

## FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1985\*

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1. REVIEWS

The magnetic and structural properties of one-dimensional  $[(\eta\text{-C}_5\text{Me}_5)_2\text{Fe}]^+$  compounds containing radical anions have been reviewed [1]. The formation and spectroscopic characterization of ferrocenium salts has been discussed by Neuse [2]. The chemistry of  $\eta$ -arene,  $\eta$ -cyclopentadienyl and related transition

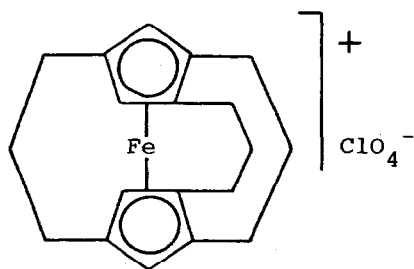
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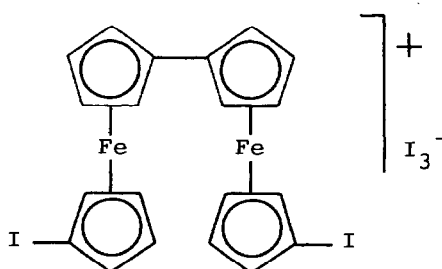
metal complexes has been surveyed [3]. Rausch has reviewed the preparation and reactions of  $\eta$ -cyclopentadienyl complexes of transition metals [4]. The chemistry of ferrocene-based enzyme electrodes has been discussed by Hill and Allen [5]. The chemistry of homo- and hetero-chain polymers containing pendant or backbone ferrocene groups has been reviewed [6]. The preparation, homopolymerization and copolymerization of vinyl and isopropenyl derivatives of ( $\eta$ -cyclopentadienyl)metal complexes has been surveyed [7].

## 2. STRUCTURAL DETERMINATIONS

The crystal structure of ferrocenecarboxylic acid has been determined by X-ray analysis. Pairs of molecules were hydrogen-bonded together so that the geometric centre of the hydrogen-bonded framework coincided with a crystallographic centre of inversion. The structure of this molecule was compared with that of ferrocene-1,1'-dicarboxylic acid [8]. The crystal and molecular structure of the ferrocenium salt



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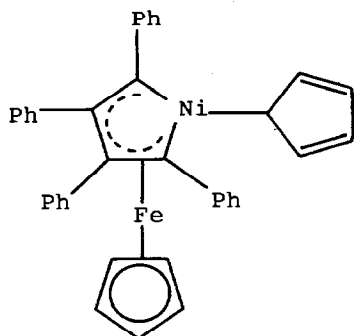


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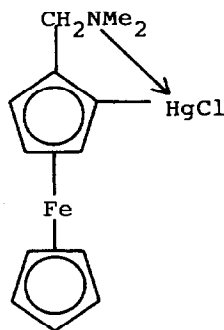
(2.1) has been determined by X-ray analysis. The iron-to-ring distance in the cation was longer than in the corresponding neutral molecule. In the cation there was also an increase in angle between the  $\alpha$ -carbon atoms and the ring planes together with an increase in the ring-ring tilt angle [9]. The crystal and molecular structure of the valence delocalized biferroceniumcation (2.2) has been determined by X-ray crystallography. The two iron atoms were located at environmentally equivalent positions in the unit cell and this favoured rapid intramolecular

electron transfer [10].

A ferrocene analogue with a nickelacyclopentadiene ring (2.3) has been prepared and characterized. X-ray crystallography confirmed that the iron atom was sandwiched between two parallel five-membered rings. The complex (2.3) underwent a reversible one-electron oxidation at  $E_{1/2} = 0.67$  V vs. Ag/AgCl and green salts of the derived cation were prepared [11]. The



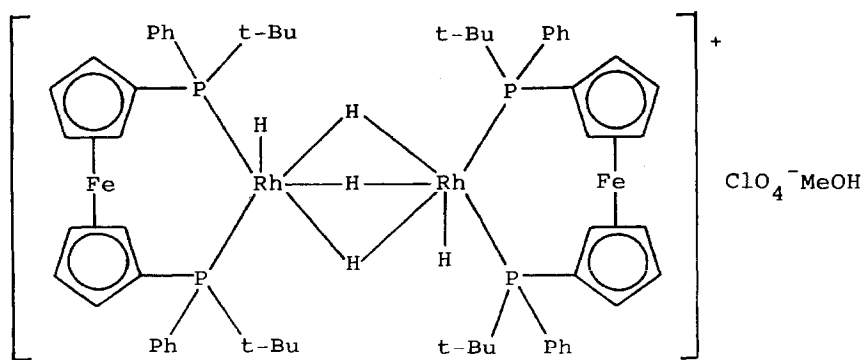
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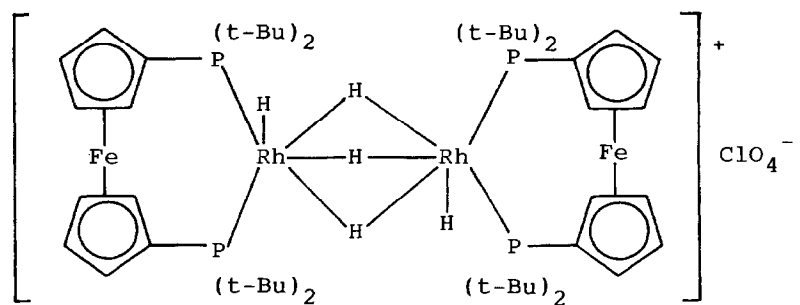
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crystal and molecular structure of 1-chloromercury-2-dimethylaminomethylferrocene (2.4) has been determined by X-ray crystallography [12]. The crystal structures of the two rhodium (III) hydride complexes (2.5 and 2.6) have been determined by X-ray analysis. In complex (2.5) each rhodium atom had three Rh-H bridging bonds, a single Rh-H terminal bond and two Rh-P bonds. It was proposed that complex (2.6) had a similar structural arrangement [13].

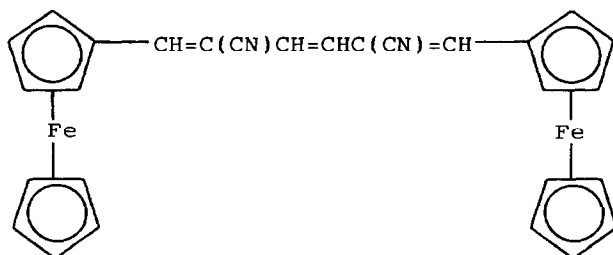
The structure of 1,6-biferrocenyl-2,5-dicyanohexa-1,3,5-triene (2.7) has been determined by X-ray analysis. The molecule was centrosymmetric with the nitrile group cis to the nearest  $\eta$ -cyclopentadienyl ring. The electrochemistry of this molecule was investigated. Thus the cyclic voltammogram exhibited two overlapping waves for the oxidation of the two ferrocene groups. The mixed-valence ion was generated and investigated in a series of solvents. The results indicated that the ion had trapped valence with a small amount of delocalization [14]. An analysis of the molecular conformation and rotational disorder in crystalline ferrocene and nickelocene



2.5



2.6



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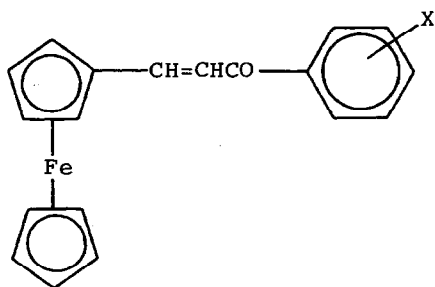
has been carried out. The results showed that ferrocene had a disordered structure at room temperature and a mechanism was proposed for the second-order phase transformation that ferrocene underwent on cooling [15].

### 3. THEORETICAL STUDIES

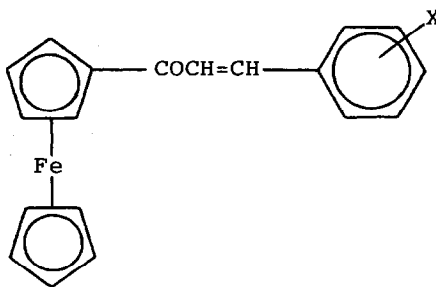
Large scale MO SCF and externally contracted CI calculations have been carried out to determine the iron to  $\eta$ -cyclopentadienyl ring distance in ferrocene. The calculated distance was 0.07 Å longer than that determined experimentally [16]. The structures of organometallic molecules have been predicted by MO calculations and compared with experimentally determined structures. The metal-to-ring distance in ferrocene has been optimized at the Hartree-Fock-Roothaan (HFR) level to predict a bond distance of 1.9 Å which compares with the experimental distance of 1.65 Å. Generalized MO CI calculations which explained the HFR bond distance error were reported. Accurate theoretical geometries for other organometallic molecules may be determined using these calculations [17]. Graph theory was used to investigate the structure of ferrocene and related molecules. Ferrocene was characterized as a three-dimensional aromatic molecule [18]. A theoretical approach has been developed for the prediction of intervalence transfer band profiles for delocalized, bridged, mixed-valence dimers [19].

### 4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

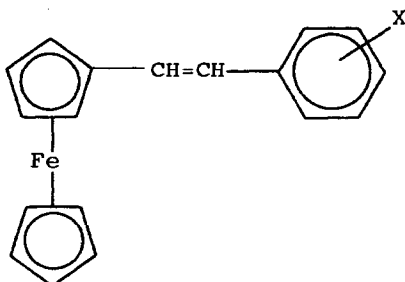
NMR spectroscopy has been used to study the kinetics and mechanism of conversion of solid diamagnetic nonamethylferrocenylcarbenium ion salts to the paramagnetic salts of bis-(nonamethylferrocenyl)ethane [20]. The electron donor-acceptor character of organic groups has been evaluated by measuring the half-wave potentials,  $^1\text{H}$  NMR and electronic spectra of the appropriate substituted ferrocenes [21]. Electron density distribution in ferrocene analogues of stilbene (4.1, 4.2 and 4.3; X = H, F, Cl, Me, CN, NO<sub>2</sub>, OMe, OEt, CHO) and the corresponding phenylferrocenes (4.4) has been investigated by  $^{13}\text{C}$  NMR spectroscopy and cyclic voltammetry [22]. The  $^{13}\text{C}$  NMR chemical shifts have been measured for a range of compounds containing vinylidene groups, including ferrocene analogues of chalcone and stilbene. The results were used to determine the



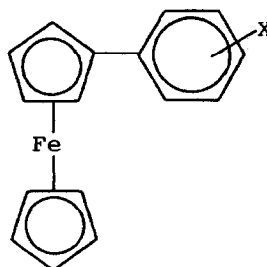
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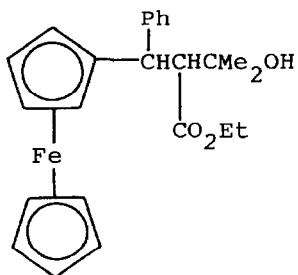
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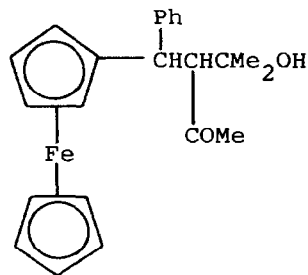
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polarizations and polarization ranges for the vinylidene groups. The effects of substituents were discussed [23].

Structural features of several 1,1'-di- and 1,2,1'-tri-substituted ferrocenes have been correlated with the  $^{57}\text{Fe}$  NMR chemical shifts [24]. Acid-base interactions between phenols and carbonylferrocenes have been investigated by IR spectroscopy. The strength of the interaction was related to the Hammett constant of the phenol [25]. Infrared and NMR spectroscopy have been used to investigate intramolecular hydrogen bonding in ferrocene containing  $\beta$ -hydroxycarbonyl compounds. Evidence of an intramolecular  $\text{Fe}\cdots\text{HO}$  hydrogen bond was found in a dilute solution of the alcohol [RS(or SR)-(4.5)]. In the solid state only  $\text{OH}\cdots\text{OH}$  and  $\text{OH}\cdots\text{O}=\text{C}$  bonds were found. In the RR (or SS) diastereoisomer and in the alcohol (4.6)



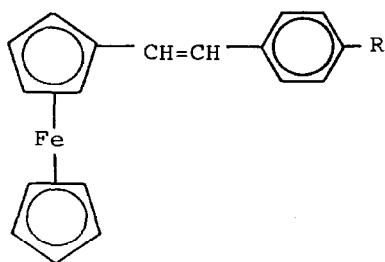
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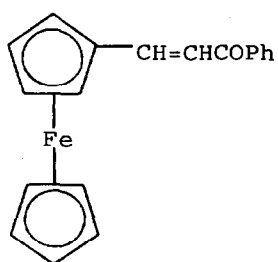
4.6

there was evidence for an  $\text{Fe} \cdots \text{HO}$  hydrogen bond [26]. The electronic absorption spectra of the charge-transfer complexes formed between ferrocene and the polyhalohydrocarbons,  $\text{CBr}_4$ ,  $\text{CClBr}_3$ ,  $\text{CHBr}_2\text{CH}_2\text{CHBrMe}$ ,  $\text{CClBr}_2\text{CH}_2\text{CH}(\text{Br})\text{Me}$ ,  $\text{CClBr}_2\text{CH}_2\text{CHBr}(\text{CH}_2)_3\text{Me}$  and  $\text{CCl}_2\text{BrCH}_2\text{CHBr}(\text{CH}_2)_2\text{CH}=\text{CH}_2$  have been recorded, assigned and discussed [27].

