

REVIEW

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Ferrocene in agriculture: from agrochemicals and soil remediation to selective chemosensors

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Abstract

Ferrocene and derivatives find numerous applications in agriculture, both as agrochemicals and as catalysts, for selective synthesis of agrochemicals. Moreover, they can be used as surfactants in soil remediation and as selective colorimetric and electrochemical chemosensors for analytes of interest in agriculture.

Keywords: Ferrocenes; Agrochemicals; Enantioselective synthesis; Soil remediation; Chemosensors

Introduction

Organometallic compounds are generally air and moisture sensitive, need to be manipulated in inert atmosphere, preferably argon, and often must be kept at very low temperature. Thus, at a first sight, that an organometallic compound, although as stable as ferrocene, is related to agriculture may sound strange. Nevertheless, there are several ways for ferrocene and derivatives to be of use in the agriculture world. Agrochemicals can be linked to the ferrocenyl system either directly (for example, ferrocene-containing herbicides and fungicides) or indirectly, as catalysts in the synthesis of organic compounds of interest for agriculture. As a matter of fact, examples are not particularly numerous, but they are quite significant, as discussed in the following. Moreover, taking advantage of reliable redox properties and robustness of ferrocenes, analytical methods were developed to detect and quantify compounds of importance in crop protection and/or soil remediation as well as for environment control.

Ferrocene (Figure 1) is a peculiar organometallic compound, with a sandwich structure where two cyclopentadienate (Cp) groups are coordinated to an iron atom, formally Fe(II). The $(\eta^5\text{-Cp})_2\text{Fe}$ has a 18 electrons closed shell, a remarkable stability at the air, especially in the solid state, and a reactivity similar to that of other aromatic species, that allowed extensive functionalization

and the introduction of a huge number of substituents [1,2]. All these aspects favored the use of ferrocene and its derivatives in biological applications and in conjugation with biomolecules [3] and prompted the synthesis of compounds with potentiality as drugs [4].

The present review is intended at offering the reader with a panorama of the most recent developments in the field. Therefore, the literature survey was limited to the last 10 years, with only occasional references to older papers.

Review

Ferrocene-containing agrochemicals

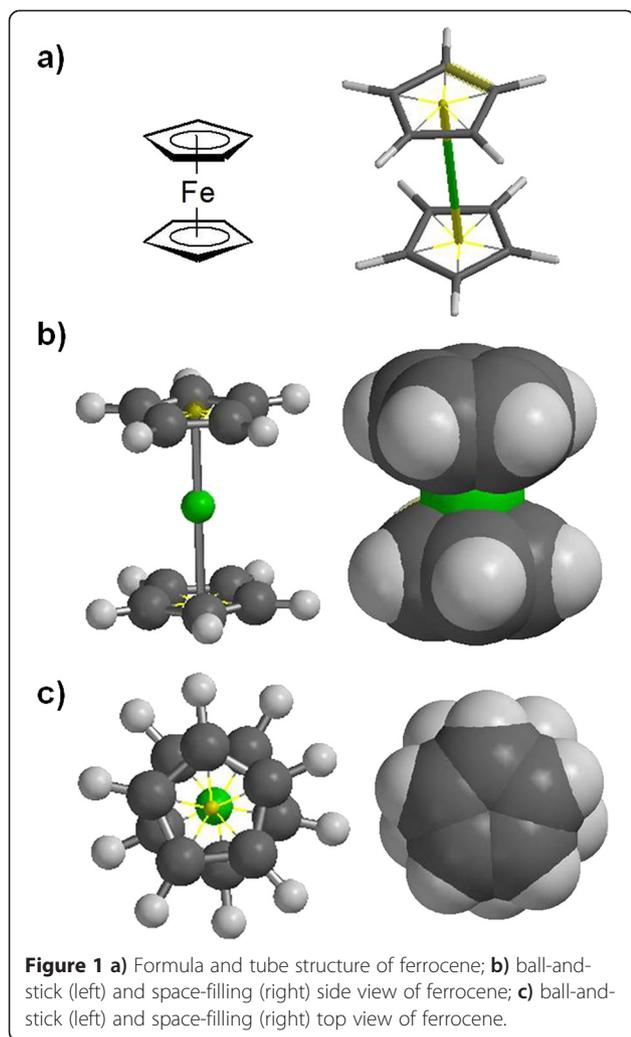
Crop protection is an important issue in agriculture, made possible, in part, by the utilization of chemicals for pest control or as herbicides. On the other hand, the increasing concern about adverse effects of pesticides on health and environment, evidenced by the introduction of new pesticide registration procedures (see, for example, the Food Quality Protection Act in the United States [5]), prompted the investigation of new pesticides, including natural product-based pesticides [6], to replace the compounds that could no longer be used, due to the new registration requirements. Examples can be found in a number of reviews [7,8]. In the attempt to obtain more efficient compounds, ferrocenyl group was introduced as a substituent in compounds known to be active.

Important systemic agents with a broad spectrum of fungicidal activity against plant pathogens are derivatives of 1*H*-1,2,4-triazole, such as those shown in Figure 2.

Therefore, it is not surprising that most of ferrocene-based agrochemicals (fungicides, herbicides) contain

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the same heterocycle. Moreover, quite often the same compounds revealed promising and somewhat unexpected plant growth regulatory activity. The synthesis is quite straightforward, starting from acetylferrocene, **1**, [9-15] or ferrocenecarbaldehyde, **2**, [16-18] and using classical organic reactions, as illustrated in Figures 3 and 4.

E and *Z* isomers of 3-aryl-1-ferrocenyl-2-triazolyl derivatives, **3**, [9] were tested for preventive fungicidal activity against powdery mildew on barley (foliar and soil drench applications) and for curative fungicidal activity against brown rust on wheat (foliar application). Selected results from foliar applications are reported in Table 1 (entry 1). *E* isomers displayed better fungicidal activity than *Z* ones, probably due to a favorable steric feature. Moreover, plant growth regulatory activity was detected, spraying apple leaves of plants grown from seeds. Reacting both isomers with phenylhydrazine (Figure 3), 5-aryl-3-ferrocenyl-1-phenyl-4-triazolyl-dihydropyrazoles, **4**, were obtained, that were tested against some bacterial strains, with results not much satisfactory.

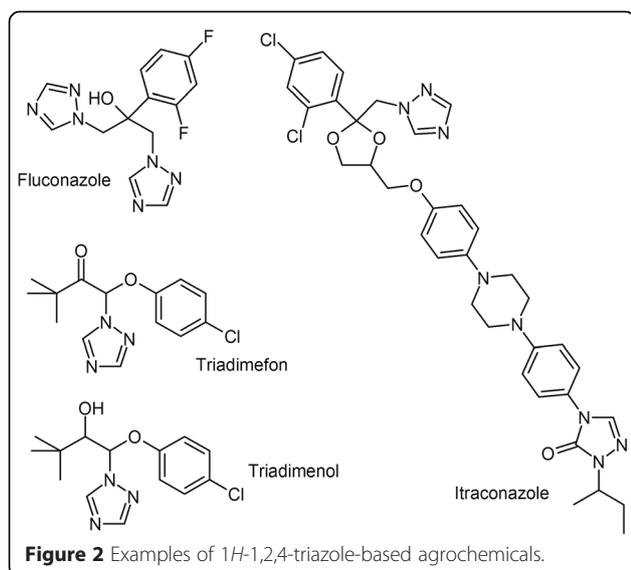
The triazolyl ring was distanced from ferrocene inserting another carbon atom [11], and the resulting (*E*)-3-aryl-1-ferrocenyl-2-triazolylmethyl derivatives, **5**, (Figure 3) were tested against some fungi (*Pratylenchus zae*, *Alternaria solani*, *Cladosporium fulvum*, *Physalospora piricola*, and *Cercospora arachidicola*), with variable activities, generally better against *A. solani* (Table 1, entry 2). The derivatives from reaction with phenylhydrazine, **6**, this time, presented an improved performance (Table 1, entry 3).

