_n$	CH_2OH	**89**, 70	81
I_2	I	**90**, 87	74
Ph_2CO	$C(OH)Ph_2$	**91**, 87	79

Scheme 14.



9 92 - 95

Electrophile	E	(R_p)-**product**, yield	% ee
Ph_2CO	$C(OH)Ph_2$	**92**, 57	99
$(TMSO)_2$	OH	**93**, 17	99
$(PhS)_2$	SPh	**94**, 46	99
$TMSCH_2N_3$	NH_2	**95**, 46	96

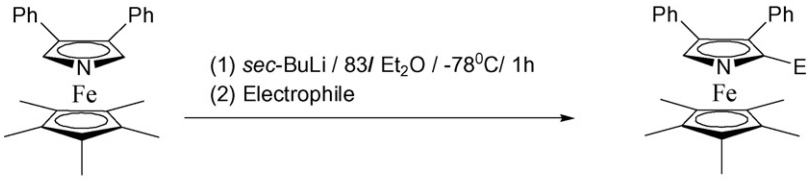
Scheme 15.

The original rationale for their work was to investigate of electrochemistry of symmetric binuclear azaferrocene systems rather than to synthesize a new ligand for catalysis.

5. Synthesis of azaferrocene derivatives *via* functional group transformations

The direct introduction of desired functional groups to azaferrocenes *via* lithiation or Friedel–Crafts reactions has been more successful than efforts to transform existing functional groups on an azaferrocene derivative. Azaferrocenes with reactive functional group attached are generally thermally and chemically less stable than their unsubstituted precursors. Despite those limitations, 2,5-dimethylazaferrocene-1′-carbaldehyde **60** proved to be a valuable starting material for the synthesis of various more complex derivatives. In 2006, the Horner–Wadsworth–Emmons reaction of **60** with diethyl benzylphosphonate, diethyl *p*-methoxybenzylphosphonate and diethyl (ferrocenylmethyl)phosphonate was reported, yielding ethenylazaferrocene derivatives **127**–**129** (Scheme 21) [80].

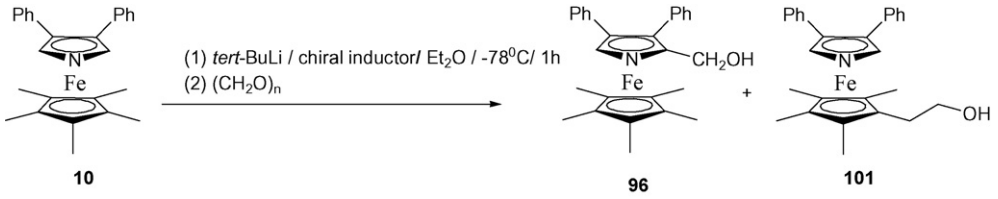
The 2,5-dimethylazaferrocene-1′-carbaldehyde **60** was also utilized for the synthesis of 1′-ethynyl-2,5-dimethylazaferrocene **130** in the course of the reaction with dimethyl-1-diazo-2-oxopropylphosphonate (Scheme 22) [81].



10 96 - 100

Electrophile	E	(S_p)-**product**, yield %	% ee
$(CH_2O)_n$	CH_2OH	**96**, 74	78
I_2	I	**97**, 84	79
TMSCl	$Si(CH_3)_3$	**98**, 61	75
$ClPPh_2$	PPh_2	**99**, 39	77
$(PhS)_2$	SPh	**100**, 88	76

Scheme 16.



10 96 101

Chiral inductor	**96**, yield %	% ee	**101**, yield %
83	-	-	80
84	72	53	-
85	72	18	-
87	31	11	41

Scheme 17.

Since **130** is an oil, its in-depth structural analysis was achieved by single crystal X-ray measurements after its transformation into the crystalline $W(CO)_5$–adduct **131** (Fig. 12) [81]. Chemical properties of complex **130** were also examined with respect to a lithiation/silylation reaction and by Cu-catalyzed coordination to a Pt center. These procedures afforded derivative **132** and the trimetallic complex **133** (Fig. 12) [81].

In the course of searching for new bimetallic, rigid-rod, electrochemically active systems, 1′-ethynyl-2,5-dimethylazaferrocene **130** was dimerized to obtain 1,4-di-(2,5-dimethylazaferrocenyl)-1,3-butadiyne **134** (Scheme 23) [82].

6. Applications of azaferrocenes

6.1. Planar chiral azaferrocenes as ligands in catalysis

In review articles published in 2000 [15] and 2006 [68], Fu and co-workers summarized the details of their synthetic investigations and the catalytic applications of chiral azaferrocenes. Herein, only a short summary of their results will be presented.

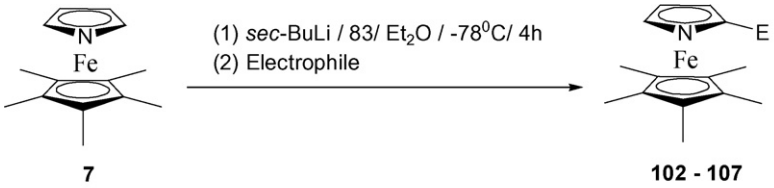
In their preliminary attempts to identify novel planar chiral nucleophilic catalysts, Fu and Ruble focused on comparative testing of azaferrocenes **7** and **66** against nitrogen containing ferrocenes **135** and **136** and **139**, all of them bearing the stable electron-rich and bulky (η^5-C_5Me_5)Fe fragment [20] (Fig. 13). The sterically demanding units (η^5-C_5Me_5)Fe or (η^5-C_5Ph_5)Fe are inherently present in all other azaferrocenes tested by this group.

Complexes **135** and **136** are planar chiral analogues of known DMAP and imidazole catalysts. Compounds **7**, **66**, **135**, and **136** were examined for their catalytic activities in the acylation of racemic mixtures of alcohols, cyanosilylation of aldehydes and addition of alcohols to ketenes reactions. Their catalytic performance was determined by ^{1}H NMR spectroscopy by monitoring the half-life for each reaction in the presence and absence of the respective catalyst. These measurements revealed that all catalysts subjected to testing were active but to different extents. Catalyst **136** appeared to be the most effective of the whole series and provided more than 100-fold acceleration for each reaction tested.

Very interesting results were also obtained for reactions catalyzed by azaferrocenes (+)-**66** and (−)-**66** in the kinetic resolutions of secondary alcohols **137** and **138** (Scheme 24).

These resolutions *via* acylation reactions with diketene proceeded with remarkable ee values ranging from 53% to 87%. In an extension of their initial studies on the kinetic resolutions of secondary alcohols, Fu's group reported an improvement of their methodology by employing the more sterically hindered DMAP analog **139** along with use of inexpensive acetic anhydride as the acylating agent [83].

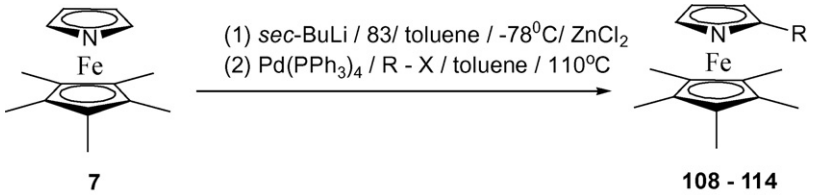
Catalytic enantioselective additions of alcohols to ketenes were also studied by Fu and co-workers with respect to planar chiral azaferrocenes **140**–**142** (Fig. 13) and **66** [84]. In contrast to previously

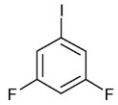
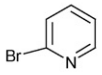
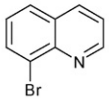
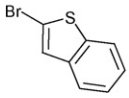


7 102 - 107

Electrophile	E	**product**, yield %	% ee	% ee after cryst.
I_2	I	**102**, 80	77	90
Ph_2CO	$C(OH)Ph_2$	**103**, 86	82	97
TMSCl	$Si(CH_3)_3$	**104**, 86	81	>99
MeI	CH_3	**105**, 93	80	-
$(PhS)_2$	SPh	**106**, 93	79	96
$ClPPh_2$	PPh_2	**107**, 93	57	86

Scheme 18.