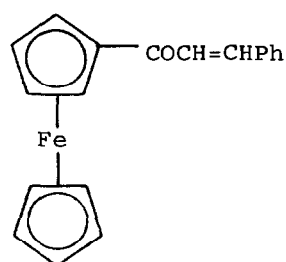
The vapour-phase far-UV absorption spectrum of ferrocene has been recorded and interpreted. It was considered that Rydberg bands originating with metal 3d and ligand  $\pi$ -orbitals made a



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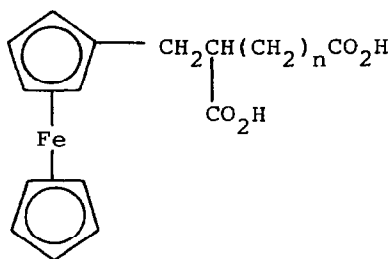


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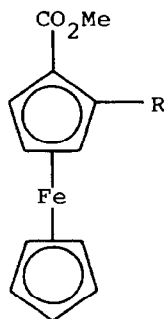


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contribution to the spectra and this interpretation was compared with the conventional charge transfer assignments [28]. Fourteen 1-aryl-2-ferrocenylethylenes (4.7) have been prepared from substituted phenylacetic acids or by the Wittig reaction. The effect of substituents on the electronic absorption spectra, especially the band at 440nm, has been examined [29]. The electronic absorption spectra of the chalcone analogues (4.8 and 4.9) have been measured and interpreted. The absorption band between 450 and 540nm showed a good correlation with the Hammett substituent constants for the ferrocene (4.8). The correlations were less good with the compound (4.9) [30]. Comparisons were made with the corresponding chalcones and stilbenes [31]. The mass spectra of a series of (1-ferrocenyl-alkyl)phenyl sulphides have been recorded. The fragment peak



4.10



4.11

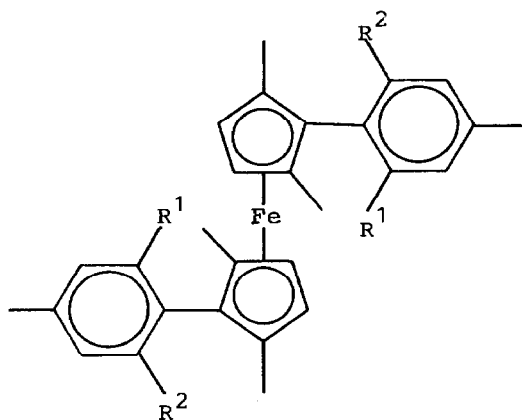
$(C_5H_5FeSPh)^{+\bullet}$  was observed in the spectra of all the compounds [32].

Low resolution mass spectra of some mono- and di-substituted ferrocenes, for example, the acids (4.10;  $n = 1, 2$ ) and the esters (4.11;  $R = CHO, CN$ ), have been recorded and interpreted [33]. Some collisionally induced dissociation experiments have been carried out by Fourier transfer mass spectrometry of benzoylferrocene, methylbenzoate and trifluoroacetic acid [34]. Monosubstituted ferrocenes with an  $\alpha$ - or  $\beta$ -olefinic bond have been examined by mass-analyzed ion kinetic energy spectrometry. Important fragmentation pathways gave the  $[M-H_2O]^{+\bullet}$  and

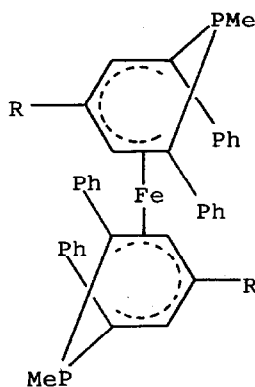


$[M-C_5H_5]^+$  ions [35]. The He(I) photoelectron spectra of [3]-ferrocenophane and 6,8-dimethyl-7-oxa[3]ferrocenophane have been recorded and interpreted. The ionization potentials and band shapes of the ligand  $\pi$ -levels were affected by the presence of the methylene bridge [36]. Phase transitions in azaferrocene have been investigated by X-ray powder diffraction in the temperature range 78 to 295K. Annealing at 220K for several hours converted the undercooled metastable monoclinic phase into two stable phases. First order transitions between the stable phases and the disordered monoclinic phase occurred at  $277 \pm 2$  and  $287 \pm 2$ K [37].

The ligand 2-(2-ethyl-4,6-dimethylphenyl)-1,3-dimethylcyclopentadiene has been converted to a mixture of two isomeric hexa-substituted ferrocenes. The exo, exo (4.12;  $R^1 = \text{Me}$ ,  $R^2 = \text{Et}$ ) and endo, endo (4.12;  $R^1 = \text{Et}$ ,  $R^2 = \text{Me}$ ) configurations were



4.12



4.13

determined by X-ray crystallography  $^1\text{H}$  NMR chemical shifts of the methyl groups suggested that ferrocene exhibited a diamagnetic anisotropy in the same way as benzene [38]. Pulse radiolysis has been used to determine the rates of reaction of ferrocenylalkylcarboxylates with the hydroxyl radical. The reaction was also investigated using a competition method with the thiocyanate ion. Discrepancies between the results obtained by the two techniques were explained by reaction of  $\text{SCN}^\bullet$  and  $\text{SCNOH}^-$  with the ferrocene compounds [39]. Moessbauer spectroscopy has been used to study the crystal-plastic phase

transition of formylferrocene at 319-329K [40]. Iron bis- ( $\eta^5$ -phosphinine) complexes (4.13; R = Me, CMe<sub>3</sub>) have been prepared from lithiated phosphinines and iron(II) chloride. Moessbauer isomer shifts were similar to those for ferrocenes while quadrupole splittings were close to those for "open ferrocene" complexes [41].

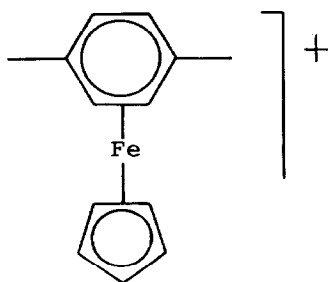
A Moessbauer spectroscopic study has been carried out on vinylferrocene, poly(vinylferrocene) and an acrylonitrile-vinylferrocene copolymer. The data was used to detect hindered side group motions below the glass transition temperature [42]. Moessbauer parameters, redox potentials and <sup>13</sup>C NMR shifts have been measured for a series of mono- and di-ketone derivatives of [3]-, [4]- and [5]-ferrocenophanes. Correlations between the effect of the carbonyl group and the molecular structure were discussed [43]. Electron-transfer reactions between ferrocene and octahedral cobalt(III) complexes in the presence of cationic, nonionic and ionic micelles have been studied by a stopped flow technique. The rate and equilibrium constants were consistent with a model in which ferrocene was partitioned between the aqueous and micellar pseudophase [44]. Rate constants and activation parameters have been determined for the oxidation of ferrocene with tris(1,10-phenanthroline)cobalt(III) in t-butanol-water and acetone-water mixtures [45].

A study of the effect of pressure on the electrical conductivity of ferrocene suggested that a slow, continuous phase transition occurred under pressure at room temperature [46]. A kinetic study of the solution thermolysis of ferrocenylsulphonyl azide revealed unusual activation parameters which were attributed to competing reactions by radical and singlet sulphonylnitrene pathways [47]. The heats of formation of 1:1 complexes of ferrocene and several other compounds with various electron acceptors have been determined calorimetrically. The relationship between the heat of mixing and the complex forming capacity of the compounds was discussed. An order of relative acceptor strengths was proposed as:  
 $\text{SO}_2\text{Cl} < \text{COCl}_2 < \text{PCl}_3 < \text{SO}_2$  [48] (sic).

##### 5. ELECTROCHEMISTRY AND PHOTSENSITIVE ELECTRODES

Cyclic voltammetric studies have been carried out on chloro-, bromo- and iodo-ferrocene in ethylene glycol dimethylether at

-45°. Electrochemical reduction caused cleavage of the carbon-halogen bonds [49]. The effect of changes in the composition of the electrical double layer on the standard rate constants for metallocene redox couples has been studied at the mercury electrode in dimethylformamide and acetonitrile. Cationic couples  $(\eta\text{-C}_5\text{H}_5)_2\text{M}^{+/0}$ , where  $\text{M} = \text{Fe}, \text{Mn}, \text{Co}$ , did not change the rate constants when the double layer structure was altered by changing the central metal atom  $\text{M}$ . However the rate constants



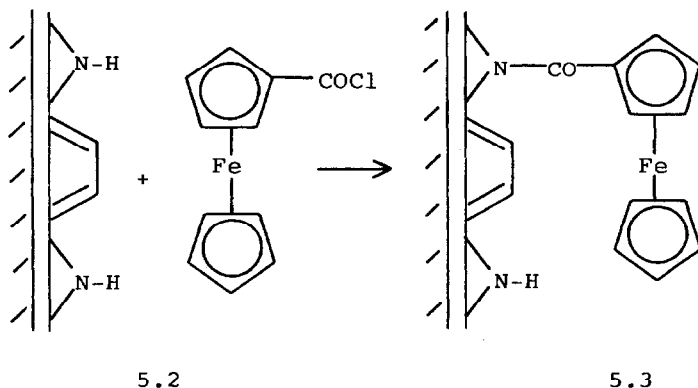
5.1

were sensitive to double layer changes when anionic couples  $(\eta\text{-C}_5\text{H}_5)_2\text{M}^{0/-}$  were used. The observations were interpreted in terms of differences in charge distribution between the central metal atom and the cyclopentadienyl ligands in cationic and anionic couples [50]. The chemistry of polymer-bound binuclear complexes as surface reactants on semiconductor electrodes in photoelectrochemical cells has been the subject of a review. Ferrocene, ferrocenophane and chromium-ferrocene complexes were included [51].

As part of a study on photoanodes, rotating ring-disc electrode experiments confirmed the regenerative behaviour of the  $n\text{-CdSe}$  and  $n\text{-InP}$  electrodes with the ferrocenemethanol-ferrocenium methanol couple in lithium perchlorate/methanol solution [52]. Semiconductor/liquid junctions derived from films of amorphous hydrogenated silicon have been investigated in methanol. The silicon anodes in 0.02M ferrocene/0.5mM ferrocenium ion/1.5M lithium perchlorate/methanol were irradiated

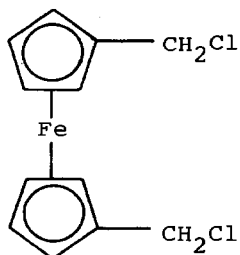
by long and short wavelength radiation and the quantum yields were determined. Photovoltages for the acetylferrocene/acetylferrocenium ion system were some of the highest reported for amorphous hydrogenated silicon anodes [53]. The design of efficient semiconductor/liquid junction interfaces has been investigated in nonaqueous solvents. The composition of the semi-conductor was varied and related with changes in interface properties at a ferrocene/ferrocenium/ $\text{Et}_4\text{NBF}_4/\text{MeCN}$  interface [54].

Photolysis of the cation (5.1) in methyl cyanide at  $-40^\circ$  produced the cation  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3\text{CN})_3]^+$  and when the solution was warmed to room temperature ferrocene and  $[\text{Fe}(\text{CH}_3\text{CN})_6]^{2+}$  were produced. A rotating photoelectrochemical electrode was used to study the  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3\text{CN})_3]^+$  intermediate [55]. Electrodes were prepared by the electro-deposition of polypyrrole-fluoroborate films on optically transparent iridium-tin oxide on glass. The coated electrodes (5.2) were treated with ferrocenylcarbonyl chloride to give a ferrocene functionalized electrode (5.3). Cyclic voltammetry of these films indicated two different redox processes corresponding to the ferrocene and polypyrrole moieties [56]. Electroactive polymer films on



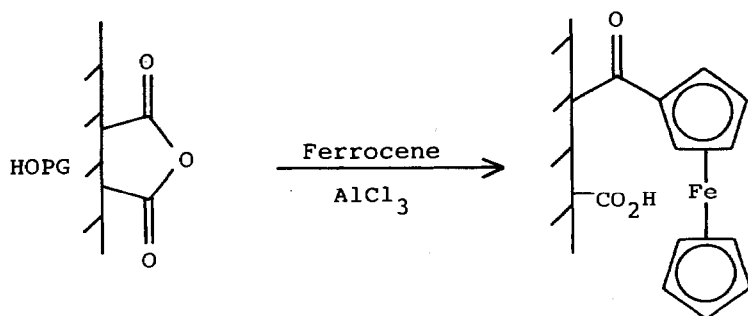
electrode surfaces have been prepared by electroreduction of 1,1'-bis(chloromethyl)ferrocene (5.4) at a glassy carbon electrode. An electrochemical study of these films showed that they behaved as a selective charge-transport mediator for the reduction of ferrocene redox couples and for the oxidation of

the couples in the ferrocenium state[57]. Friedel-Crafts alkylation and acylation of ferrocene via lactones (5.5) anhydrides, acids (5.6) and alcohols on the edges of highly ordered pyrolytic graphite (HOPG) electrodes has been carried out. These electrodes were investigated via cyclic voltammetry and the results were consistent with the ferrocene being attached to the HOPG surface in the manner shown (5.5, 5.6) [58].

