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AZINYLFERROCENES: SYNTHESIS AND PROPERTIES

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Abstract – The present review gives an account of the various synthetic routes to azinyl ferrocenes. Magnetic, catalytic, redox, physiologically active and other properties of these derivatives are considered.

INTRODUCTION

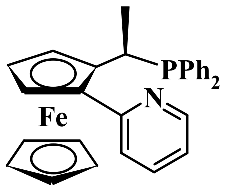
More then fifty years passed since the first ferrocene derivatives were obtained, however a growing interest to this class of compounds has been demonstrating during the last two decades. Indeed, the monographs[1] and a number of review articles[2-6] have recently been dedicated to the chemistry of ferrocenes, including development of new synthetic methods and elucidation of properties of their numerous derivatives.

The interest in ferrocene-based compounds is currently enormous because of their potential use in a wide range of applications: ligands in molecular sensors,[7,8] photosensitizers in complexes[9,10] for the water splitting reaction, physiologically active compaunds,[11-13] monomers for extended stacked complexes and even as unit for self-assembly. Ferrocene is arranged as a rigid matrix which is able to retain the skeleton atoms in definite positions of space; this is why ferrocenyl ligands are among the most widely used in active homogeneous catalysis utilizing transition metal complexes.[14-16]

The unique feature of ferrocenes is their ability to give planar chiral derivatives, which are scarcely vulnerable to racemization. Chiral ferrocenes bearing azinyl fragments, for instance enantiomerically pure ligands **1-3**, are of a special importance, and these compounds have already found application as catalysts in a variety of organic reactions, including those used for asymmetric syntheses.[1-6, 17,18]

There are two general approaches to azinylferrocenes:

– the first one involves the formation of a heterocyclic subunit on the ferrocene matrix by using a variety of functional groups which are attached to the ferrocene moiety (Approach A);



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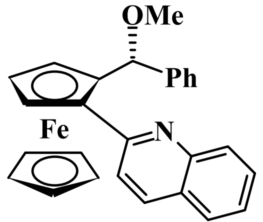

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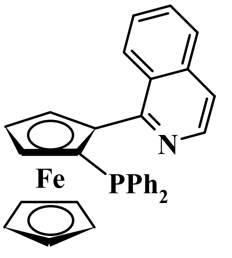

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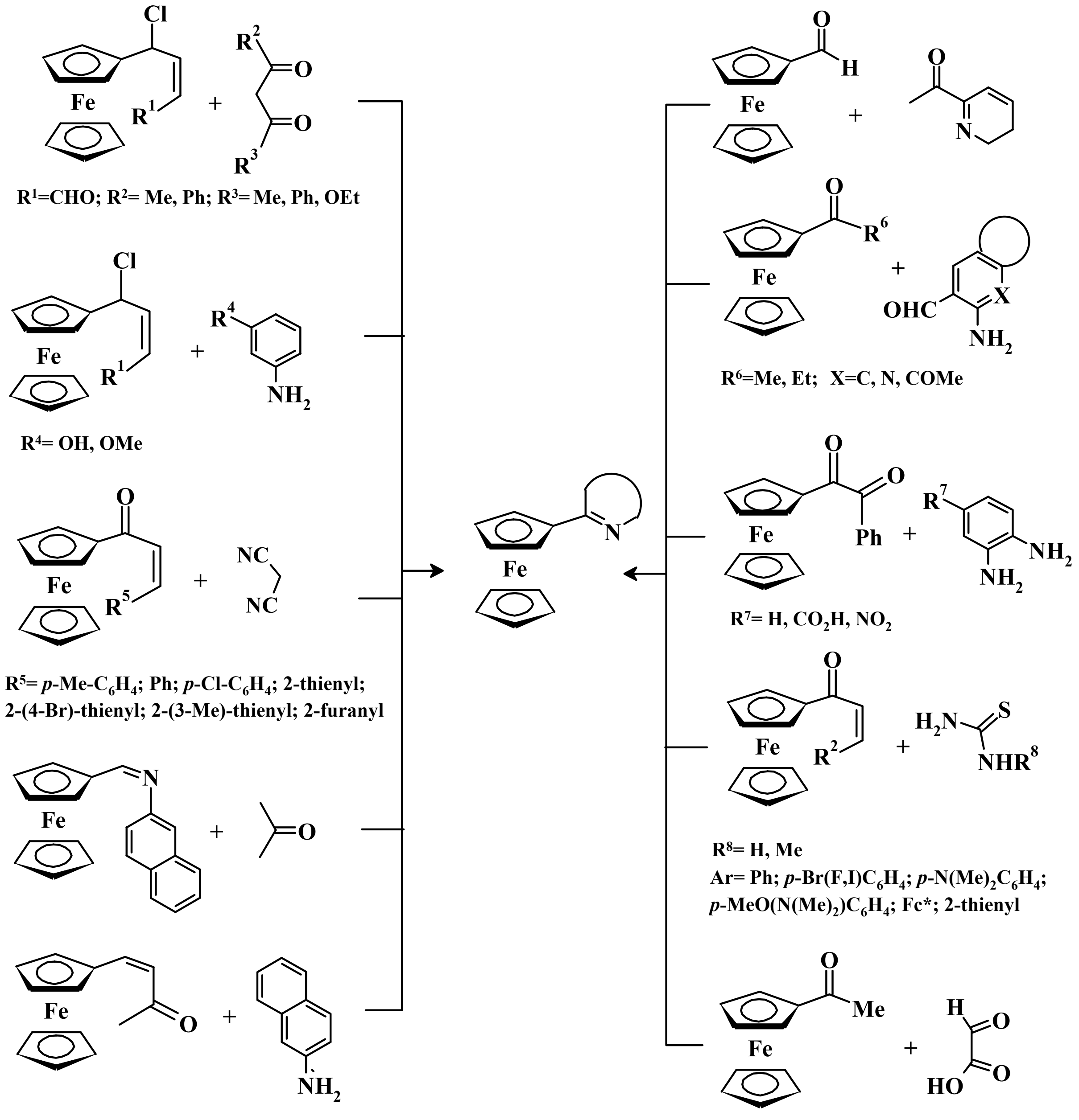
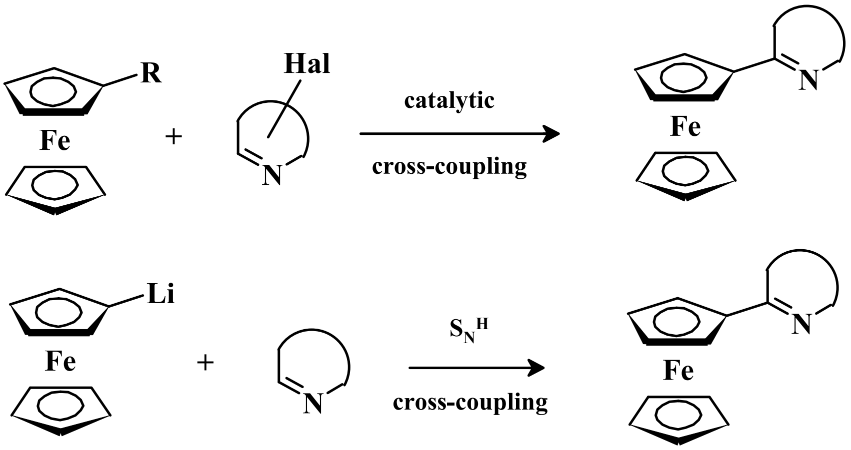


Approach A

*Here and then Fc=ferrocene

– the second way suggests use of coupling reactions in order to incorporate heterocyclic fragments into the core structure of ferrocenes (Approach B).



Approach B

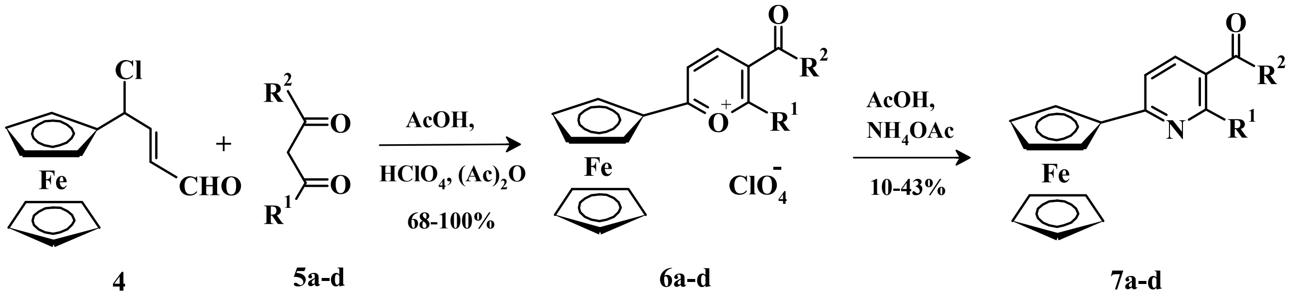
In this review article we would like to consider new synthetic methods in the chemistry of ferrocenes, and to discuss reactivity of their heterocyclic derivatives. Special attention will be paid to direct ferrocenylation of azaheterocycles by using the actively progressing developing methodology of nucleophilic substitution of hydrogen in π-deficient azaaromatics (S_N^H-reactions).[19]

2. Synthesis of azinylferrocenes through the formation of a new heterocyclic subunit

A relatively small number of syntheses of hetaryl substituted derivatives from ferrocene-containing building blocks have been performed, since not all synthetic methods can be applied to this specific system, and due to a tedious procedure to obtain appropriately functionalized starting materials.

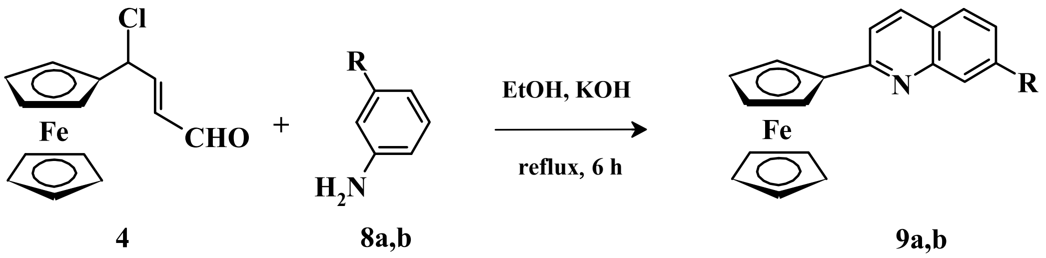
β-Chloro-*β*-ferrocenyl acrolein (**4**), resulting from acetylferrocene via the Vilsmeier-Haack reaction, appears to be a suitable staring material to obtain pyridyl- and quinolinyl substituted ferrocenes (**Scheme 1**). Condensation of **4** with *β*-carbonyl compounds **5** in acetic acid in the presence of perchloric acid and acetic anhydride affords the pyrilium salts **6,** which can further be transformed into the corresponding pyridylferrocenes **7** in 10-43% yields on reflux in a mixture of glacial acetic acid and ammonium acetate.[20]

A short-time heating of **4** with *m*-anisidine **8a** or *m*-aminophenol **8b** (Scheme 2) in benzene leads to the formation of quinolinyl ferrocenes **9a**,**b**.[21]



a) $R^1 = R^2 =$ Ph; b) $R^1 = R^2 =$ Me; c) $R^1 =$ Me, $R^2 =$ OEt; d) $R^1 = R^2 = -CH_2C(Me)_2CH_2-$

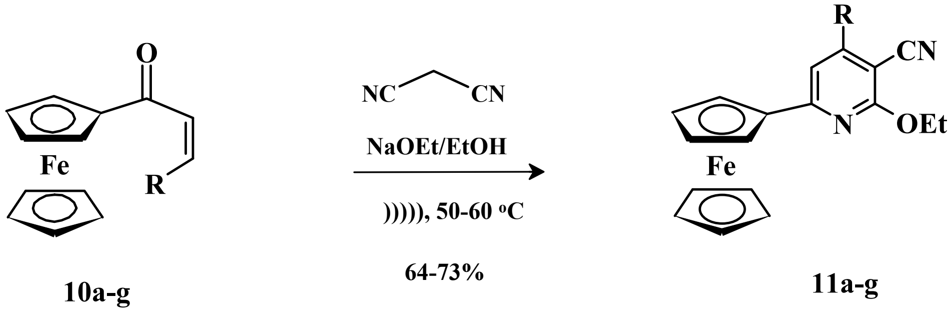
Scheme 1



R= a) OMe (44%), b) OH (15%)

Scheme 2

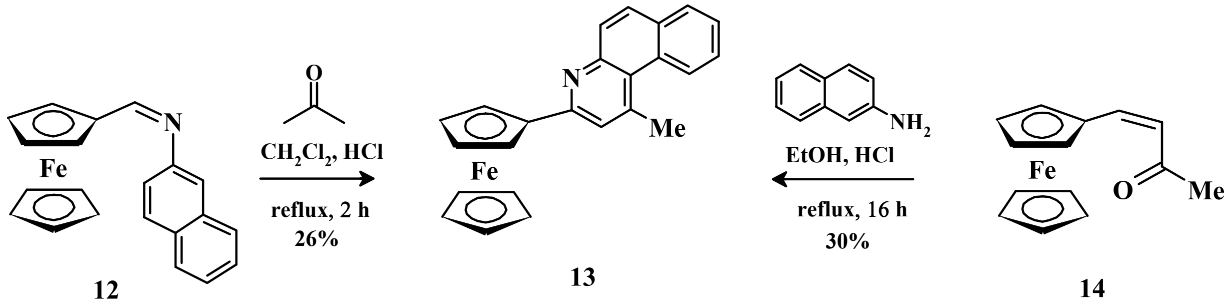
Condensation of chalcones **10** with malodinitrile in sodium ethoxide solution under ultrasonic irradiation affords ferrocenyl substituted 3-cyanopyridines (**Scheme 3**).[22] Cyanopyridines are of a special interest because effective pharmaceuticals and structural analogues of vitamins have been found in this series.[23,24]