R-X	product, yield %	% ee
PhI	**108**, 77	~80
	**109**, 68	~80
	**110**, 70	80
	**111**, 68	80
	**112**, 62	77
	**113**, 72	80
	**114**, 61	~80

Scheme 19.

studied reactions wherein planar chiral DMAP derivatives provided a higher degree of stereoselection than azaferrocenes, for enantioselective additions of alcohols to ketenes metallocenyl DMAP analogues appeared ineffective at inducing asymmetry. Examination of a model reaction of MeOH addition to phenylmethyl ketene indicated that the stereoselectivity correlates with the steric demand of the substituent at the α-pyrrolyl position of the respective catalyst (Scheme 25).

Thus, small substituents of catalysts **66** and **140** provided ~28% ee for the products while the larger substituent in **142** provided 68% ee. The best results, however, were obtained for the medium-sized substituent present in **141** which gave the desired alcohol with 77% ee. Moreover, Fu's studies showed that the ee of the products varies linearly with the ee of the azaferrocene catalyst applied in the reactions. The practical usefulness of catalyst **141** was then shown in an elegant synthesis of methyl esters of ibuprofen, naproxen, and fenoprofen drugs with high ee and chemical yields.

In the course of other studies, catalyst (+)-**141** was employed in the synthesis of β-lactams *via* Staudinger reactions of ketene with imines; these reactions provided almost racemic products [85].

Development of novel nucleophilic azaferrocene-derived catalysts by the Fu group is also reflected in the synthesis of the first η^5-indolyl and η^5-tetrahydroindolyl complexes **143**–**145** and **65** (Fig. 14) [71].

The attempted use of **143** as a catalyst for the addition of alcohols to phenylethyl ketene was unsuccessful because **143** decomposed

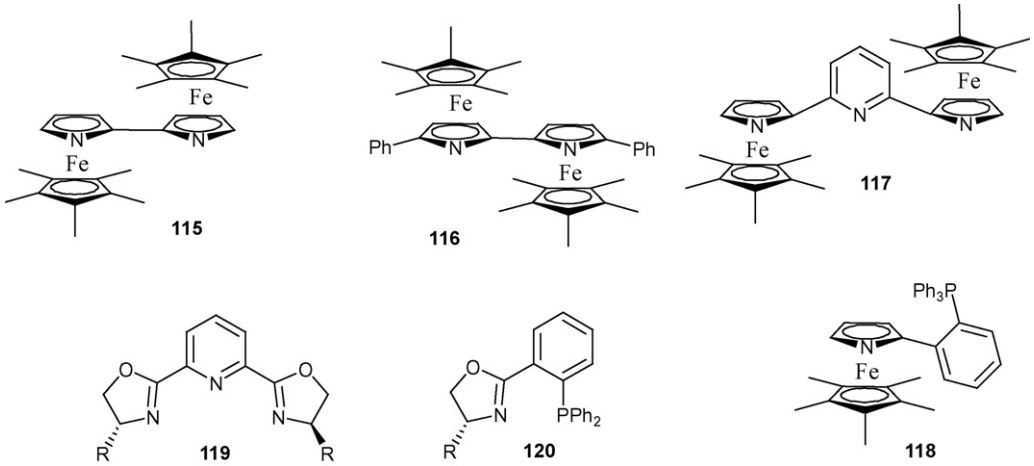
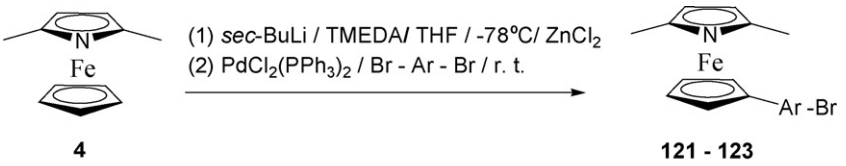
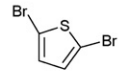
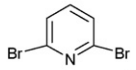
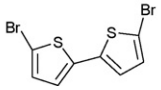


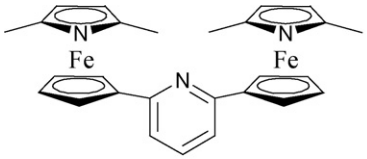
Fig. 10. The structures of chiral azaferrocenes **115**–**118** and their organic counterparts **119**–**120**.



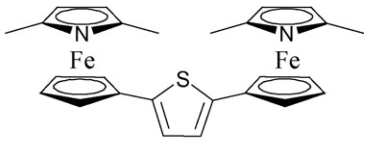
4 **121 - 123**

Br-Ar-Br	**product**, yield %
	**121**, 46
	**122**, 43
	**123**, 45

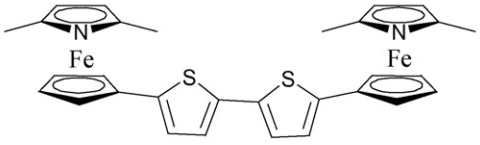
Scheme 20.



124

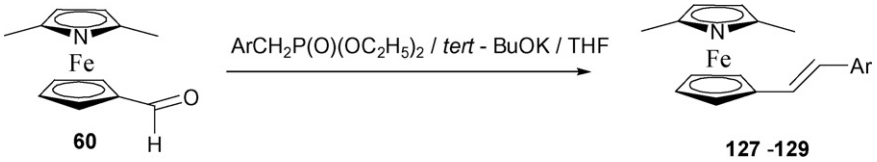


125



126

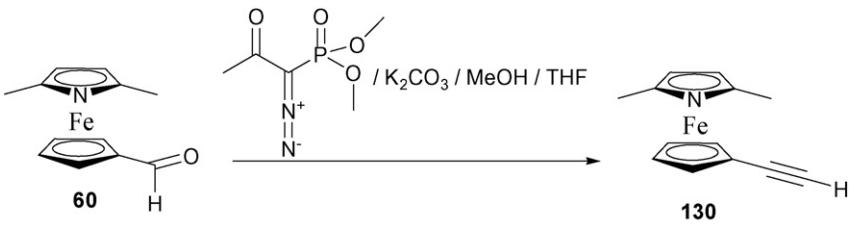
Fig. 11.



60 **127 -129**

Ar-$CH_2P(O)(OC_2H_5)_2$	**product**, yield %
Ph-	**127**, 70
p-MeOPh-	**128**, 27
Fc-	**129**, 60

Scheme 21.



60 **130**

Scheme 22.

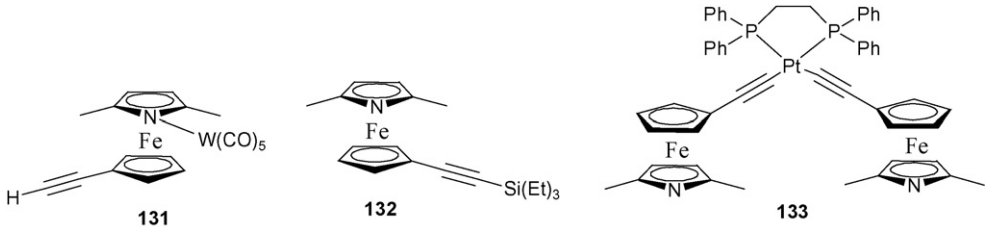
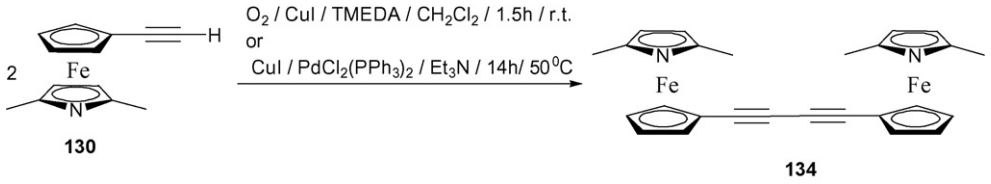


Fig. 12. The structures of complexes **131**–**133**.



Scheme 23.