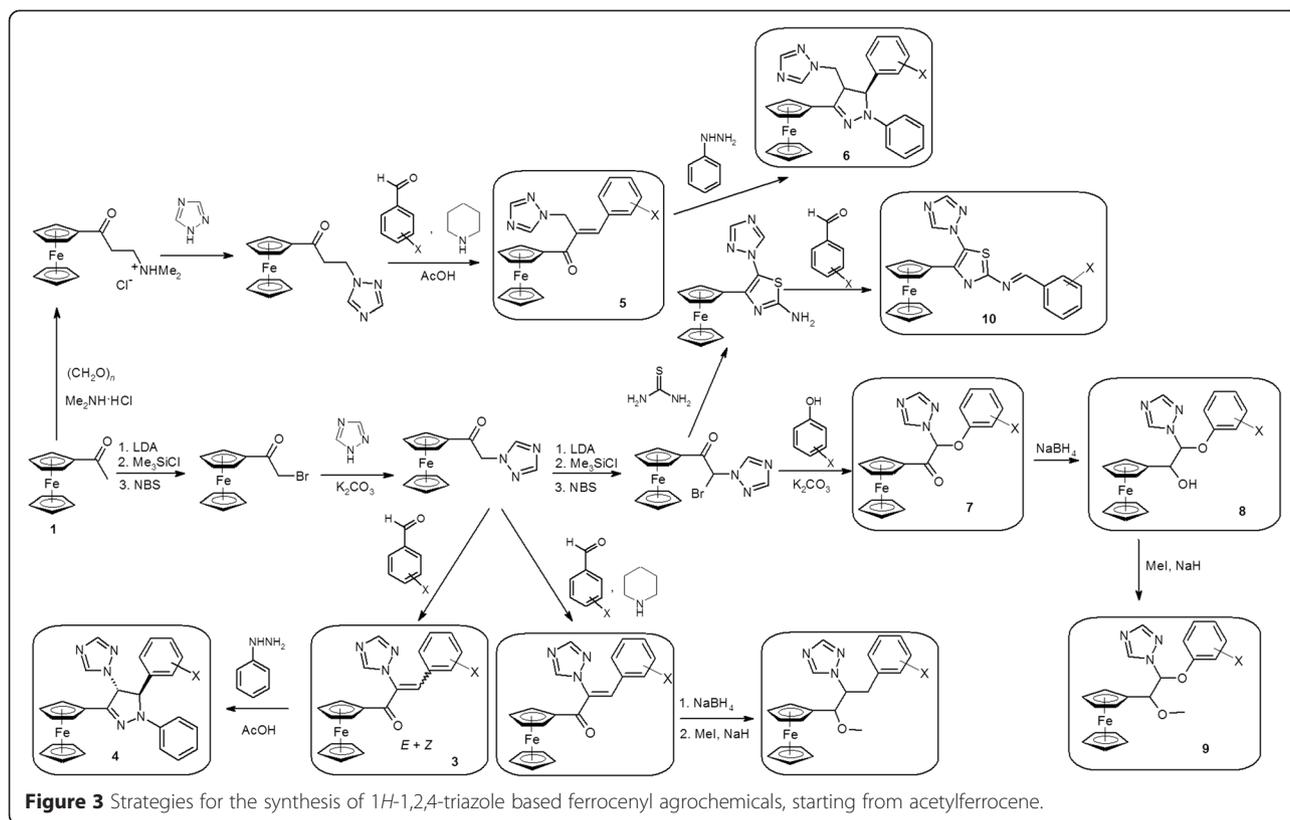
Ferrocenyl analogs of triadimefon, **7**, [12] were tested for antifungal activities against mildew and rusts on intravital wheat plants (*Isariopsis clavispora*, *Bremia lactucae*, *C. fulvum*, *Erysiphe graminis*, and *Alternaria mali*), but, disappointingly, all the tested compounds showed lower antifungal activity (see examples in Table 1, entry 4) against all fungi than parent triadimefon (92.8% and 96.6%, respectively). Instead, plant regulatory activity, assayed using cucumber cotyledon rhizogenesis method, resulted excellent.

By reducing analogs of triadimefon, the corresponding ferrocenyl analogs of triadimenol, **8**, were obtained [13]. They were tested as indicated above for the triadimefon analogs and generally did not exhibit any antifungal activity (Table 1, entry 5); however, all of them showed excellent plant growth regulatory ability, even larger than the keto precursors.

A slight structural variation was the change from OH to OMe, **9** [14]. Five fungi (*P. zae*, *A. solani*, *C. fulvum*, *P. piricola*, and *C. ara*) were used, with modest results (see, for selected examples, Table 1, entry 6). Interesting results were obtained from plant growth regulatory activity, determined by wheat gemmae elongation and cucumber cotyledon rootage methods.

N-substituted benzylidene-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine derivatives, **10**, were





synthesized by condensation of substituted benzencarbaldehydes with 2-amino-4-ferrocenyl-5-(1H-1,2,4-triazol-1-yl)-1,3-thiazole that, in turn, was obtained from 1-bromo-2-ferrocenyl-1-(1H-1,2,4-triazolyl)ethanone and thiourea (Figure 3) [15]. Fungicidal activities *in vitro*

of these imines were examined against four fungi (*P. zaeae*, *A. solani*, *P. piricola*, and *C. ara*), and plant growth regulatory activities were tested by a rape hypocotyl test. According to the authors, although the results of the screening (some of them reported in Table 1, entry 7) are

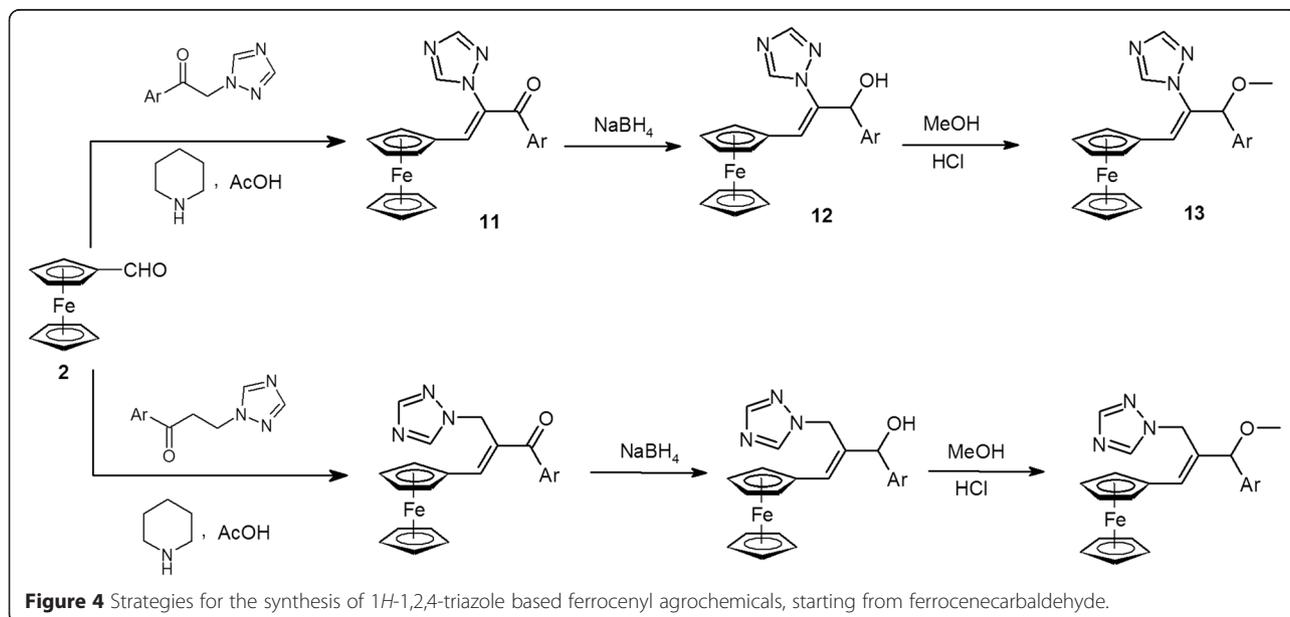
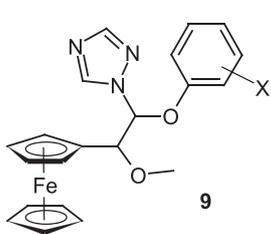


