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Metal-Catalyzed Cross-Coupling Reactions for Ferrocene Functionalization: Recent Applications in Synthesis, Material Science and Asymmetric Catalysis

V. Mamane*

Laboratoire SRSMC, Equipe Synthèse Organométallique et Réactivité, UMR CNRS-UHP 7565, Faculté des Sciences et Techniques, Nancy-Université, BP 239, 54506 Vandoeuvre-Lès-Nancy, France

Abstract: Recent examples on the functionalization of the ferrocene core by means of cross-coupling reactions are reported in this review. Several methods are discussed including Negishi, Suzuki and Stille couplings for ferrocene-aryl bond formation and Sonogashira reaction for ferrocene-alkyne coupling. The properties in material science and asymmetric catalysis of the prepared ferrocenyl compounds are briefly discussed.

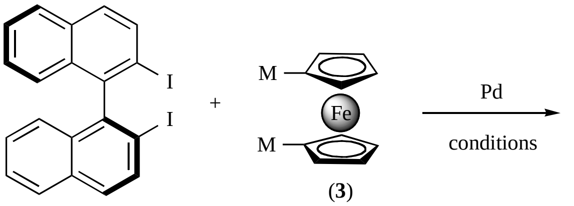
Keywords: Cross-coupling, palladium, ferrocene, material chemistry, asymmetric catalysis.

1. INTRODUCTION

Due to its interesting inherent electrochemical properties and to its planar chirality, 1,2 or 1,3-disubstituted ferrocene has found a wide application in material science [1] and in homogeneous (asymmetric) catalysis [2]. Therefore, several methods to introduce substituents on the cyclopentadienyl (Cp) rings of ferrocene, have been developed. Among these methods, metal-catalyzed cross-coupling reactions [3] have become a powerful tool to achieve highly efficient and selective transformations on one or both Cp rings. This review will focus on recent examples employing cross-coupling reactions to create C-C and C-Heteroatom bonds directly on the ferrocene core.

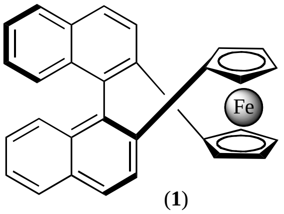
2. FERROCENE-ARYLE BOND FORMATION

A recent study on the synthesis of nonracemic C_2-symmetric 1,1'-binapht-2,2'-yl bridged ferrocene (**1**) was reported by Kasak and colleagues [4]. For this purpose, they used several palladium-catalyzed reactions to couple enantiopure 2,2'-diiodo-1,1'-binaphtyl (**2**) with 1,1'-dimetalloferrocenes (**3**), including the Negishi [5], Suzuki [6] and Stille [7] cross-couplings. The Negishi protocol gave the desired product with the highest yield and with stereoconservation, whereas Suzuki and Stille reactions led to complete racemization of binaphthyl moiety (Fig. (**1**)).



(**2**) 95% ee

(**3**)



(**1**)

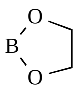
M	yield (%)	ee (%)
ZnCl	35	95
	12	0
$SnMe_3$	11	0

Fig. (1).

These results explain the fact that the Negishi cross-coupling reaction has found numerous applications. However, during the last decade, the Suzuki coupling has gained in interest due to the facile access to the boronic species. The use of the Stille coupling is still limited, particularly due to its strong sensitivity to steric hindrance.

2.1. Negishi Coupling

The ferrocenylzinc intermediate necessary for the cross-coupling is generated by transmetallation of the lithio derivative, which can be obtained by direct lithiation of ferrocene [8], by directed orthometallation (DoM) [9] or by halogen-lithium exchange [10]. In early studies, $PdCl_2$(dppf) (dppf = diphenylphosphinoferrocene) was described as the best catalyst to perform the Negishi coupling but it has been shown later that $Pd(PPh_3)_4$ and more interestingly $PdCl_2(PPh_3)_2$ were good catalysts for this reaction. The first example was reported in 1985 by Rosenblum's group for the synthesis of cofacial ferrocenes [11]. Among several mono-metallated ferrocenes tested in the cross-coupling with 1,8-diiodonaphtalene (**4**), the ferrocenylzinc intermediate led to the best results with formation of the bis-coupled product (**5**) in good yield in presence of $PdCl_2$(dppf) as the catalyst. If one of the two ferrocenes is replaced by a Cp group such as in (**6**), face-to-face metallocene triads (**7**) [12] and polar cofacially fixed sandwich complexes (**8**) for Second Harmonic Generation (SHG) [13] could be prepared. While a "through space" interaction exists no SHG intensity could be observed (Fig. (**2**)).

Interferrocenic communication in molecules having two or more redox centers is fundamentally interesting for the study of multi-electron transfer processes via mixed valence state derived from these multi-metallic systems [14]. In this field, the Negishi cross-coupling has been widely used to install two or several ferrocene moities around different scaffolds. Two ferrocene fragments could be introduced by Ogawa and colleagues on thianthrene, leading to a new type of multi-steps reversible redox organic-organometallic hybrid molecule (**9**) [15]. Vollhardt's group has succeeded in the introduction of five ferrocene units around the Cp ring in $[(C_5H_4)Mn(CO)_3]$ to give (**10**) [16] and six ferrocene units around a benzene ring to furnish (**11**), albeit in poor yield [17]. These new multinuclear ferrocenic compounds are of potential interest since their architecture apparently allows for considerable electronic interaction (Fig (**3**)).

Another family of highly symmetric hexaferrocenyl complexes (**12**) was previously described by Mamane and colleagues [18, 19]. These compounds having six chiral ferrocene units around a hexaarylbenzene core were prepared by a [2+2+2] cyclotrimerization reaction of the corresponding alkyne monomer (**13**), itself obtained by a double Negishi coupling of chiral ferrocenylzinc (**14**) intermediate with bis-(*p*-bromophenyl)acetylene (**15**). Intermediate (**14**) was used by the same group for the design of new C_3 symmetric chiral architectures (**16**) bearing organometallic donor-acceptor fragments [20]. These octupoles possessing good SHG properties showed a significant electronic interaction between the three 1-D arms through the benzene ring (Fig. (**4**)).

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*Address correspondence to this author at the Laboratoire SRSMC, Equipe Synthèse Organométallique et Réactivité, UMR CNRS-UHP 7565, Faculté des Sciences et Techniques, Nancy-Université, BP 239, 54506 Vandoeuvre-Lès-Nancy, France; E-mail: victor.mamane@sor.uhp-nancy.fr

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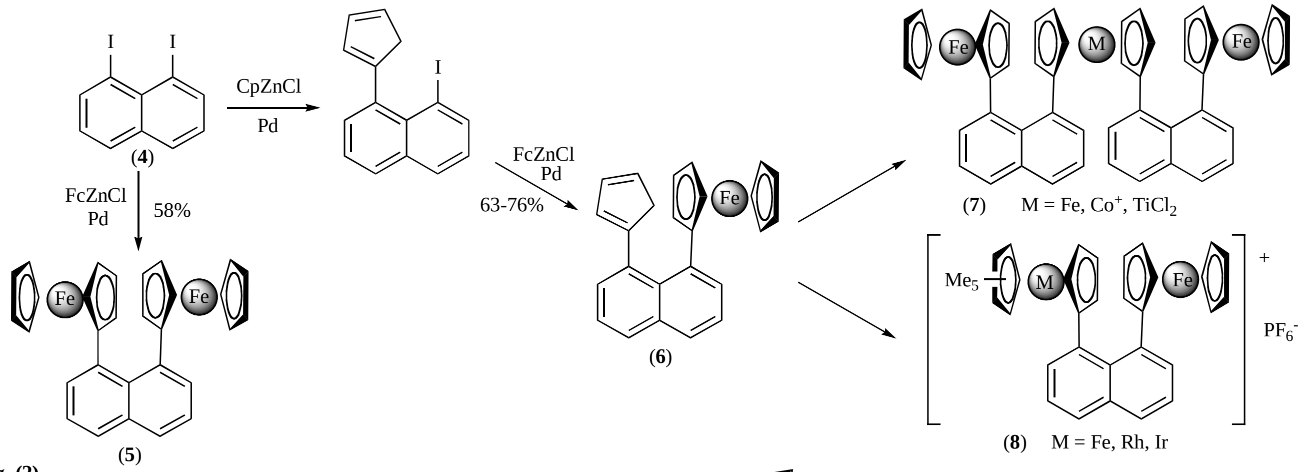


Fig. (2).