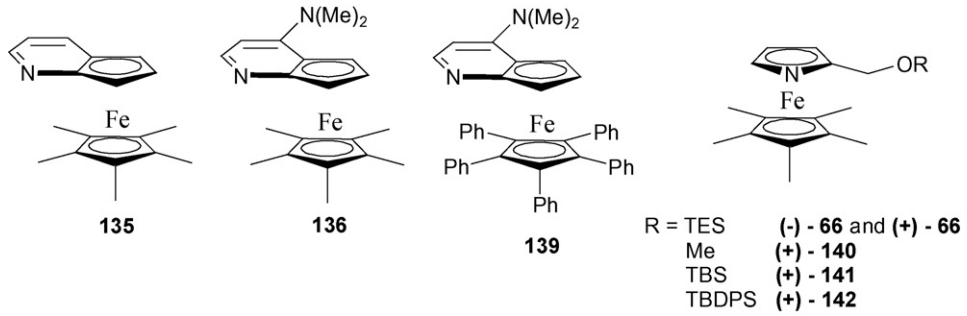
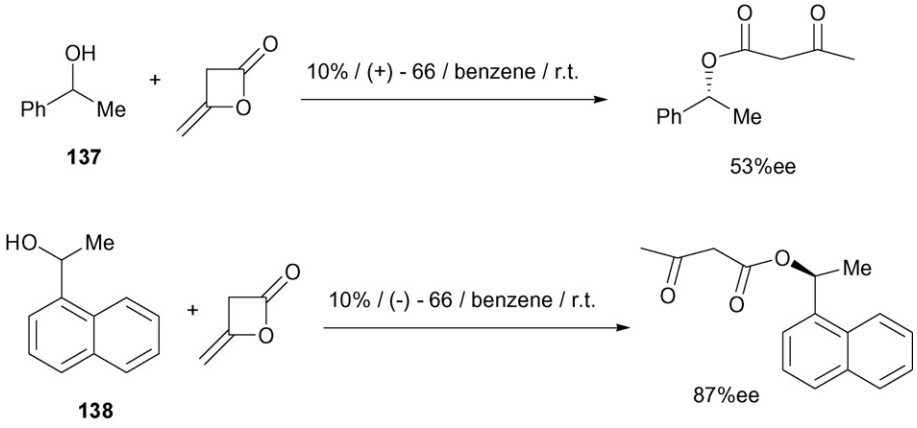
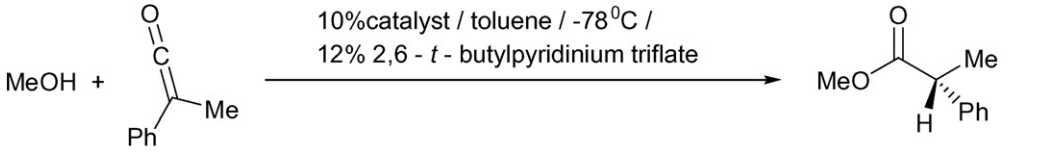


Fig. 13. The structures of planar chiral catalysts **135**–**142**.



Scheme 24.



catalyst (%ee of the product): **66** (28% ee), **140** (27% ee), **141** (77% ee), **142** (68% ee)

Scheme 25.

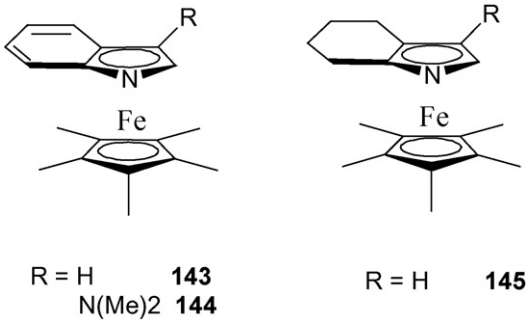


Fig. 14. The molecular structures of planar chiral azaferrocenes **143**–**145**.

during the course of the reaction. However, hydrogenation of **143** yielded the more air-stable complex **145**. To investigate the electron donating effects of the $-N(Me)_2$ group on the catalytic activity, complex (−)-**65** was obtained in 6 overall steps followed by a preparative chiral HPLC separation. Complexes **145** and (−)-**65** are of comparable stability. Their catalytic activities were investigated toward several reactions and were then compared to the activity exhibited by simple azaferrocene **7**. For the addition of benzyl alcohol to phenylethyl ketene, catalyst **145** increased the reaction rate 3-fold over the rate catalyzed by **7**. This result clearly illustrated that the fused six membered ring in **145** has superior influence over the steric factor. The ^{1}H NMR measurements of the half-life of the reaction catalyzed by **65** indicated an additional 2-fold enhancement of the reaction rate as compared to **145**. The catalytic activities of **7**, **65**, and **145** were compared for the acylation of 1-phenylethanol with diketene or acetic anhydride and for the rearrangement of *O*-acylated azalactones. In all of these cases, a similar pattern of activity was recorded, with the most active species being **65** and **7** being the least active ones. Reactions catalyzed by **145** were 1.3–1.5 times more rapid than those catalyzed by **7**. An additional 3–4-fold acceleration of rate in relation to **145** was provided by the derivative **65**. Since enantiomers of **65** were accessible by HPLC separations, asymmetric versions of the reactions for addition of methanol to phenylmethyl ketene, kinetic resolution of 1-phenylethanol with acylating agents along with rearrangement of *O*-acylated azalactones were investigated [71]. The stereoselectivities achieved by enantiomers of **65** in those reactions were comparable to those furnished by **66**.

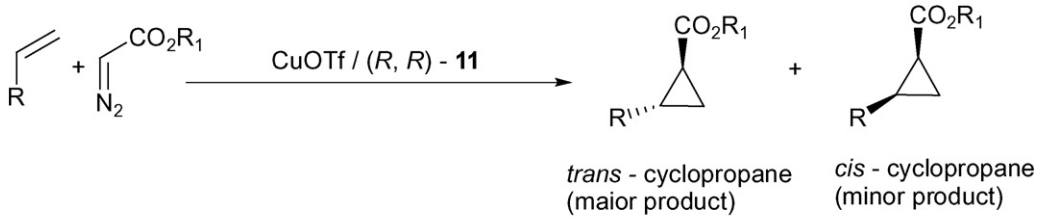
In 1998, Lo and Fu described the synthesis of bidentate C_2-symmetric planar chiral bisazaferrocene (+)-(*R*,*R*)-**11** (Fig. 2) [24]. This complex proved its value as a chiral ligand in various Cu(I) catalyzed reactions. Firstly, it was utilized in the enantioselective Cu(I)-catalyzed cyclopropanation of olefins (Scheme 26) [24].

The outcome of these studies showed that the steric demands of the R_1 group of the diazo ester component is a critical factor influencing both the *trans*:*cis* selectivity of the reactions and the enantiomeric excess values. The more sterically demanding the R_1 group, the higher were the yields of *trans*-cyclopropenes along with higher ee. In this regard, the most sterically demanding BHT diazo ester yielded almost exclusively the *trans*-cyclopropane (*trans*:*cis* ratio 96:4) with 94% ee. The enantioselective Cu(I)-catalyzed cyclopropanation of olefins was also tested with respect to an array of differently substituted olefins. These studies revealed that the CuOTf/(*R*,*R*)-**11** catalytic system is efficient not only for asymmetric cyclopropanation of styrenes but also for alkyl- and silyl-substituted olefins.

Bisazaferrocenes (*R*,*R*)-**11** and (*S*,*S*)-**11** were utilized as ligands in the Cu(I)-catalyzed asymmetric ring expansion of oxetanes to tetrahydrofurans (Scheme 27) [86].

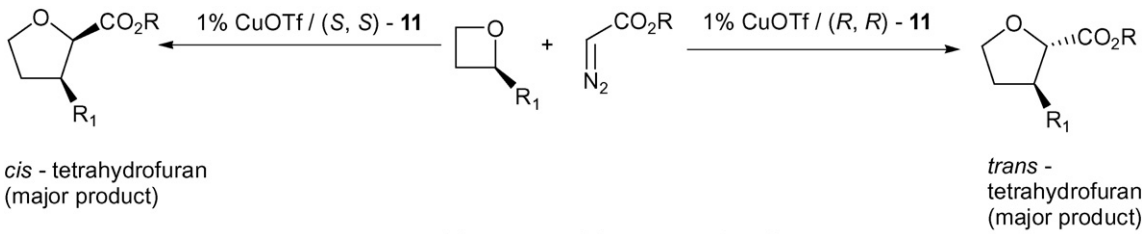
Similarly to the Cu(I)-catalyzed cyclopropanation of olefins, the stereoselection increased as the bulkiness of the R substituent in the diazo ester increased. Thus, in the ring expansion reaction, the highest selectivity was achieved for the most sterically hindered diazo ester with the $CMeCy_2$ substituent, with the major *trans*-product having an ee of ∼98%. In general, the Cu(I)–**11** catalytic system effectively catalyzed ring expansion of a range of differently functionalized 2-oxetanes with good selectivity. Importantly, in the course of their studies, Fu's group showed that the stereochemistry of the azaferrocenyl ligand, but not the oxetane substrate, governed the absolute stereochemistry of the newly generated stereocenter of the tetrahydrofuran derivative.