Table 1 Selected biological activities of 1H-1,2,4-triazole based ferrocenyl agrochemicals (Continued)

6			<i>C. fulvum</i>	<i>P. piricola</i>	Wheat	Cucumber	14
		H	33.3	0	-22.8	+10.5	
		4-Me	0	0	-22.3	+63.1	
		4-OMe	0	0	-22.3	+63.1	
		2-Cl	33.3	0	-20.4	+26.3	
		4-Cl	33.3	25.0	-20.4	+2.6	
		4-F	50.0	0	-12.6	+126.3	

^a2-naphth = 2-naphthyl.

quite disappointing, biological activity resulted higher than that of the same compounds with a phenyl group instead of the ferrocenyl one.

A different approach to synthesize ferrocene derivatives containing triazole was to start from ferrocenecarbaldehyde and α -bromo arylketones that allowed structural variations (Figure 4) [16-18].

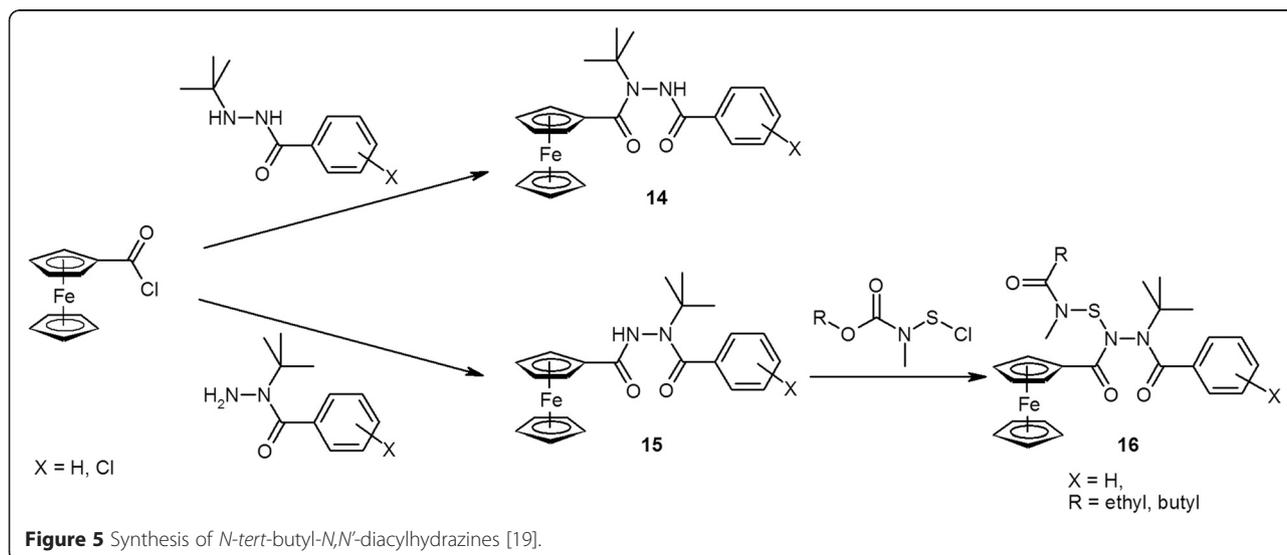
The three families of compounds (with CO, **11**, OH, **12**, and OMe, **13**, functionalities, respectively) were tested for biological activities. Scarce plant growth regulatory activity (wheat coleoptile and cucumber cotyledon tests) was observed, a little less so with ketones. Some antifungal *in vitro* activity was registered (vs. *Gibberella zeae*, *A. solani*, *Cercospora arachidicola*, *P. piricola*, *Phomopsis asparagi*, *Cladosporium cucumerinum*, *Sclerotinia sclerotiorum*, and *Pyricularia oryzae*), but it was not significant, according to the authors, if compared with known commercial agents. A few selected data are shown in Table 1 (entries 8 to 10).

Ferrocenyl derivatives with different functionalities were also investigated. It is noteworthy that one of the

first attempts to have biologically active ferrocenes introduced aroylhydrazines as substituents (Figure 5 [19]): more than a decade later, it was acknowledged the importance of natural hydrazine-containing compounds, also with respect to biological activities [20].

N-tert-butyl-N,N'-diacylhydrazines, mimicking the action of 20-hydroxyecdysone to activate the ecdysone receptor, lead to lethal premature molting, thus constituting a class of insect growth regulators useful in crop protection. The larvicidal activities were tested against Southern armyworm by foliar application. Results (Figure 6) indicate a good larvicidal activity, in comparison with the reference RH5849 (*N-tert-butyl-N,N'*-dibenzoylhydrazine) only when the *tert*-butyl group was far from ferrocenyl moiety.

1,1'-Disubstituted ferrocenes with different keto-ester, hydroxy-ester, and dihydroxy functionalities on both cyclopentadienyl rings were prepared (Figure 7 [21]) and assayed *in vitro* for antifungal activity against *G. zeae*, *A. solani*, *C. arachidicola*, *P. piricola*, and *Fusarium oxysporum*. The compounds showed relatively low fungicidal activity.



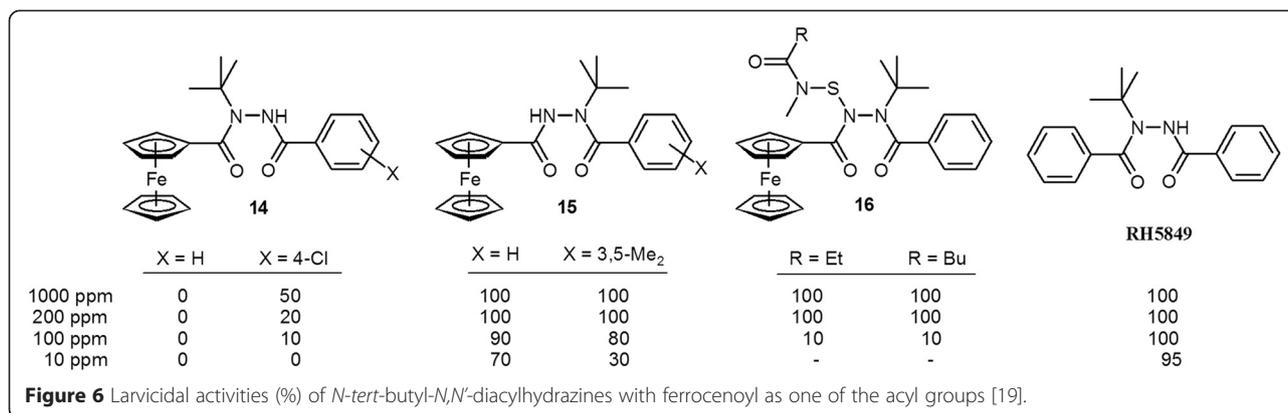


Figure 6 Larvicidal activities (%) of *N-tert-butyl-N,N*-diacylhydrazines with ferrocenoyl as one of the acyl groups [19].

Instead, ferrocenyl ethers [22], much easier to prepare (Figure 8) than previous diferrocenyl derivatives, showed moderate activity against two plant fungi, *Botrytis cinerea* and *Penicillium species* (Table 2).

Among herbicides, it is important to mention a series of cyanoacrylates containing ferrocene (Figure 9 [23]), that exhibited, according to the authors, excellent herbicidal activities against rape weeds.