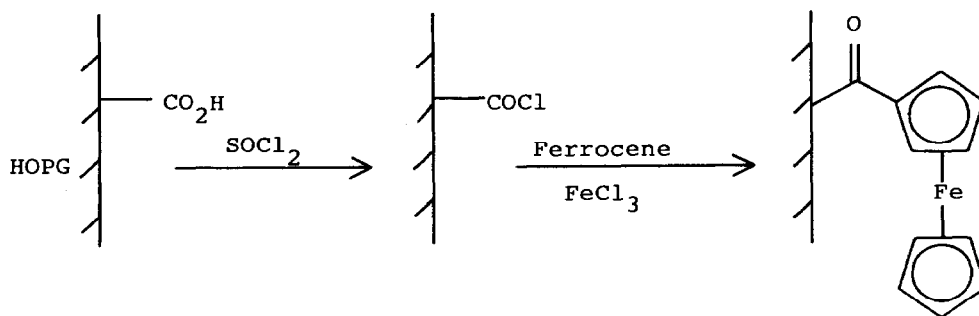


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The temperature dependence of the voltammetric response of thin electroactive polymer films has been investigated with poly(vinylferrocene) modified electrodes. The solvent swelling of the films was an important factor in determining the size of the response [59]. The rates of heterogeneous charge transfer to ferrocene groups in poly(vinylferrocene) coated electrodes have been measured under semi-infinite conditions. The rate constants ( $k^{\circ}$ ) were  $10^{-4} \geq k^{\circ} \geq 10^{-5} \text{ cm s}^{-1}$  and were some two orders of magnitude smaller than those measured for similar species in homogeneous solution [60]. The electrochemical properties of platinum and glassy carbon electrodes coated with a vinylferrocene, N-vinylcarbazole copolymer have been investigated in, dichloromethane, acetonitrile and aqueous solutions. Apparent diffusion coefficients in the polymer film were determined by cyclic voltammetry and chronoamperometry [61]. The influence of the experimental conditions on the cyclic voltammetric response has been investigated using poly(vinylferrocene) coated electrodes [62].



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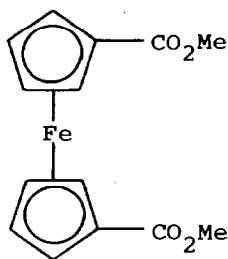


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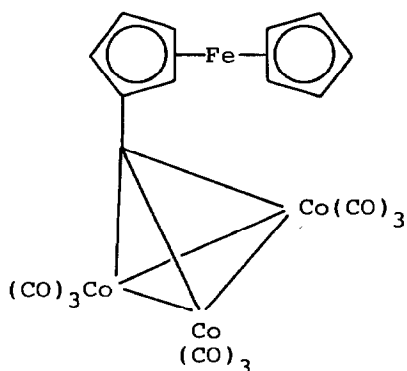
A glassy carbon electrode has been coated with a plasma-polymerized vinylferrocene film and used to determine ascorbic acid [63]. The styrene-tetraphenylarsonium *p*-styrenesulphonate-vinylferrocene copolymer has been studied by cyclic voltammetry as an electroactive cation exchanger. When the copolymer was coated on electrodes the number of ferrocene-ferrocenium redox waves was dependent on the number of sulphonate groups. In the reduced form the copolymer film behaved as a cation exchanger while in the oxidized form it behaved as a counter ion for sulphonate groups [64]. The ferrocene-ferrocenium couple in Nafion coated electrodes behaved differently from other cationic couples in the polymer. It showed a large negative shift in half wave potential and two oxidation waves for ferrocene. This behaviour was rationalized in terms of differences between

the oxidized and reduced forms in binding to the polymer [65].

Electrodes have been modified by a thick crystalline deposit of an organic compound such as phenazine; however, only those molecules near to the electrode surface were electroactive. A redox couple, such as ferrocenecarboxylic acid-ferrocenium carboxylic acid, in which both forms were soluble increased the amount of the deposit that was electroactive [66]. An electrode coated with a hydrophobic liquid membrane has been used to distinguish between organic and inorganic depolarizers. Thus the cyclic voltammogram of ferrocene carboxylic acid showed a reversible redox wave while hexacyanoferrate(II) showed no wave in the region around its equilibrium potential [67]. Poly(styrene sulphonate) has been used as a matrix for the mediated oxidation of ferrocene-1,1'-disulphonate (FDS) in acetonitrile with electrostatically bound tris(2,2'-bipyridine)osmium(III). Current-voltage curves for the oxidation of the FDS were obtained [68]. Zinc bis(0,0-diethyl phosphorodithioate-S,S')  $[(EtO)_2PS_2]_2Zn$  and zinc bis[0,0-bis(1-methylethyl)phosphorodithioate-S,S']  $\{[(CH_3)_2CH]_2PS_2\}_2Zn$  were irreversibly oxidized at a glassy carbon electrode at a potential of +1.5V. This charge-transfer process was irreversible due to a fast homogeneous reaction that produced the corresponding disulphides. In the presence of the ester (5.7), which behaved as a mediator, the oxidation occurred at +0.9V and the disulphides were obtained in high yields [69].

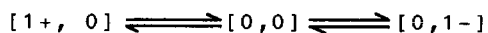


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5.8

Ferroceneboronic acid has been used as the mediator of the anodic reaction in the enzyme-catalyzed electrochemical oxidation of *p*-cresol to *p*-hydroxybenzaldehyde [70]. The use of platinum microelectrodes of radius  $< 1\mu\text{m}$  for electrochemical investigations in low temperature glasses of nonaqueous solvents such as methylcyanide and acetone has been investigated. Data was presented for the oxidation of ferrocene in these very high resistance media [71]. The ferrocene-tricobalt carbon cluster compound (5.8) and its derivatives have been characterized as multiple redox species by electrochemical and spectroscopic techniques. The cluster was shown to be a reduction centre while the ferrocenyl group formed the positive site. Thus the reversible redox series:



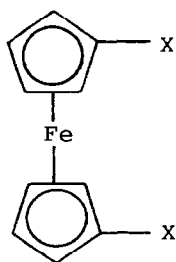
was established. The  $[1+,1+]$  species was accessible when an additional Lewis base was coordinated to the cluster. The experimental results indicated a weak interaction between the redox sites [72].

The ferrocene-ferrocenium ion couple has been proposed as a reference redox system for use in tetrahydrofuran on the basis of polarographic and cyclic voltammetry tests [73]. Rate constants and activation parameters have been determined electrochemically for the electron exchange between bis( $\eta$ -benzene)-chromium and five metallocene couples in non-aqueous solvents. The results indicated that conventional transition-state theory may not apply to electron-transfer reactions when the free-energy barrier arose from solvent reorganisation [74].

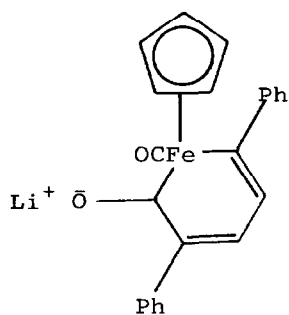
## 6. PREPARATIONS OF FERROCENE

The reaction of iron atoms with cyclopentadiene in an argon matrix at 14K gave cyclopentadienyliron hydride. No evidence was obtained for the formation of ferrocene under these conditions [75]. Ferrocene has been prepared electrochemically from iron and cyclopentadiene. It was a one step process where ferrocene was formed directly by dissolution of an iron anode in the presence of bis(cyclopentadiene) in an electrolyte solution of sodium bromide in dimethylformamide [76]. Iron(II) acetylacetonate combined with lithium pentamethylcyclopentadienide to form  $(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\text{acac})$  which was converted to  $(\eta\text{-C}_5\text{Me}_5)\text{-}$

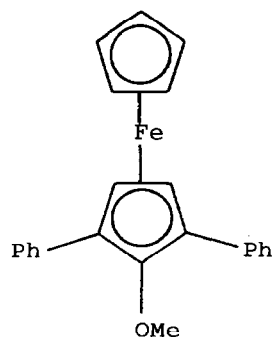




6.1



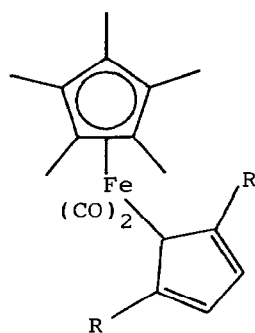
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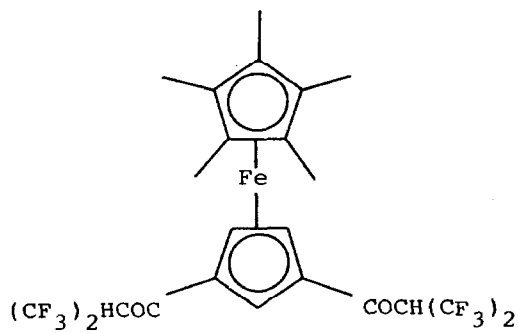
6.3

$\text{Fe}(\text{C}_5\text{H}_5)$  with sodium cyclopentadienide [77]. Reaction of  $(\eta\text{-cyclopentadienyl})\text{thallium}$  with  $N\text{-halosuccinimides}$  or iodine produced chloro-, bromo or iodo-cyclopentadiene. Treatment of these cyclopentadienes with thallium(I) ethoxide gave the corresponding  $(\eta\text{-halocyclopentadienyl})\text{thallium}$  compounds. These compounds were used in the preparation of the 1,1'-disubstituted ferrocenes (6.1;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and other organometallic derivatives [78].

Reaction of  $(E,E)\text{-1,4-dilithio-1,4-diphenyl-1,3-butadiene}$  with  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  produced the unstable ferrabenzene intermediate, (6.2). Treatment of this intermediate with  $(\text{CH}_3)_3\text{OBF}_4$



6.4



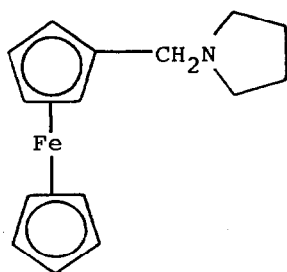
6.5

resulted in reductive elimination, loss of a terminal carbonyl and methylation to give 1,3-diphenyl-2-methoxyferrocene (6.3) [79]. Reaction of  $(\eta\text{-Me}_5\text{C}_5)\text{Fe}(\text{CO})_2\text{I}$  with silver tetrafluoroborate, cyclopentadiene and triethylamine produced the  $\eta^1$ -cyclopentadiene complex (6.4; R = H). Treatment of this latter complex with the ketene  $(\text{F}_3\text{C})_2\text{C}=\text{CO}$  gave the ring addition product [6.4; R =  $\text{COCH}(\text{CF}_3)_2$ ] which lost two molecules of carbon monoxide on heating to give the corresponding ferrocene (6.5) [80].

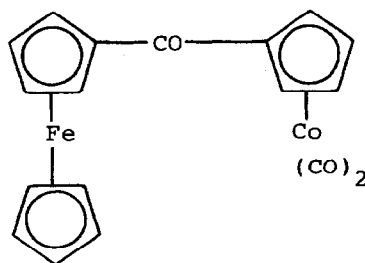
## 7. REACTIONS OF FERROCENE

The formation of an electron donor-acceptor complex between ferrocene and tetranitromethane has been investigated as a function of solvent and concentration [81]. Aryl, alkyl, carbonyl, carboxyl and haloalkyl groups have been introduced into ferrocene and ruthenocene by photochemical substitution. Charge transfer complexes formed between the metallocene and a halogenated compound were implicated as intermediates. The photoethoxycarbonylation of thiophene, benzothiophene, azulene and naphthalene was catalyzed by ferrocene derivatives [82]. Pyrrolidinylmethylferrocene (7.1) has been obtained directly from ferrocene by treatment with pyrrolidene and formaldehyde [83]. Treatment of ferrocene with butyllithium in the presence of tetramethylethylenediamine (TMEDA) gave a red solid of stoichiometry  $[(\eta\text{-C}_5\text{H}_4\text{Li})_2\text{Fe}]_3[\text{TMEDA}]_2$ . The compound was characterized by X-ray crystallography and contained lithium in one type of 4-coordinate environment and in two types of 3-coordinate environment [84].

The gas phase reaction of ferrocene with organomercury compounds, for example,  $\text{Me}_2\text{Hg}$  and  $\text{Et}_2\text{Hg}$ , has been studied. The mercury compounds underwent radical decomposition and homolytic substitution of the ferrocene occurred. Similar reactions in the liquid phase were studied [85]. Ethylferrocene has been formed in the pyrolysis of diethylzinc with ferrocene [86]. The reaction of ferrocene with  $(\eta\text{-chloroformylcyclopentadienyl})\text{-dicarbonylcobalt}$  in the presence of aluminium chloride produced the bimetallic product (7.2) [87]. Ferrocene and nickelocene have been attacked by butadiene and isobutene complexes of iron, cobalt and nickel in the gas phase to form mixed metal metallocenes  $[\text{M}^1\text{M}^2(\eta\text{-C}_5\text{H}_5)_2]^+$ , where  $\text{M}^1, \text{M}^2 = \text{Fe}, \text{Ni}, \text{M}^1 = \text{Co}$ . These



7.1



7.2

intermediates underwent metal switching and condensation with ferrocene and nickelocene [88].