Copper-catalyzed enantioselective O–H insertions are further example of reactions in which the azaferrocene (*R*,*R*)-**11** was uti-



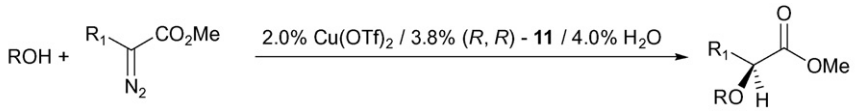
1. R = Ph; R_1 = Et, *t* - Bu, (+) - menthyl, (-) - menthyl, BHT
2. R = Ph, *p* -$(CF_3)C_6H_4$, *p* -$(MeO)C_6H_4$, $PhCH_2$, *n*-hex, Et_3Si; R_1 = BHT

Scheme 26.



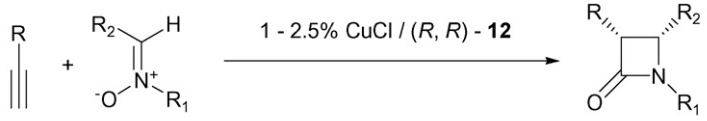
1. R_1 = Ph; R = Et, *t* - Bu, (+) - menthyl, (-) - menthyl, $CMeCy_2$
2. R_1 = Ph, *p* - $(CF_3)C_6H_4$, *p* - $(MeO)C_6H_4$, 1 - naphthyl, *n* - C_7H_{15} - acetylene ; R = $CMeCy_2$

Scheme 27.



1. R = Me, Et, *i*-Pr, *t* - Bu, CH_2CH_2TMS, CH_2CF_3, $PhCH_2$, *p* - $(MeO)C_6H_4$, allyl, Ph; R_1 = Ph
2. R = CH_2CH_2TMS; R_1 = Ph, *o* - $(MeO)C_6H_4$, *o* - MeC_6H_4, *o* - ClC_6H_4, *o*-FC_6H_4, *m* - $(MeO)C_6H_4$, *m* - ClC_6H_4, *p* - $(MeO)C_6H_4$, *p* - $(NHAc)C_6H_4$, *p* - PhC_6H_4, *p* - BrC_6H_4, *p* - FC_6H_4, *p* - $(CF_3)C_6H_4$, 2 - naphthyl, $C_7H_5O_2$, 3-thienyl

Scheme 28.



1. R = Ph; R_1 = Ph, *p* -$(MeO)C_6H_4$, *p* -BrC_6H_4, *p* -$(CO_2Et)C_6H_4$; R_2 = Ph
2. R = Ph; R_1 = *p* -$(MeO)C_6H_4$; R_2 = Ph, *p* -$(CF_3)C_6H_4$, *p* -$(MeO)C_6H_4$, Cy, PhCO
3. R = Ph, *p* -$(CF_3)C_6H_4$, *p* -$(MeO)C_6H_4$, $PhCH_2$; R_1 = *p* -$(MeO)C_6H_4$; R_2 = Cy
4. R = Ph, Cy ; R_1 = Ph ; R_2 = PhCO

Scheme 29.

lized as a chiral ligand. Maier and Fu examined them with respect to a range of alcohols and α-aryl-α-diazo esters (Scheme 28) [87].

2-Trimethylsilyl ethanol was recognized as a particularly attractive substrate. Its insertion products were obtained in high chemical yield and with moderate to high enantiomeric excess. Moreover, they can by easily deprotected without racemization yielding α-hydroxy esters.

Catalytic activity of the copper/bisazaferrocene (*R*,*R*)-**11** catalytic system was also tested in the synthesis of the β-lactam ring *via* enantioselective cycloaddition of phenylacetylene with *N*,α-

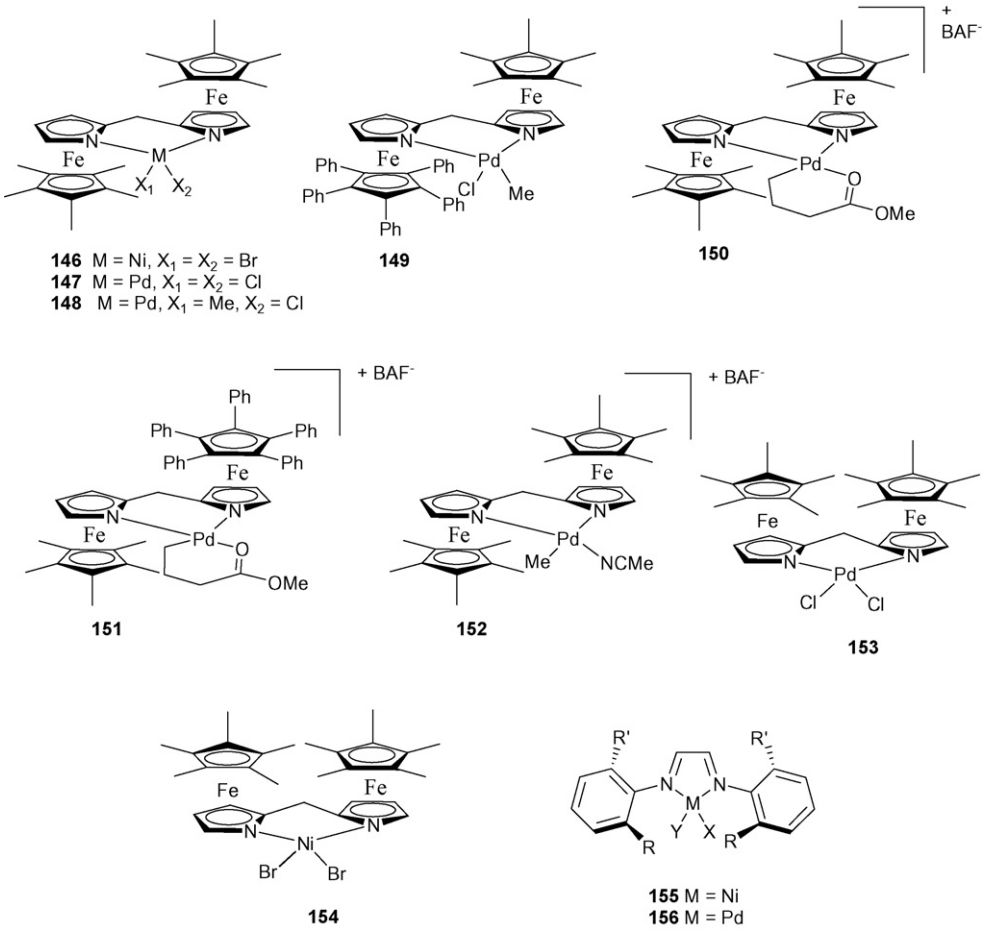
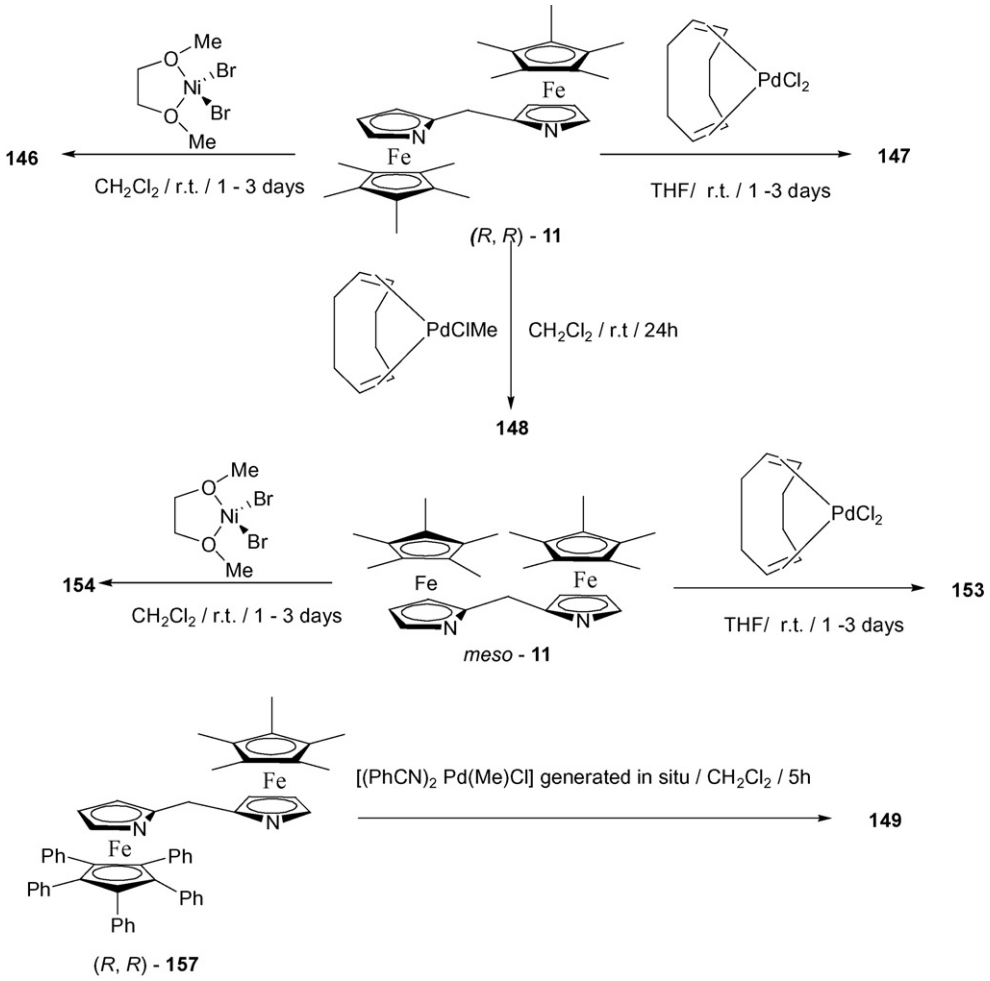