More recently, a series of ferrocenes substituted with pyrimidines (17 to 20, Figure 10) were prepared [24,25], because of their potentialities as herbicides and plant growth regulators, but the biological activities have not been tested yet. The same holds for trifluoromethylsulfanylferrocene, 21, (trifluoromethylsulfanyl)ethynylferrocene, 22 [26], and (*N*-ferrocenylmethyl)benzenecarbamide, 23 [27], shown in Figure 10.

Ferrocenes as catalysts in the synthesis of agrochemicals

The importance of agrochemicals is evident, although the environmental consequences of their use must not be underestimated. Therefore, it is important to limit the amount of chemicals introduced in the environment. Moreover, it became increasingly apparent that biological properties of chiral agrochemicals are related to the absolute configuration. The not active enantiomer is unnecessary or even noxious, so that enantioselective synthesis became a must. The problem is well illustrated by the case of (*S*)-metolachlor (Figure 11, IUPAC: (*S*)-*N*-(2-ethyl-6-methyl)phenyl-*N*-(1-methyl-2-methoxy)ethyl-2-chloroethanamide), the most important herbicide of Novartis Crop Protection Division [28] (>20,000 ton/year).

It has been produced since 1978, first as a racemic mixture, then (from 1997) as enantiomerically enriched

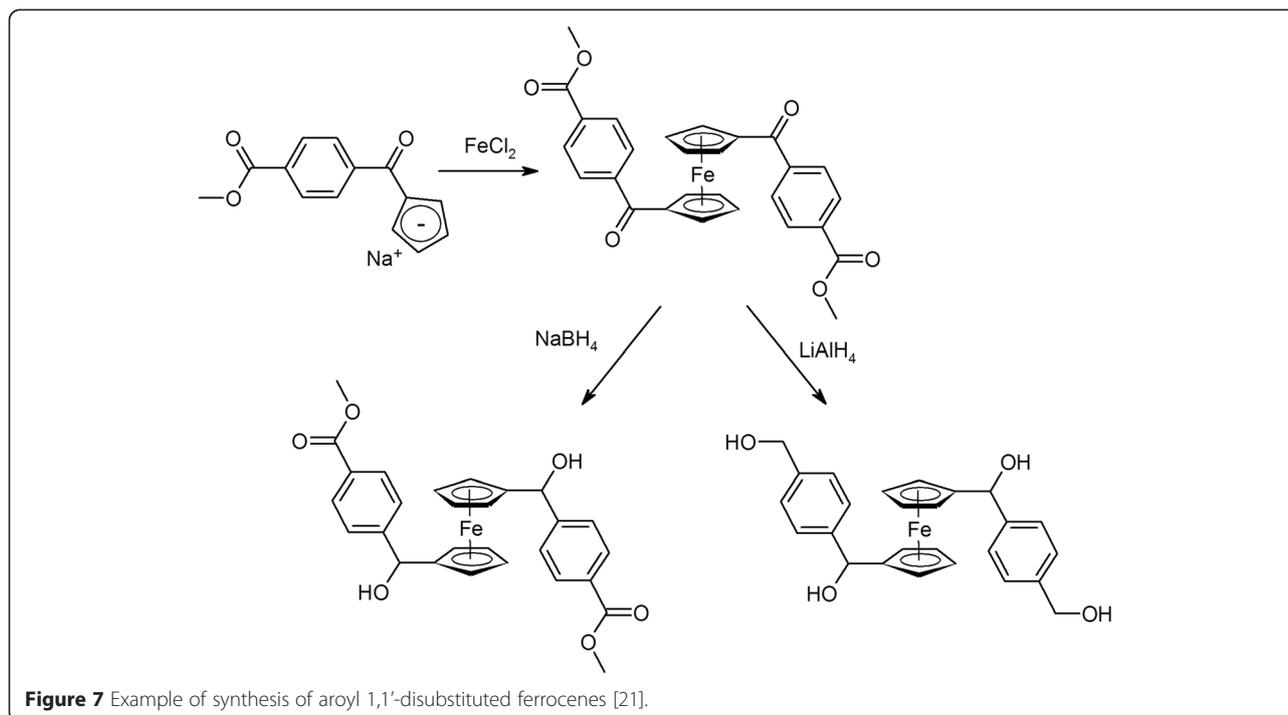


Figure 7 Example of synthesis of aryl 1,1'-disubstituted ferrocenes [21].

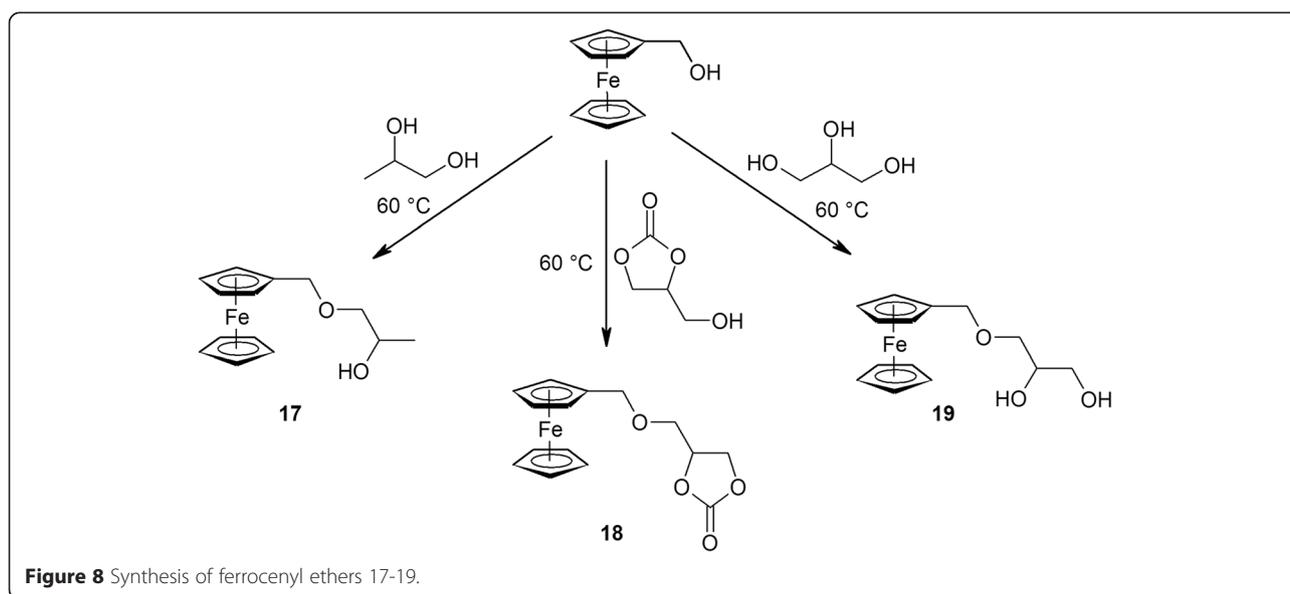
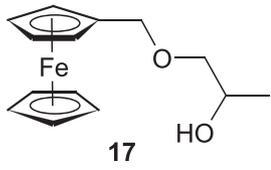
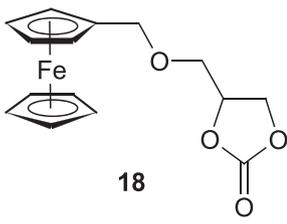
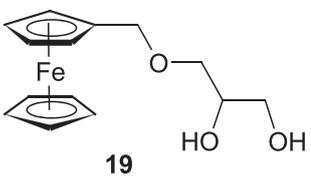
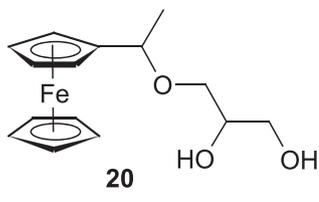
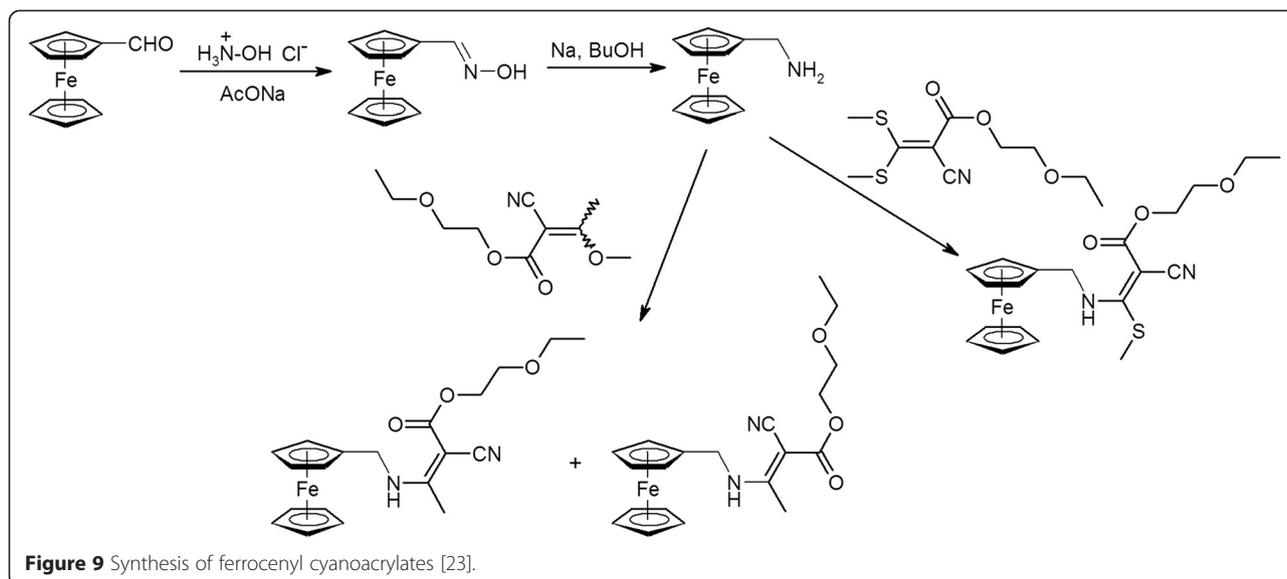