R= a) *p*-Me-C_6H_4; b) Ph; c) *p*-Cl-C_6H_4; d) 2-thienyl; e) 2-(4-Br)-thienyl;
f) 2-(3-Me)-thienyl; g) 2-furanyl

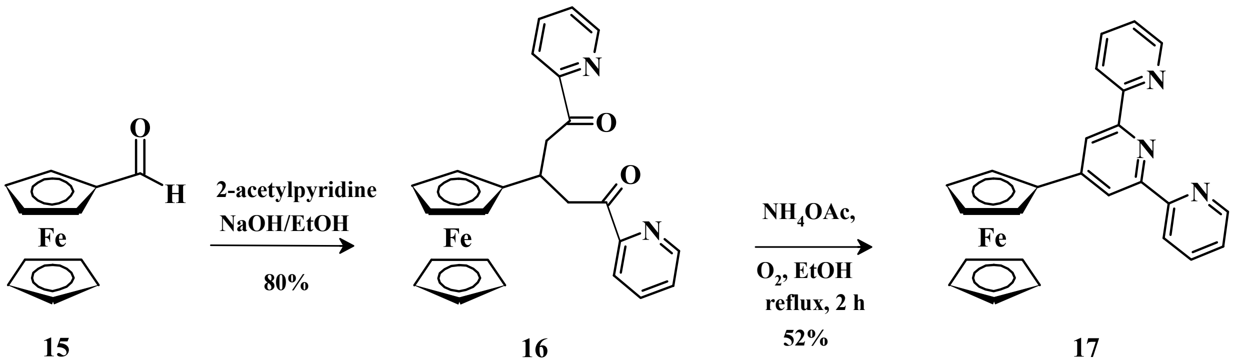
Scheme 3

2-Ferrocenyl-4-methylbenzo[5,6]quinoline (**13**) can be obtained by the reaction of azomethine **12** with acetone, while **12** is derived from condensation of the corresponding formylferrocene with *β*-naphthylamine;[25] the same compound **13** is formed on treatment of ferrocenyl-1-buten-1-one (**14**) with *β*-naphthylamine (**Scheme 4**).[26]



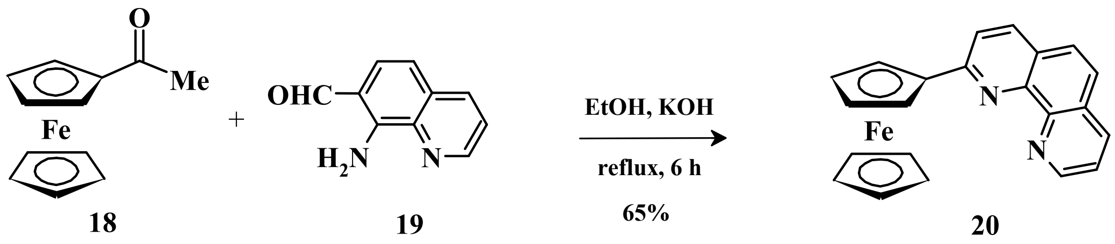
Scheme 4

Building block methodology can be applied for the synthesis of terpyridyl substituted ferrocene derivatives. Indeed, interaction of aldehyde **15** with 2-acetylpyridine followed by cyclization of 2-ferrocenyl-1,5-bis(2-pyridyl)-1,5-pentanedione (**16**) with ammonium acetate in refluxing ethanol have been shown to result in the formation of terpyridine **17** (**Scheme 5**).[27,28] The same strategy has been used to incorporate six pyridine fragments into ferrocenes.[29] Compound **17** appears to be a promising ligand for coordination chemistry;[30] photo and redox properties of complexes of **17** with Co(II), Ru(III), Zn(II), Fe(II) have extensively been studied.[31,32]



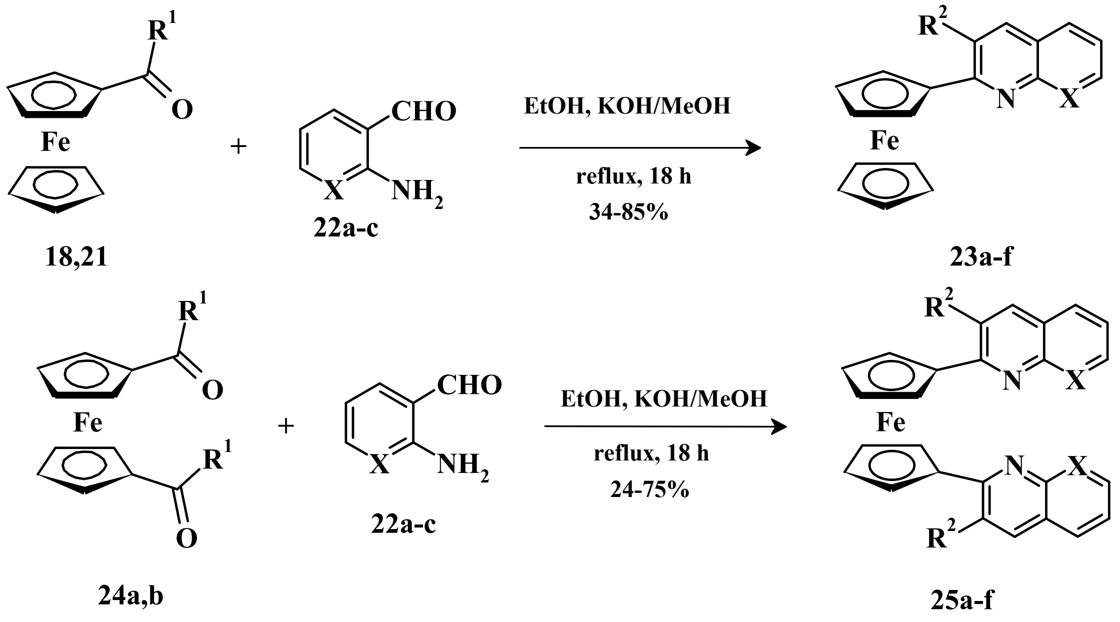
Scheme 5

Also, the Friedlander condensation seems to be an appropriate synthetic tool to obtain azaheterocyclic ferrocene derivatives. So, the synthesis of **20** has been accomplished through cyclization of acetylferrocene **18** with 8-amino-7-quinolinyl aldehyde (**19**) in ethanolic solution of potassium hydroxide (65% yield) (**Scheme 6**).[33] It has been shown that phenanthrolinyl substituted ferrocene takes part in the cyclopalladation reaction to give the corresponding racemic mixtures. Their resolution becomes possible provided enantiomerically pure phosphine ligand [(*R*)-Ph-BINEPINE] is incorporated into the inner sphere of palladium complexes followed by crystallisation of obtained diastereomers.



Scheme 6

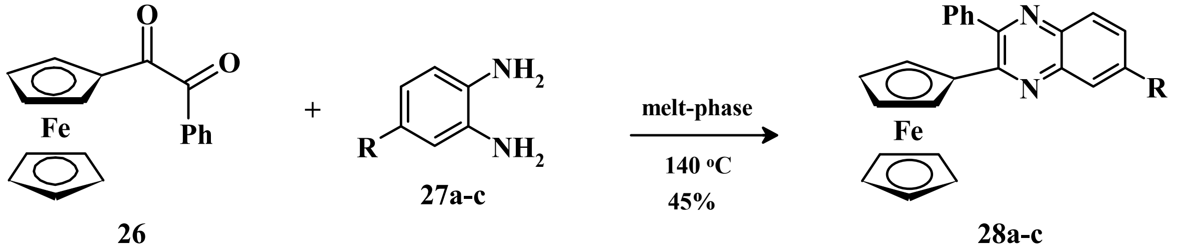
Heating of acetyl- or propionylferrocenes **18**, **21**, **24a**,**b** with *o*-amino arylaldehydes **22a-c** in methanol in the presence of potassium hydroxide results in the formation of 2-quinolinyl-, 2-naphthyridinyl- and 2-methoxyquinolinyl substituted ferrocenes, respectively (**Scheme 7**).[34] Such compounds, for example derivatives **26b**, **28b**, can be exploited as ligands to prepare bimetallic macrocycles bearing Cu(I), Ag(I), Zn(II), and Co(II) ions.[35,36]



21: R^1= Et;
22: X= a) CH, b) N, c) COMe;
24: R^1= a) Me, b) Et;
23, 25: a) R^2= H, X= CH; b) R^2= H, X= N; c) R^2= H, X= COMe; d) R^2= Me, X= CH; e) R^2= Me, X= N; f) R^2= Me, X= COMe

Scheme 7

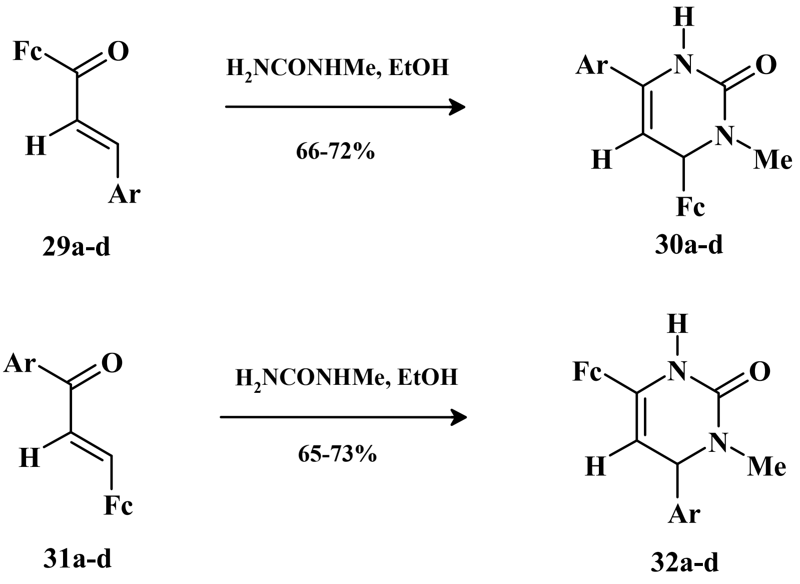
A convenient synthetic route to ferrocenyl quinoxalines from the corresponding glyoxal **26** and aromatic diamines, as starting materials, has been advanced.[37,38] So, the reaction of 1-ferrocenyl-2-phenyl-ethanedione (**26**) with 1,2-diaminobenzenes **27a-c** takes place on heating in melt to afford derivatives **28a-c** (**Scheme 8**); electrochemical properties of compounds **28a-c** have been studied.[38]



R= a) H, b) CO_2H, c) NO_2

Scheme 8

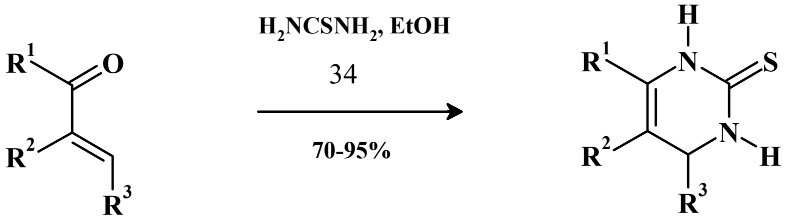
Syntheses and properties of ferrocene-based dihydropyrimidinones and dihydropyrimidinthiones, which appear to have structural similarities with the natural nucleic acids and, as a sequence, can exhibit anticancer, antiviral, antibacterial, and antiflammatory activities,[39,40] have extensively been studied. N-Methyldihydropyrimidinones **30a-d**, **32a-d** were obtained by condensation of methylurea with the corresponding ferrocenyl chalcones **29a-d**, **31a-d** (**Scheme 9**).[41]



Ar= a) Ph; b) *p*-BrC_6H_4; c) *p*-$MeOC_6H_4$; d) Fc

Scheme 9

A convenient route to build dihydropyrimidin-2-thiones **35a-l** is interaction of ferrocene-containing *α,β*-unsaturated carbonyl compounds **29a-c**, **31a**,**c**, **33a-g** with thiourea, which proceeds very smoothly and regioselectively to give the corresponding pyrimidinylferrocenes **35a-l** in good yields (**Scheme 10**).[42]