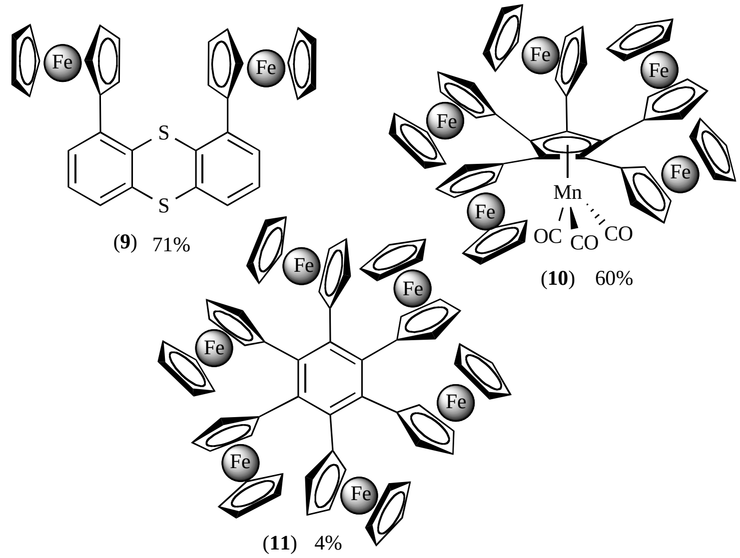


Fig. (3).

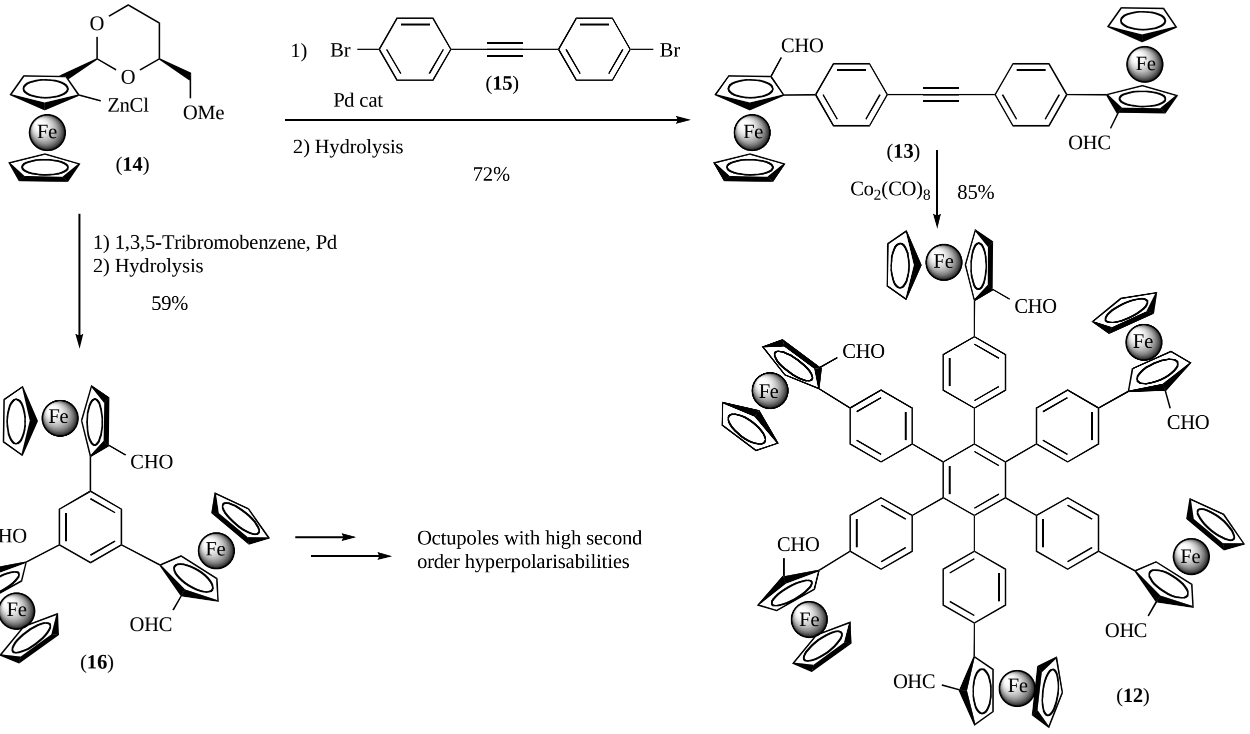


Fig. (4).

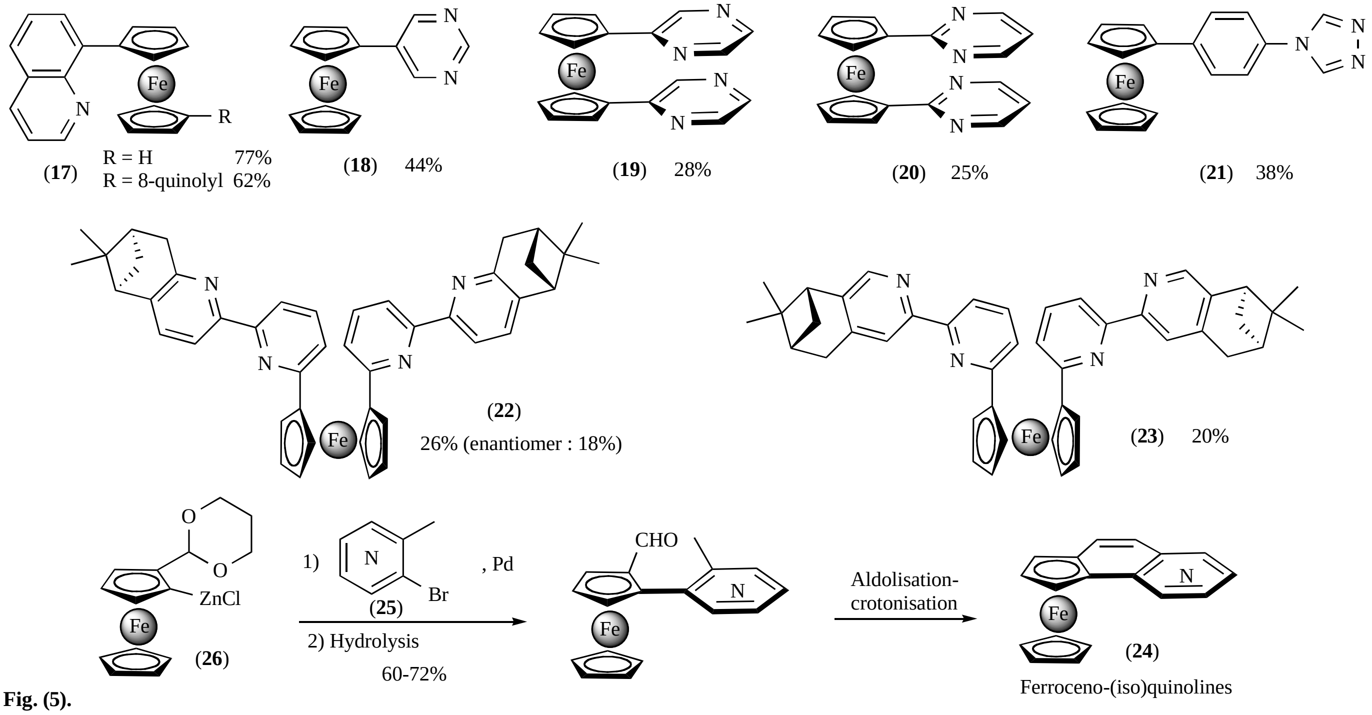


Fig. (5).

Several nitrogen-containing heterocycles has been used as the coupling partner of ferrocene in the Negishi cross-coupling reaction. Enders and colleagues described the reaction of the quinolyl group at the 8-position with ferrocene [21]. The coupling could be realized in good yields once or twice for furnishing compound (**17**) which showed interesting coordination behavior. In the same field, Mochida's group designed several ferrocene-containing ligands (**18**)-(**21**) by coupling pyrazines, pyrimidines and phenylazoles with the ferrocenylzinc complex under palladium catalysis [22, 23, 24]. Chiral ligands (**22**) and (**23**) with ferrocene bridging units for chiral induction in self-assembled helicates were described by Quinodoz and colleagues [25]. During their study, they compared the Suzuki and the Negishi reactions for performing the bis-coupling of 1,1'-dimetalloferrocene (**3**) with chiral bipiridines. The Negishi cross-coupling gave the best results although the yields were moderate in all cases. In their synthesis of new chiral ferroceno-(iso)quinolines (**24**) as potential molecules in asymmetric catalysis and material chemistry, Mamane and Fort used different picolines (**25**) in the coupling reaction with racemic (**26**) or enantiopure ferrocenylacetal (**14**) in good yields [26] (Fig. (**5**)).