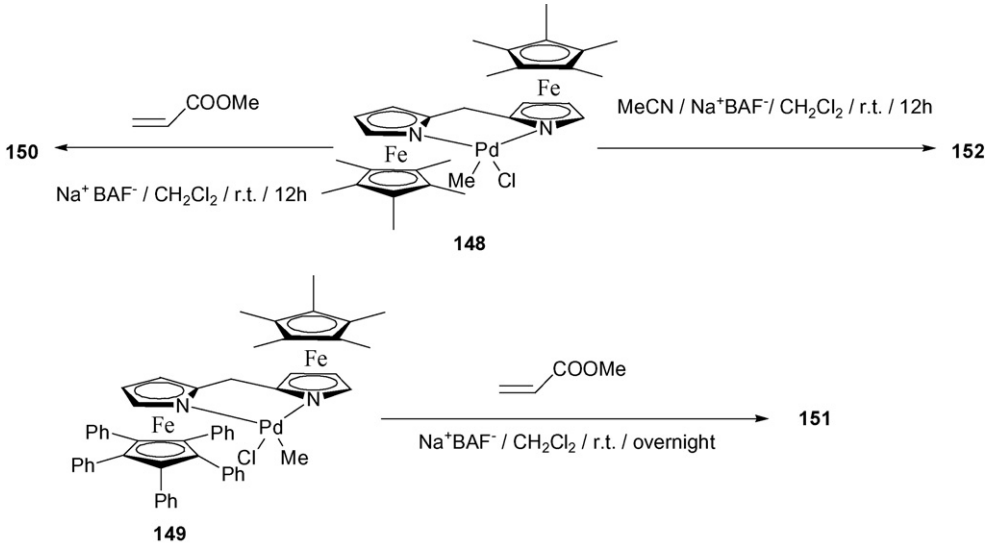
Fig. 15. The structures of catalysts **146**–**156**.

diphenylnitrone. The stereochemical outcome of these reactions was, however, rather modest. To overcome this disadvantage, Lo and Fu replaced bisazaferrocene (*R*,*R*)-**11** with the sterically more demanding bisazaferrocene (*R*,*R*)-**12**. The Cu(I) catalyzed enantioselective couplings of alkynes with nitrones in the presence of (*R*, *R*)-**12** yielded almost exclusively *cis*-configured lactams within up to 89% ee (Scheme 29) [25].

In addition, the Cu(I)/(*R*,*R*)-**11** catalytic system tolerated the presence of a variety of substituents in both the acetylene and nitrone reagents.



Scheme 30.



Scheme 31.

6.2. Olefin polymerization

Late transition metal catalysts for olefin polymerization have been met with great attention [88–90]. In the course of searching for novel late transition metal catalysts for olefin polymerization, Salo and Guan described a series of C_2-symmetric and asymmetric bisazaferrocene complexes **146**–**154** with M(II) (Ni, Pd) centers and evaluated their catalytic properties toward ethylene polymerization (Fig. 15) [91]. Complexes **146**–**154** are structurally related to the highly active and versatile Ni(II) and Pd(II) aryl-substituted α-diimine complexes of the general formulae of **155** and **156** as developed by Brookhart (Fig. 15) [92,93].

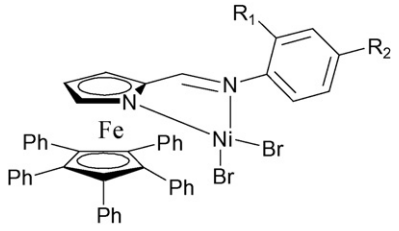
As a justification for choosing bisazaferrocenes as ligands, these authors considered their combined bulkyness and chelate-forming properties. The final steps of the syntheses of **146**–**149**, **153**, and **154** have been achieved by a one-step coordination of appropriate Ni- or Pd-containing precursors to the respective free (*R*,*R*)-**11**, *meso*-**11**, or (*R*,*R*)-**157** bisazaferrocenes (Scheme 30).

Preparations of the preactivated catalysts **150**–**152** demanded, after initial coordination of the Pd(Me)Cl fragment, further ligand exchange in the Pd coordination sphere (Scheme 31).

Following activation with methylaluminoxane (MAO), complexes **146**, **147**, **153**, and **154** exhibited very low activities for polymerization of ethylene and yielded only trace amounts of polymers. Better results were obtained with preactivated catalysts **150** and **151**, which were tested toward ethylene polymerization at various (catalyst loading, pressure, temperature, time) conditions. Both preactivated catalysts yielded oligomeric PEs with number-averaged molecular weights (M_n) ranging from 200 to 600 g/mol and branching density from 20 to 60 total branches per 1000 carbons. Complex **150** exhibited a higher productivity in comparison to its asymmetrical counterpart **151**, but both of them have demonstrated weaker productivity than the Brookhart α-diimine catalysts. Interestingly, thermal stability of both complexes was higher than the "purely organic" α-diimine complexes (complex **150** remained active in the ethylene polymerization reaction at temperatures as high as 120 °C). The low activity of the Pd(II) bisazaferrocene complexes toward ethylene polymerization was explained by the authors as a result of unfavorable enthalpic and entropic factors.

More recently, Watanabe disclosed a series of 2-azaferrocenylimine Ni(II) complexes **158**–**167** and tested their catalytic activity in the ethylene polymerization reaction (Fig. 16) [94].

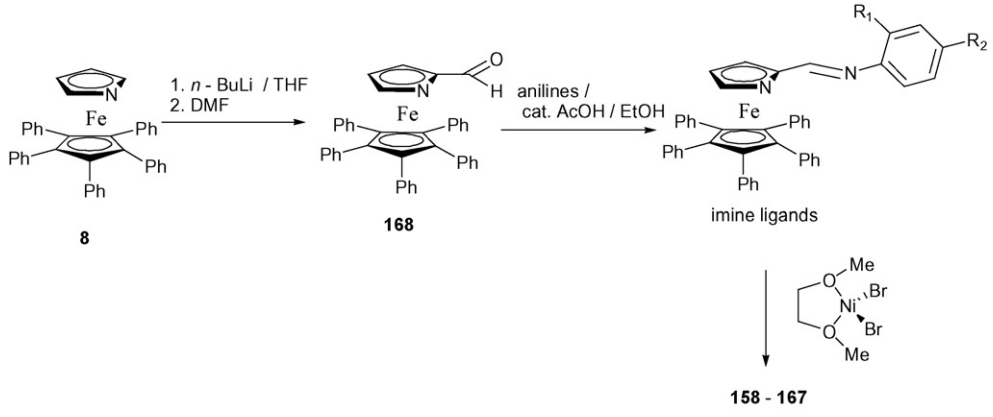
Complexes **158**–**167**, all bearing the bulky pentaphenylcyclopentadienyl fragment, were designed to shield against access to the axial positions of the square planar coordination sphere of the Ni(II) center. To obtain their catalysts, Watanabe and coworkers developed a simple and generally applicable three-step route utilizing lithiation/formylation of azaferrocene **8** yielding 1′,2′,3′,4′,5′-penthaphenylazaferrocene-2-carbaldehyde **168**. Carbaldehyde **168** was then reacted with the respective anilines in AcOH/EtOH to give imine ligands. In a final step, the imine ligands were converted to complexes **158**–**167** by treatment with $NiBr_2$(DME) in dichloromethane (Scheme 32).