29a-c; 31a,c; 33a-g

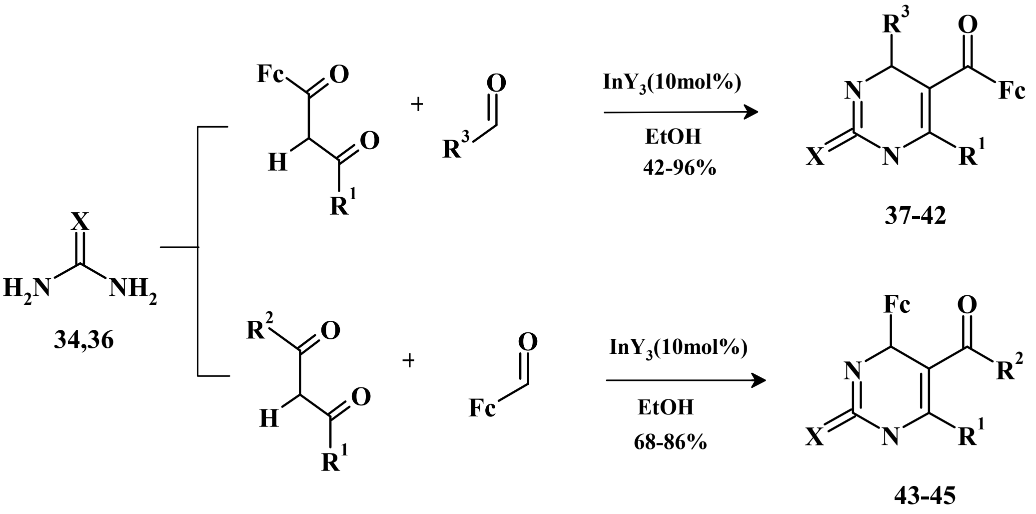
35a-l

33: a) R^1= Fc, R^2= H, R^3= *p*-F-C_6H_4;
b) R^1= Fc, R^2= H, R^3= *p*-I-C_6H_4;
c) R^1= Fc, R^2= H, R^3= 2-thienyl;
d) R^1= Fc, R^2= H, R^3= *p*-N(Me)$_2$-C_6H_4;
e) R^1= Fc, R^2= H, R^3= *p*-Me-C_6H_4;
f) R^1= Fc, R^2= H, R^3= $C_5H_4Mn(CO)_3$;
) R^1= *p*-N(Me)$_2$-C_6H_4, R^2= H, R^3= Fc;

35: a) R^1= Fc, R^2= H, R^3= Ph;
b) R^1= Fc, R^2= H, R^3= *p*-Br-C_6H_4;
c) R^1= Fc, R^2= H, R^3= *p*-MeO-C_6H_4;
d) R^1= Ph, R^2= H, R^3= Fc;
e) R^1= *p*-MeO-C_6H_4, R^2= H, R^3= Fc;
f) R^1= Fc, R^2= H, R^3= *p*-F-C_6H_4;
g) R^1= Fc, R^2= H, R^3= *p*-I-C_6H_4;
h) R^1= Fc, R^2= H, R^3= 2-thienyl;
i) R^1= Fc, R^2= H, R^3= *p*-N(Me)$_2$-C_6H_4;
j) R^1= Fc, R^2= H, R^3= *p*-Me-C_6H_4;
k) R^1= Fc, R^2= H, R^3= $C_5H_4Mn(CO)_3$;
l) R^1= *p*-N(Me)$_2$-C_6H_4, R^2= H, R^3= Fc

Scheme 10

Dihydropyrimidinones **37-45** can also be obtained by condensation of *β*-ketoesters, aldehydes with urea (the Biginelli reaction) catalyzed by indium trihalides (**Scheme 11**).[43]

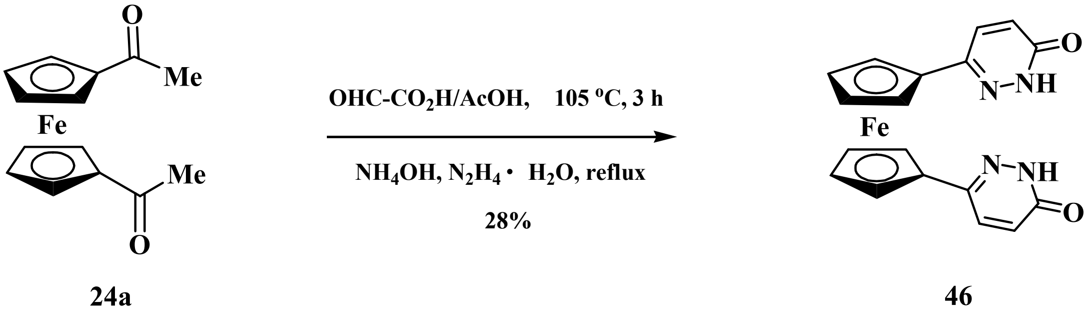


36: X= O

DHPM	37	38	39	40	41	42	43	44	45
R^1	Me	Me	Me	Me	Me	Ph	Me	Me	Me
R^2	-	-	-	-	-	-	OEt	OMe	OEt
R^3	Ph	*p*-Me-C_6H_4	*p*-Cl-C_6H_4	*p*-NO_2-C_6H_4	Ph	Ph	-	-	-
X	O	O	O	O	S	O	O	O	S
Y	Br	Cl, Br	Br	Cl	Br	Br	Cl, Br	Cl	Cl

Scheme 11

Cyclisation of 1,1'-diacetylferrocene with glyoxylic acid and hydrazine hydrate is the only example of the synthesis of ferrocenyl substituted pyridazinone **46**, although yield of the latter is moderate (**Scheme 12**). Compound **46** can be regarded as a precursor for the synthesis of novel ferrocenophanes, as polydentate ligands for homogenous catalysis.[44]

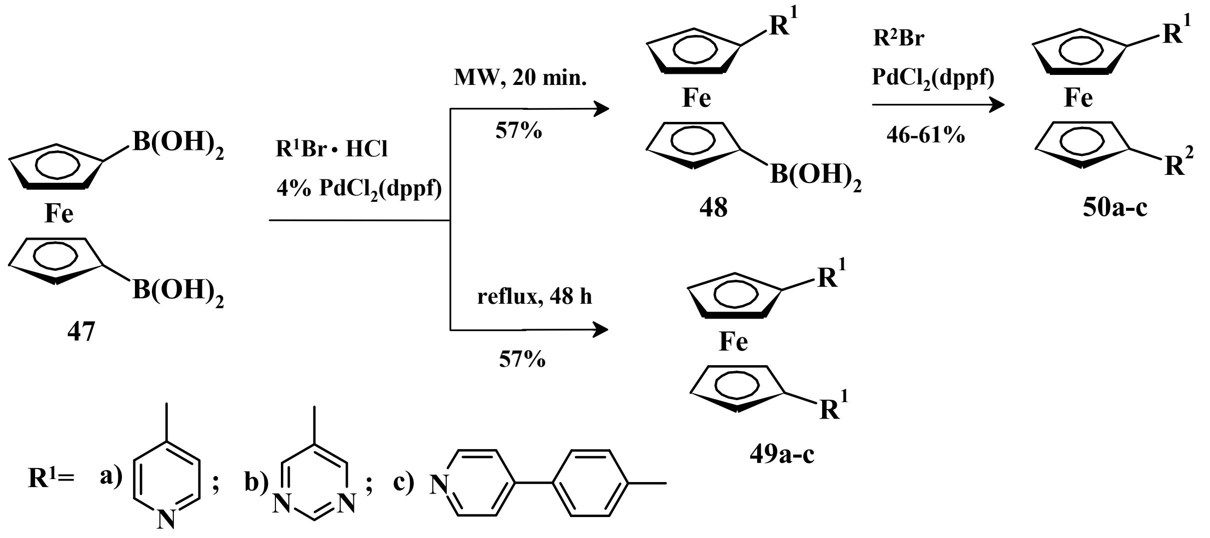


Scheme 12

3. The C-C coupling of heterocyclic fragments with ferrocenes

3.1. Metal catalyzed cross-coupling reactions

Organic boronic acids proved to be suitable starting materials to build new carbon-carbon bonds (the Suzuki cross-coupling reaction). There are two preparative procedures for using of this methodology to obtain hetarylferrocenes including azinyl derivatives. In the first case the reaction is carried out in dioxane, while halogenated heterocycles are added into the reaction in the form of hydrochrorides (**Scheme 13**).[45]

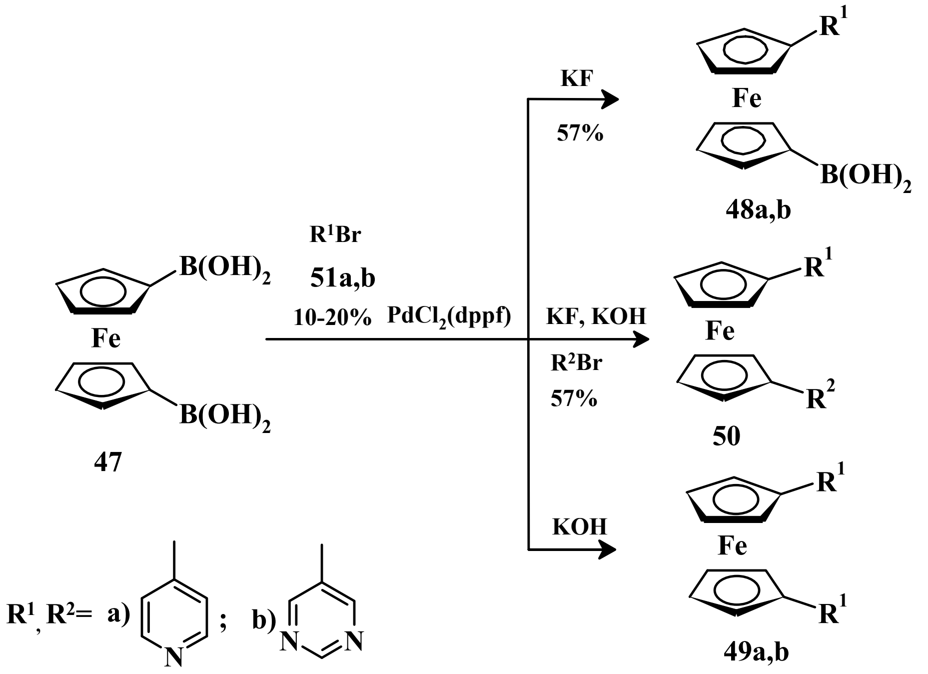


Scheme 13

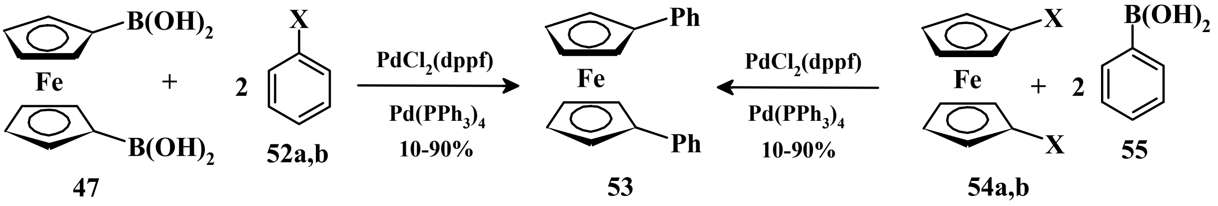
An alternative procedure is a kind of solvent-free solid-state reaction, which is a more attractive one due to the principles of green chemistry (**Scheme 14**).[46]

In both cases the formation of new C-C bond takes place in the presence of $PdCl_2$(dppf). The methods described above have been used for the synthesis of asymmetrical 1,1’-disubstituted ferrocenes. Coordination ability of ligands **48-50** with Ni(II), Ag(I), Cd(II), Zn(II), Cu(II) ions[47] as well as their electrochemical properties have been elucidated.[48]

Aryl derivatives of ferrocene can be prepared via the Suzuki-Miyaura reaction. Ferrocene-1,1’-diboronic acid **47** has been established to react smoothly with halobenzenes in the presence of palladium catalysts to give 1,1’-diphenylferrocene. Compound **53** is also formed on treatment of phenylboronic acid **55** with haloferrocenes **54a,b** (**Scheme 15**). Depending on the reaction conditions and the nature of starting materials yields of the final products are varied from 10 to 90%.[49] Compounds **53** can be undoubtedly used in the synthesis of appropriate quinolines according to known methods.[50]



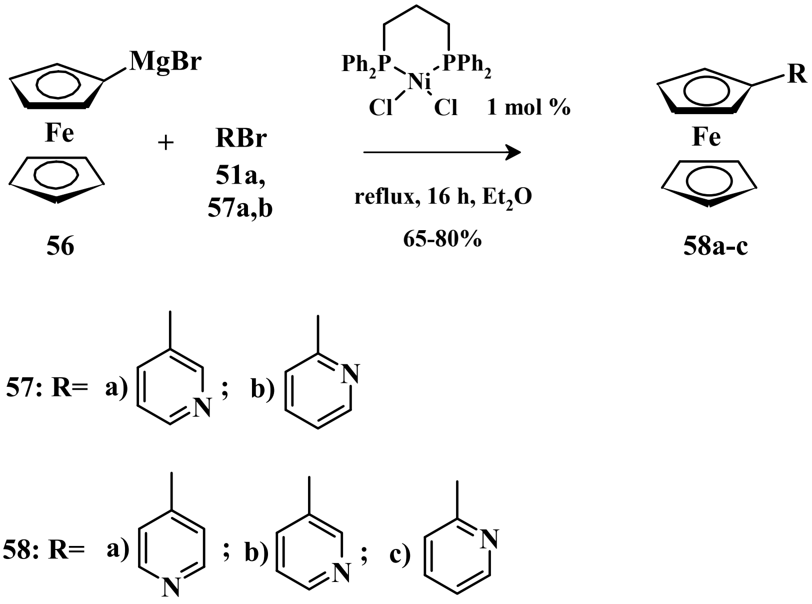
Scheme 14



a) X = Br, b) X = I

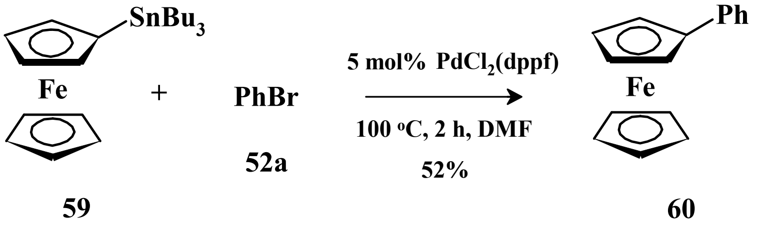
Scheme 15

Pyridylferrocenes **58a-c** were synthesized via the Kumada cross-coupling reaction. In particular, it has been shown that the Grignard reagent **56** interacts with bromopyridines **57a-c** in diethyl ether in the presence of the Ni catalyst for 16 hours to form the corresponding pyridinyl ferrocenes **58a-c** (**Scheme 16**). Metal complexes of the obtained ligands with Pd(II), Pt(II), Rh(II) were found to exhibit a significant cytotoxic activity *in vitro*, which is comparable with that of "cisplatin", the famous anti-cancer drug. Effect of the ferrocene fragment in this case is closely related with a reversibility of redox processes for the ferrocene/ferrocenium ion system *in vivo*, and generation of active oxygen radicals, for example, the hydroxyl one, prevents a cell fission and is responsible for biological damage of cancer cells through the formation of radical metabolites.[51]