Ferrocene-based phosphine ligands are widely used in asymmetric catalysis, and during the last decade cross-coupling reactions allowed the synthesis of new families of arylphosphinoferrocenes. The Negishi coupling was then used with success by several groups in

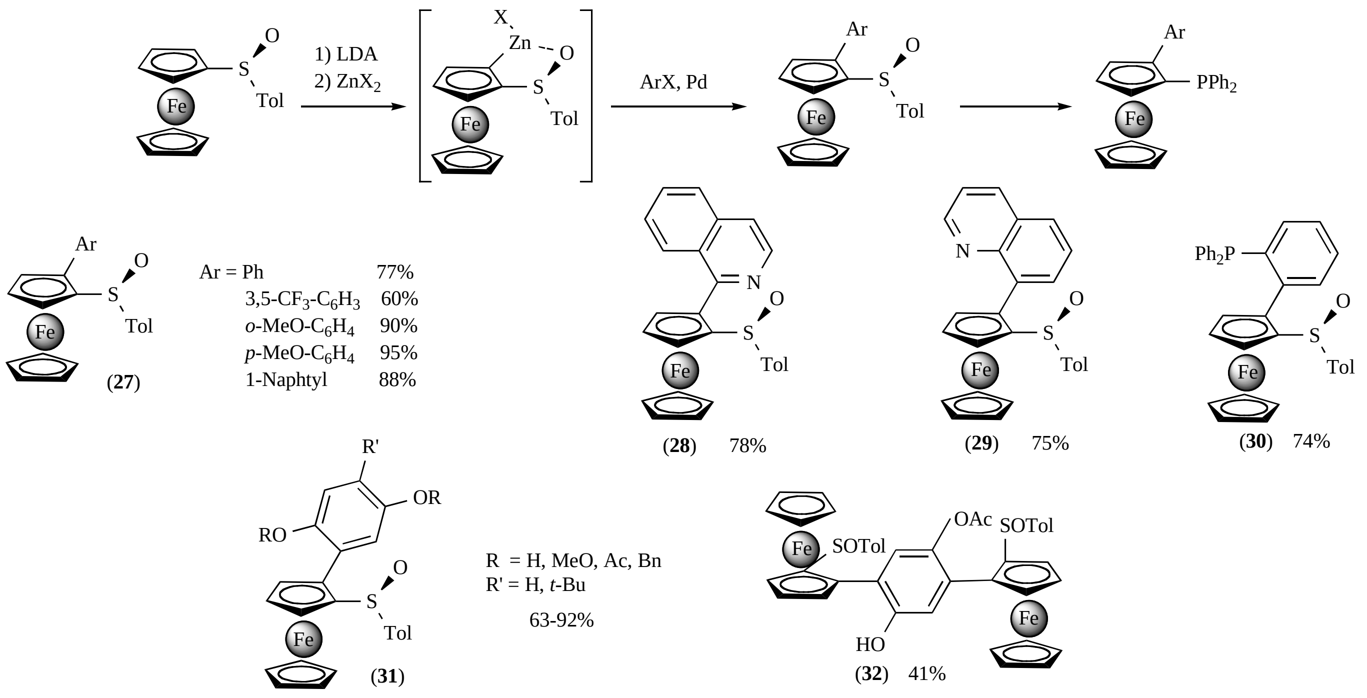
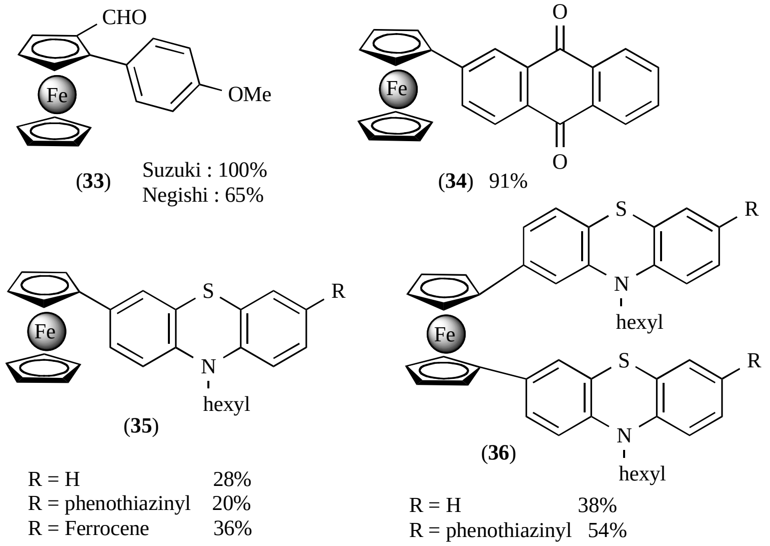


Fig. (6).



(**33**) Suzuki : 100%
Negishi : 65%

(**34**) 91%

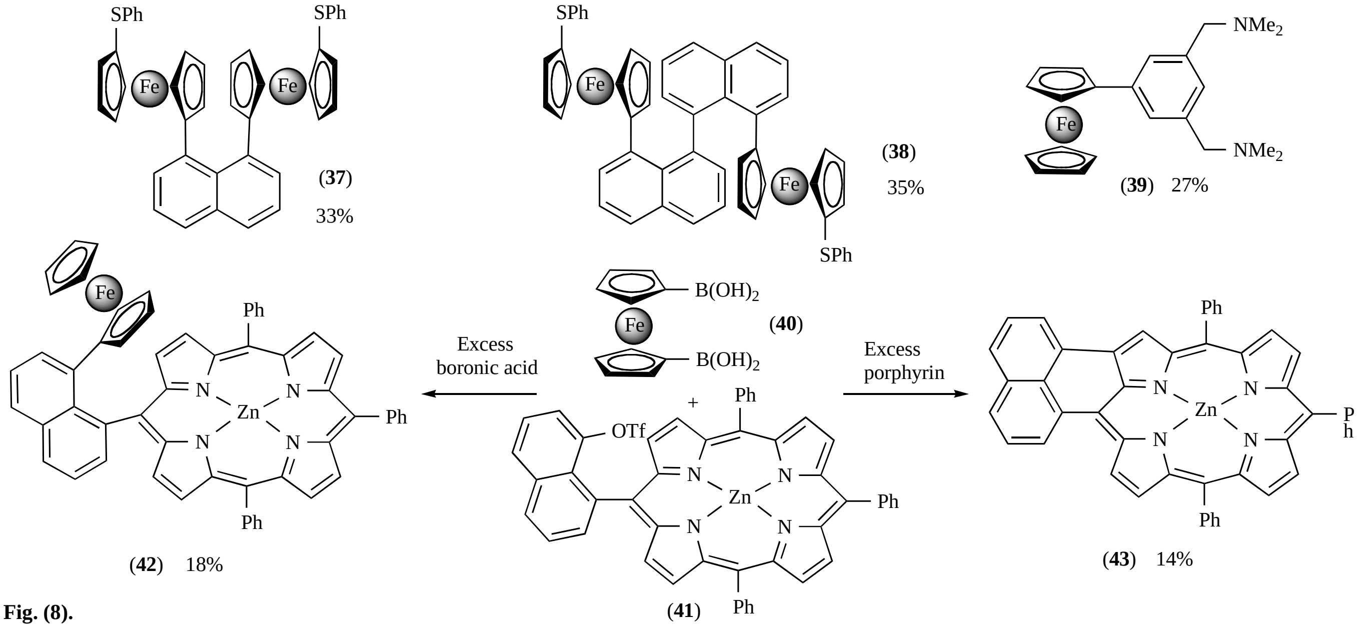
(**35**)

R = H 28%
R = phenothiazinyl 20%
R = Ferrocene 36%

(**36**)

R = H 38%
R = phenothiazinyl 54%

Fig. (7).



(**37**) 33%

(**38**) 35%

(**39**) 27%

(**40**)

(**41**)

(**42**) 18%

(**43**) 14%

Fig. (8).

order to introduce an aryle group in α-position of a chiral sulfoxide which served as a directing group and could be easily transformed to a diphenylphosphine group. Pedersen and Johannsen described the synthesis of compounds (**27**), leading after transformation to monophosphine ligands which showed high catalytic activities in hydrosilylation of styrene [27]. Starting from derivatives (**28**)-(**30**), Knochel's group reported the use of diphosphines and aminophosphines in palladium-catalyzed allylic alkylation and amination [28, 29]. The sulfoxide group can be maintained in the molecule as described by Bäckvall's group in the synthesis of a new class of chiral ferrocene-based quinone ligands (**31**) and (**32**). Most of the ligands decomposed during the deprotection of the OR groups except for one (R' = R = H in (**31**)) and a poor enantioselectivity was obtained when used in the asymmetric diacetoxylation of cyclohexadiene [30] (Fig. (**6**)).

2.2. Suzuki Coupling

The Pd-catalyzed cross-coupling reaction between halobenzenes and ferrocene-1,1'-diboronic acid was reported for the first time by Knapp and Rahahn [31]. 1,1'-Diphenyl- and 1,1'-bis(halophenyl)-substituted ferrocenes bearing fluoro, chloro and bromo substituents were obtained in good yields. In 1999, Imrie and colleagues reported a systematic study on the use of Suzuki reaction for the synthesis of monoarylferrocenes from haloferrocenes and arylboronic acids [32]. They found that the use of strong bases such as barium hydroxide or potassium carbonate in the presence of Pd(OAc)$_2$ as a catalyst was necessary to achieve good conversions. These conditions were later utilized by different groups for the synthesis of ferrocene-containing molecules of potential interest in material chemistry. Mamane and Riant obtained an excellent yield of aldehyde (**33**) in the coupling of a chiral iodoferrocene compound with *p*-methoxyphenylboronic acid showing that this method is a good alternative to the Negishi coupling [33]. Butler and colleagues generated ferrocenylanthraquinone compound (**34**) in good yield by changing the catalyst to Pd(PPh$_3$)$_4$ [34]. Recently, Sailer and colleagues described several ferrocene-phenothiazine systems (**35**) and (**36**) with interesting electronic properties [35] (Fig. (**7**)).