Table 2 Selected fungicidal activities (%) of ferrocenyl ethers, at 250 µg/mL

Entry	Ferrocene derivative	<i>Penicillium</i> spp.		<i>Botrytis cinerea</i> spp.		References
		Surface	Inclusion	Surface	Inclusion	
1		77.0	84.2	68.1	62.0	[22]
2		72.2	72.6	44.1	39.0	
3		53.9	56.0	59.1	57.6	[22]
4		50.6	59.6	66.5	38.2	[22]

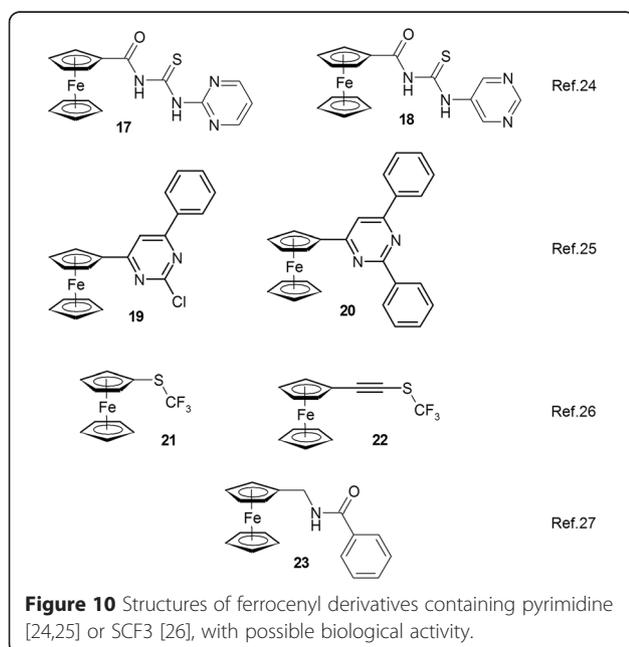


form, that allowed a 40% reduction of the environmental load. One of the most important strategies of asymmetric synthesis is the use of chiral catalysts. The turning point to asymmetric synthesis of metolachlor was the use of an iridium catalyst [29], made chiral by a chiral ferrocenylphosphane ligand, Josiphos. The catalyst was robust enough to ensure very high turnover number (TON) and turnover frequency (TOF).

For the reader not familiar with ferrocenes, it is sufficient to say that two different substituents in the same cyclopentadienyl ring give rise to two enantiomers, that present a planar chirality (Figure 12). Each enantiomer is indicated as R_p or S_p (where p stands for planar), according to Schögl's rules: the observer looks along the C_5 axis of ferrocene

from the side of the more highly substituted Cp ring, and the absolute configuration is given depending on the shortest arc to descend in priority, either clockwise or counterclockwise.

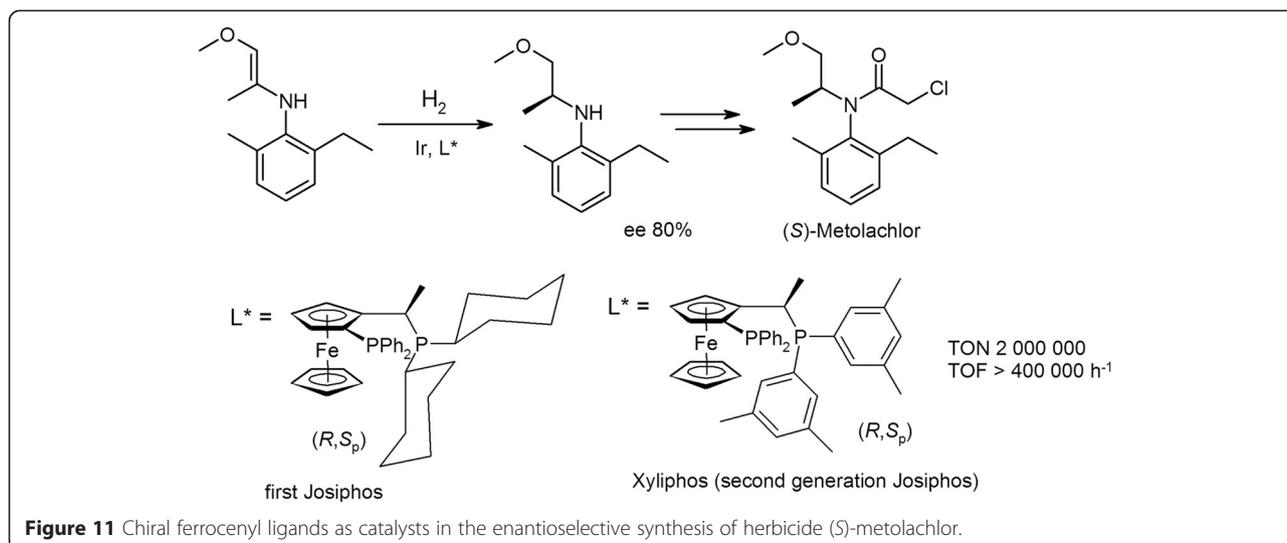
The success of Josiphos and its Xyliphos modification boosted both industrial applications of chiral catalysts [30-32] and the synthesis of new chiral ferrocenes [33-37] as well as their use in asymmetric synthesis [38-42]. Thus, the first Josiphos was the parent compound for a family of effective chiral ligands that found application in enantioselective synthesis of other compounds useful in agriculture. To give just an example, the asymmetric allylation of tertiary α -fluoroketones, molecules useful for applications toward drugs, agrochemicals, and functional materials, was performed, *inter alia*, with chiral ferrocenyl catalysts (Figure 13, [43]). Unfortunately, e.e.s are too low to be useful.