Scheme 16

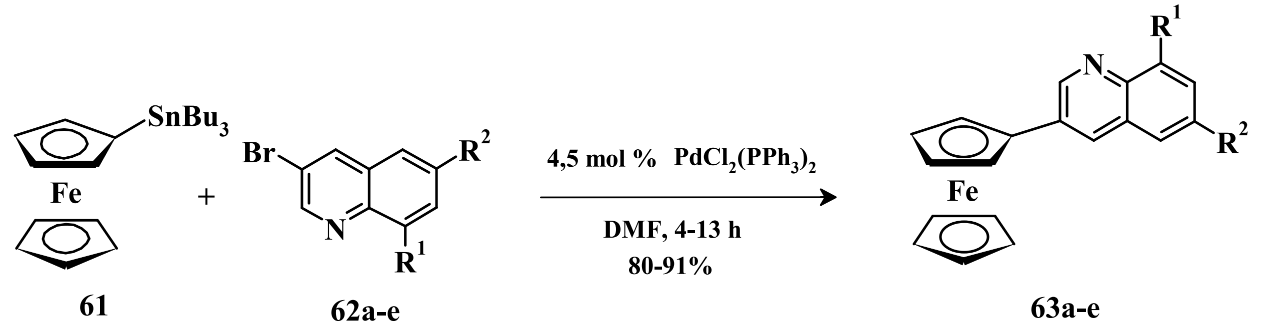
Another efficient method to modify the structure of ferrocene derivatives is the Stille cross-coupling reaction. Heating of tri(*n*-butyl)stannylferrocene (**59**) with bromobenzene in DMF in the presence of a catalytic amount of Pd(II) affords phenylferrocene in 52% yield (**Scheme 17**).[52]



Scheme 17

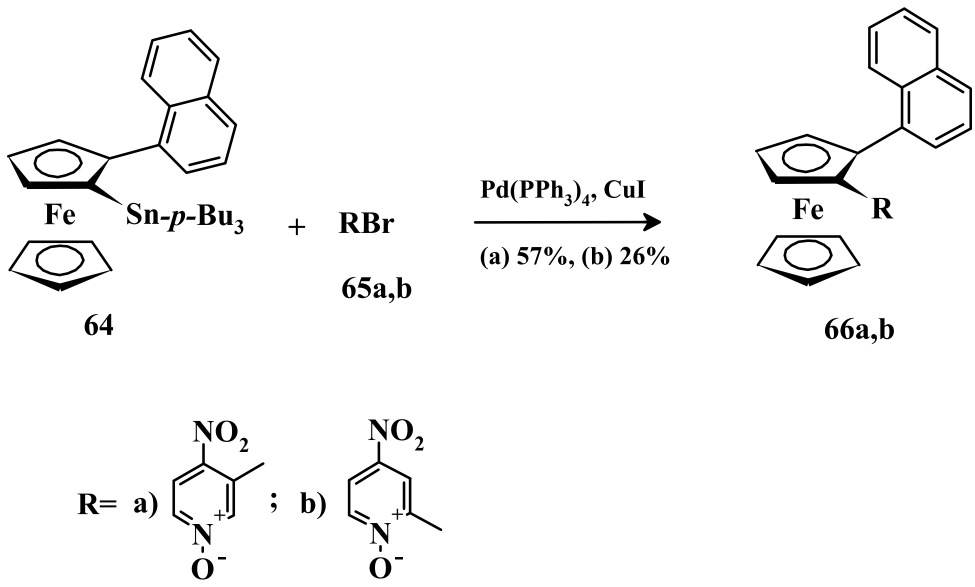
According to this procedure a number of haloquinolines **62** were transformed into the corresponding quinolinylferrocenes **63** in 80-91% yields (**Scheme 18**). The reaction was carried out in DMF at 100-130 °C for 4-13 hours in the presence of Pd (0). This method allows one to obtain ferrocene-based pyridines, thiophenes, and oxazoles.[53]

In some cases the Stille cross-coupling reaction appears to be a convenient tool for the synthesis of chiral 1,2-disubstituted ferrocenes. For instance, compounds **66a,b** (**Scheme 19**) have been obtained by the catalytic reaction with bromo derivatives of 4-nitropyridin-1-oxides in the presence of Pd(0) and CuI as catalysts. Reduction of **66** gave the corresponding pyridylferrocenes.[54]



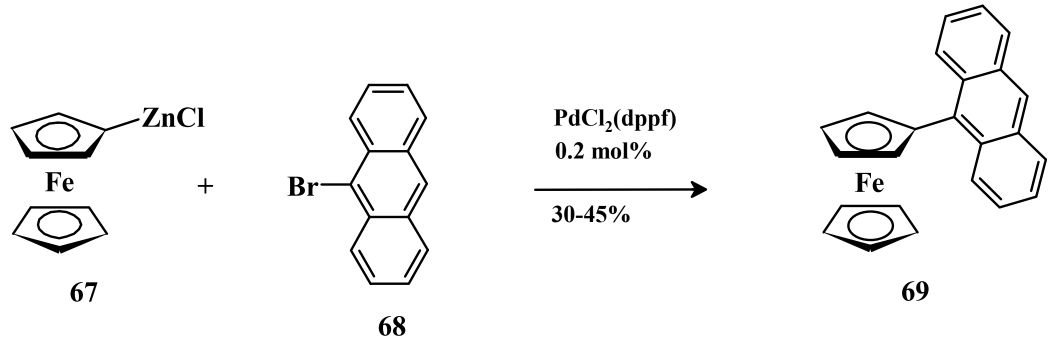
63: a) R^1= NO$_2$, R^2= Me; b) R^1= Me, R^2= NO$_2$; c) R^1= NO$_2$, R^2= OMe; d) R^1= OMe, R^2= NO$_2$; e) R^1= NO$_2$, R^2= Cl

Scheme 18



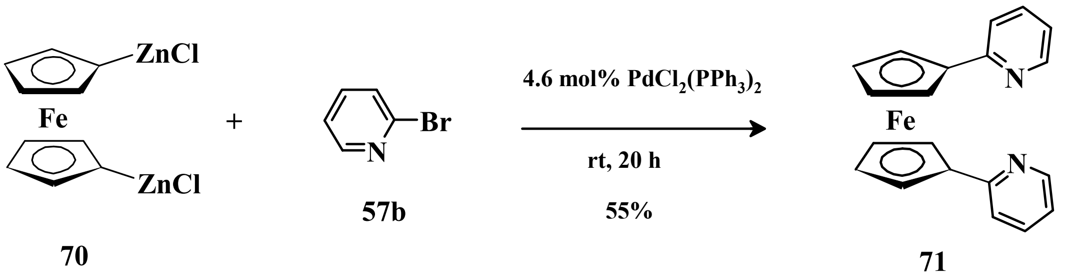
Scheme 19

A wide-spread method to incorporate a heterocyclic unit into the ferrocene skeleton is the Negishi cross-coupling reaction. It has been established that ferrocenyl anthracene **69** is formed when ferrocenyl zinc chloride **67**, derived from the lithium salt of ferrocene, reacts with bromoanthracene in the presence of a palladium catalyst (**Scheme 20**).[55] Structural analogues of compound **69** were shown to be used as fluorescent sensors.[56]



Scheme 20

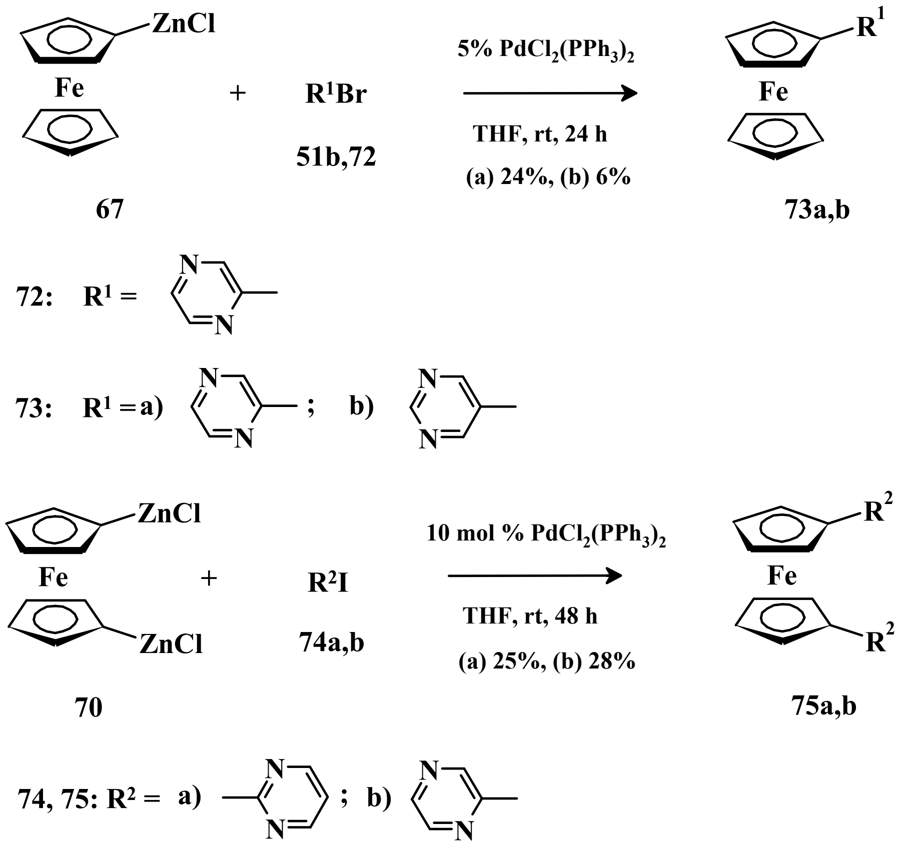
Further studies have shown that dilithioferrocene can easily be involved into the transmetalation reaction to give organozinc derivative **70**, which being treated with bromopyridine in the presence of catalytic amounts of palladium salt is transformed into the corresponding dipyridylferrocene **71** (**Scheme 21**). Elucidation of coordination properties of the obtained ligand towards Pd(II), Pt(II) (Pd(COD)(Me)Cl, $K[PtCl_3(CH_2{=}CH_2)]$ have revealed that a number of these metal complexes proved to be unstable.[57]



Scheme 21

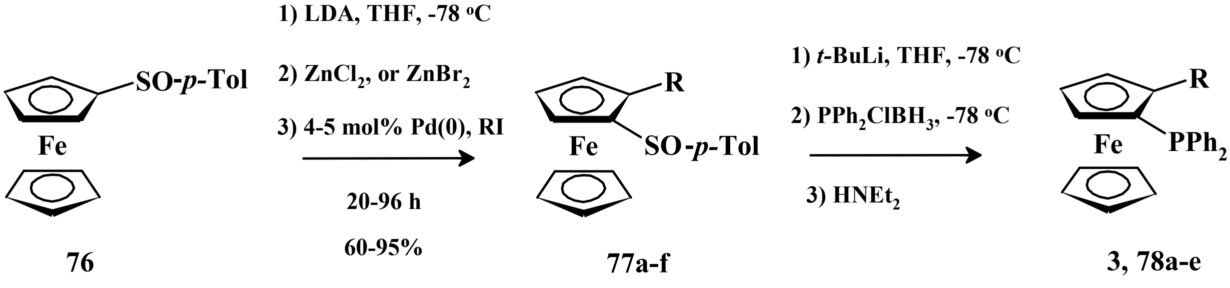
Pyrimidine and pyrazine fragments can be incorporated into the ferrocene structure by the palladium-catalyzed Negishi-coupling. The reaction of **67**, **70** with haloheterocycles **51b**, **72**, **74a**,**b** has been found to proceed smoothly in THF at room temperature, resulting in hetarylferrocenes **73a**,**b**, **75a**,**b** (**Scheme 22**). The compounds obtained proved to be appropriate components to form metal complexes with Ag(I), Co(II), Cu(II), Mn(II), Ni(II), Pt(II), Zn(II) ions. Also, such ligands have been exploited in design of supramolecular organometallic assemblies.[58]

Ferrocenes with an asymmetric skeleton can easily be lithiated in enantioselective manner, and a subsequent transmetalation reaction enables one to retain their configuration. Finally, arylation by means of the Negishi-coupling reaction affords planar chiral derivatives **77a-e** (**Scheme 23**).