Other methods involving ferroceneboronic acids have been used to perform the Suzuki reaction. Hua and colleagues described the coupling between 2,4,6-tris(1'-phenylthio-1-ferrocenyl)boroxin and 1,8-diio-donaphtalene to give (**37**) or 1,8-diidobinaphtyl to yield (**38**) in presence of Pd(PPh$_3$)$_4$/NaOH system in moderate yields [36]. With

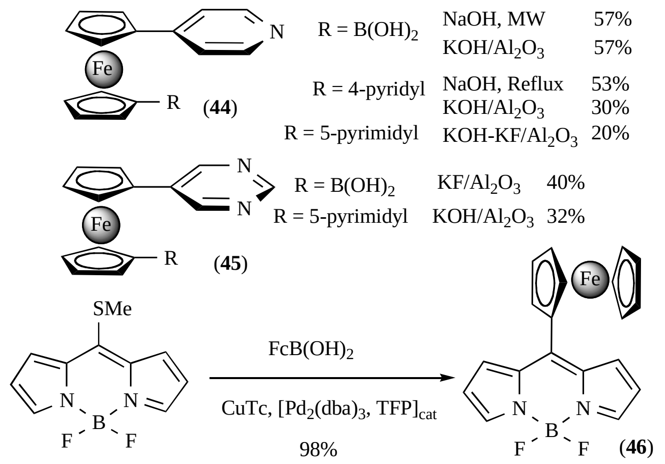


Fig. (9).

$PdCl_2$(dppf)/NaOH system, Köcher and colleagues obtained a low yield of (**39**) by coupling 3,5-(dimethylamino)methyl iodobenzene with ferrocene. Compound (**39**) was then used for NCN pincer complexes synthesis [37]. $Ba(OH)_2$ was used as the base by Cammidge and colleagues for the synthesis of face-to-face porphyrin-ferrocene systems [38]. It has been shown that changing the ratio between 1,1'-ferrocene diboronic acid (**40**) and porphyrin (**41**) modified the reaction pathway. While excess boronic acid delivered the ferrocene-porphyrin dyad (**42**) with loss of one boronic acid group, excess porphyrin yielded an unexpected product (**43**) resulting from the intramolecular cyclization with no incorporation of ferrocene (Fig. (**8**)).

The Suzuki reaction has been applied to the coupling of several heterocycles with ferrocene mono- or di-boronic acid. During its work on molecular crystal engineering involving organometallics building blocks, Braga's group described the synthesis of pyridine and pyrimidine ferrocenyl derivatives (**44**) and (**45**). Methods such as microwaves [39] or KF/alumina [40] in the presence of $PdCl_2$(dppf) as the catalyst were used for the selective preparation of mono-, homo-bis and hetero-bis-functionalized ferrocene starting from 1,1'-ferrocene diboronic acid (**40**). A very efficient method for Bodipy functionalization involving a thiomethyl group in the cross-coupling with boronic acids was reported recently by Pena-Cabrera and colleagues [41]. Bodipy (**46**) incorporating ferrocene in 8-position could be prepared by this method with an excellent yield (Fig. (**9**)).

A number of chiral ferrocenyl ligands having an aryle group directly attached to one or both Cp rings were developed during the last years. Laufer and colleagues described the synthesis and application in asymmetric diethylzinc addition to benzaldehyde of a C_2-symmetric planar chiral ferrocene diamide (**47**) [42]. Although the yield of the coupling was low, the ligand was obtained with unchanged ee (enantiomeric excess) comparing to the starting material. A similar ligand was prepared in a better yield by the Stille coupling but the ee was not determined. Johannsen's group improved its own synthesis of aryl-ferrocenyl phosphines by using the Suzuki coupling instead of the Negishi protocol [43]. The new conditions using a chiral ferrocene boronic acid allowed the formation of compounds (**48**) containing free amino and hydroxyl groups. Anderson and colleagues reported the preparation and evaluation of ferrocenyloxazoline palladacycle catalysts derived from ligands (**49**) in catalytic asymmetric synthesis of chiral allylic amines [44]. A new class of ferrocenylphosphines (**50**) was prepared by Stead and Xiao starting from ferrocene diboronic acid (**40**) and bromoarenes bearing a diphenylphosphine oxide group [45]. A subsequent reduction in presence of $HSiCl_3$ yielded the free phosphines. A series of precursor phosphine ligands (**51**) containing aryl groups was recently obtained in high yields by Wang and colleagues [46]. After transformation to 1,2,3-trisubstitued ferrocenyl diphos-phines (**52**) containing a phenyl or a xylyl group, these ligands were compared to other known phosphines in asymmetric hydrogenations (Fig. (**10**)).

2.3. Stille Coupling

Ma's groups reported the synthesis of a variety of heteroaryl ferrocenes by using the Stille cross-coupling. In presence of $PdCl_2(PPh_3)_2$ as the catalyst, tributylstannylferrocene and electron-poor heteroaryls gave the desired coupling products (**53**)-(**58**) with good yields. Less electron-poor substrates required the use of $Pd(PPh_3)_4$/CuO system to achieve good conversions [47]. With 1,1'-bis (tributylstannyl)ferrocene (**59**), only electron-poor heterocycles were described to perform efficient stepwise coupling to give (**60**) and (**61**) respectively [48]. The intermediary 1-tributylstannyl, 1'-heteroaryl ferrocenes (**60**) were also homocoupled in presence of copper to yield bis(heterocyclyl)biferrocene compounds (**62**) [49] (Fig. (**11**)).

In order to perform the cross-coupling between electron-rich and sterically demanding partners, methods involving ligands such as $AsPh_3$ or P*t*-Bu_3 were recently described. Song and colleagues used $AsPh_3$ as ligand for palladium to prepare pyrimidine nucleosides (**63**) incorporating a ferrocene moiety as a redox probe to study the electron transfer in DNA [50]. The same catalyst system was recently

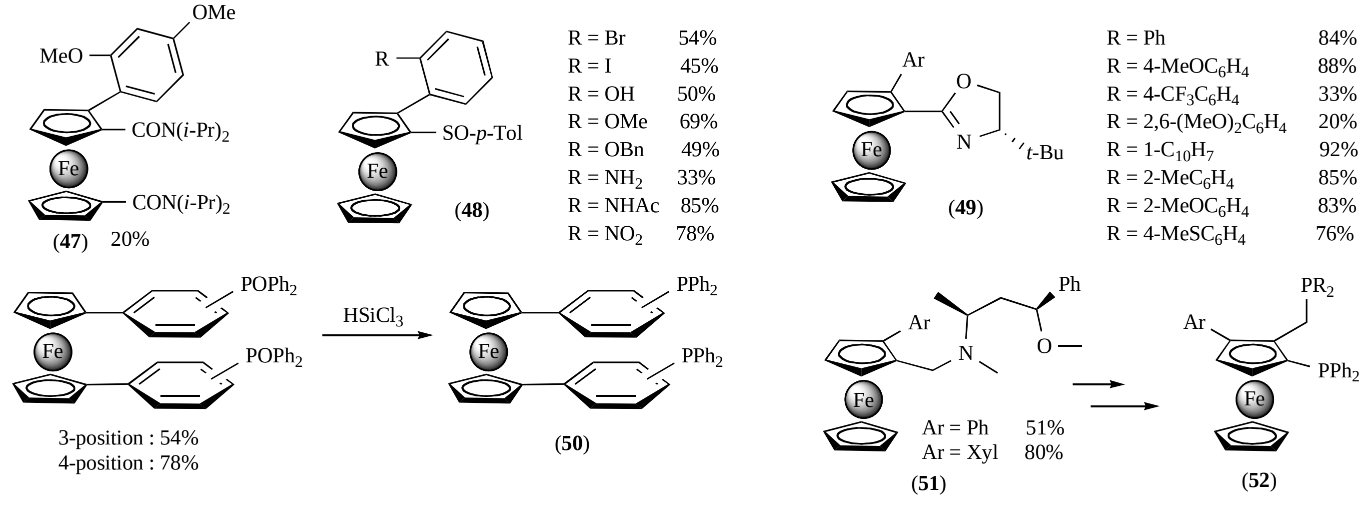


Fig. (10).