Ferrocenes in soil remediation

Native clays emerged as an active component of soils that influence the sorption of cations, anions, and hydrophobic organic chemicals. Therefore, their importance in removing and retaining pollutants is increasing [44], also because iron ions within the clay lattice participate in redox reactions, that can be useful against metal ion pollution [45]; for example, researchers at the Hanford site in Washington could decrease the amount of Cr(VI) in the water supply from 1 ppm to below detection limits (7 to 8 ppb) reducing it to the less toxic and less soluble Cr(III), taking advantage of clay structural iron, previously reduced to Fe(II) [46].

For the remediation of contaminated soils, the application of surfactants is gaining importance [47-51]. Ferrocene-based surfactants have the advantage to act both as surfactants and as redox-active compounds. Therefore, a series of ferrocenyl surfactants of varying chain lengths was



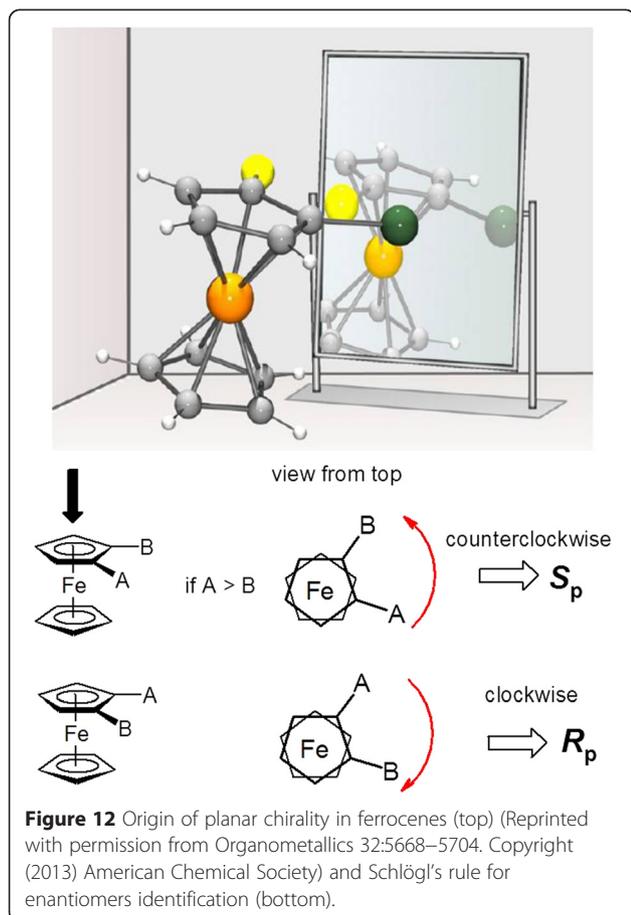
employed as intercalants, in order to determine the conditions when electronic transfer takes place in clay structural Fe. By this investigation, a better general knowledge of Fe activity in natural silicates could be achieved [52]. Ferrocenyl surfactants (**25** and **26** in Figure 14a) used as intercalants, having different chain lengths, ensured both a range of

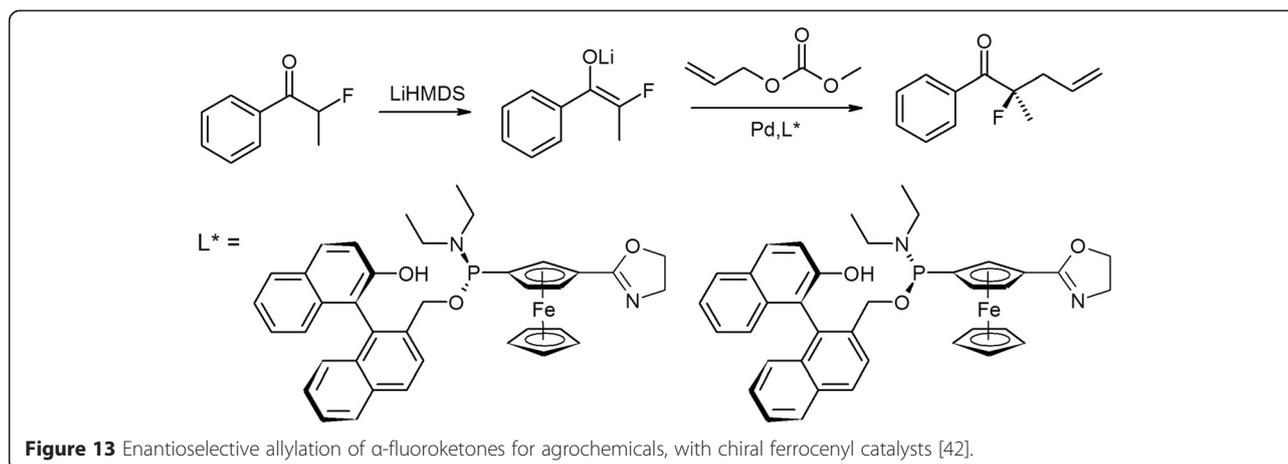
potentials and a range of possible conformations; as clay, standard Wyoming montmorillonite (SWy-1), of formula $(Al_{2.88}Fe_{0.68}Mg_{0.47})(Si_{7.7}Al_{0.29})O_{20}(OH)_4$, was used.

The results indicated that ferrocenyl trimethylammonium derivatives with C6 (**25**) and C11 (**26**) chains can be oxidized by structural Fe(III) in clay, whereas ferrocenylmethyl trimethylammonium (**24**) is not oxidized (Figure 15).

Later, other ferrocenyl surfactants (**27** and **28** in Figure 14b) were used to verify the possibility to exploit them as reversible surfactants [53]. In fact, although the surfactant washing of contaminated soils and groundwater may be an effective approach, operating costs result high and the surfactants need to be recycled, in order to optimize surfactant-enhanced remediation (SER). As discussed in ref. [53], the methods developed are not satisfactory. From this study, it resulted that the solubilization of benzene, toluene, and ethylbenzene with ferrocenyl surfactants was better than that of with commonly used cationic (hexadecyltrimethylammonium bromide (CTABr)) or anionic (sodium dodecyl sulfate (SDS)) surfactants. Moreover, the removal efficiency was higher at low ferrocenyl surfactant concentrations, and finally, oxidation to ferrocenium cation allowed separation from organic compounds and, therefore, recycling of the surfactant.

It is worth mentioning that ferrocenes proved useful into evidencing the redox properties of Fe(II) adsorbed onto mineral surfaces [54]. The measurement of meaningful rest potentials in environmental and geochemical systems has been very difficult in the past, due, among *alia*, to the slow electron transfer between the solid sensing electrode (typically Pt) and the redox active species. Instead, the ferrocene-mediated electron transfer approach generated mobile solution probes that can react with the redox active species sufficiently fast to provide a measurable current, thus providing a direct measure of redox reactivity (i.e., electron transfer rates) of adsorbed redox active species.