158 R_1 = *iso* - Pr ; R_2 = H
159 R_1 = Me ; R_2 = H
160 R_1 = TMS ; R_2 = H
161 R_1 = *tert* - Bu; R_2 = H
162 R_1 = CF_3 ; R_2 = H
163 R_1 = Ph ; R_2 = H
164 R_1 = H ; R_2 = H
165 R_1 = Me ; R_2 = Me
166 R_1 = Me ; R_2 = OMe
167 R_1 = Me ; R_2 = F

Fig. 16. The structures of catalysts **158**–**167**.

The polymerization of ethylene was examined with catalysts **158**–**167** at 1.0 MPa ethylene pressure for 1 h after activation with MAO in toluene. All complexes exhibited efficient ethylene polymerization activities. The best results were achieved with complex **158** which was highly active and produced 7.0 kg (PE) mmol $(Ni)^{-1}\,h^{-1}$ at 25 °C. The molecular weight of the polyethylene was $2.0 \times 10^5\,g\,mol^{-1}$ and the branching density was 63 total branches per 1000 carbons. Both of these factors exceed those obtained for α-diiminonickel (II) complexes under similar polymerization conditions [95]. In general, Watanabe's studies showed that the penthaphenylcyclopentadienyl group effectively blocks an axial face of the square planar of Ni(II) catalysts to give high molecular weight polyethylene polymers. Also the *ortho*- and *para*-substituents of the aniline moieties have significant influence on catalytic activity of the complexes and on the physical properties of the polymers obtained.



Scheme 32.

7. Electrochemistry of azaferrocenes

7.1. Electrochemical studies on mono and bis(azaferrocenes)

From the electrochemical point of view, the ferrocenyl moiety exhibits fast electron transfer kinetics in one-electron oxidation–reduction processes and is characterized by significant chemical stability of its oxidized ferrocenium radical cation. Early electrochemical studies of heteroferrocenes have mainly focused on the influence of heteroatom substitutions of CH groups on the redox potentials and on the chemical stabilities of the associated heteroferrocenium radical cations. In the Group 15-element heteroferrocenes, there is a general consensus that incremental CH substitution by P or N increases $E_{1/2}$ and renders the associated cations more susceptible to nucleophilic attack or deprotonation [96–99]. An in-depth cyclic voltammetry study performed by Audebert's group [99] for azaferrocene **2** and 2,5-dimethylazaferrocene **4** revealed the highly unstable nature of the electrogenerated radical cations $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ in several solvents, under various conditions of basicity and nucleophilicity. It their experiments, Audebert and co-workers were able to record chemically reversible CVs of **2** and **4** in dichloromethane as a solvent only at high scan rates (20 V s^{-1} and 1 V s^{-1}, respectively). All the data collected indicated that under the same experimental conditions radical cation $\mathbf{4}^{\bullet+}$ was about 100 times less reactive (thus more stable) than $\mathbf{2}^{\bullet+}$. A subsequent cyclic voltammetry study of azaferrocenes also confirmed the lack of stability of the electrogenerated corresponding azaferrocenyl radical cations [80–82]. This limited stability of the oxidized forms of azaferrocene compromised the accurate assessment of their $E_{1/2}$ potentials and, in the case of homobinuclear complex **134** made it impossible to gain deeper insights into the 'electronic communication' phenomena in the $\mathbf{134}^{\bullet+}$ radical cation [82].

Recently, Kowalski and Winter reinvestigated the electrochemistry of **2** by cyclic and square wave voltammetry techniques. In their hands, **2** gave a nearly ideal diffusion controlled one-electron wave even at sweep rates as low as 0.025 V s^{-1} with peak current ratios $I_{p,cathodic}/I_{p,anodic}$ of ≥0.95 and peak-potential separations ΔE_p and forward-wave half-widths $E_{p,f} - E_{p,f/2}$ that are very similar or identical to those of the internal decamethylferrocene or ferrocene standards (Fig. 17) [79]. The $E_{1/2}$ redox potential of **2** is 170 mV higher than that of the ferrocene/ferrocenium standard redox couple. They also observed an additional irreversible oxidation at distinctly higher potential which may be due to electron abstraction from the N lone pair.

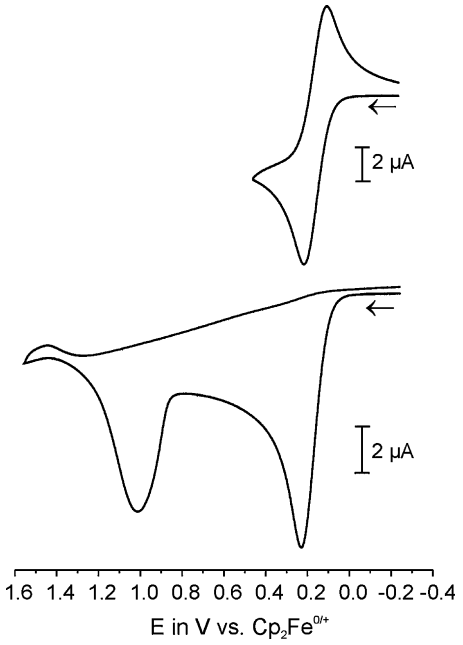
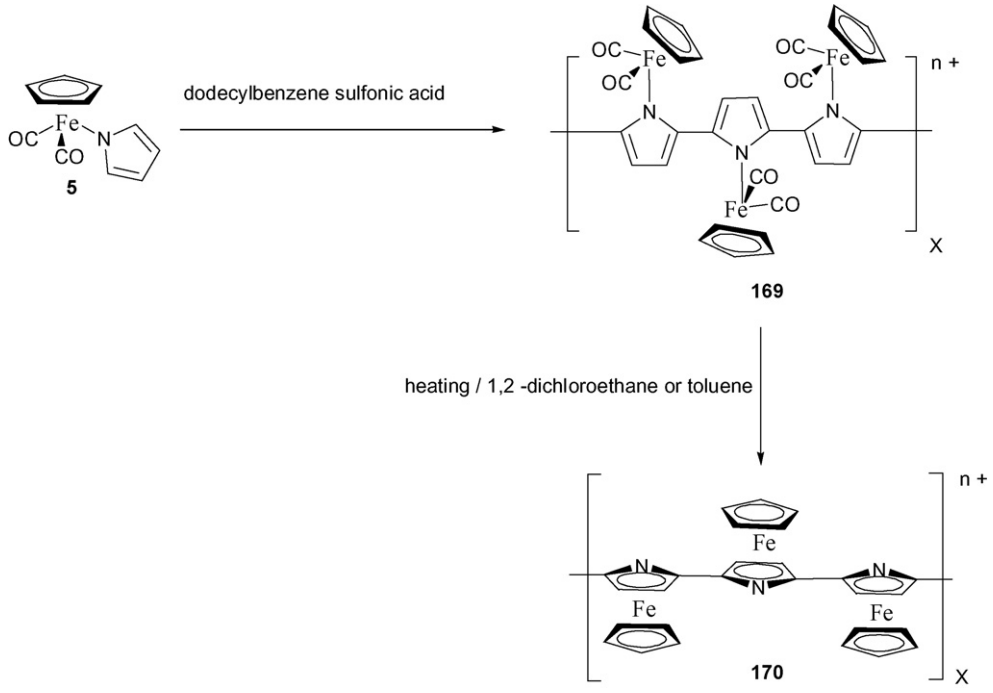


Fig. 17. Voltammograms of **2** in CH_2Cl_2/NBu_4PF_6 (0.1 M, RT) at $\nu = 0.1$ V/s (lower curve) and at $\nu = 0.05$ V/s (upper curve) [79].