Scheme 22

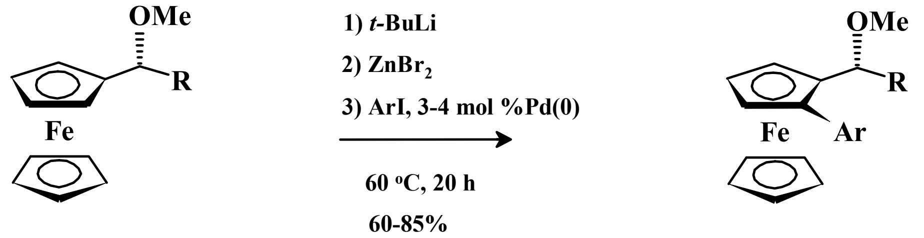
The reaction proceeds (**Scheme 23**) in THF at room temperature and takes from 20 to 96 hours. Catalytic activity of ligands **78** has been tested for the palladium-catalyzed asymmetric hydrosilylation of styrene, and depending on the nature of starting materials enantioselectivity proved to vary from 25 to 86%.[59] The methodology described above was used to obtain ferrocene-containing analogue of the well-known ligand for asymmetric catalysis (QUINAP) **78f**. An efficiency of palladium complex of this ligand has been elucidated for both allylic alkylation and amination reaction; enantioselectivity proved to be in the range of 59-86% ee.[17]



a) R = Ph; b) R = 3,5-$(CF_3)_2$-C_6H_3; c) R = *o*-OMe-C_6H_4;
d) R = *p*-MeO-C_6H_4; e) R = 1-naphthyl

Scheme 23

It has been found that, when heated at 60 ºC zinc derivatives **79** are subjected to a palladium (0)-catalyzed cross-coupling reaction with pyridyl, quinolinyl and pyrimidinyl iodides to give the corresponding ferrocenes **80** in 60-80% yields (**Scheme 24**).[18] It is noteworthy that complexes of these ligands with Rh(II) exhibit a high catalytic activity in hydroboration of styrenes (>99% ee).

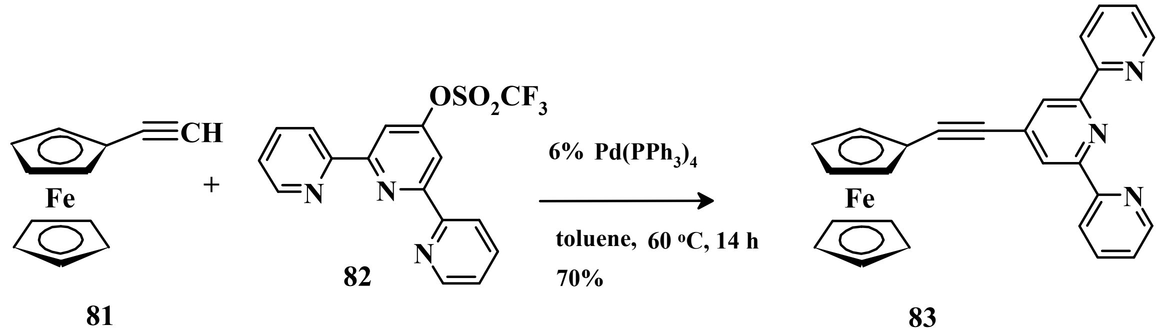


79a-i **2, 80a-h**

a) R = Ph, Ar = 2-pyridyl; b) R = Ph, Ar = pyrimidin-2-yl;
c) R = *o*-tolyl, Ar = 2-pyridyl; d) R = *o*-tolyl, Ar = pyrimidin-2-yl;
e) R = *o*-tolyl, Ar = quinolin-2-yl; f) R = 3,5-xylyl, Ar = 2-pyridyl;
g) R = 3,5-xylyl, Ar = pyrimidin-2-yl; h) R = 3,5-xylyl, Ar = quinolin-2-yl

Scheme 24

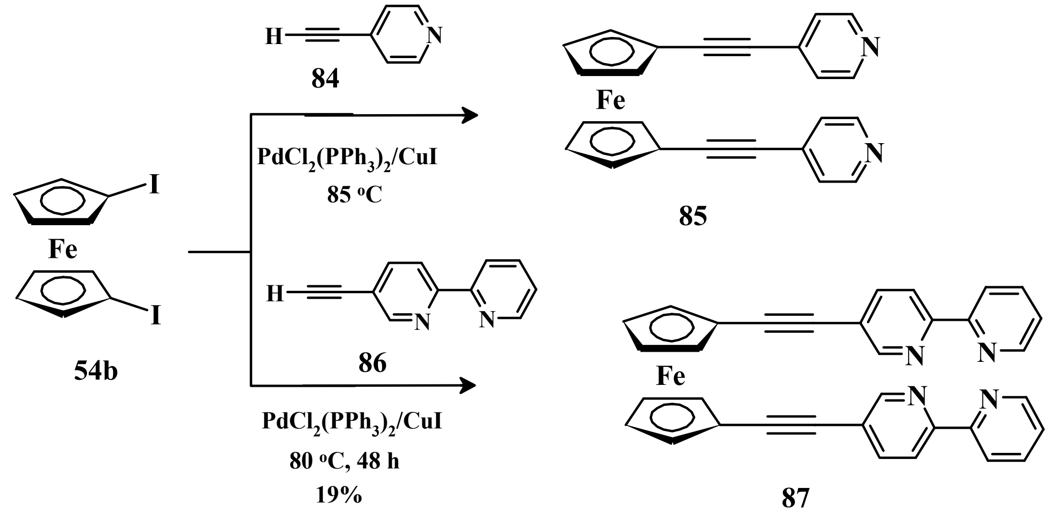
The next type of cross-coupling reactions used for the synthesis of azinylferrocenes is the Sonogashira reaction. This method affords heterocyclic ferrocenes in which substituents are attached to the cyclopentadienyl ring through a rigid acetylene fragment (**Scheme 25**). Electrochemical, spectrophotochemical, photophysical and redox-active properties for the complexes of **83** with Ru(II), Fe(II), Zn(II) have extensively been studied.[60]



81 **83**

Scheme 25

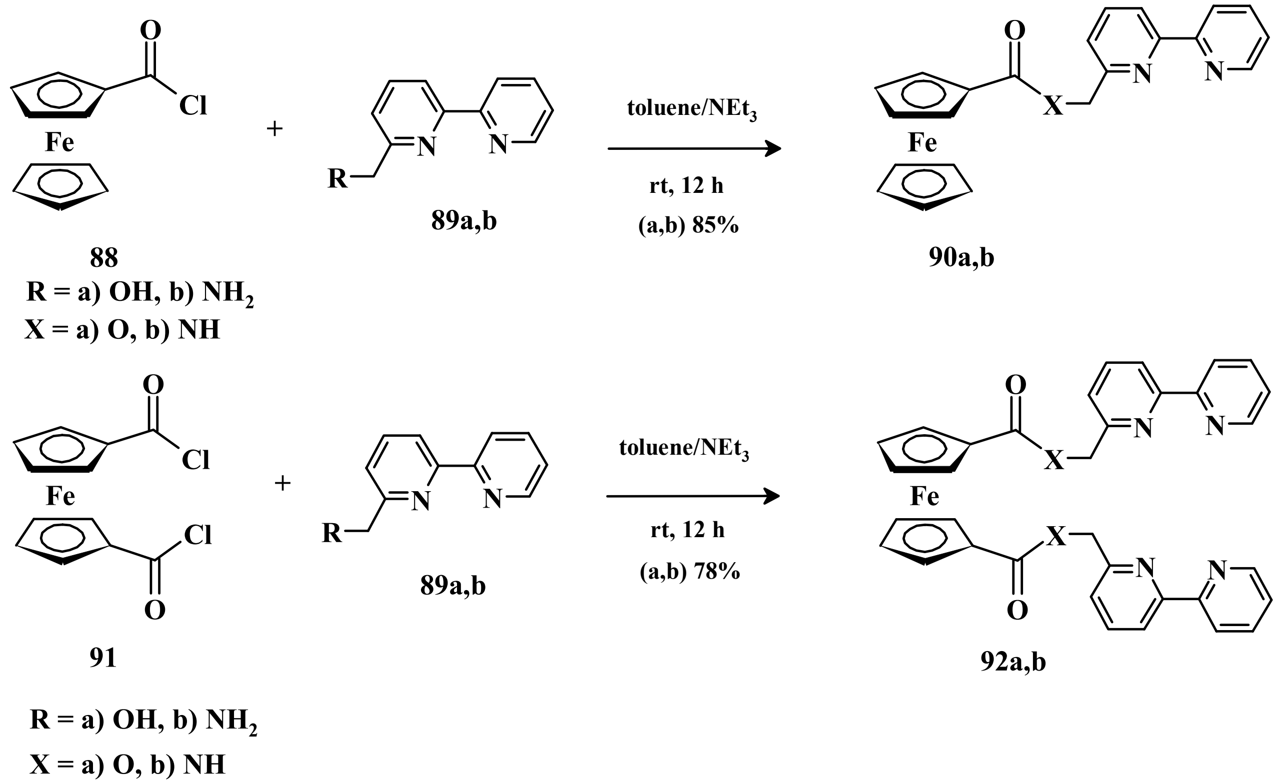
The Sonogashira-reaction has been exploited to obtain heteroannular disubstituted pyridyl- and bipyridylethynyl ferrocenes from 1,1’-diiodoferrocene (**Scheme 26**). The reaction has been shown to proceed in diisopropylamine at 80 ºC for two days and affords the final products **85**, **87**;[61] their complexes with Ag(I), Ni(II), Pd(II) ions have been obtained and their redox properties were studied.



Scheme 26

Thus, a variety of cross-coupling reactions allow one to functionalize the ferrocene moiety with a number of aromatic and heterocyclic substituents.

An alternative procedure for direct incorporation of dipyridine-based ligands into the structure of ferrocenes is interaction of carbonyl compounds **88**, **91** with hydroxy- and aminomethyl derivatives of 2,2'-bipyridine **89a**,**b**. It seems to be a promising approach to ligands for coordination chemistry **90**, **92a**,**b** (**Scheme 27**)[62] and their complexes with Cu(II), Ni(II), Hg(II), Fe(II), and Ag(I), which exhibit interesting electrochemical properties.[63]

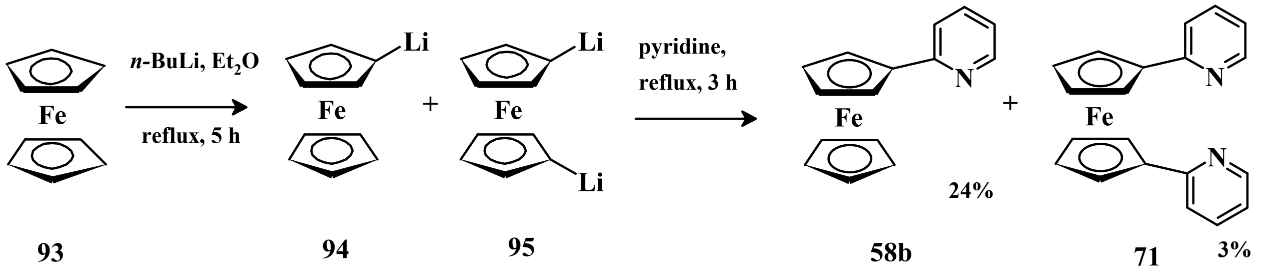


Scheme 27

3.2. S_N^H cross-coupling of lithioferrocene with azines

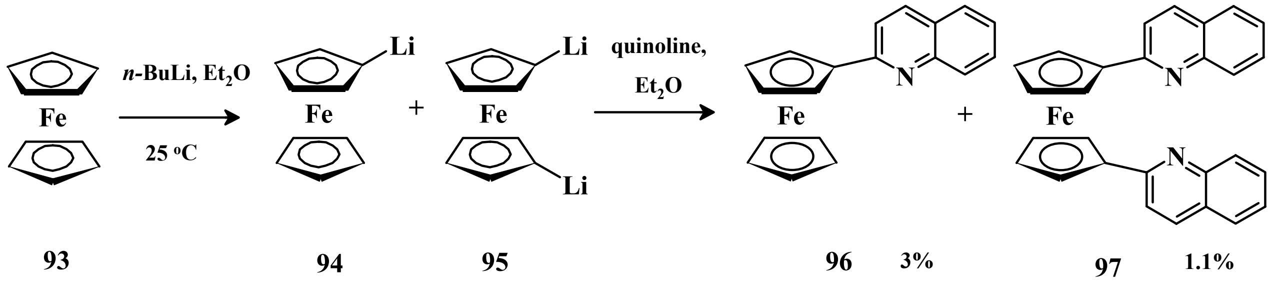
In the series of cross-coupling reactions a special role belongs to the S_N^H - reactions of lithioferrocene with a variety of heteroarenes. These reactions provide the formation of C-C bonds between ferrocene and azaheterocycles without use of any metal catalysts and halogenated compounds.