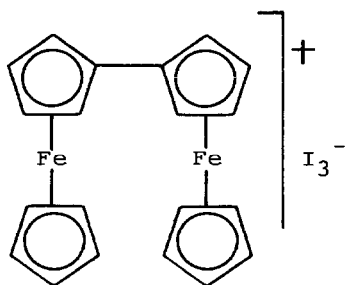
#### 8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

X-ray crystallography, Moessbauer spectroscopy and differential scanning calorimetry have been used to demonstrate that lattice dynamics control the intramolecular electron transfer in mixed-valence biferrocenes such as biferrocenium triiodide (8.1) [89]. X-ray crystallography and Moessbauer spectroscopy have been used to investigate the rate of intramolecular electron transfer in mixed-valence biferrocenium triiodides (8.2). The unsubstituted complex (8.2; R = H) showed different Moessbauer spectra depending on crystal size and the history of the sample with the ratio of delocalized to localized molecules varying from  $\sim 0$  to  $\sim 1$  at 300K. However at 375K average-valence behaviour was observed. X-ray crystallographic results for the dibutyl compound (8.2; R = Bu) were temperature dependent with the two halves of the cation inequivalent at 150K, at higher temperatures the butyl group was dynamically disordered. The bibenzyl salt (8.2; R = CH<sub>2</sub>Ph) showed valence localization at 300K which charged to valence delocalization on crystallization. It was concluded that solid state dynamics controlled the electron transfer rates [90].

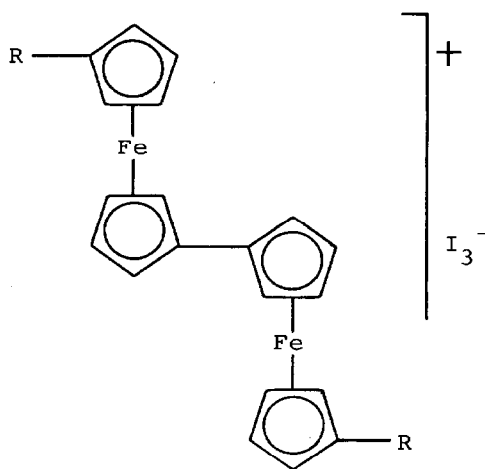
Electron transfer self-exchange reactions in ferrocene-ferrocenium and in other metallocenes has been studied in the gas-phase by Fourier transform ion cyclotron resonance mass

spectrometry. The results were consistent with a small barrier to self-exchange in which the free energy associated with the reorganization of the solvent was predominant in solution [91]. Conditions for the preparation of ferrocenium tetrachloroferrate (III) free from diferrocenium salts have been examined. IR, UV, Moessbauer and photoelectron spectra have been obtained for the purified complex. The low measured magnetic moment indicated weak inter- or intra-molecular antiferromagnetic interaction in the crystal [92]. A kinetic study has been made of the electron transfer reactions between aquoiron(III) and ferrocene or alkylferrocenes in the presence of cationic (CTAN) and non-ionic (Triton X-100) micelles at 20°C. The reaction was inhibited to the same extent by the two surfactants for a given ferrocene compound, but alkylation had a marked effect on the rate [93].

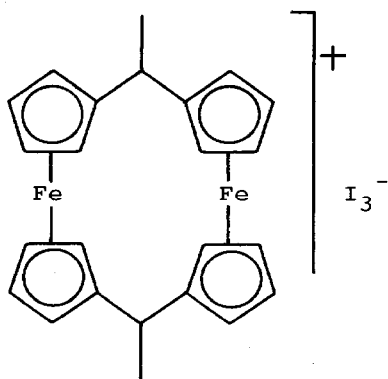
The ferrocenium cation has been used as an oxidizing agent to convert the neutral dinuclear complexes  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ ,



8.1



8.2



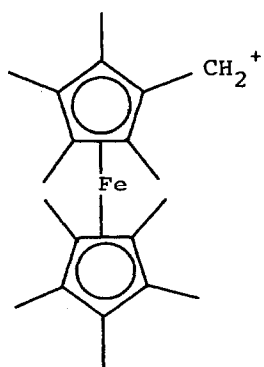
8.3

$\text{Co}_2(\text{CO})_8$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{NiCO}]_2$  in the presence of triphenylphosphine to the cations  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PPh}_3]^+$ ,  $[\text{trans-Co}(\text{CO})_3\text{-}(\text{PPh}_3)_2]^+$  and  $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{PPh}_3)_2]^+$  in high yield [94]. The oxidation of ferrocene by different amounts of iodine has been investigated. Iodine to ferrocene ratios up to and including 1.5 produced the salt  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+\text{I}_3^-$ . Iodine to ferrocene ratios of 2-15 gave mixtures of polyiodides  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}\cdot\text{I}_x$ , where  $x = 4-10$ , and distinct compounds ranging in composition from  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}\cdot\text{I}_4$  to  $(\eta\text{-C}_5\text{H}_5)_2\text{Fe}\cdot\text{I}_{7.5}$  were isolated [95]. The mechanism of oxidation of ferrocene, cobaltocene and nickelocene by  $\text{RNO}_2\text{-HBF}_4\cdot\text{Et}_2\text{O}$ , where  $\text{R} = \text{Me}, \text{Pr}, \text{Ph}$ , to give the corresponding metallocenium tetrafluoroborate salts has been investigated. In the reaction  $[\text{RNO}_2\text{H}][\text{BF}_4]$  was formed initially and this oxidized the metallocene in the presence of  $\text{H}^+$  to give the metallocenium ion,  $\text{RNO}$  and  $\text{H}_2\text{O}$  [96]. The molecular and electronic structure of the [1.1]ferrocenophanium salt (8.3) has been investigated by X-ray crystallography and Moessbauer spectroscopy. The two metallocene groups were not equivalent, one corresponded to  $\text{Fe}(\text{II})$  and the other to  $\text{Fe}(\text{III})$ . The valence-localized character of the species was supported by magnetic susceptibility, EPR and IR evidence [97].

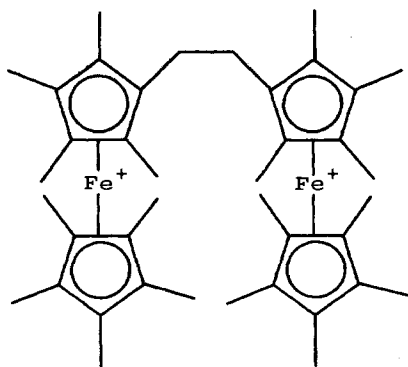
### 9. FERROCENYL CARBENIUM IONS

Conversion of the diamagnetic nonamethylferrocenylcarbenium ion (9.1) to the paramagnetic bis(nonamethylferroceniumyl)-ethane ion (9.2) has been studied by NMR spectroscopy in solution and in the solid phase. The nature of the anions present and the aggregate state of the sample influenced the rate of conversion and the reaction proceeded through an intermediate paramagnetic nonamethylferrocenium cation [98]. Protonation of the ferrocenyl-alkyne (9.3) in trifluoroacetic acid- $\text{SO}_2\text{ClF}$  generated the  $\alpha$ -ferrocenyl-vinyl cation (9.4).  $^{13}\text{C}$  NMR spectroscopy indicated significant charge delocalization into the ferrocenyl group of this species. The spectroscopic data was in accord with a linear sp-hybridized vinyl cation [99].

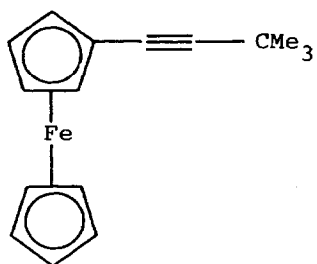
The hydroxyl group in the ferrocenylacetylenes (9.5;  $\text{R} = \text{H}, \text{Me}$ ) has been attacked by  $\text{HBF}_4$  and  $\text{HClO}_4$  to give onium salts (9.6;  $\text{R} = \text{H}, \text{Me}$ ;  $\text{X} = \text{BF}_4, \text{ClO}_4$ ) [100]. Several (2-ferrocenylethyl)methyl ethers (9.7;  $\text{X} = \text{OH}, \text{OMe}, \text{OPr}^i, \text{SCH}_2\text{CO}_2\text{H}, \text{N}_3$ ) have been prepared from the 1-ferrocenyl-2-methoxy-ethylion ion by



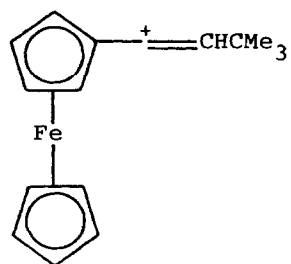
9.1



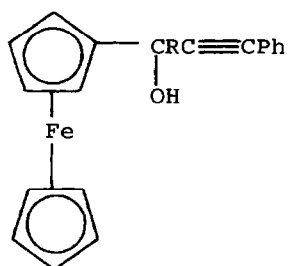
9.2



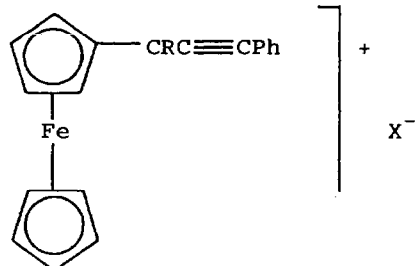
9.3



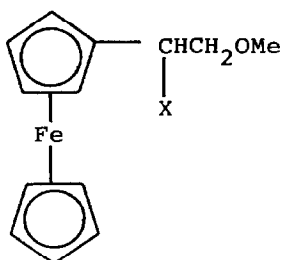
9.4



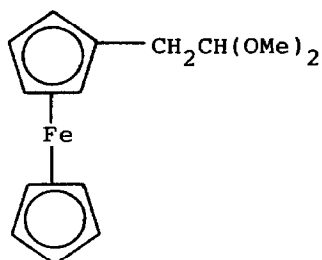
9.5



9.6



9.7



9.8

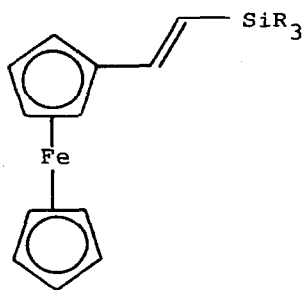
treatment with the appropriate nucleophile. The alcohol (9.7; X = OH) was attacked by methanol and hydrochloric acid to give the dimethyl acetal of ferroceneacetaldehyde (9.8) [101].

## 10. FERROCENE CHEMISTRY

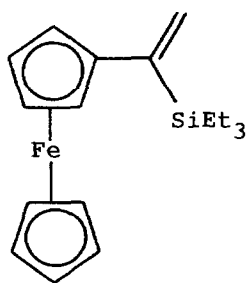
### (i) Derivatives containing other metals (metalloids)

The hydrosilylation of ferrocenylacetylene by the silanes  $R_3SiH$ , where  $R = Et, Ph$ , in the presence of Speiers catalyst has been studied. The reaction proceeded with high stereospecificity to give the corresponding trans-isomers (10.1). Triphenylsilane afforded only the  $\beta$ -adduct (10.1,  $R = Ph$ ) whereas triethylsilane produced an 80:20 mixture of the  $\beta$ -adduct (10.1;  $R = Et$ ) and the  $\alpha$ -adduct (10.2) [102]. The condensation of lithioferrocene with chloromethylphenylsilane produced ferrocenylmethylphenylsilane which was converted to the chlorosilane (10.3) by treatment with palladium(II) chloride. Reaction of the chlorosilane (10.3) with  $LiC\equiv CR$ , where  $R = Ph, SiEt_3, SiPh_3$ , gave the corresponding ferrocenylsilylethyne (10.4). The condensation of the chlorosilane (10.3) with  $R_2Si(C\equiv CLi)_2$ , where  $R = Ph, Et$ , produced the diferrocenyl compound (10.5) [103]. The diacetylenic derivative (10.6) was prepared similarly [104].

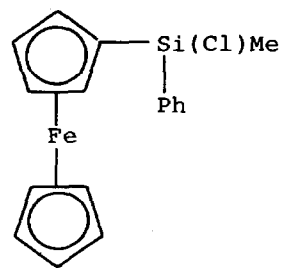
Ferrocenylsilanes have been prepared by treatment of chlorosilanes with 1-ferrocenylethanol in the presence of triethylamine. Thus the chlorosilanes,  $RSiCl_3$  gave the products (10.7;  $R =$



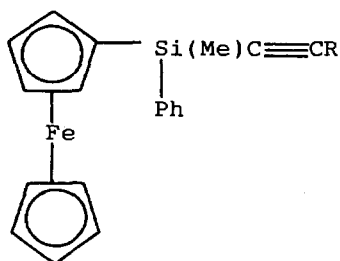
10.1



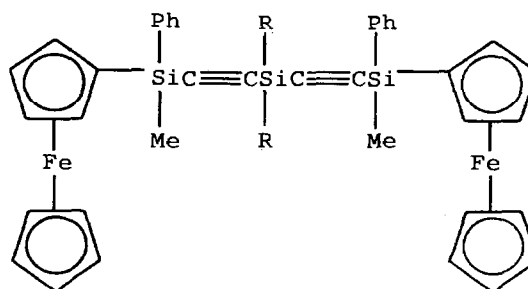
10.2



10.3



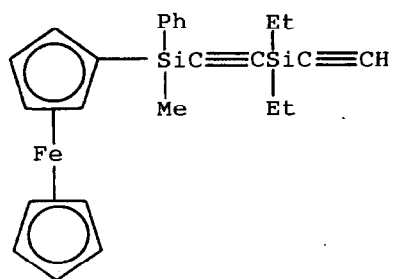
10.4



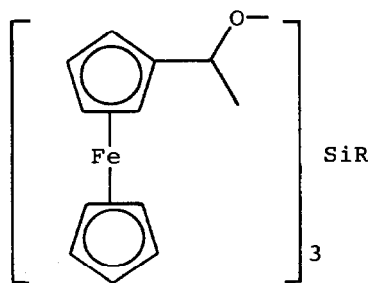
10.5

$\text{CH}_2\text{CH}_2\text{F}$ ,  $\text{CH}_2\text{CH}_2\text{CN}$ ,  $\text{CH}=\text{CH}_2$ ) [105]. Phosphino- and diphosphino-ferrocenes have been prepared by treatment of lithioferrocenes and 1,1'-dilithioferrocene with chlorophosphines  $\text{ClPR}_2$ . Metal complexes were prepared using the phosphinoferrocenes, for example the bis(diphenylphosphine) (10.8), as ligands (L). The complexes  $\text{PdCl}_2\text{L}$ ,  $\text{NiX}_2\text{L}$  and  $[\text{RhL}(\text{norbornadiene})]\text{ClO}_4$  were characterized and the crystal and molecular structures of three complexes where  $\text{L} = (10.8)$  were determined [106]. The ferrocenyl-Wittig reagents (10.9;  $\text{R} = \text{Ph}$ , substituted Ph, 2-furyl, ferrocenyl) have been prepared from the corresponding ferrocene-methanol and triphenylphosphine. Benzaldehyde attacked the compound (10.9;  $\text{R} = \text{Ph}$ ) to give the diene (10.10) [107]. Reaction of 1,1'-dilithioferrocene-tetramethylethylenediamine with dichlorophenyl-phosphine, -arsine or -stibine in ethylene-glycol dimethylether produced a polymer that formed complexes