These initial studies have been followed by further detailed electrochemical investigations of mono- and binuclear azaferrocene heteroaromatic systems **121**–**126** (Scheme 20 and Fig. 11) [44,79]. The comproportionation constants (K_c) calculated from the $\Delta E_{1/2}$ values of symmetric binuclear heteroaryl bridged



Scheme 33.

azaferrocenes **124**–**126** indicated that the thermodynamic stability of their monooxidized forms **124**$^{\bullet+}$–**125**$^{\bullet+}$ with respects to disproportionation exceeded those of analogous ferrocenes [44].

Very recently, cyclic voltammetry techniques along with FTIR spectroelectrochemical measurements have been successfully applied to evaluate of the usefulness or $W(CO)_5$-containing azaferrocenes **38**–**39** as IR-active spectroelectrochemical markers of biomolecules [54].

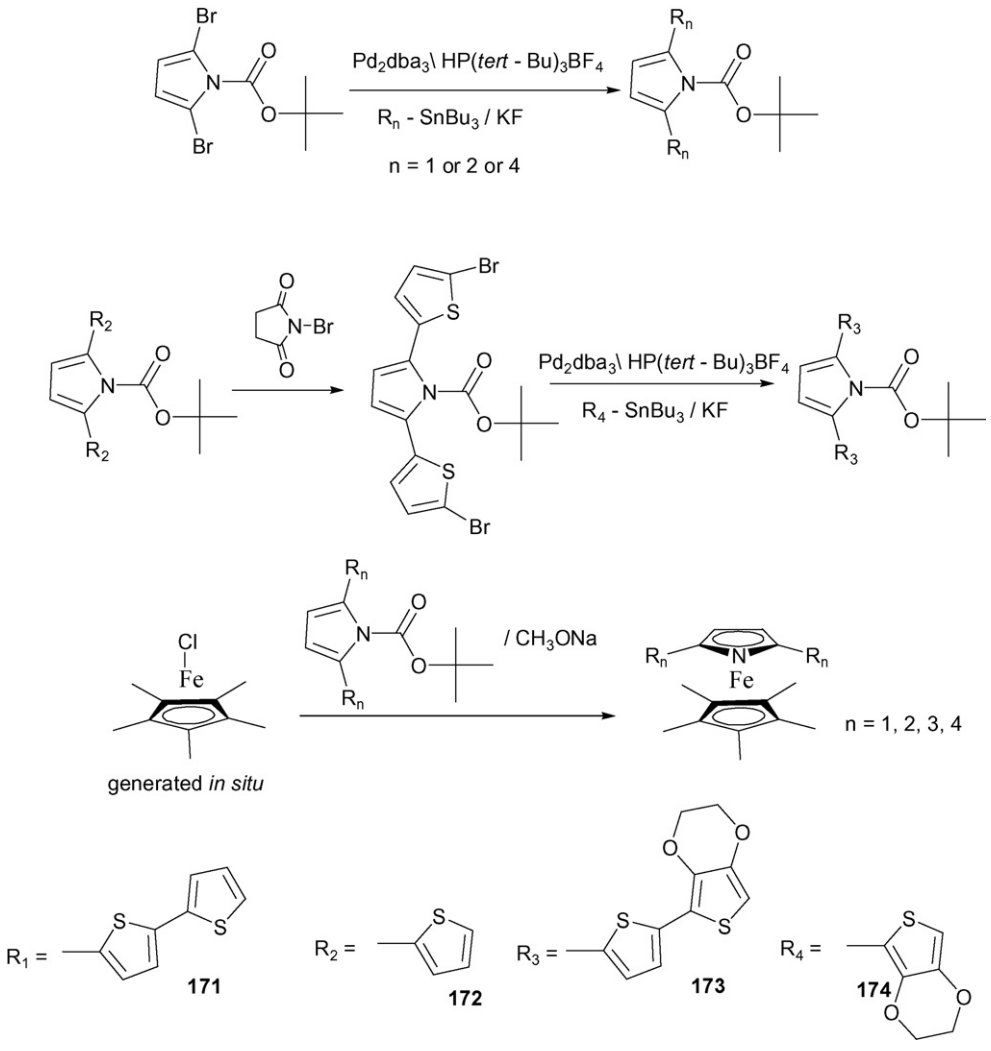
7.2. Preparation and electrical conductivity of azaferrocene-containing polymers

To the best of author knowledge, two reports have been published dealing with azaferrocene-containing polymers. Martin and Hanks described the synthesis of azaferrocene polymer **170** by thermally induced decarbonylation and $\eta^1 \rightarrow \eta^5$ ring slippage reactions of the half-sandwich precursor **169** (Scheme 33) [100].

Swager and co-workers also reported the electropolymerization of well defined thiophene-azaferrocenyl monomers along with detailed electrochemical and spectroelectrochemical studies of their polymerization products [101]. The rationale for their work was to obtain a fully conjugated polymer with the iron atom bound to the polymer backbone in a π fashion. These co-authors predicted that such a type of architecture would maximize the polymer-to-metal and metal-metal interactions and would provide access to control the bulk electronic/magnetic properties of such an organometallic-polymeric material. Practical realization of this aim started with synthesis of monomers **171**–**174** *via* Stille coupling of *N*-protected 2,5-dibromopyrrole with appropriate Sn-containing thiophenes. After deprotection, the pyrroles were allowed to react with *in situ* generated (η^5-C_5Me_5)FeCl to give the expected monomers **171**–**174** (Scheme 34).

Monomers **171**–**174** were anodically polymerized to give polymers **175**–**178** (Fig. 18).

The cyclic voltammetry study of polymers **175**, **176** and **178** displayed two waves. The first wave with half-wave potentials ($E_{1/2}$) of 0.00 V (**177**), 0.17 V (**175**) and 0.33 V (**176**) was assigned to the Fe^{2+}/Fe^{3+} redox couple and the second one at higher potential was categorized as the oxidation of the thiophene organic fragment of the polymer. In the case of polymer **178**, cyclic voltammetry shows only one broad oxidation peak at −0.02 V and two unresolved reduction peaks at −0.31 V and −0.66 V. This overlapping of the half-wave potentials was triggered by the presence of the 3,4-ethylenedioxythiophene (EDOT) group in the polymer structure. However, the CV of polymer **177**, which also contains the EDOT group, displays a larger separation between oxidation and reduction peaks than **178**. The *in situ* conductivity profile of the investigated polymers was limited by the azaferrocenyl fragment oxidation potential from one side and the thiophene fragment oxidation potential from the other. In general, it was concluded that all polymers investigated displayed metal-based redox conductivity. However, EDOT polymers **177** and **178** were better conductors



Scheme 34.

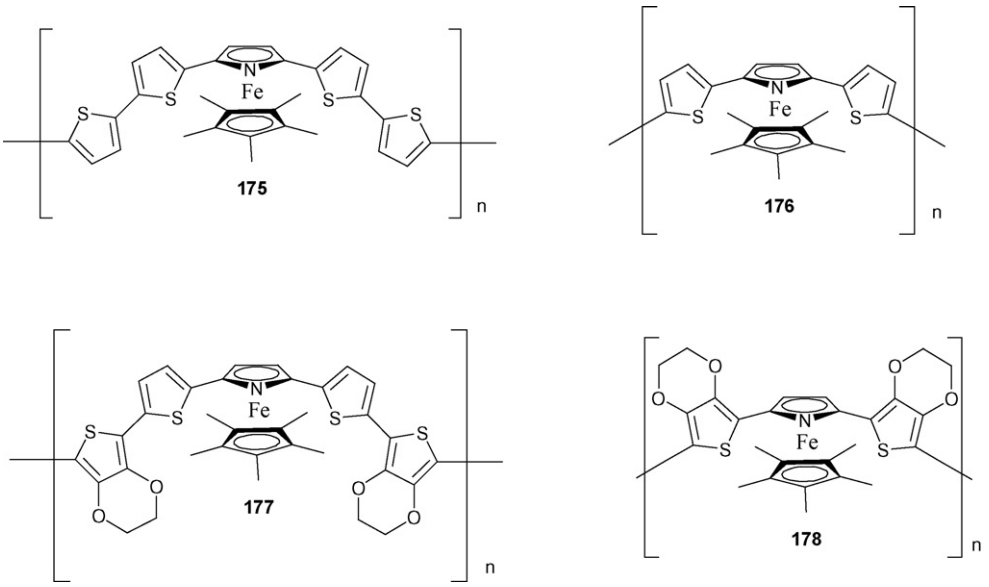


Fig. 18. The molecular structures of conductive polymers **175**–**178**.

than their non-EDOT analogues **175** and **176**. Another factor controlling the conductivity properties was the number of thiophene units that bridged the metallocene centers in the polymeric chains. The values of *in situ* conductivities of the investigated polymers increased as the length of organic thiophene fragments spanning the azaferrocenes decreased. This effect is more evident when **175** is compared with **176** than when **177** is compared to **178**. Additionally, the onset of conductivity of a polymer with two thiophene units bridging the metallocene centers occurs at a lower potential than does the onset of conductivity of a polymers with four thiophenes bridging the metallocene centers. The superexchange mechanism was proposed as being responsible for the lowering of these conductivity onsets.