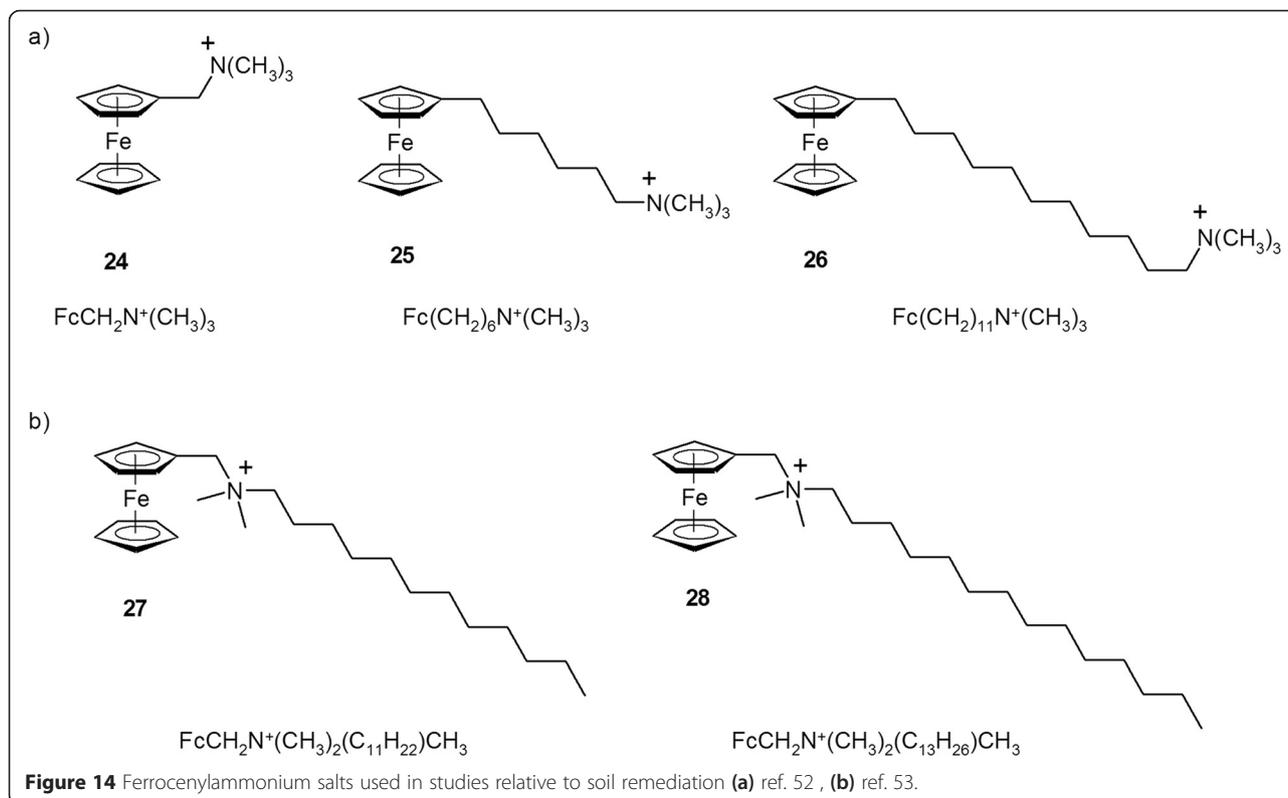


Ferrocenes as sensors

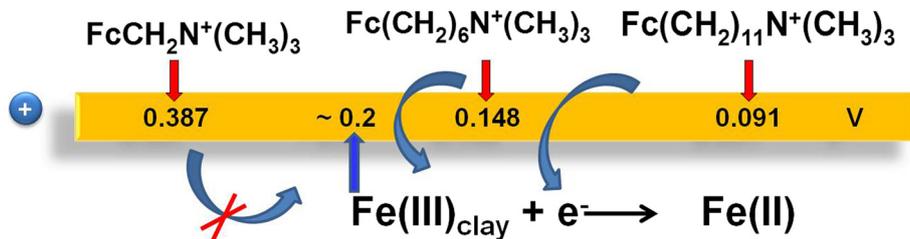
Ferrocene derivatives can work both as optical and electrochemical sensors. When opportunely substituted, they can coordinate anions or cations, with a consequent potential shift or color change [2]. Only selected recent examples will be reported here.

- a) *Neutral compounds.* Hydrazine and derivatives are used in agriculture as pesticides but enter in the environment also by industrial emissions. Because of their toxicological hazard, sensitive, reliable, and fast analytical methods are required. A number of instrumental

techniques are available [55], but electroanalytical ones might provide portable, cheap, and rapid procedures, the somewhat kinetically sluggish hydrazine oxidation notwithstanding [55]. Exploiting carbon nanotubes, the electrocatalytic determination of phenylhydrazine and hydrazine was accomplished contemporarily, with a ferrocene-modified carbon nanotube paste electrode [55]. Such an electrode resulted stable and easy to prepare and to undergo surface renewal. It displayed improved selectivity and allowed detection of hydrazine and phenylhydrazine in the same sample, contemporarily.



Electron donor



Electron acceptor

Figure 15 Energy scheme for redox reactions of ferrocenyl surfactants with structural Fe(III) in clay [52].

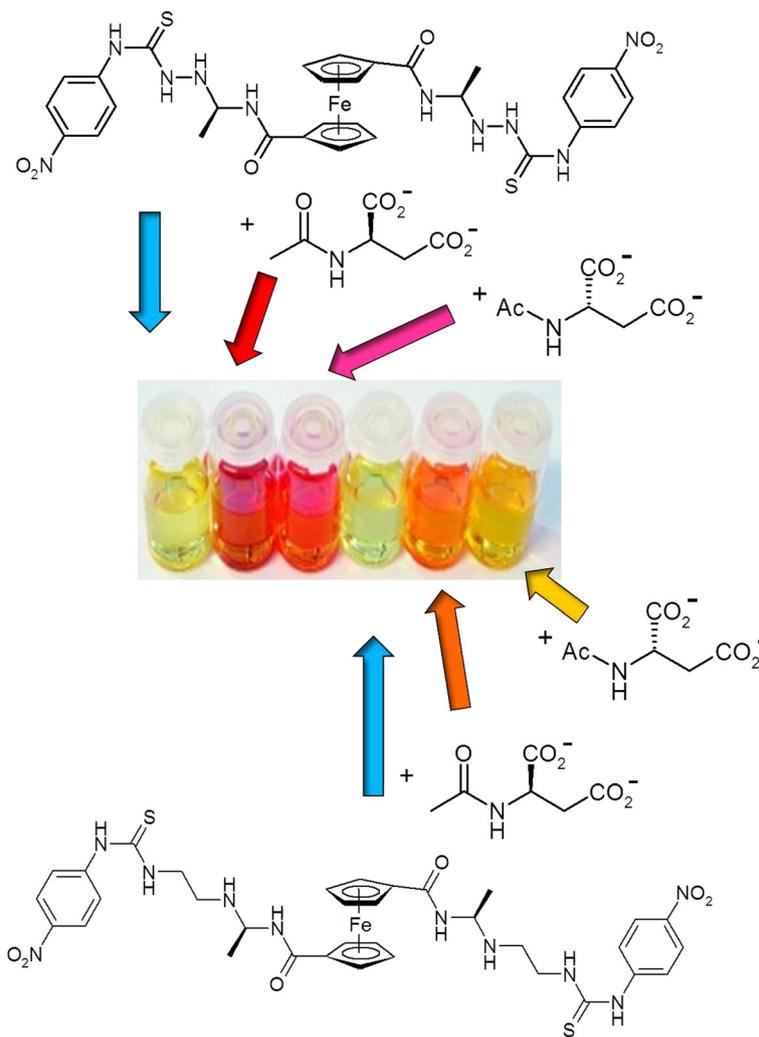
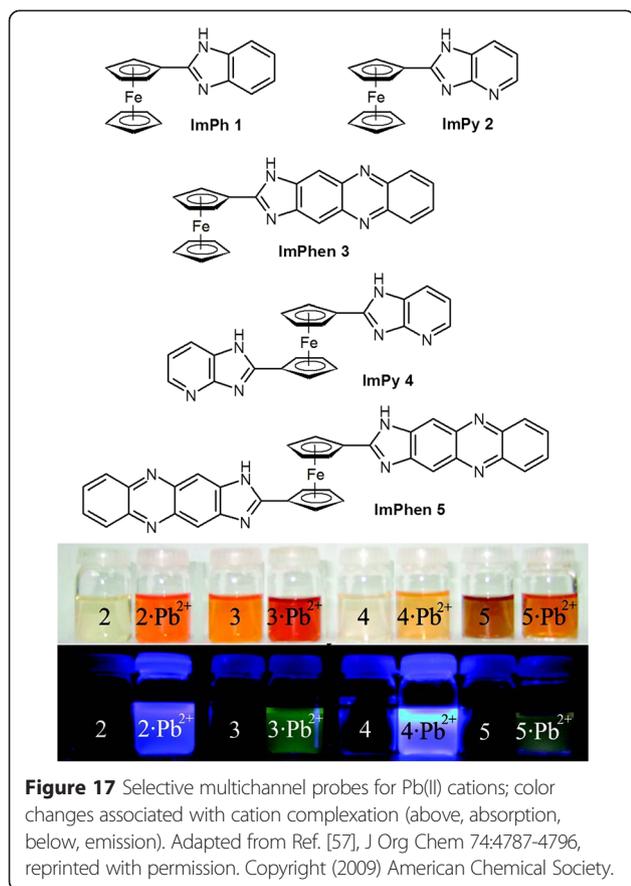


Figure 16 Colorimetric ferrocene-based sensor for *N*-acetylaspartate. From left to right: ferrocenyl derivative above, the same + *L*-*N*-acetylaspartate, the same + *D*-*N*-acetylaspartate; ferrocenyl derivative below, the same + *L*-*N*-acetylaspartate, the same + *D*-*N*-acetylaspartate. Adapted from Ref. [56], *Eur J Org Chem* 841-849. Reprinted with permission. Copyright (2009) Wiley.