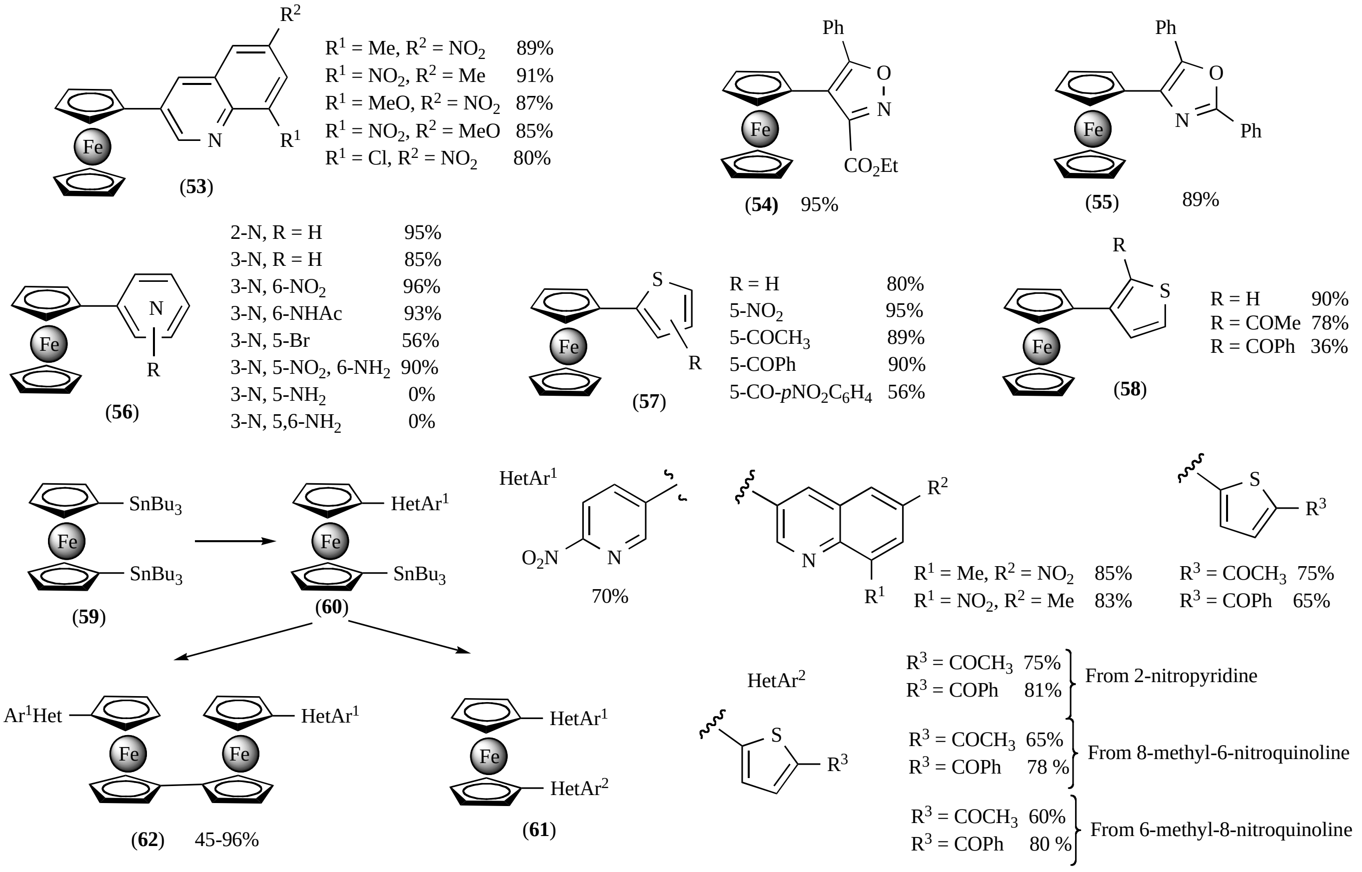


Fig. (11).

used by Weber and colleagues for the synthesis of 1,2-disubstituted planar-chiral ferrocene ligands (**64**) [51]. The P*t*-Bu$_3$ ligand was shown to allow an efficient cross-coupling reaction between tributylstannylferrocene and a bromopyridine containing the 2,5-dimethyl pyrollidine group to furnish (**65**) [52] (Fig. (**12**)).

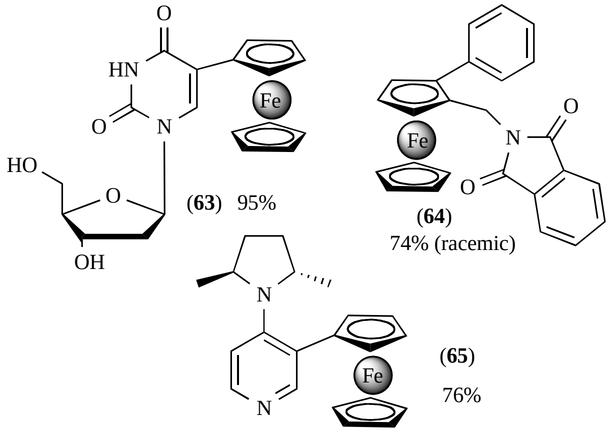


Fig. (12).

2.4. Miscellaneous

Ferrocenyl pyridines (**66**) were prepared in good yields by using the nickel-catalyzed Kumada coupling between ferrocenyl Grignard intermediates and 4-bromopyridine [53]. The mono-coupling of 1,1'-dibromoferrocene was not selective and furnished the desired compound in a poor yield. Bis(ferrocenyl)mercury reagents were coupled with aryl iodides in presence of a palladium catalyst to give a variety of ferrocenyl aryl products (**67**)-(**69**) in good yields [54]. A nickel-assisted intramolecular coupling was used to perform the synthesis of new chiral aryl-ferrocenyl ligands (**70**) [55]. A cobalt-catalyzed cross-coupling reaction involving a ferrocenyl cuprate formed in situ was recently described to give (**71**) [56] (Fig. (**13**)).

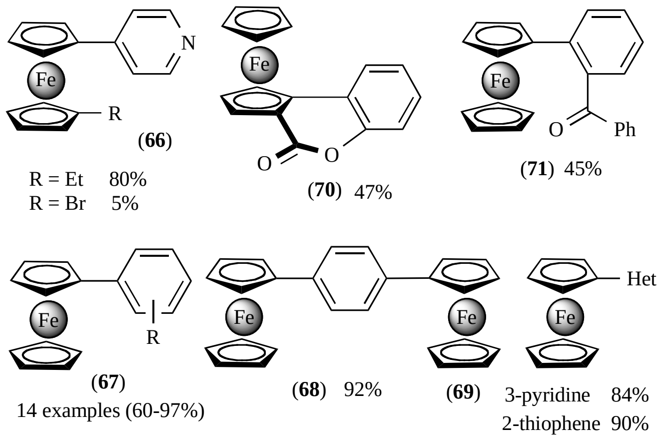


Fig. (13).

3. OTHER FERROCENE-CARBON BOND FORMATION

3.1. Ferrocene-Alkyne Bond: the Sonogashira Reaction

The triple bond spacer is widely used in ferrocene-based materials because it allows a good electronic communication between the ferrocene unit and other electro-active groups. In this regard, the Sonogashira reaction is the method of choice to couple alkynes and iodoferrocenes [57].

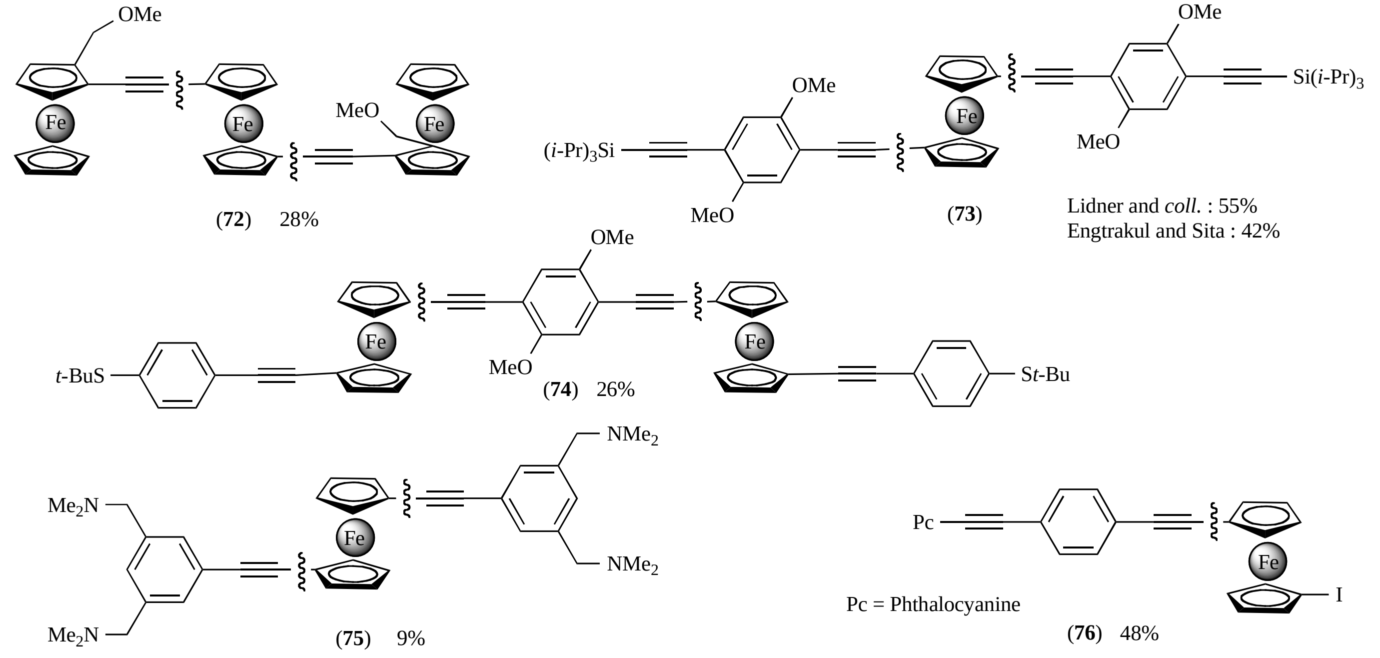


Fig. (14).