8. Applications of azaferrocenes in biology

Ferrocene and its derivatives have been recognized as molecules of central importance in bioorganometallic chemistry [102–104]. In contrast, heteroferrocenes have been far less explored with regard to their biological activity. Until the present, only one phosphaferrocene derivative **179** has been synthesized and tested for its anticancer activity (Fig. 19) [105,106].

The bioorganometallic chemistry of azaferrocenes also remains an unexplored area. However, azaferrocenes, due to the presence of the lone electron pair of the nitrogen atom, are more soluble in water, which is a common biological medium, than their ferrocene and phosphaferrocene counterparts. Moreover, simple *N*-methylation of azaferrocenes can produce their even more water soluble salts.

The first azaferrocenes obtained with the goal of being biologically tested were *N*-methyl-2,5-dimethylazaferrocenyl phosphonate iodides **180** and **181** (Fig. 19) [64]. Their cytotoxic properties were evaluated in two cell lines: the non-tumorigenic immortalized murine fibroblast (cell line NIH 3T3) and HeLa cell lines. The same tests were performed with for the simple *N*-methyl-2,5-dimethylazaferrocenyl iodide **15**. The results obtained indicate that of the three complexes tested, the best anti-metabolic activity was exhibited by salt **181** which was preferentially active towards the cancerous HeLa cell line but not the non-cancerous NIH 3T3 cell line. However, that biological effect required high milimolar concentrations of the azaferrocene. Azaferrocenes **2** and **4**, along with their corresponding *N*-methylated derivatives, have been tested against an *in vivo* DNA scission activity test. These experiments indicated a high cleavage activity of both azaferrocenes and their *N*-methyl derivatives. In addition, DNA cleavage activity was slowed by the addition of a free radical scavenger or was triggered by addition of a reducing agent. These observations may suggest a 'free radical' mechanism of DNA fragmentation caused by azaferrocenes [46].

Applications of azaferrocenes in biology have not been limited only to their anticancer activity testing. Very recently, two $W(CO)_5$-containing azaferrocenes **38** and **39** were obtained with the aim of

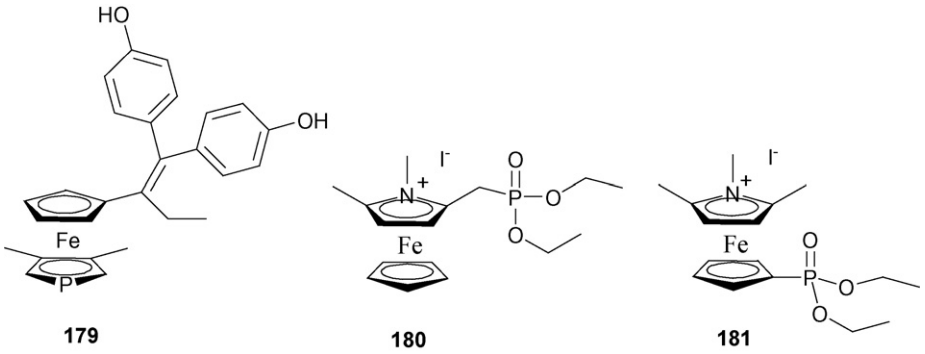
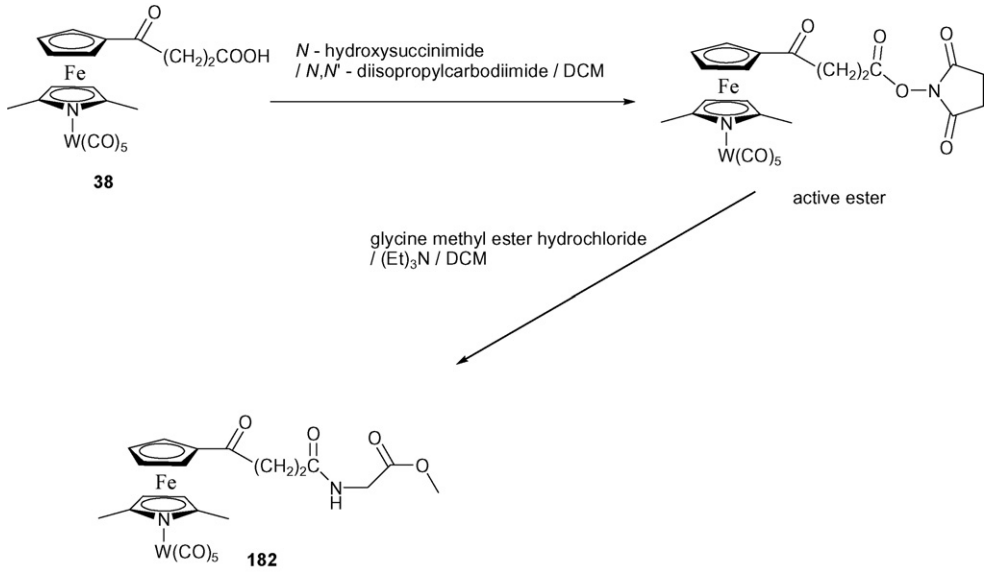


Fig. 19. The molecular structures of bioactive heteroferrocenes **179**–**181**.



Scheme 35.

developing new IR-detectable metal-carbonyl tracers for the amino function [54]. Both complexes were thermally stable and displayed sharp, intense absorption bands of tungsten-coordinated CO ligands at ca. 1923 cm^{-1}. Importantly, complexes **38** and **39** can be also detected by common cyclic voltammetry techniques. FTIR spectroelectrochemical measurements of **38** and **39** indicated that the IR band shift of the $W(CO)_5$ moiety is highly sensitive toward a change in the azaferrocene oxidation state. The usefulness of **38** in amino acid labelling was tested *via* a two-step synthesis of azaferrocenyl glycine amide **182** (Scheme 35).

It is clear that the examination of applications of azaferrocenes in biology has just been initiated and progress in that field will strongly depend on developments in the synthetic chemistry of these heterometallocenes.

9. Summary and conclusions

In this review, author has tried to emphasize that azaferrocene chemistry, despite still lagging behind that of ferrocene, has been intensively explored over recent years. The numbers of new azaferrocene derivatives have dramatically increased due to the development of effective lithiation procedures and Friedel–Crafts type reactions. This review has covered the elegant and general methods leading to planar chiral azaferrocenes which serve as a good examples of the progress in this field. Moreover, azaferrocenes have proved their value as effective planar chiral ligands in catalysis. Electrochemical investigations of azaferrocenes have shown that these heteroferrocenes, just like ferrocenes, may each be reversibly oxidized and reduced by a single electron. Also the comproportionation constants (K_c) calculated for some binuclear azaferrocenyl radical cations emphasized their greater thermodynamic stability with respect to disproportionation than analogous binuclear ferrocenes. Furthermore, the metal-carbonyl azaferrocenes have undergone greater advances over the ferrocenes with respect to the number of their available detection methods. While for the vast majority of ferrocenes electrochemical detection methods are usually employed, metal-carbonyl azaferrocene adducts can be detected by either IR-spectroscopy, cyclic voltammetry techniques, or by a combination of both. The data presented in this review suggests that azaferrocene chemistry has the potential for rapid expansion in the near future.

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