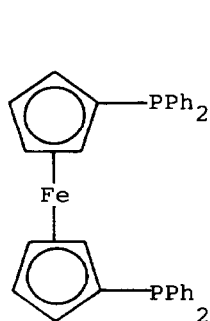


10.6

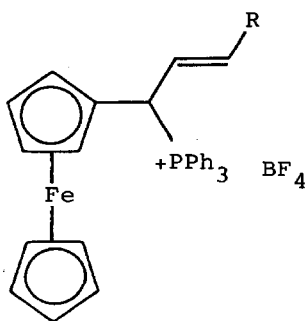


10.7

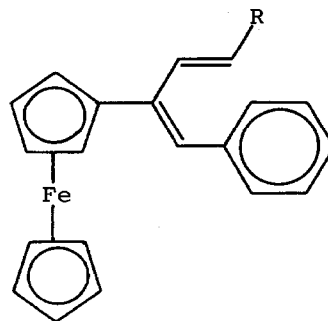
with Group VIII metals. Cobalt carbonyl in the presence of this polymer converted 1-hexene, in the presence of hydrogen and carbon monoxide at  $190^\circ$  under pressure into a mixture of hexane,  $C_7$  aldehydes and alcohols and heptyl formate [108].



10.8

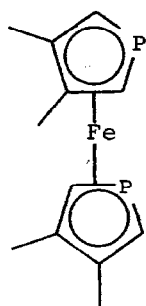


10.9

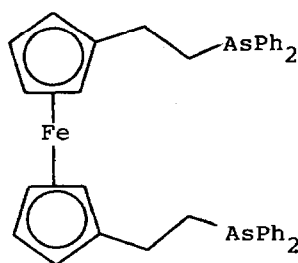


10.10

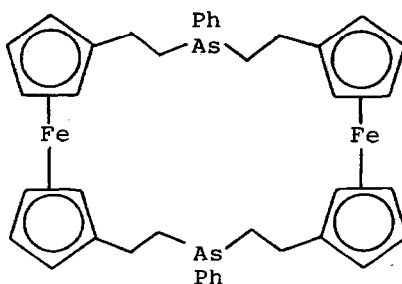
The diphosphaferrocene (10.11) underwent a reversible one-electron reduction in propylene carbonate. Metal complexes,  $M(CO)_5$ , where  $M = Cr, Mo, W$ , of the phosphoferrocene underwent similar reversible reductions but also showed irreversible reduction liberating the anion  $[M(CO)_5]^-$  [109]. The ferrocenyl-



10.11

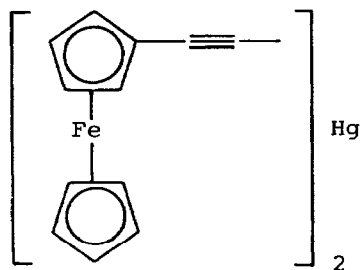


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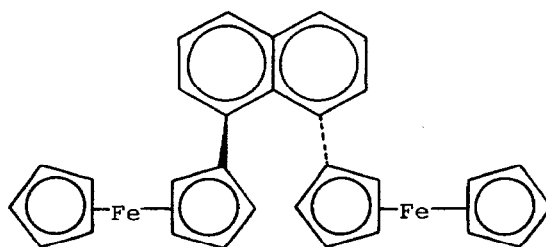


10.13

ethylarsines (10.12 and 10.13) have been prepared by reaction of the corresponding substituted cyclopentadienes with iron(II) chloride [110]. The reaction of ethynylferrocene with mercury(II) acetate in methanol has been investigated and the composition of the products was dependent on the reaction time. When the reaction was quenched immediately after the addition of the mercury(II) acetate, bis(ferrocenylacetylide)mercury (10.14) was obtained quantitatively. When the reaction was allowed to proceed for three days, acetylferrocene was obtained quantitatively. Intermediate reaction times gave several additional products [111]. Mercuration of ferrocene with mercury(II) acetate and trifluoro-



10.14



10.15

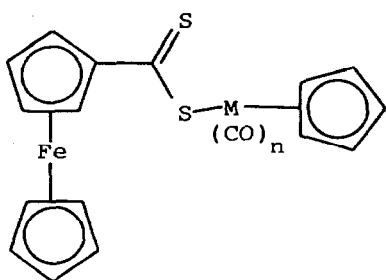
acetic acid gave either the mono- or 1,1'-di-mercuriacetates depending on the proportions of reagents [112].

The reaction of diferrocenyl- or dicymantrenyl-mercury with the elemental lanthanides samarium, europium or ytterbium produced the corresponding diferrocenyl- or dicymantrenyl-lanthanide [113]. The coupling of 1,8-diiodonaphthalene with ferrocenylzinc chloride in the presence of dichloro[1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) as the catalyst produced 1,8-diferrocenyl-naphthalene (10.15) with 94% selectivity. X-ray analysis showed that the naphthalene ring and bonds from the peri-carbon atoms to the  $\eta$ -cyclopentadienyl rings were distorted. The substituted  $\eta$ -cyclopentadienyl rings were rotated by approximately  $46^\circ$  from the perpendicular to the naphthalene ring [114]. Monodentate ferrocenedithiocarboxylato complexes (10.16;  $M = \text{Cr, Mo, W}$ ;  $n = 3$ ;  $M = \text{Fe, } n = 2$ ) have been prepared by treatment of the carbonylmetal cations,  $[(\eta\text{-C}_5\text{H}_5)_n\text{M}(\text{CO})_n\text{L}]^+$ , where  $n = 3$ ,  $M = \text{Cr}$ ,  $L = \text{MeCN}$ ,  $M = \text{Mo}$ ,  $L = \text{CH}_2\text{Cl}_2$ ,  $M = \text{W}$ ,  $L = \text{CO}$ ;  $n = 2$ ,  $M = \text{Fe}$ ,  $L = \text{MeCN}$ , with the ferrocenedithiocarboxylate anion. The complexes (10.18) were converted to chelate complexes by thermal decarbonylation. Similar reactions were carried out with the complexes  $[\text{M}(\text{CO})_5(\text{MeCN})]^+$ , where  $M = \text{Mn, Re}$  [115]. The ferrocene carbodithioateoxomolybdenum complexes (10.17;  $n = 1, 2$  and 10.18) have been prepared. The complex (10.18) underwent disproportionation in solution where it existed as an equilibrium mixture of the compounds (10.17;  $n = 1$  and 2). The cyclic voltammograms of the latter two complexes exhibited quasi-reversible couples arising from stepwise redox reactions of the molybdenum and the iron [116].

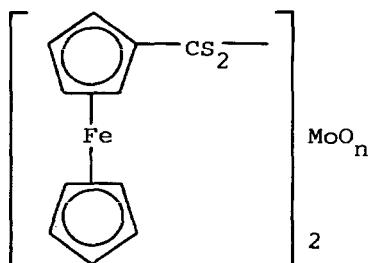
The reaction of the benzoylhydrazine derivative of formyl ferrocene with dioxobis[2,4-pentanedionato]molybdenum(VI) produced the complex (10.19). The structure of this complex was determined by X-ray analysis. The molybdenum atom had a distorted octahedral geometry with the two bidentate ligands coordinated through the oxygen and azomethine nitrogen atoms. The electrochemical properties of the complex were investigated [117]. The Fe-S and Mo-Fe-S cluster compounds  $\{\text{Fe}_4\text{S}_4[(\eta\text{-C}_5\text{H}_4\text{S})\text{Fe}(\eta\text{-C}_5\text{H}_5)]_4\}^{2-}$  and  $\{\text{Mo}_2\text{Fe}_6\text{S}_8\text{X}_3[(\eta\text{-C}_5\text{H}_4\text{S})\text{Fe}(\eta\text{-C}_5\text{H}_5)]_6\}^{3-}$ , where  $X = \text{EtS}$  or  $\text{MeO}$ , have been prepared as the tetraalkylammonium salts. The reduction potentials of these clusters were more negative than those containing benzenethiolate and it was concluded that ferrocene thiolate was a stronger

electron donor than benzenethiolate. The ability of the ferrocene containing clusters to catalyze the reduction of ethyne in water at pH 7 under controlled potential electrolysis conditions was investigated [118].

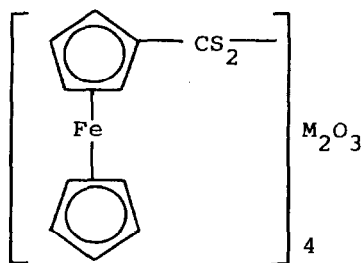
Transition metal carbene complexes with ferrocenyl substituents  $(\eta\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Mn}=\text{C}(\text{XPh})(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)$ , where X = S, Se, Te, have been prepared [119]. The crystal and molecular structure of the ferrocene carbene complex (10.20) has been determined by X-ray crystallography and the presence of a bridging ketenyl ligand confirmed [120]. Catalysts for the hydroformylation of olefins have been prepared from a ferrocene ligand such as 1,1'-bis(diphenylphosphino)ferrocene, a platinum compound such



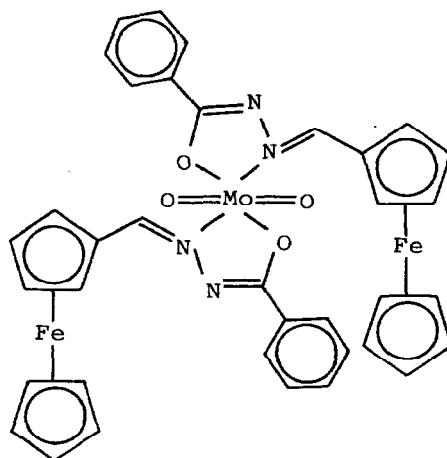
10.16



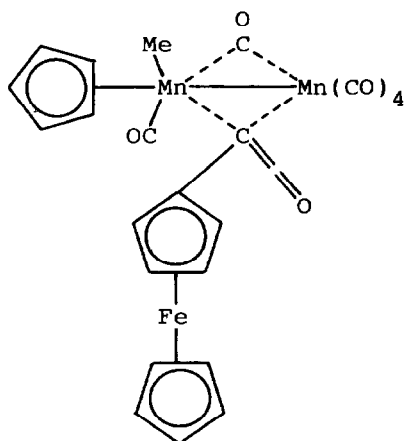
10.17



10.18



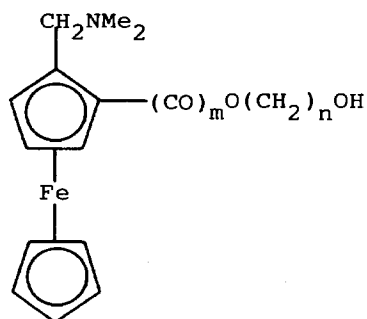
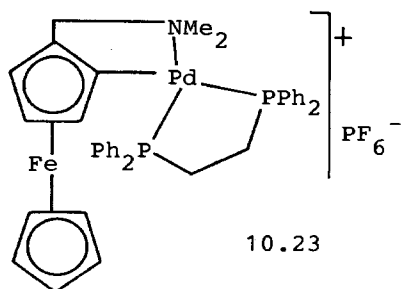
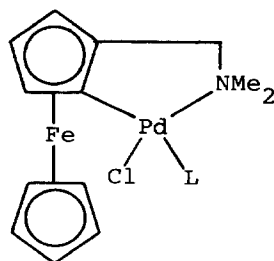
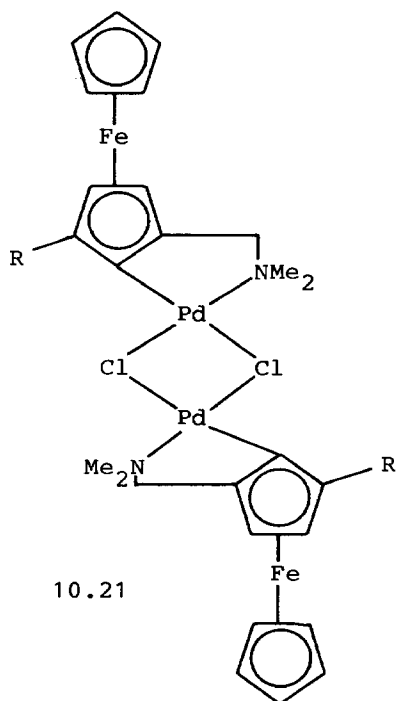
10.19



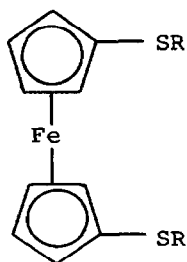
10.20

as the acetylacetonate and a group IVB metal halide such as tin(II) chloride [121]. Treatment of dimethylaminomethylferrocene with the tetrachloropalladate(II) anion resulted in intramolecular metallation to produce the complex (10.21; R = H). The chloride bridges in this complex were cleaved on treatment with a series of ligands L, where L = PR<sub>3</sub> (R = Ph, OPh, OMe, OEt), AsPh<sub>3</sub> or Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>-TlPF<sub>6</sub> to give the corresponding ferrocene derivatives (10.22 and 10.23) respectively [122]. Carbonylation of the dimethylaminomethylferrocene-palladium complex (10.21; R = H) with carbon monoxide in the presence of the diols HO(CH<sub>2</sub>)<sub>n</sub>OH, where n = 6, 10, produced the carbon monoxide insertion products [10.21; R = (CO)<sub>m</sub>O(CH<sub>2</sub>)<sub>n</sub>OH, m = 1, 2; n = 6, 10 and 10.24; m = 1, 2; n = 6, 10] [123].