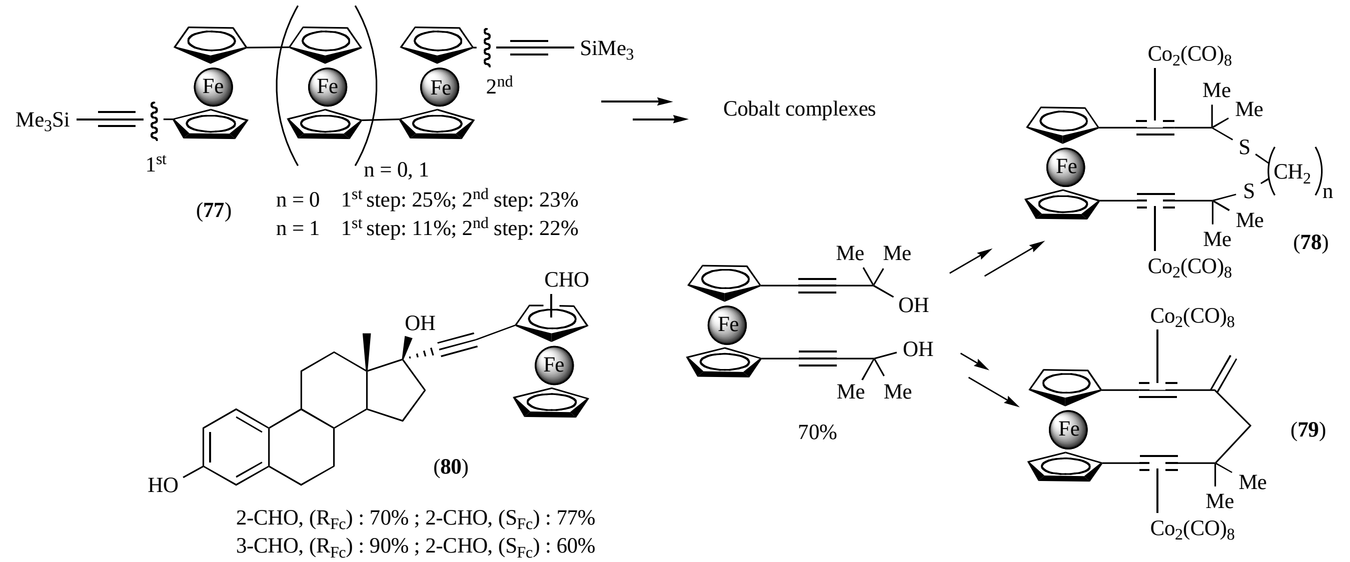


Fig. (15).

Plenio and colleagues described the synthesis of several optically and redox-active ferroceneacetylene polymers and oligomers such as derivative (**72**) [58]. While the reaction is high yielding with 1-iodo, 2-substituted ferrocene derivatives, the yield dropped when using 1,1'-dioodoferrocene. The main reason could be the steric hindrance generated after the first coupling. Lindner and colleagues [59], and recently Engtrakul and Sita [60] noted that the solubility of the resulting compounds was of major importance for the bis-coupling success. The presence of methoxy and tri-isopropylsilyl groups in the alkyne moiety allowed the formation of π-extended molecules (**73**) in good yields. Moderate yields were reported by Ma and colleagues by using *tert*-butylsulfanyl groups in the substrates for the synthesis of (**74**), a precursor for symmetrical molecular wires [61]. A low yield of bis-product (**75**) was obtained by Köcher and colleagues during the preparation of 4-ferrocenyl-NCN pincer complexes [62], whereas no expected product was isolated by Gonzalez-Cabello and colleagues [63]. In this last case the obtained mono-coupling product (**76**) was reused in a second Sonogashira reaction but again the bis-phthalocyanine ferrocene derivative was not formed (Fig. (**14**)).

The alkyne functionality was used respectively by Robinson's and Woods' groups as a ligand for cobalt complexes. In the first case, it was shown that polyferrocenes in (**77**) can serve as a communicator linkage between $Co_2(CO)_4$dppm units [64]. In the second application, new ferrocenophane derivatives (**78**) and (**79**) bearing two $Co_2(CO)_8$(alkyne) complexes were isolated and studied by electrochemistry [65]. Jaouen's group showed that the alkyne group can serve as a linker between chiral ferrocene and oestradiol through the synthesis of (**80**) [66] and that the estrogen receptor was capable to recognize preferentially one diastereoisomer [67]. During this work, the authors noted that the Sonogashira coupling was more efficient with iodoferrocene compounds, whereas the Stille coupling was more

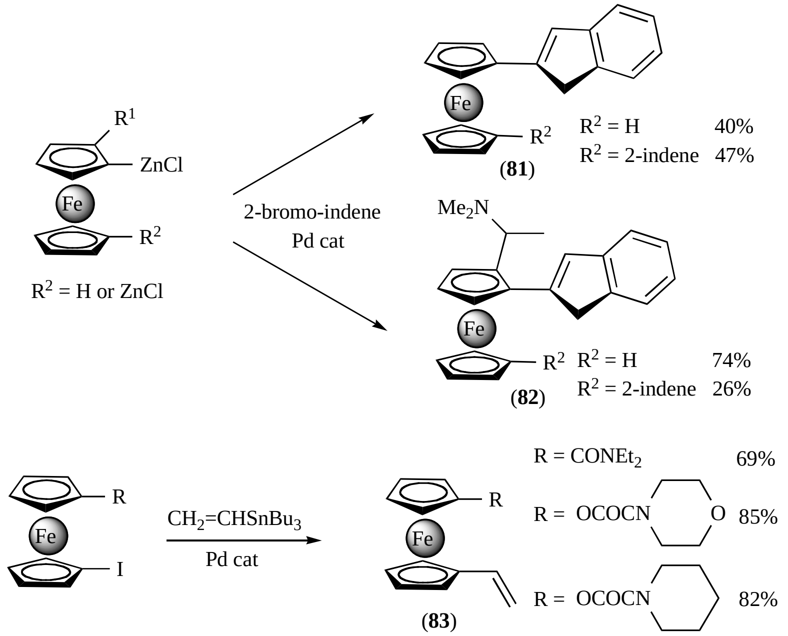
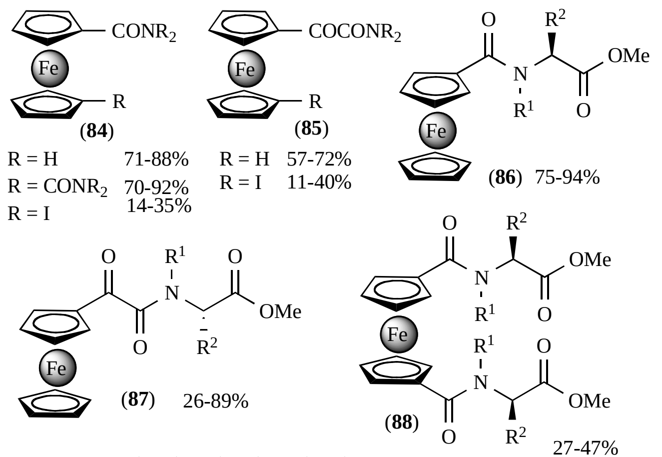


Fig. (16).



R = Et, *n*-Bu, -$(CH_2)_5$-, -$(CH_2)_2$-O-$(CH_2)_2$

Amino acids : Gly-OMe, L-Ala-OMe, L-Phe-OMe, L-Met-OMe, L-Pro-OMe

Fig. (17).

practical for other iodocyclopentadienyl complexes (Mn, Re). The explanation for these interesting observations was reported recently by Amatore and colleagues [68] (Fig. (**15**)).

3.2. Ferrocene-Alkene Bond

Two recent examples described the formation of a ferrocene-alkene bond on the basis of cross-coupling reaction. A Negishi coupling was used by Anderson and *colleagues* to introduce one or two indenyl ligands on the ferrocene to give (**81**) and (**82**) [69]. 1-Substituted, 1'-vinylferrocenes (**83**) were prepared in good yields by Szarka and colleagues by a Stille coupling in presence of vinyltributyltin [70] (Fig. (**16**)).