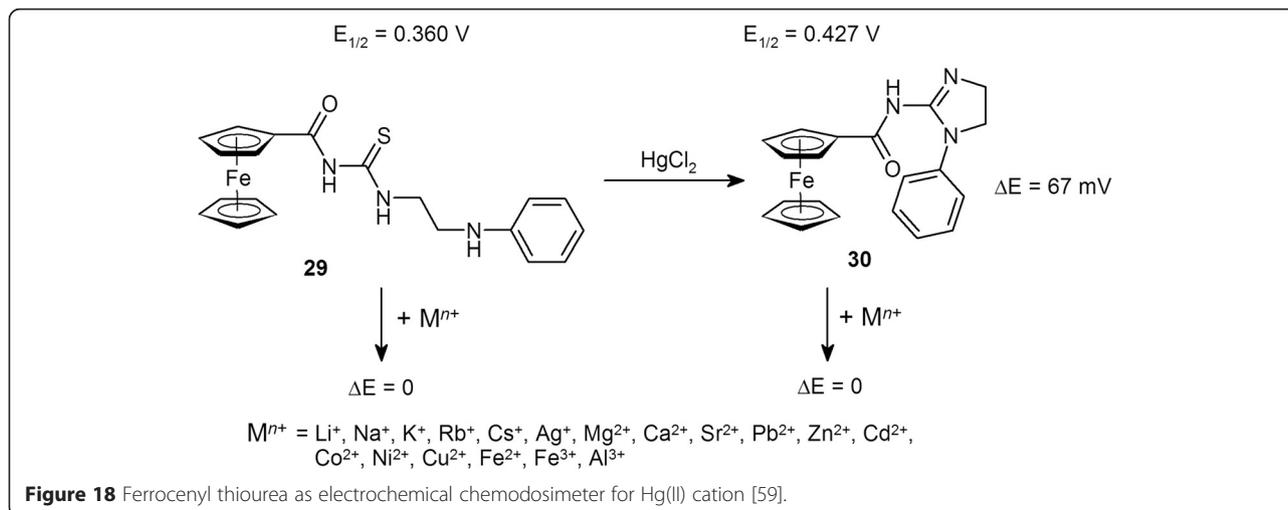
b) *Anions*. The importance of aspartate is undeniable: like many chiral anions, it enters in biological and chemical processes, not to speak of the industrially important aspartame. On the other hand, the enantioselective recognition by artificial host molecules is of increasing interest [56]. A number of 1,1'-disubstituted ferrocenes, with a chiral carbon atom and a thiourea moiety in the substituents, were prepared,

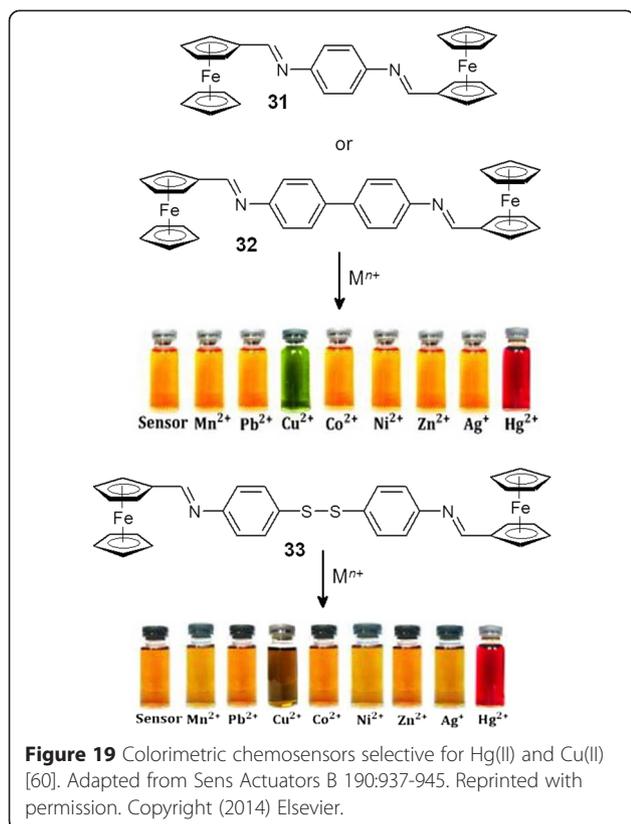
and their enantioselective recognition was tested. At least two of them exhibited good chiral recognition, as shown by optical titration with either L- or D-N-acetylaspartate in dimethyl sulfoxide (DMSO) solution. Changes in color are significant, as illustrated in Figure 16, thus rendering these ferrocenes 'naked eye' colorimetric sensors.

c) *Cations*. Detection of heavy metal cations in environment is of great importance, due to their diffusion from industrial sources and their treat to health. In particular, lead poisoning is still one of the most common environmentally caused diseases and detection of Pb(II) ions is absolutely necessary, especially in drinking water [57]. After succeeding in recognition of phosphate-related anions by a ferrocenylimidazophenanthroline, that worked both as colorimetric and electrochemical sensor [58], the same authors prepared ferrocenes substituted with imidazopyridine (ImPy) or imidazophenazine (ImPhen) (Figure 17), that acted as selective receptors toward Pb(II) cations [57].

The compounds, reported in Figure 17, show highly selective affinity for Pb(II) ions over a range of other metal ions, through different channels, i.e., as redox, chromogenic, and fluorescent chemosensors. For example, compound **ImP2** showed, upon complexation with Pb(II) cation, an oxidation redox peak anodically shifted ($\Delta E_{1/2} = 150$ mV), a red-shifted absorption maximum ($\Delta\lambda = 44$ nm) and an emission with an important chelation-enhanced fluorescence effect.

Mercury is a highly poisonous element, for which numerous analytical methods were developed; among them, the chemodosimetric approach for Hg(II) ion is noteworthy. It involves a chemosensor based on chemical reaction. Using a ferrocenyl-substituted thiourea, **29**, a ferrocene-based electrochemical chemodosimeter **30** was prepared [59]. The reaction promoted by Hg(II) cation





(Figure 18) resulted in a significant shift of redox potential that, on the contrary, was not affected by the presence of other cations, such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+} .

Other ferrocene-based chemosensors, one selective for Hg(II) cation and the other selective for Cu(II) cation, were developed introducing 1,4-benzenediamine **31**, 4,4'-biphenyldiamine **32**, or 4,4'-diaminobenzenedisulfide, **33** [60]. The compounds resulted highly sensitive colorimetric chemosensors for Cu(II) and Hg(II), with changes that allowed 'naked eye' detection, as can be seen in Figure 19.

Conclusions

This survey was intended at showing the multiform aspects of ferrocene contribution to agriculture. The applications emerged in the last 10 years are significant, but the feeling is that much more can be done and the best has yet to come. The wish is that the present review might raise curiosity and interest in the field.

Competing interests

The author declares that she has no competing interests.

Received: 12 February 2015 Accepted: 26 March 2015

Published online: 25 June 2015

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