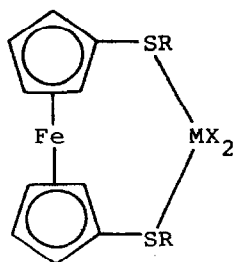
Lithiation of ferrocene and treatment with disulphides has given ferrocene sulphides (10.25; R = Me, CHMe<sub>2</sub>, CH<sub>2</sub>CHMe<sub>2</sub>, Ph, CH<sub>2</sub>Ph) which formed chelate complexes (10.26; M = Pd, Pt, X = Cl, Br) with palladium(II) and platinum(II) halides. The crystal and molecular structure of one complex (10.26; R = CH<sub>2</sub>CHMe<sub>2</sub>, M = Pd, X = Cl) has been determined by X-ray crystallography. The complex was fluxional in solution with the metal atom flipping from side to side of the Fe-S-S plane [124]. Copper(II) acetate combined with ferrocenecarboxylic acid in THF to give the antiferromagnetic complex tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II) (10.28). The



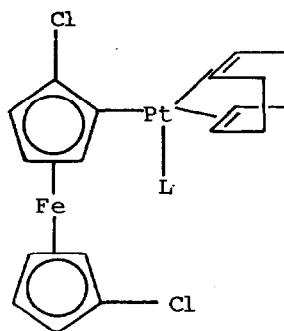
crystal and molecular structure has been determined by X-ray crystallography to show two copper(II) ions mutually linked by four carboxylate groups and with each copper ion coordinated to a THF ligand. Electrochemical oxidation and reduction revealed processes corresponding to the ferrocene-ferrocenium and copper(II)-copper(I) couples respectively [125]. Lithiated 1,1'-dichloroferrocene combined with (*cis*, *cis*-cycloocta-1,5-diene)diodoplatinum(II) to form the diferrocenyl platinum complex (10.27;  $L = (\eta\text{-C}_5\text{H}_4\text{Cl})\text{Fe}(\eta\text{-C}_5\text{H}_3\text{Cl})$ ) which was characterized by X-ray crystallography. The related complexes (10.27;  $L = \text{Cl}, \text{Br}, \text{I}, \text{Me}, \text{CH}_2\text{Ph}$ ) were also prepared [126].



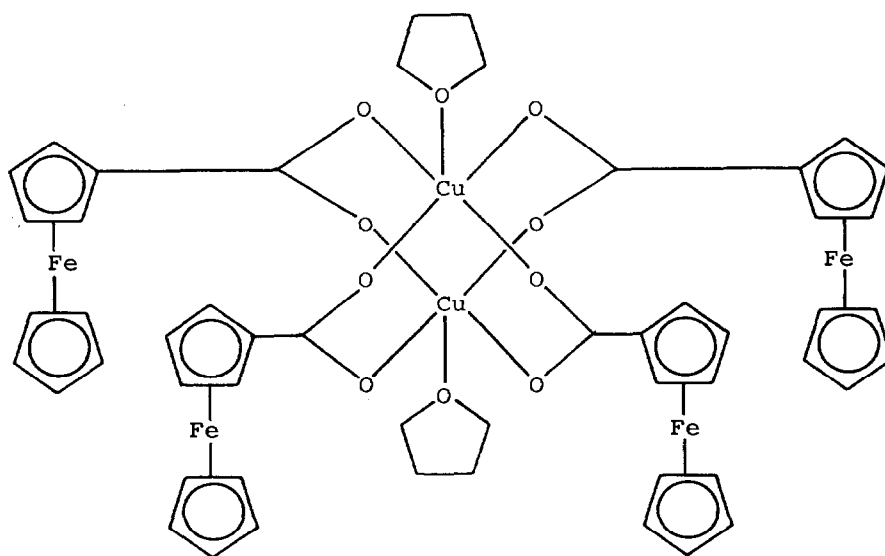
10.25



10.26



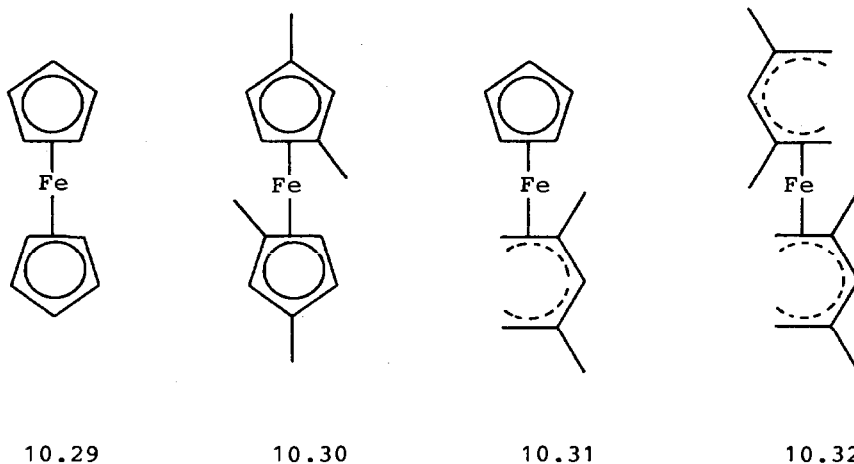
10.27



10.28

(ii) General Chemistry

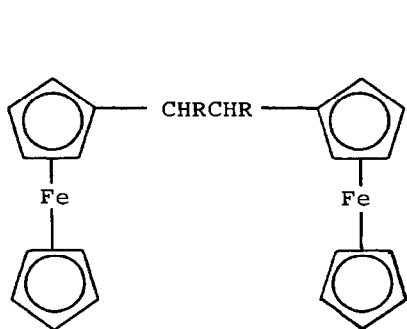
A series of "closed" "half-open" and "open" ferrocenes (10.29-10.32) have been compared by cyclic voltammetry and ESR spectroscopy. Sequential opening of the cyclopentadienyl rings caused a cathodic shift of the redox potential for the ferrocene-ferrocenium couple; an increase in chemical lability and a greatly decreased  $g$  anisotropy in the ESR spectra of respective radical cations. The results were interpreted on the basis of electronic structures as predicted by INDO MO calculations [127].



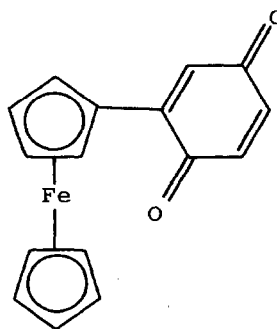
The rates of isotopic exchange of  $\eta$ -cyclopentadienyl ring protons in hexamethylferrocene and octamethylferrocene with  $\text{MeCO}_2\text{D}$  or  $\text{F}_3\text{CCO}_2\text{D}$  have been investigated. The rates were  $10^4$ - $10^5$  higher than with unsubstituted ferrocene [128]. The effect of steric hindrance on the reaction of ferrocene derivatives with organo-mercury compounds has been investigated. The reactions of 1,1'-diethyl- and 1,1'-di-*t*-butyl-ferrocenes with diethyl-, diphenyl- and diisooamyl-mercury have been studied [129].

Ferrocenemethanol and  $\alpha$ -phenylferrocenemethanol underwent coupling with  $\text{HBF}_4$  and  $\text{HClO}_4$  in the two-phase system dichloro-methane-water in the presence of copper to give the diferrocenyl-ethanes (10.33;  $\text{R} = \text{H}, \text{Ph}$ ) respectively [130]. 2,5-Dimethoxy-phenylferrocene has been demethylated with boron tribromide and then oxidized with silver(I) oxide to give 2,5-benzoquinonyl-ferrocene (10.34) in 54% yield. Twenty similar benzoquinonyl-ferrocenes were prepared in the same way [131]. Reaction of



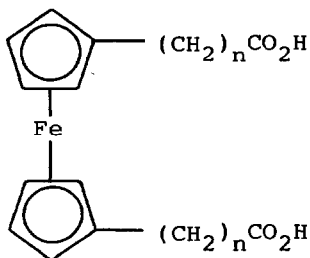


10.33

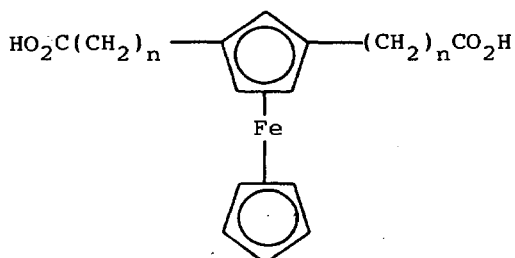


10.34

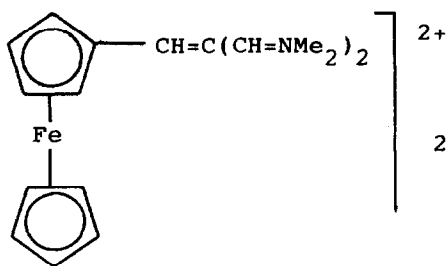
the ferrocenedialkanoic acids (10.35 and 10.36;  $n = 2,3$ ) with  $\alpha, \beta, \alpha, \beta$ -tetrakis(*o*-aminophenyl)porphyrin in the presence of 2-chloro-1-methylpyridinium iodide and tri-*n*-butylamine produced the corresponding ferrocenoporphyrinophanes [132]. The condensation of the salt  $\text{Me}_2\text{NCH}=\text{CHCH}=\text{NMe}_2^+\text{ClO}_4^-$  with formylferrocene produced the intermediate (10.37) which was hydrolysed to give the dialdehyde (10.38) [133]. Ferrocenylphenylthioketone (10.39) combined with the cyclopentadienide and dicarbonyl( $\eta$ -cyclopentadienyl)iron anions to form ferrocenylphenylfulvene (10.40) [134].



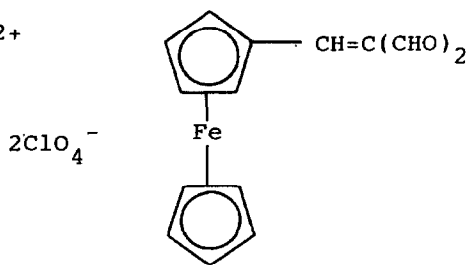
10.35



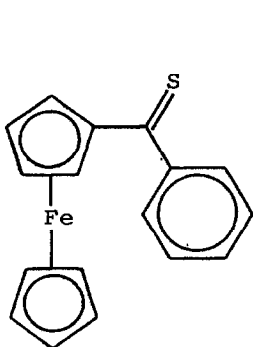
10.36



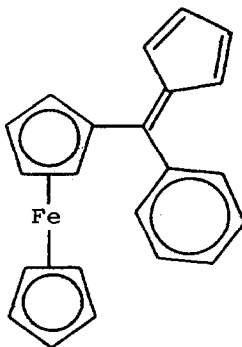
10.37



10.38

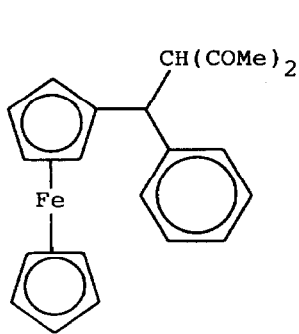


10.39

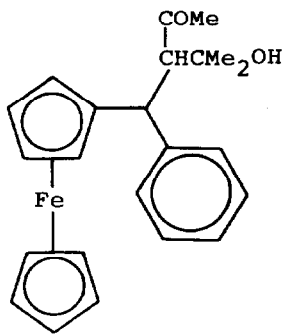


10.40

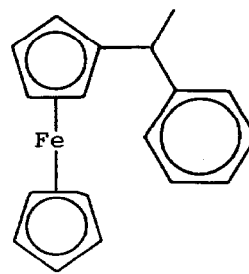
The reaction of ferrocene containing  $\beta$ -dicarbonyl compounds with methylmagnesium iodide has been investigated. For example, the dicarbonyl compound (10.41) produced the three ferrocene containing products (10.42, 10.43 and 10.44). The origin of these reaction products was investigated [135]. Arenes underwent arylation with chloro- and 1,1'-dichloro-ferrocene in the presence of aluminium and aluminium(III) chloride. Reductive dechlorination accompanied the reactions to give aryl- and 1,1'-diaryl-ferrocenes [136]. Ultra-violet irradiation of haloferrocenes in aqueous alcohols produced the corresponding alkoxyferrocenes (10.45; R = Me, Et, Pr, CHMe<sub>2</sub>, CMe<sub>3</sub>). The order of reactivity of the haloferrocenes was iodoferrocene > bromoferrocene > chloroferrocene [137]. The ferrocene-borane salts [10.46 and 10.47; X = (CH<sub>2</sub>)<sub>2</sub>, C≡C; Y = 2 B<sub>3</sub>H<sub>8</sub><sup>-</sup>, B<sub>10</sub>H<sub>10</sub><sup>2-</sup>, B<sub>12</sub>H<sub>12</sub><sup>2-</sup>] have been