A number of reports concerning direct synthesis of hetarylferrocenes by using lithioferrocene as the starting material can be found in the literature. The first example of such coupling reactions was shown by Nesmeyanov and co-workers in 1962 cross-coupling of pyridine and ferrocenyllithium. They established that a mixture of lithioferrocenes **94**, **95** reacted with pyridine into mono- and 1,1'-dipyridinyl-ferrocenes (**Scheme 28**). Yields of mono- and disubstituted products proved to be 20% and 3% respectively.[64]



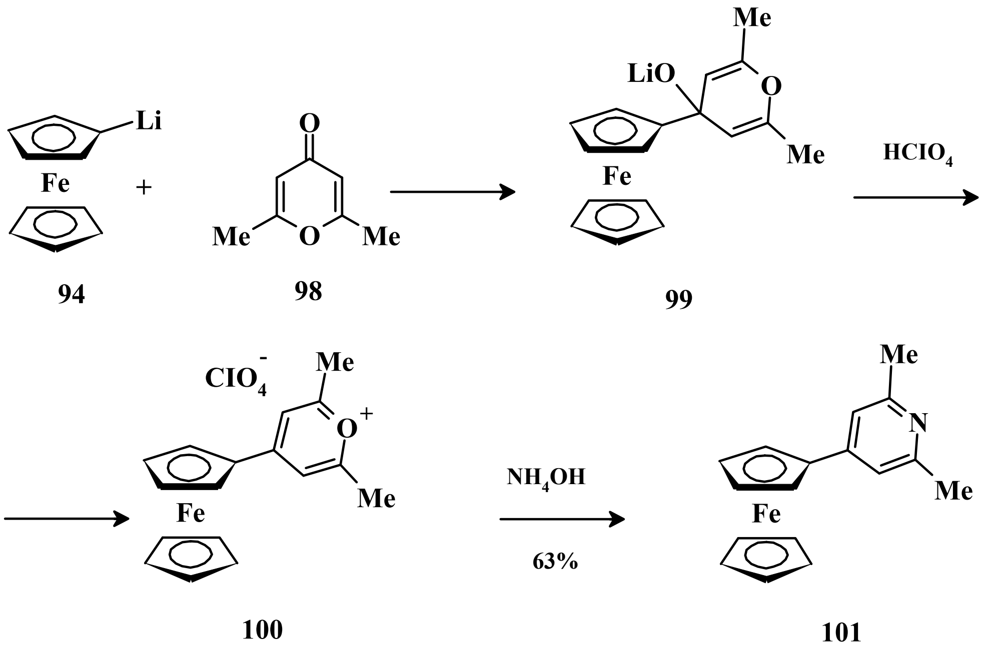
Scheme 28

The same methodology was used for the synthesis of quinolinyl substituted ferrocenes **96**, **97** in a very poor 3% yield.[65] It should be mentioned that the reactions were carried out in inert atmosphere (**Scheme 29**).



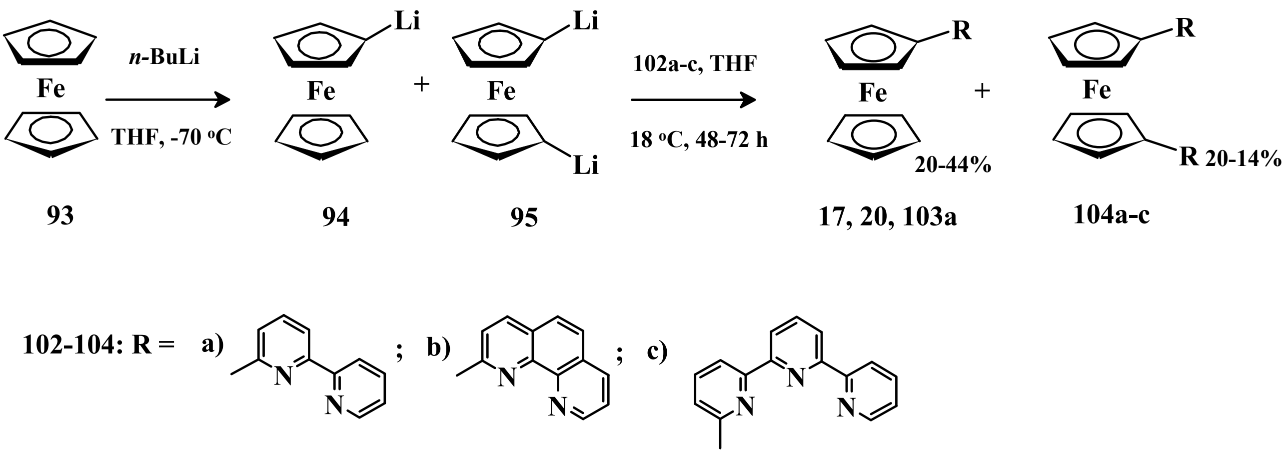
Scheme 29

The reaction of lithioferrocene with 2,6-dimethyl-γ-pyrrone (**98**) results in the formation of carbino late **99**, which on treatment with chloric acid is transformed into 2,6-dimethyl-4-ferrocenyl-pyrilium perchlorate (**100**) (**Scheme 30**). Addition of ammonium hydroxide solution to the salt **100** causes the ring transformation reaction, affording 2,6-dimethyl-4-ferrocenylpyridine (**101**).[66]



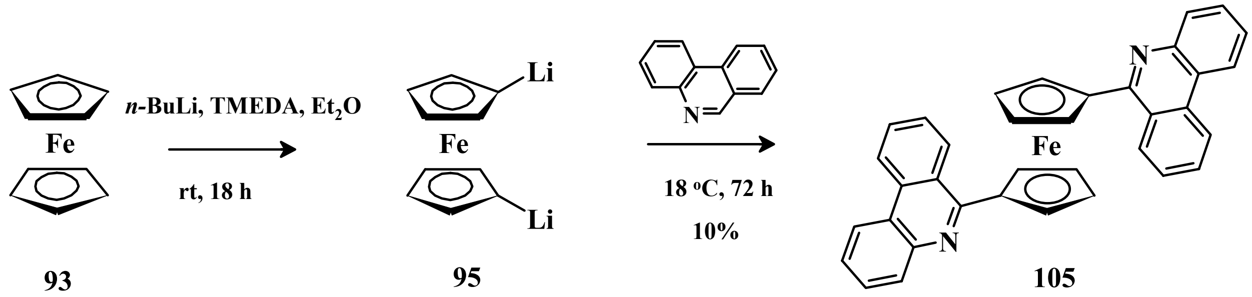
Scheme 30

A number of azinylferrocenes with metal complexing properties has been synthesized. In particular, a mixture of mono and dilithio ferrocenes **94**, **95** were found to react with 2,2'-bipyridine, [1,10]-phenantroline and 2,2':6',2''-terpyridine in THF to result in the formation of the corresponding mono- and disubstituted ferrocenes (**Scheme 31**). The reactions were carried out at 18 ºC for three days to give monosubstituted products **17**,**20**,**103a** in 20-44% yields, while 1,1'-disubstituted derivatives **104a-c** were obtained in 14-20% yields.[67]



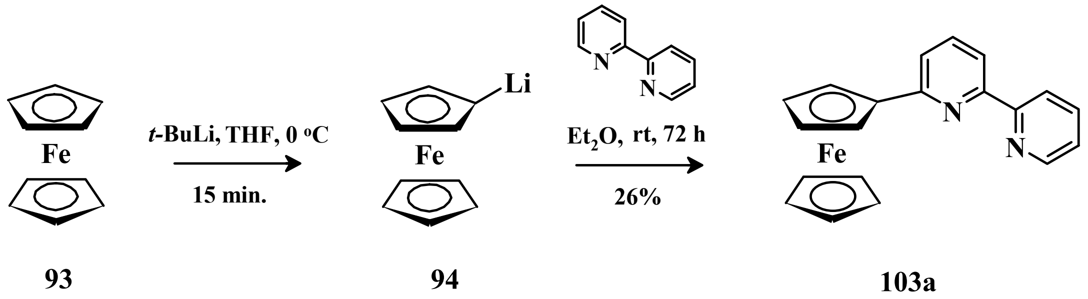
Scheme 31

1,1'-Dilithioferrocene **95**, generated on treatment of ferrocene with *n*-BuLi in diethyl ether in the presence of TMEDA, was shown to react with phenanthridine in the same manner to give 1,1'-bis(5-phenanthridine)ferrocene (**105**) in 10%yield (**Scheme 32**).[68]



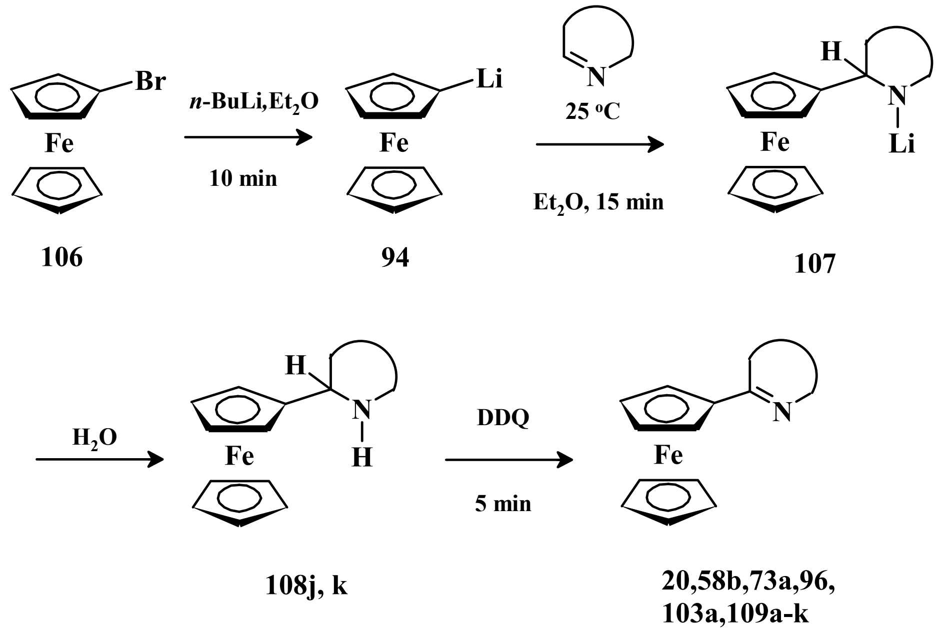
Scheme 32

When ferrocene reacts with *t*-BuLi only monolithiated compound is formed, but yield of he corresponding 6-ferrocenyl-2,2'-bipyridine (**103a**) proved to be rather poor (only 26%) (**Scheme 33**).[69] It is worth mentioning that the method for obtaining of monolithioferrocene has first been offered in the paper.[70]



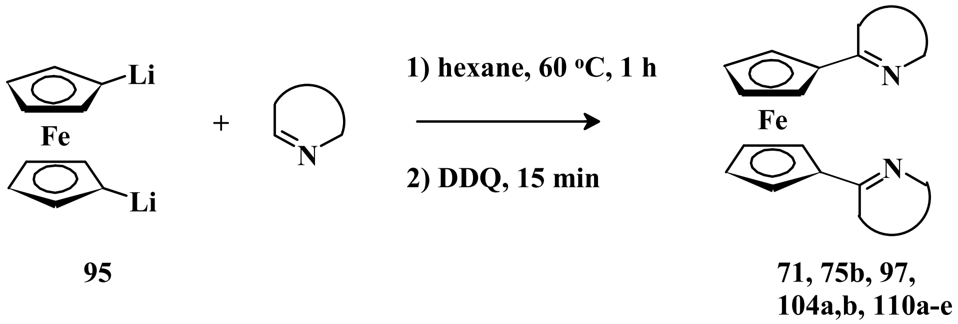
Scheme 33

In the examples presented above the mechanism for interaction of lithioferrocene with azines has not been elucidated in detail, and the formation of σ^H-adducts (dihydro derivatives resulting from the addition of the lithiated ferrocenyl anion to azines) has only been postulated.[67] Many details concerning intricate mechanism for elimination of hydrogen from σ^H-adducts have so far been unclear, which was an obstacle to prepare the S_N^H products in satisfactory yields. We have studied the mechanism of this reaction.[71] Following the general concept[19] of oxidative nucleophilic substitution of hydrogen (the S_N^H (AO) process) takes place in two steps. The first one involves an addition of nucleophilic agent to aromatic compounds bearing electron-withdrawing substituents, which leads to σ^H-adducts **108**. The second step, oxidation, is accompanied by aromatization of these intermediates to give the corresponding S_N^H-products. We have succeeded to perform the synthesis of hetarylferrocenes **20**, **58b**, **73a**, **103a**, **109a-k** (**Table 1**) under appropriate oxidative conditions (**Scheme 34**). The best results have been obtained with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as oxidative agent.[71] The stability of σ^H-adducts of lithioferrocene with azines is varied greatly from very unstable short-lived species to rather stable dihydro compounds. Indeed, most of them are subjected to ‘spontaneous’ aromatization due to the contact with air. The formation of intermediate in the reaction of lithioferrocene with pyrazine **107** can be registered by ^{1}H NMR, in which the characteristic signal of proton at the *sp*^{3}-carbon is observed at $\delta=5.59$. The σ^H-adducts of such highly electrophilic reagents as 1,2,4-triazines were isolated in crystal form. The structures of σ^H-adducts were confirmed by X-ray analysis performed for stable Zn(II) complex.[72]



Scheme 34

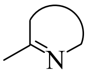
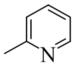
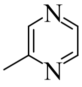
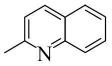
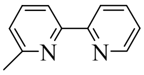
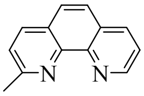
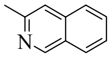
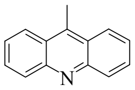
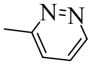
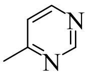
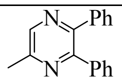
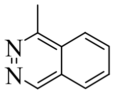
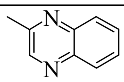
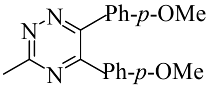
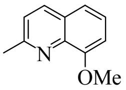
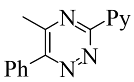
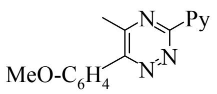
The above-mentioned techniques developed for monosubstituted hetaryl derivatives of ferrocene was slightly modified and used for the synthesis of 1,1’-diazinylferrocenes. The latter are of interest as ligands for complexation with metals. It is known that 1,1’-dilithioferrocene can be prepared by the reaction of ferrocene with *n*-BuLi in the presence of TMEDA (**Scheme 35**).[73,74] 1,1’-Dilithioferrocene **95** smoothly reacts with a twofold excess of azines to give heteroannular-substituted 1,1’-bis-azinylferrocenes **71**, **75b**, **97**, **104a**,**b**, **110a-e** (**Table 2**). Aromatization of the intermediates also proceeds by the action of DDQ.