3.3. Ferrocene-CO Bond: Aminocarbonylation

The aminocarbonylation reaction of iodoferrocene compounds catalyzed by palladium was intensively used by Skoda-Földes' group for the synthesis of amides (**84**) and α-ketoamides (**85**) [70-72]. The reaction was described to proceed with both 1-iodoferrocene and 1,1'-diiodoferrocene with moderate to good yields. A nice entry to ferrocenyl amino acid derivatives (**86**)-(**88**) was also described by using protected amino-acids as the amine partners in the reaction [73, 74] (Fig. (**17**)).

4. FERROCENE-HETEROATOM BOND FORMATION

Only a few examples described the direct formation of a ferrocene-heteroatom bond. Copper in catalytic or stoechiometric amounts is generally preferred to effect these transformations. For the

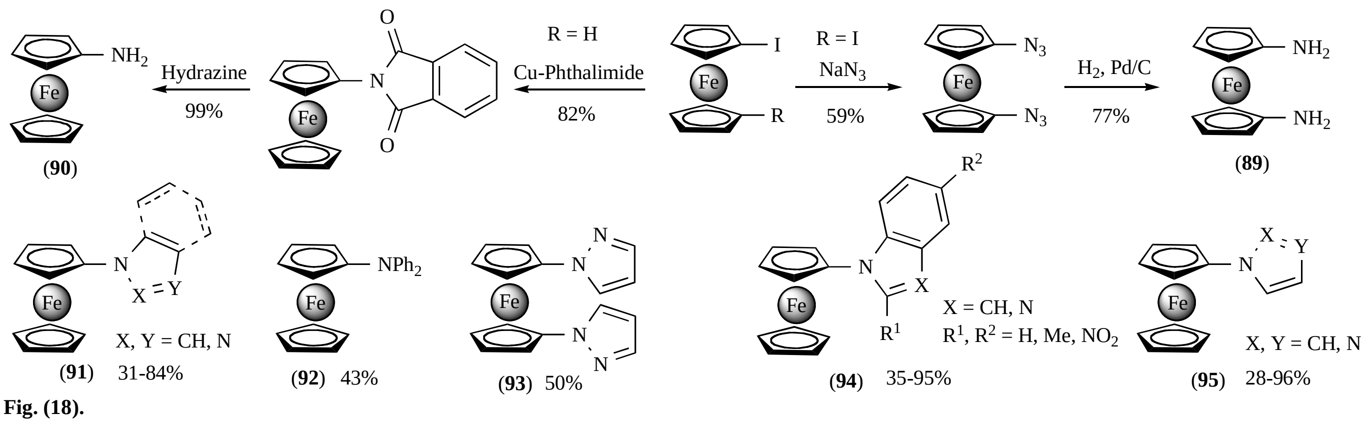
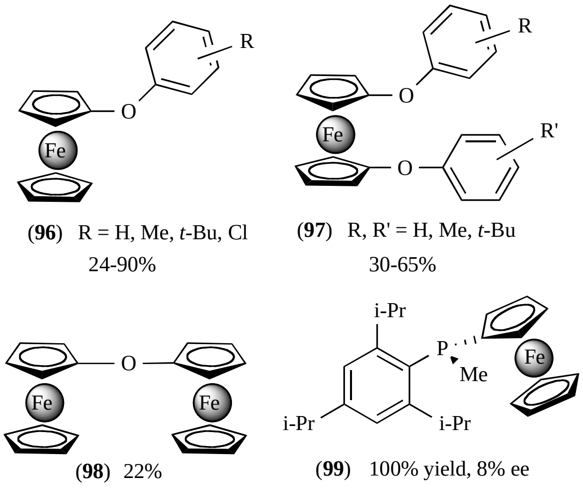


Fig. (18).

preparation of 1,1'-diaminoferrocene (**89**) and 1-aminoferrocene (**90**), improved procedures were reported. Shafir and colleagues described the synthesis of (**89**) in two steps from the readily available 1,1'-dibromoferrocene [75]. Heinze and Schlenker obtained (**90**) in good yield and purity by reacting iodoferrocene with a pre-formed Cu-phtalimide complex following by deprotection [76]. Recently, Bolm's group described the direct synthesis of N-substituted ferrocenes (**91**)-(**93**) using stoechiometric amount of CuI in DMSO [77]. A catalytic protocol for the Ulmann-type coupling was then reported by Nagarkar's group for the efficient preparation of a range of N-substituted ferrocenes (**94**) and (**95**) [78] (Fig. (**18**)).

Plenio's group reported the copper-catalyzed synthesis of ferrocenyl aryl ethers (**96**)-(**98**) from iodo-and bromo-ferrocenes in moderate to good yields [79]. 2,2,6,6-Tetramethylheptane-3,5-dione (TMHD) was found to be an efficient ligand for copper when this reaction was carried out in N-methylpyrrolidinone (NMP) solvent using Cs_2CO_3 or K_3PO_4 bases. During their study on the palladium-catalyzed asymmetric phosphination of iodoarenes, Blank and colleagues reported one example using iodoferrocene [80]. Product (**99**) was obtained in quantitative yield but in low ee (Fig. (**19**)).



(**96**) R = H, Me, *t*-Bu, Cl
24-90%

(**97**) R, R' = H, Me, *t*-Bu
30-65%

(**98**) 22%

(**99**) 100% yield, 8% ee

Fig. (19).

5. CONCLUSION

Metal-catalyzed cross-coupling reactions have allowed the formation of new compounds which are not accessible or obtained with low yields by other methods. These reactions thus widened the utilization of ferrocenyl compounds in material science and asymmetric catalysis. Direct introduction of heteroatoms on the ferrocene core is still limited and one could suppose that new methods involving the formation of ferrocene-heteroatom bonds will appear in the near future.