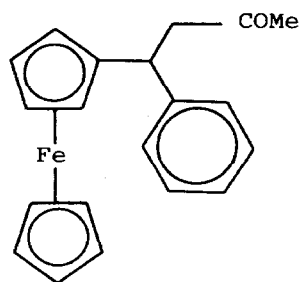
10.41



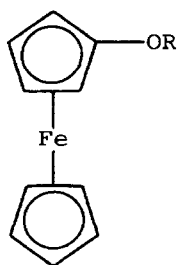
10.42



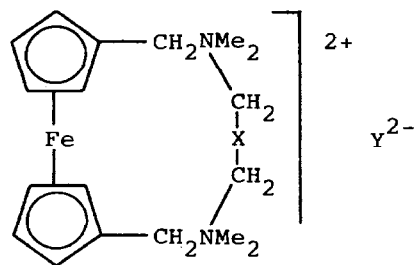
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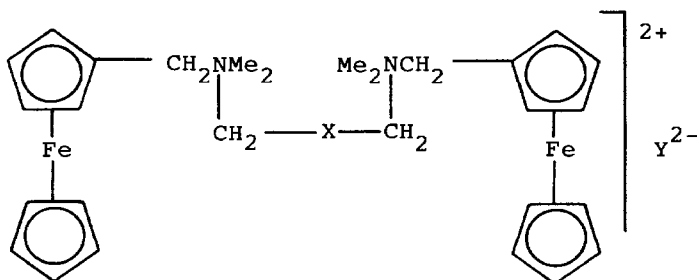
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10.45



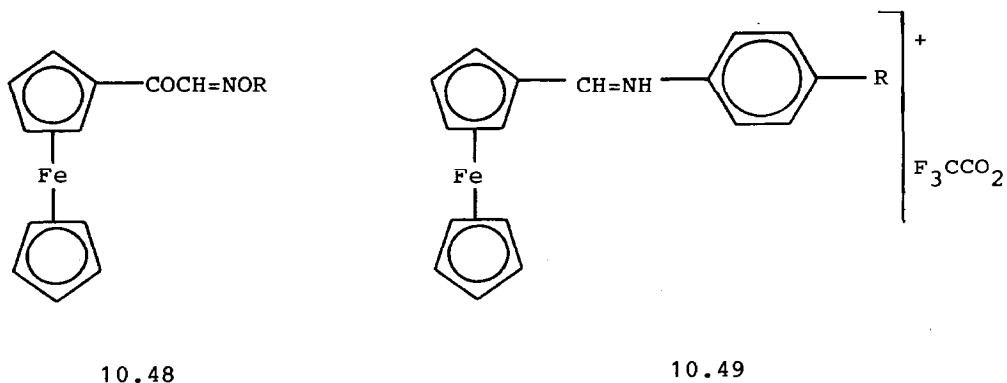
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10.47

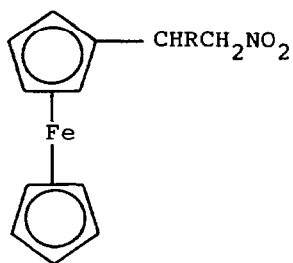
obtained from the corresponding ferrocene quaternary ammonium salts and tetraethylammonium boranes. Thermal stability of the complexes (10.46 and 10.47) increased with increasing size of the borane anion [138].

$\alpha$ -Ferrocenylalkylureas have been prepared by treatment of ferrocenylcarbinols with substituted ureas in acetic acid [139]. Oxidation, reduction and substitution in the oxime (10.48; R = H) has been studied. Treatment with acetic anhydride at 60°C gave the acetate (10.48; R = COMe) in 77% yield [140].

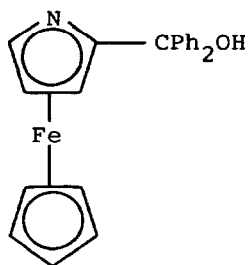


Ferrocenylimines have been attacked by trifluoroacetic acid to give immonium salts (10.49; R = Me, OMe) and charge transfer complexes [141]. Reaction of 1-ferrocenyl-2-nitroethene with the Grignard reagents PhMgBr, MeMgI and  $\text{CH}_2=\text{CHCH}_2\text{MgCl}$  produced the corresponding substituted ethanes (10.50; R = Ph, Me,  $\text{CH}_2=\text{CHCH}_2$ ) [142].

The metallation of azaferrocene with *n*-butyllithium-tetra-methylethylenediamine at  $-50^\circ$  followed by condensation of the lithio intermediate with benzophenone produced the alcohol (10.51) as the only product. The structure of this latter compound was established by X-ray analysis [143]. The azaferrocene and azacymantrene complexes  $[(\eta\text{-C}_4\text{H}_4\text{N})\text{Fe}(\eta\text{-C}_5\text{H}_5)]_2\text{MCl}_2$  and  $[(\eta\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3]_2\text{MCl}_2$ , where M = Pd, Pt, have been prepared by the reaction of azaferrocene and azacymantrene with  $\text{K}_2\text{PtCl}_4$  and  $(\text{PhCN})_2\text{PdCl}_2$  respectively [144].



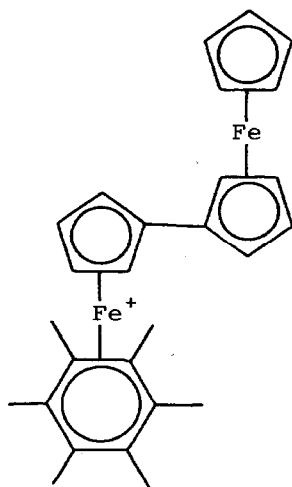
10.50



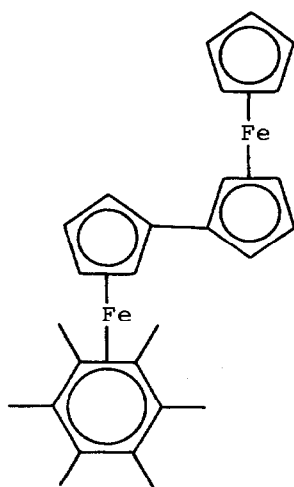
10.51

### 11. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

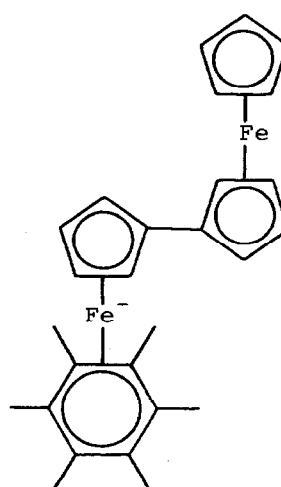
The reaction of biferrocene with hexamethylbenzene in the presence of aluminium chloride gave the Fe(II)-Fe(III) complex (11.1). The voltammogram of this complex showed three quasi reversible waves at 20° and on the mercury cathode two reduction waves were observed corresponding to the formation of the 37- and 38-electron molecules (11.2 and 11.3) [145]. Biferrocene underwent ligand exchange with benzene in the presence of aluminium



11.1



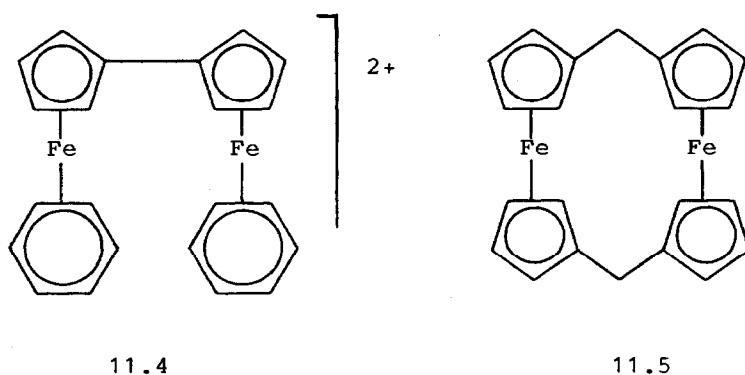
11.2



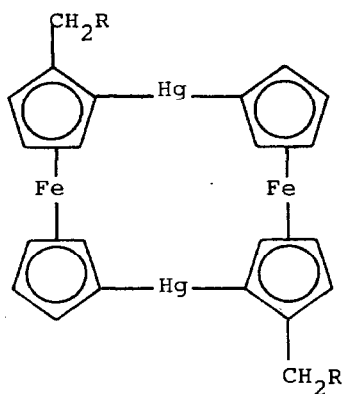
11.3

chloride to give the dication (11.4). A similar exchange took place with hexamethylbenzene. The dication (11.4) was used in an investigation of organometallic "electron reservoir" complexes [146].

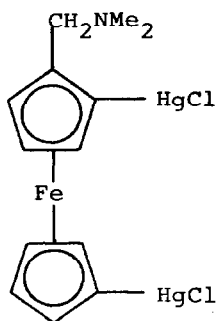
The liberation of hydrogen by [1.1]ferrocenophanes (11.5) and strong acids has been the subject of a kinetic study. The rate constants for hydrogen formation were first order in [1.1]ferrocenophane. Electrochemical and kinetic evidence indicated a three-stage mechanism with two successive protonation steps followed by  $H_2$  formation as the rate-determining step [147].



Reaction of the ferrocenophane (11.6;  $R = NMe_2$ ) with methyl iodide produced the corresponding methiodide (11.6;  $R = NMe_3I$ ) and reaction with mercury(II) chloride gave the ferrocene mercurichloride (11.7) [148]. Treatment of the ferrocenophane (11.8) with phenyllithium produced 1-lithio-1'-(diphenylphosphino)ferrocene. Reaction of this lithioferrocene with hexacarbonylchromium or -tungsten and  $Me_3OBF_4$  gave the corresponding zwitterionic complexes (11.9;  $M = Cr, W$ ) and the metal-carbene ferrocenophanes (11.10;  $M = Cr, W$ ) [149]. Lithioferrocenes have been attacked by chloroisopropylphosphines to form the corresponding isopropylphosphinoferrocenes. Thus 1,1'-dilithioferrocene combined with chloro-diisopropylphosphine to give 1,1'-bis(diisopropylphosphino)ferrocene while the tetramethylethylenediamine adduct of 1,1'-dilithioferrocene gave, with dichloro-



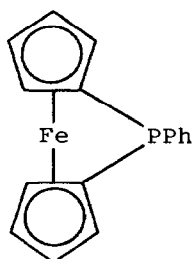
11.6



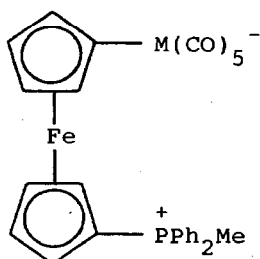
11.7

isopropylphosphine the [1]ferrocenophane (11.11) [150].

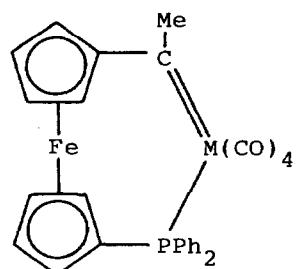
The [3]ferrocenophanes (11.12; X = S, Se; Y = P, As) have been prepared by the reaction of ferrocene-1,1'-dithiol or ferrocene-1,1'-diselenol with  $\text{PhPCl}_2$  or  $\text{PhAsCl}_2$ . The structure of the complex (11.12; X = S; Y = As) has been determined by X-ray analysis [151]. The [3]ferrocenophanes (11.13; X = S, Se; Y = Ge, Sn) and the spiro compounds (11.14; X = S, Se; Y = Ge, Sn) have been prepared by the reaction of ferrocene 1,1'-dithiol



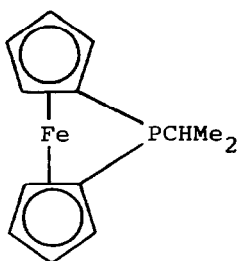
11.8



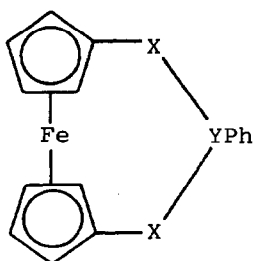
11.9



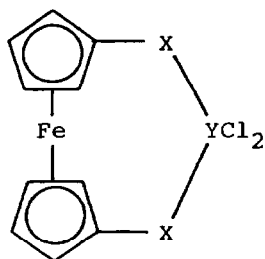
11.10



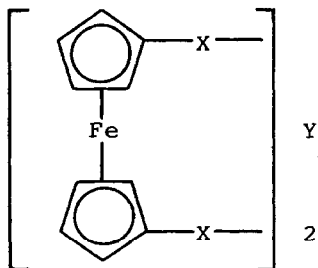
11.11



11.12



11.13

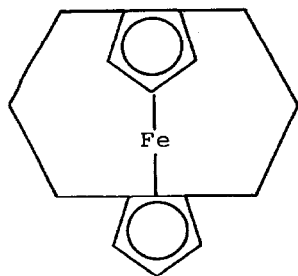


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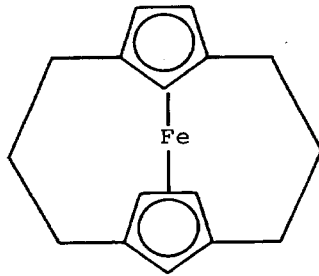
and ferrocene 1,1'-diselenol with germanium and tin tetrahalides. Spectroscopic studies indicated that in solution the compounds were fluxional by a bridge reversal process. The crystal structure of the [3]ferrocenophane (11.13; X = Se; Y = Ge) was determined by X-ray diffraction [152]. The metallation of 1,1',2,2'-, 1,1',3,3'-bis(trimethylene)ferrocene (11.15 and 11.16) and 1,1',2,2',4,4'-tris(trimethylene)ferrocene (11.17; R = H) with butyllithium-tetramethylethylenediamine or potassium t-butoxide followed by treatment with carbon dioxide produced the corresponding mono- and di-carboxylic acids. The dibromo compound (11.17; R = Br) was prepared and the structure was determined by X-ray analysis [153].