Scheme 35

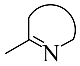
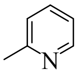
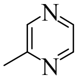
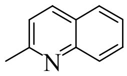
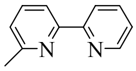
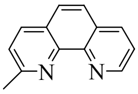
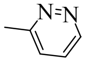
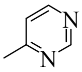
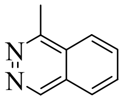
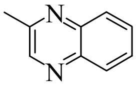
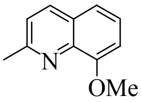
Yields of monoazinylferrocenes **20**, **58b**, **73a**, **103a**, **109a-k**

Table 1

Compound	Azinyl residue		Yield, %
58b	pyridyl-2		67
73a	pyrazin-2-yl		61
96	quinolin-2-yl		67
103a	2,2'-dipyridyl-6		78
20	[1,10]-phenanthrolin-2-yl		80
109a	iso-quinolin-3-yl		60
109b	acridin-9-yl		80
109c	pyridazin-3-yl		75
109d	pyrimidin-4-yl		79
109e	2,3-diphenylpyrazin-5-yl		68
109f	phthalazin-1-yl		68
109g	quinoxalin-2-yl		70
109h	5,6-di-*p*-methoxyphenyl-1,2,4-triazinyl-3		67
109i	8-methoxyquinolin-2-yl		85
109j	1-[6-(4-methoxyphenyl)-3-(pyridyl-2)-4,5-dihydro-4(*H*)-1,2,4-triazin-5-yl]		75
109k	1-[6-(4-phenyl)-3-(pyridyl-2)-4,5-dihydro-4(*H*)-1,2,4-triazin-5-yl]		76

Yields of diazinylferrocenes **71**, **75b**, **97**, **104a**,**b**, **110a-e**

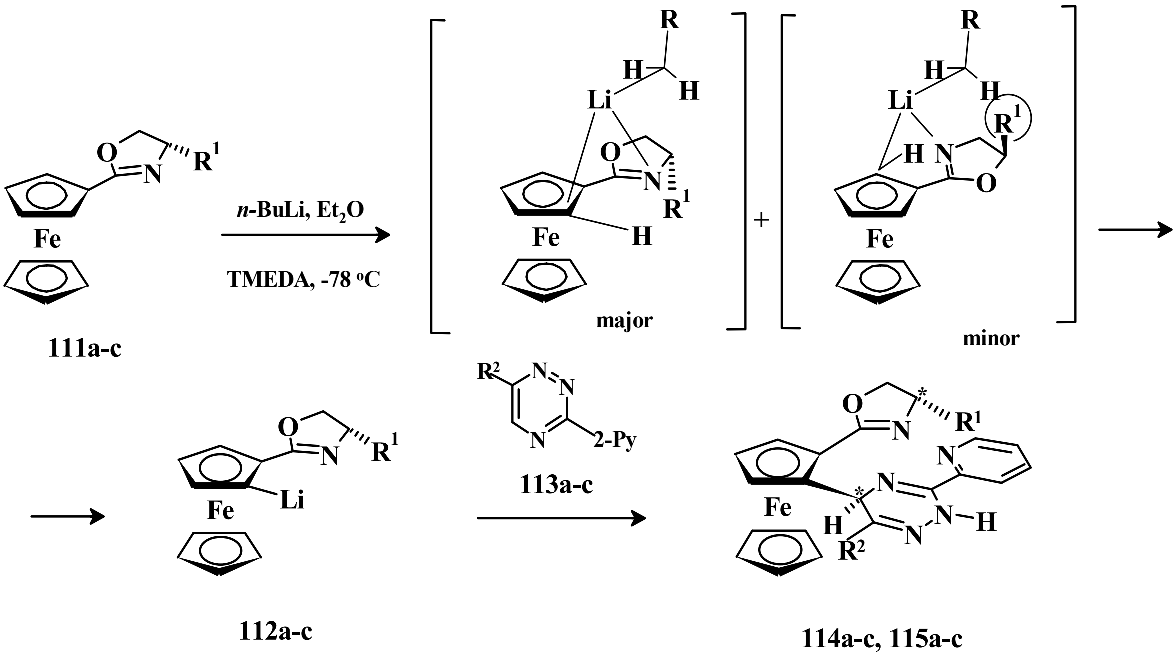
Table 2

Compound	Azinyl residue		Yield, %
71	pyridyl-2		63
75b	pyrazin-2-yl		60
97	quinolin-2-yl		61
104a	2,2'-dipyridyl-6		63
104b	[1,10]-phenanthrolin-2-yl		65
110a	pyridazin-3-yl		60
110b	pyrimidin-4-yl		62
110c	phthalazin-1-yl		70
110d	quinoxalin-2-yl		60
110e	8-methoxyquinolin-2-yl		64

The modification of pyridyltriazines with the chiral lithium salt of the oxazolinyl ferrocenes **111a-c** is based on the S_N^H-process, which provides an access to new derivatives of metal complexes, including those possessing planar chirality (**Scheme 36**).[75]

Interaction of chiral ferrocenes **111a-c** with 3-(pyridyl-2-)1,2,4-triazines gave 1,2-disubstituted derivatives **114a-c**, **115a-c** with the definite configuration and in 86-99% optical purity. The absolute configuration of **114**, **115** was also established by X-ray crystallography for **114b**-NiPiv$_2$ complex, as shown in Figure 1.

Attempts to cause aromatization of compounds **114a-c, 115a-c** and to isolate the corresponding final S_N^H-products failed, probably, because of sterical tensions in these molecule.



(Oz=oxazoline; Tr=triazine)

111 (*S*-Oz)-: a) R^1=Me; b) R^1=*i*-Pr; c) R^1=Ph; 112 (*S*-Oz, *R*p): a) R^1=Me; b) R^1=*i*-Pr; c) R^1=Ph

113: R= a) Ph, b) *p*-MeOPh;

114 (*S*-Oz, *R*p, *S*Tr): a) R^1=Me, R^2=Ph; b) R^1=*i*-Pr, R^2=Ph; c) R^1=Ph, R^2=Ph;

115 (*S*-Oz, *R*p, *S*Tr): a) R^1=Me, R^2=*p*-MeOPh; b) R^1=*i*-Pr, R^2=*p*-MeOPh;

c) R^1=Ph, R^2=*p*-MeOPh

Scheme 36

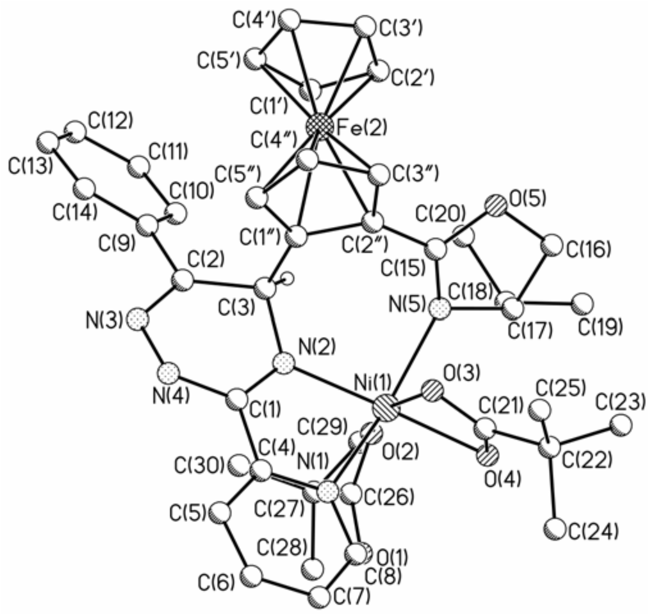
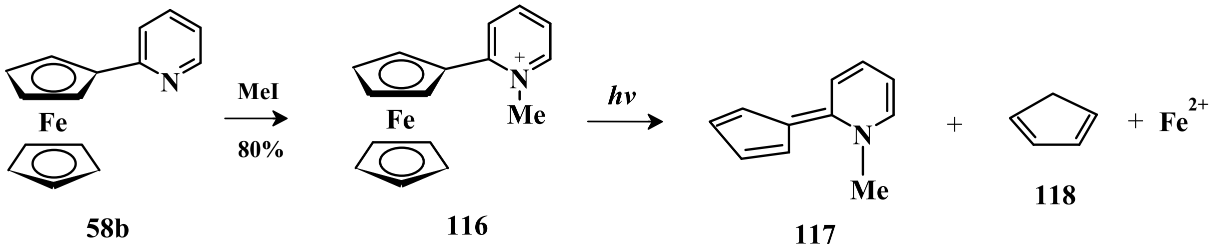


Figure 1. The molecular structure of (*S,S,R*$_p$)-**114b**-NiPiv$_2$ complex

Some properties azinylferrocenes

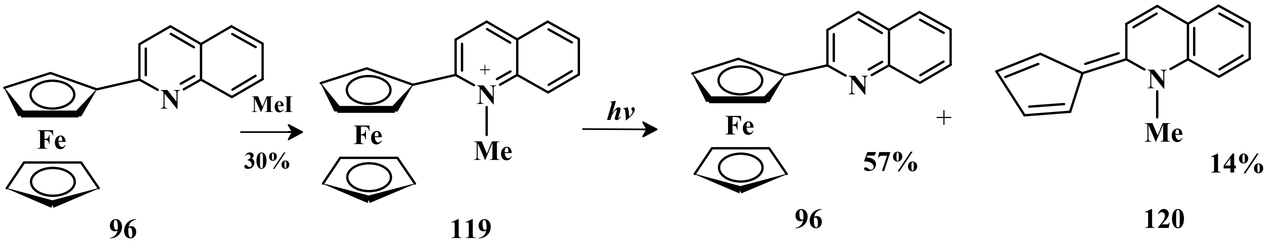
Azinyl subsituted ferrocenes proved to be colored from orange to dark purple, and as a rule, they have a more deep color, than ferrocene. Melting points of monosubstituted ferrocenes are lower than those of 1,1'-disubstituted derivatives. In the ^{1}H NMR spectra of monoazinylferrocenes protons of cylopentadienyl rings resonate at δ=2.9-5.2 ppm and are observed as a combination of singlet from five equivalent protons of the cyclopentadienyl ring which is free of substituents, and two multiplets assigned to the resonance of α– and β-protons in the substituted ring. In case of disubstituted compounds the ferrocene unit is characterized by a couple of multiplets.