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REFERENCES

[1] Togni, A.; Hayashi, T. *Ferrocenes*, VCH-Wiley: Weinheim, Germany, **1995**.
[2] Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.*, **2004**, *33*, 313.
[3] De Meijere, A., Diederich, F. *Metal Catalyzed Cross-Coupling Reactions*, VCH-Wiley: Weinheim, Germany, **1998**.
[4] Kasak, P.; Miklas, R.; Putala, M. *J. Organomet. Chem.*, **2001**, *637-639*, 318-326.
[5] *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.; Ed; Wiley-Interscience: New-York, **2002**; vol. *1*, Part III.
[6] Miyaura, N.; Suzuki, A. *Chem. Rev.*, **1995**, *95*, 2457-2483.
[7] Espinet, P.; Echavarren, A. M. *Angew. Chem. Int. Ed.*, **2004**, *43*, 4704-4734.
[8] Guillaneux, D.; Kagan, H. B. *J. Org. Chem.*, **1995**, *60*, 2502-2505.
[9] Ferber, B.; Kagan, H. B. *Adv. Synt. Catal.*, **2007**, *349*, 493-507.
[10] Helberg, F. L.; Rosenberg, H. *Tetrahedron Lett.*, **1969**, *10*, 4011-4012.
[11] Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics*, **1985**, *4*, 539-547.
[12] Hudson, R. D. A.; Foxman, B. M.; Rosenblum, M. *Organometallics*, **2000**, *19*, 469-474.
[13] Malessa, M.; Heck, J.; Kopf, J.; Garcia, M. H. *Eur. J. Inorg. Chem.*, **2006**, 857-867.
[14] Barlow, S.; O'Hare, D. *Chem. Rev.*, **1997**, *97*, 637-669.
[15] Ogawa, S.; Muraoka, H.; Sato, R. *Tetrahedron Lett.*, **2006**, *47*, 2479-2483.
[16] Yu, Y.; Bond, A. D.; Leonard, P. W.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem. Int. Ed.*, **2006**, *45*, 1794-1799.
[17] Yu, Y.; Bond, A. D.; Leonard, P. W.; Lorenz, U. J.; Timofeeva, T. V.; Vollhardt, K. P. C.; Whitener, G. D.; Yakovenko, A. A. *Chem. Commun.*, **2006**, 2572-2574.
[18] Mamane, V.; Gref, A.; Lefloch, F.; Riant, O. *J. Organomet. Chem.*, **2001**, *637-639*, 84-88.
[19] Mamane, V.; Gref, A.; Riant, O. *New J. Chem.*, **2004**, *28*, 585-594.
[20] Mamane, V.; Ledoux-Rak, I.; Deveau, S.; Zyss, J.; Riant, O. *Synthesis*, **2003**, 455-467.
[21] Enders, M.; Kohl, G.; Pritzkow, H. *J. Organomet. Chem.*, **2001**, *622*, 66-73.
[22] Horikoshi, R.; Nambu, C.; Mochida, T. *Inorg. Chem.*, **2003**, *42*, 6868-6875.
[23] Mochida, T.; Okazawa, K.; Horikoshi, R. *Dalton Trans.*, **2006**, 693-704.
[24] Mochida, T.; Shimizu, H.; Suzuki, S.; Akasaka, T. *J. Organomet. Chem.*, **2006**, *691*, 4882-4889.
[25] Quinodoz, B.; Labat, G.; Stoeckli-Evans, H.; von Zelewsky, A. *Inorg. Chem.*, **2004**, *43*, 7994-8004.
[26] Mamane, V.; Fort, Y. *J. Org. Chem.*, **2005**, *70*, 8220-8223.
[27] Pedersen, H. L.; Johannsen, M. *J. Org. Chem.*, **2002**, *67*, 7982-7994.
[28] Lotz, M.; Kramer, G.; Knochel, P. *Chem. Commun.*, **2002**, 2546-2547.
[29] Kloetzing, R. J.; Knochel, P. *Tetrahedron Asymmetry*, **2006**, *17*, 116-123.
[30] Cotton, H. K.; Huerta, F. F.; Bäckvall, J.-E. *Eur. J. Org. Chem.*, **2003**, 2756-2763.
[31] Knapp, R.; Rehahn, M. *J. Organomet. Chem.*, **1993**, *452*, 235-240.
[32] Imrie, C.; Loubster, C.; Engelbrecht, P.; McCleland, C. W. *J. Chem. Soc. Perkin Trans. 1*, **1999**, 2513-2523.
[33] Mamane, V.; Riant, O. *Tetrahedron*, **2001**, *57*, 2555-2561.
[34] Butler, I. R.; Caballero, A. G.; Kelly, G. A. *Inorg. Chem. Commun.*, **2003**, *6*, 639-642.
[35] Sailer, M.; Rominger, F.; Müller, T. J. J. *J. Organomet. Chem.*, **2006**, *691*, 299-308.
[36] Hua, D. H.; McGill, J. W.; Lou, K.; Ueki, A.; Helfrich, B.; Desper, J.; Zanello, P.; Cinquantini, A.; Corsini, M.; Fontani, M. *Inorg. Chim. Acta*, **2003**, *350*, 259-265.
[37] Köcher, S.; Lutz, M.; Spek, A. L.; Prasad, R.; van Klink, G. P. M.; van Koten, G.; Lang, H. *Inorg. Chim. Acta*, **2006**, *359*, 4454-4462.
[38] Cammidge, A. N.; Scaife, P. J.; Berber, G.; Hughes, D. L. *Org. Lett.*, **2005**, *7*, 3413-3416.
[39] Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Sturba, L.; Grepioni, F. *Organometallics*, **2003**, *22*, 2142-2150.
[40] Braga, D.; D'Addario, D.; Polito, M.; Grepioni, F. *Organometallics*, **2004**, *23*, 2810-2812.
[41] Pena-Cabrera, E.; Aguilar-Aguilar, A.; Gonzalez-Dominguez, M.; Lager, E.; Zamudio-Vazquez, R.; Godoy-Vargas, J.; Villanueva-Garcia, F. *Org. Lett.*, **2007**, *9*, 3985-3988.
[42] Laufer, R. S.; Veith, U.; Taylor, N. J.; Snieckus, V. *Org. Lett.*, **2000**, *2*, 629-631.
[43] Jensen, J. F.; Sotofte, I.; Sorensen, H. O.; Johannsen, M. *J. Org. Chem.*, **2003**, *68*, 1258-1265.
[44] Anderson, C. E.; Donde, Y.; Douglas, C. J.; Overman, L. E. *J. Org. Chem.*, **2005**, *70*, 648-657.
[45] Stead, R.; Xiao, J. *Lett. Org. Chem.*, **2004**, *1*, 148-150.
[46] Wang, Y.; Weissensteiner, W.; Spindler, F.; Arion, V. B.; Mereiter, K. *Organometallics*, **2007**, *26*, 3530-3540.
[47] Liu, C.-M.; Chen, B.-H.; Liu, W.-Y.; Wu, X.-L.; Ma, Y.-X. *J. Organomet. Chem.*, **2000**, *598*, 348-352.
[48] Liu, C.-M.; Guo, Y.-L.; Wu, X.-L.; Liang, Y.-M.; Ma, Y.-X. *J. Organomet. Chem.*, **2000**, *612*, 172-175.
[49] Liu, C.-M.; Liang, Y.-M.; Wu, X.-L.; Liu, W.-M.; Ma, Y. X. *J. Organomet. Chem.*, **2001**, *637-639*, 723-726.
[50] Song, H. S.; Li, X.; Long, Y.; Schatte, G.; Kraatz, H.-B. *Dalton Trans.*, **2006**, 4696-4701.
[51] Weber, I.; Heinemann, F. W.; Bakatselos, P.; Zenneck, U. *Helv. Chim. Acta*, **2007**, *90*, 834-845.
[52] Nguyen, H. V.; Motevalli, M.; Richards, C. J. *Synlett*, **2007**, 725-728.
[53] Chen, Y. J.; Kao, C.-H.; Lin, S. J.; Tai, C.-C.; Kwan, K. S. *Inorg. Chem.*, **2000**, *39*, 189-194.
[54] Tsvetkov, A. V.; Latyshev, G. V.; Lukashev, N. V.; Beletskaya, I. P. *Tetrahedron Lett.*, **2000**, *41*, 3987-3990.
[55] Bringmann, G.; Hinrichs, J.; Peters, K.; Peters, E.-M. *J. Org. Chem.*, **2001**, *66*, 629-632.
[56] Korn, T. J.; Schade, M. A.; Cheemala, M. N.; Wirth, S.; Guevara, S. A.; Cahiez, G.; Knochel, P. *Synthesis*, **2006**, 3547-3574.
[57] Chinchilla, R.; Najera, C. *Chem. Rev.*, **2007**, *107*, 874-922.

[58] Plenio, H.; Hermann, J.; Sehring, A. *Chem. Eur. J.*, **2000**, *6*, 1820-1829.

[59] Lindner, E.; Zong, R.; Eichele, K.; Ströbele, M. *J. Organomet. Chem.*, **2002**, *660*, 78-84.

[60] Engtrakul, C.; Sita, L. R. *Organometallics*, **2008**, *27*, 927-937.

[61] Ma, J.; Vollmann, M.; Menzel, H.; Pohle, S.; Butenschön, H. *J. Inorg. Organomet. Polym.*, **2008**, *18*, 41-50.

[62] Köcher, S.; Walfort, B.; van Klink, G. P. M.; van Koten, G.; Lang, H. *J. Organomet. Chem.*, **2006**, *691*, 3955-3961.

[63] Gonzalez-Cabello, A.; Vasquez, P.; Torres, T. *J. Organomet. Chem.*, **2001**, *637-639*, 751-756.

[64] Hore, L.-A.; McAdam, J.; Kerr, J. L.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *Organometallics*, **2000**, *19*, 5039-5048.

[65] Woods, A. D.; Alcalde, G.; Golovko, V. B.; Halliwell, C. M.; Mays, M. J.; Rawson, J. M. *Organometallics*, **2005**, *24*, 628-637.

[66] Ferber, B.; Top, S.; Welter, R.; Jaouen, G. *Chem. Eur. J.*, **2006**, *12*, 2081-2086.

[67] Ferber, B.; Top, S.; Vessières, A.; Welter, R.; Jaouen, G. *Organometallics*, **2006**, *25*, 5730-5739.

[68] Amatore, C.; Godin, B.; Jutand, A.; Ferber, B.; Top, S.; Jaouen, G. *Organometallics*, **2007**, *26*, 3887-3890.

[69] Anderson, J. C.; White, C.; Stenson, K. P. *Synlett*, **2002**, 1511-1513.

[70] Szarka, Z.; Kuik, A.; Skoda-Földes, R.; Kollar, L. *J. Organomet. Chem.*, **2004**, *689*, 2770-2775.

[71] Szarka, Z.; Skoda-Földes, R.; Kollar, L. *Tetrahedron Lett.*, **2001**, *42*, 739-741.

[72] Szarka, Z.; Skoda-Földes, R.; Kuik, A.; Berente, Z.; Kollar, L. *Synthesis*, **2003**, 545-550

[73] Kuik, A.; Skoda-Földes, R.; Balogh, J. Kollar, L. *J. Organomet. Chem.*, **2005**, *690*, 3237-3242.

[74] Kuik, A.; Skoda-Földes, R.; Janosi, L. Kollar, L. *Synthesis*, **2007**, 1456-1458.

[75] Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics*, **2000**, *19*, 3978-3982.

[76] Heinze, K.; Schlenker, M. *Eur. J. Inorg. Chem.*, **2004**, 2974-2988.

[77] Özçubukçu, S.; Schmitt, E.; Leifert, A.; Bolm, C. *Synthesis*, **2007**, 389-392.

[78] Purecha, V. H.; Nandurkar, N. S.; Bhanage, B. M.; Nagarkar, J. M. *Tetrahedron Lett.*, **2008**, *49*, 1384-1387.

[79] an der Heiden, M. R.; Frey, G. D.; Plenio, H. *Organometallics*, **2004**, *23*, 3548-3551.

[80] Blank, N. F.; Moncarz, J. R.; Brunker, T. J.; Scriban, C.; Anderson, B. J.; Amir, O.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *J. Am. Chem. Soc.*, **2007**, *129*, 6847-6858.

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