It should be noted that up to now reactions of azinylferrocenes are scarcely investigated. Some ferrocenes, especially those bearing a positively charged group attached to the cyclopentadienyl ring, undergo decomposition with a rupture of Fe-C bonds by action of the sun light. In particular, iodide of 1-methyl-2-pyridinium ferrocene (**116**) is destroyed in an alkali solution for one hour, affording *N*-methyl-2-cyclopentadienyliden-1,2-dihydropyridine (**117**) and cyclopentadiene (**Scheme 37**). Also, the photolysis of 2-pyridinylferrocene was found to occur in acid aqueous solutions.[76]



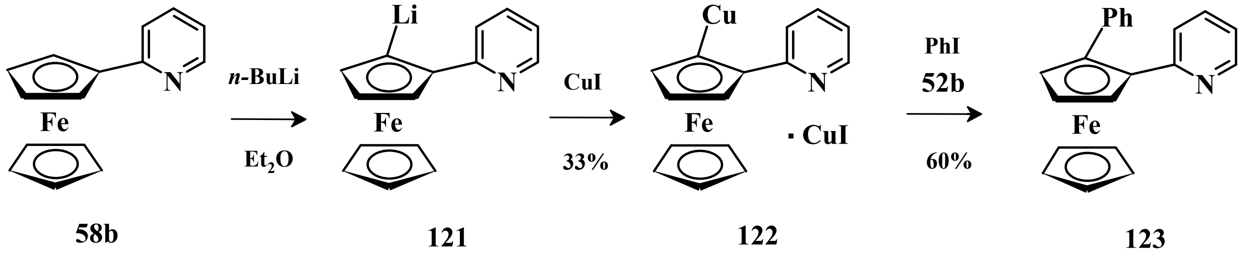
Scheme 37

Iodide 1-methyl-2-ferrocenylquinoliium (**119**) is decomposed under the same conditions into *N*-methyl-2-cyclopentadienyliden-1,2-dihydroquinoline **120** in 15% yield, in addition to the formation of 2-quinolinylferrocene **96,** which is the major product (**Scheme 38**).[77]



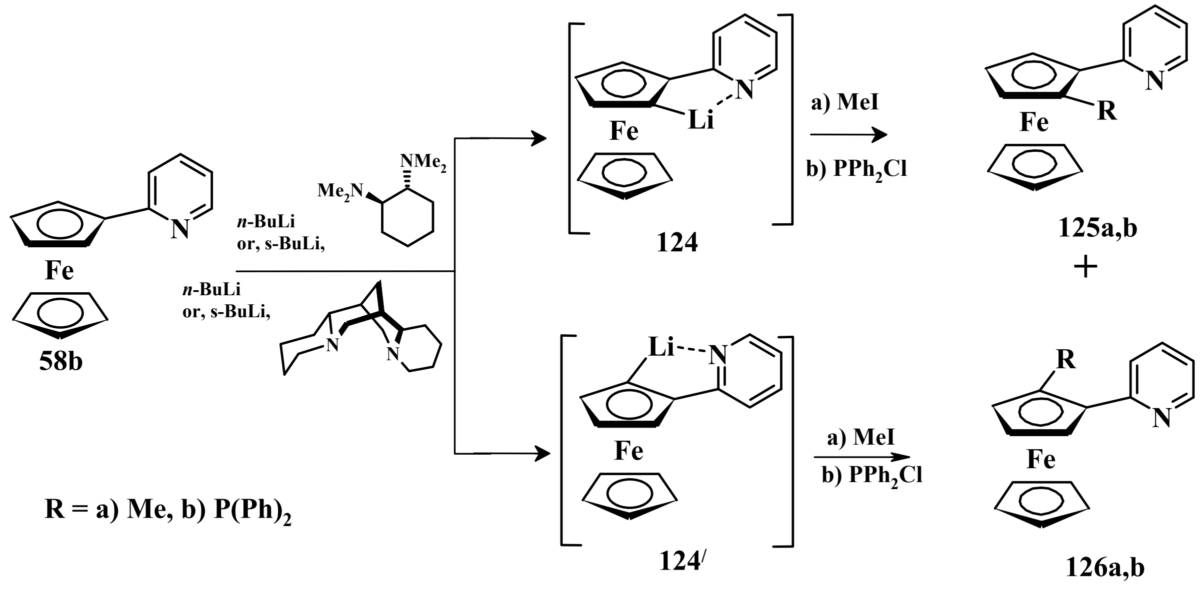
Scheme 38

Pyridylferrocene has been found to undergo metalation with *n*-BuLi in diethyl ether, affording derivative **121**, which on treatment with copper iodide is transformed into rather stable complex **122**. The reaction of **122** with PhI yields 1-pyridyl-2-phenylferrocene (**123**) (**Scheme 39**).[78]



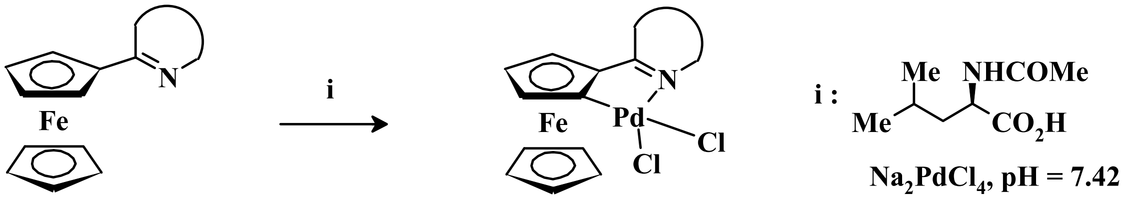
Scheme 39

In order to prepare enantiomerically pure compounds on the basis of azinyl ferrocenes we have tried to use asymmetric syntheses. It is known that the presence of an azinyl unit in the ferrocene structure may play the role of a promoter for regioselective lithiation, affording exclusively the *ortho*-substituted products (CIPE-effect),[79] because of the N-Li bonding in intermediates **124**, **124'** (**Scheme 40**). The formation of complex compounds of *n-*, *s-* or *t*-BuLi with asymmetric reagents is a prerequisite for asymmetric induction and transformation of the starting materials into the planar chiral lithioferrocenes. Indeed, both stereoisomers are formed under the above mentioned conditions with a poor stereoselectivity, which, however, can be improved considerably by using of external asymmetric catalysts, such as (-)-sparteine or *R,R*-diaminocyclohexane, by application of TMEDA for stabilization of lithio derivatives, as well as by a search of appropriate reagents and reaction conditions. Compounds **125**, **126** were obtained with enantioselectivity 20%.[75] Enantiomeres **125b**, **126b** were purified by using preparative HPLC column with chiral sorbent "Chiralcel" OD-H.



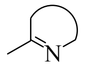
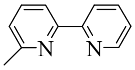
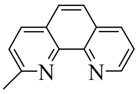
Scheme 40

Cyclopalladation of azinyl ferrocenes have been carried out, but the corresponding final products **127a**,**b** were obtained in racemic forms.[67,80]A possibility to obtain planar chiral cyclopalladated hetarylferrocenes by using *N*-acetyl-D-leucine salt as an external asymmetric catalyst has been demonstrated.[81,82] Optical purity and absolute configuration of the prepared compounds were determined by chiroptic methods and X-ray analysis, respectively (**Scheme 41**). In the present case, ferrocene acts as a five-electron-donor system. Optical purity and absolute configuration of prepared compounds were determined by chiroptic investigations and X-ray crystallography respectively. A high stability of C-Pd bonds in the obtained derivatives should be noted.



20, 103a

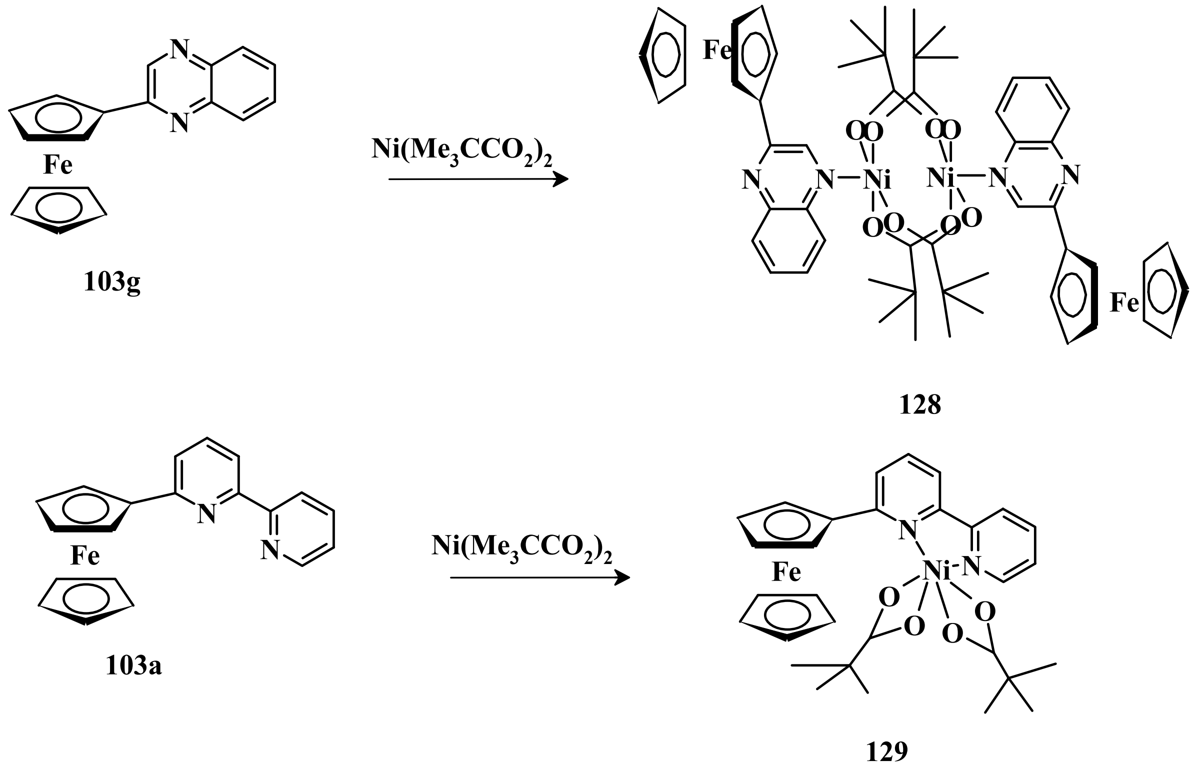
127a,b

Compound		Yield, %
127a		96
127b		95

Scheme 41

Role of metal complexes of ferocenes in development of supramolecular chemistry have became more evident last few years. Nowdays major goals are a design, assembly and evaluation of new materials to be exploited as push-pull systems, molecular switches, logic gates, and systems based on intramolecular charge transfer. In this context, the choice of suitable bridging ligands in the communication among metal centers is of prime importance.

Heterocyclic derivatives of ferrocene demonstrate a high ability to bind metal ions in different modes, including monodentate, bidentate and polydentate chelating, or bi- or polynuclear (**Figure 2**) bridging, thus promoting utilization of these ligands to build various metal supramolecular architectures (**Figure 3**). For design of such complexes a wide range of metal salts have been utilized in appropriate stoichiometry ratio. Interaction of quinoxalinyl ferrocene or bipyridyl ferrocene (**Scheme 42**) with Ni(Piv)$_2$ provides an access to corresponding complexes of hetaryl substituted ferrocenes.[75]



Scheme 42

Magnetic and redox properties, as well as physiological activity of organometal complexes Pt(II), Pd(II), Ir(II), Rh(II), Ni(II), Co(II), Ru(II) have been studied extensively. Complexes of planar chiral ferrocenes are widely used as catalysts in asymmetric syntheses.[3,4]

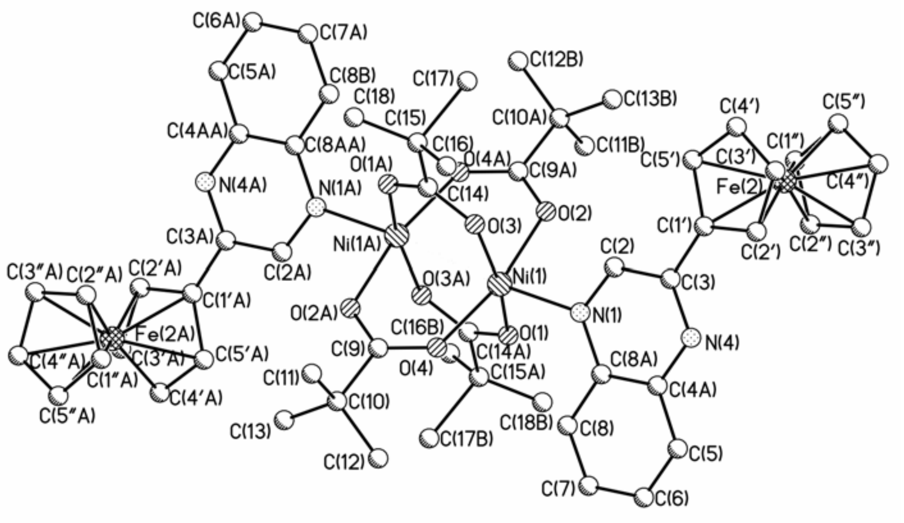


Figure 2. The molecular structure of compound (**128**)

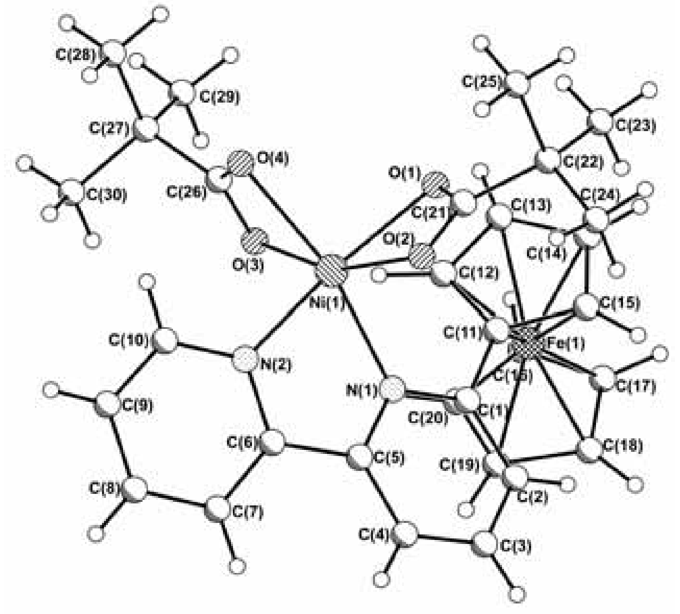


Figure 3. The molecular structure of compound (**129**)

In conclusion, in this article we have tried to focus on azinylferrocene-based ligands, which are of great importance for many branches of chemistry, and have already found many technical applications due to a unique set of magnetic, catalytic, and redox properties, as well as because of their physiological activity. A growing interest in this class of compounds observed during the last decade shows that the problems considered in this review article are both actual and challenging for organic chemists, dealing with a search and development of new methods for the synthesis of azinylferrocenes.

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