The [3]ferrocenophanes [11.18;  $R^1 = R^2 = H$ , X = H, H;  $R^1 = R^2 = H$ , X = O,  $R^1 = COCH_3$ ,  $R^2 = H$ , X = H, H;  $R^1 = H$ ,  $R^2 = COCH_3$ , X = H, H;  $R^1 = CH_3CH(OH)$ ,  $R^2 = H$ , X = H, H;  $R^1 = H$ ,  $R^2 = CH_3CH(OH)$ ;  $R^1 = R^2 = H$ , X = H, OH] have been studied by  $^{57}Fe$  Moessbauer and  $^1H$  NMR spectroscopy. The symm-

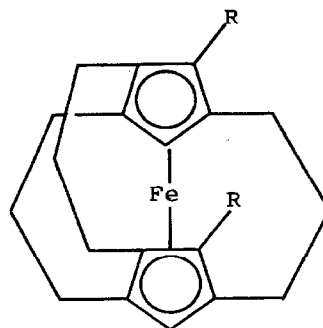




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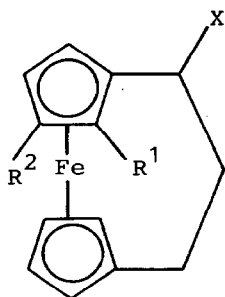


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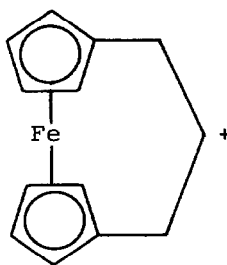


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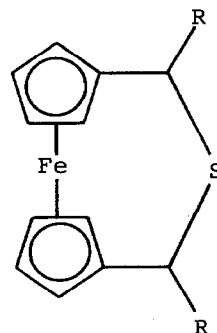
etrical carbenium ion (11.19) showed exalted quadrupole splitting values in the Moessbauer spectrum which were indicative of iron  $e_{2g}$  orbital overlap [154]. The sulphur containing ferrocenophanes (11.20; R = H, Me, Et, Ph) were tested as antiwear-antifriction additives in lubricating oils. In one of the tests the ferrocenophane (11.20; R = Et) behaved in a manner similar to that of  $(\text{PhCH}_2)_2\text{S}_2$  [155]. The reaction of disodium 1,1'-ferrocenedithiolate with polymethylene dibromides at high



11.18



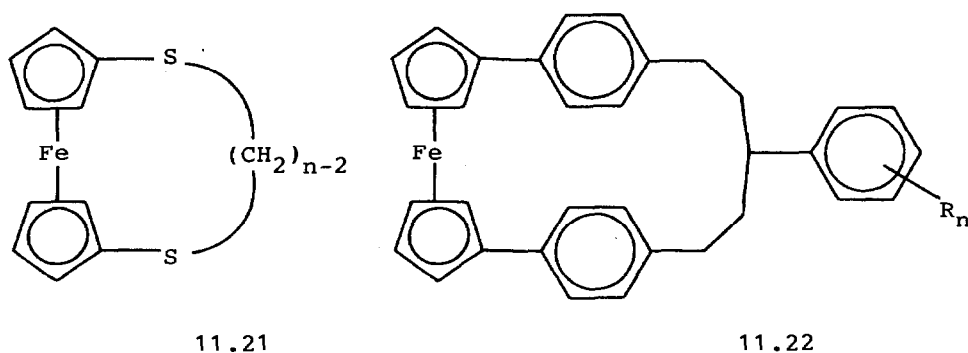
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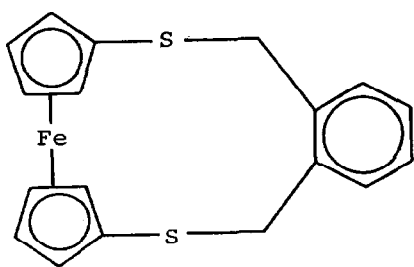
dilution produced the corresponding 1,n-dithia[n]ferrocenophanes (11.21;  $n = 4-10$ ). The electronic and  $^{13}\text{C}$  NMR spectra and the redox potentials of these compounds were recorded. The ferrocenophane (11.21;  $n = 7$ ) showed the largest shift in the electronic and  $^{13}\text{C}$  NMR spectra and the largest decrease in the redox potential. These effects were interpreted in terms of an interaction between the sulphur and the iron atoms [156].

Aromatic aldehydes have been condensed with 1,1'-bis(p-acetylphenyl)ferrocene to give the [0]paracyclo[5]paracyclo[0](1,1') ferrocenophanes (11.22;  $R = \text{H, OMe}$ ;  $n = 1-3$ ) [157]. Several

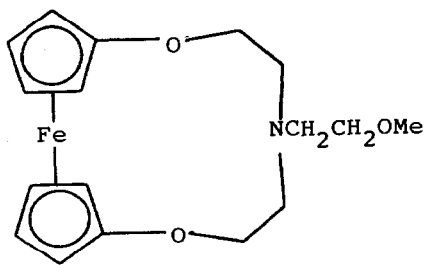


dithioferrocenophanes have been prepared by treatment of 1,1'-ferrocenedithiol with dihalides. Thus *o*-xylene dibromide gave the ferrocenophane (11.23) in 38% yield. *m*-Xylene dibromide, 2,6-bis(bromomethyl)pyridine and 2,5-bis(chloromethyl)furan were also used as reagents [158].

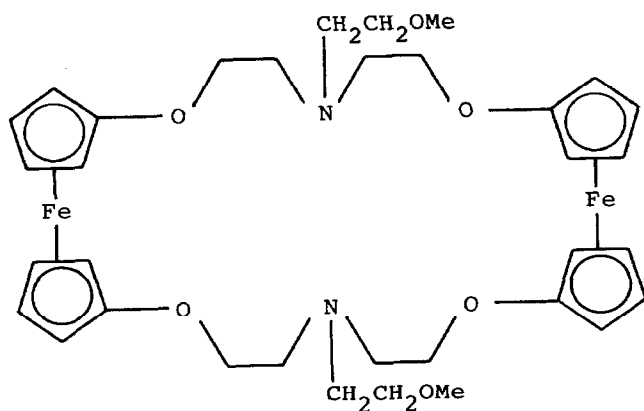
Ferrocenocrown ethers have been prepared by treatment of the dipotassium salt of 1,1'-dihydroxyferrocene with *N*-substituted bis(2-chloroethyl)amines. Thus  $\text{MeOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$  gave the diether (11.24) and the tetraether (11.25) in yields of 26% and 2% respectively. The reaction of 1,1'-bis(2-chloroethoxy)ferrocene with *N*-substituted bis(2-hydroxyethyl)amines as the disodium salts also gave ferrocenocrown ethers [159]. Condensation of 1,1'-bis(chlorocarbonyl)ferrocene with two azacrown ethers gave the ferrocene bis-crown ethers (11.26;  $n = 1, 2$ ). Rotation about the *N*-CO bond was demonstrated by



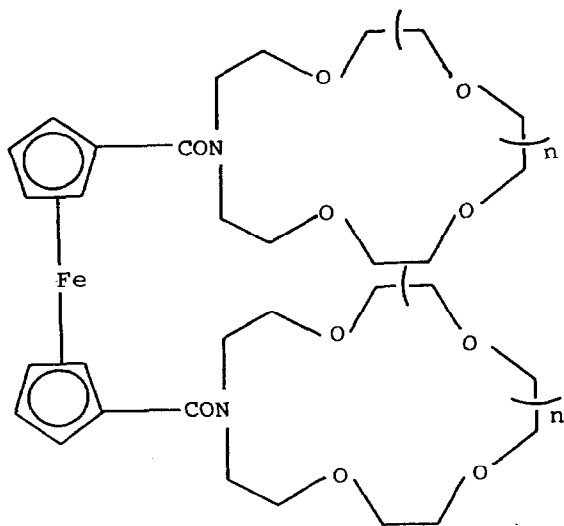
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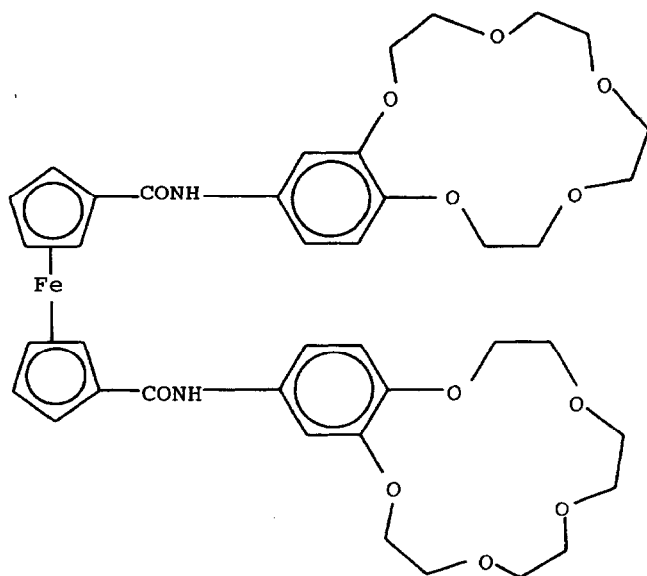
10.24



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11.26

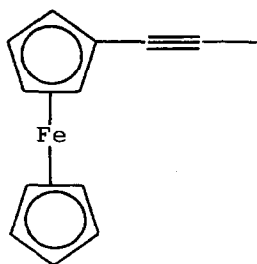


11.27

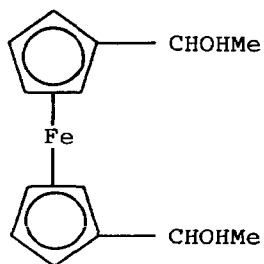
variable temperature NMR spectroscopy [160]. Treatment of 1,1'-bis(chlorocarbonyl)ferrocene with 4-aminobenzo-15-crown-5 gave the ferrocene bis(crown ether) (11.27). Fast atom bombardment mass spectrometry demonstrated the high selectivity of the crown ether (11.27) for the potassium cation [161].

## 12. FERROCENE CONTAINING POLYMERS

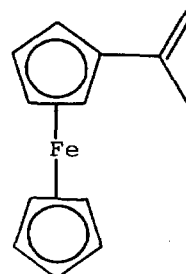
1-Ferrocenyl-1-propyne (12.1) has been polymerised in the presence of a  $WCl_6$ - $Ph_4Sn$  catalyst to give a product of molecular weight 11,000-16,000 with a backbone of alternating double bonds and pendant ferrocenyl groups. The polymer was thermally stable up to 380°C in nitrogen and 350°C in air [162]. Ferrocene containing polyester resins were prepared by the condensation of fumaric acid with diethylene glycol in the presence of 1,1'-bis-(1-hydroxyethyl)ferrocene (12.2), 1,1'-ferrocenedicarboxylic acid or 1,1'-ferrocenediacetic acid. The presence of the ferrocene derivatives increased the rate of the polyesterification process. The effect of the ferrocene compounds incorporated into the polyester backbone on copolymerization with styrene was investigated [163]. The radical initiated copolymerization of butadiene and vinylferrocene has been studied at several temperatures, pressures and in the presence of a solvent with weak transfer capability [164]. The polymerization and copolymerization of isopropenylferrocene (12.3) by cationic initiators



12.1



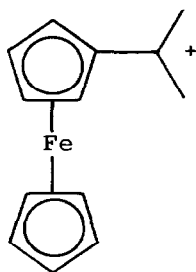
12.2



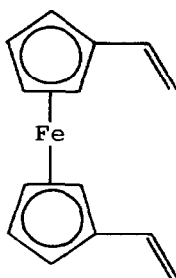
12.3

has been studied. Low molecular weight homopolymers and copolymers with styrene and *p*-methoxy- $\alpha$ -methylstyrene were obtained. The high stability of the  $\alpha$ -ferrocenylcarbenium ion (12.4) was considered to be the reason for limited polymerization [165].

High polymers have been obtained by the terminal polymerization of transannular-linked cyclotriphosphazines  $(\eta\text{-C}_5\text{H}_4\text{N}_3\text{P}_3\text{F}_5)_2\text{M}$ , and the monosubstituted metallocenes  $(\eta\text{-C}_5\text{H}_4\text{N}_3\text{P}_3\text{F}_5)(\eta\text{-C}_5\text{H}_5)\text{M}$ , where M = Fe, Ru. The fluoro groups in both the monomers and polymers were displaced by  $\text{CF}_3\text{CH}_2\text{O}^-$  to give air-stable products.



12.4



12.5

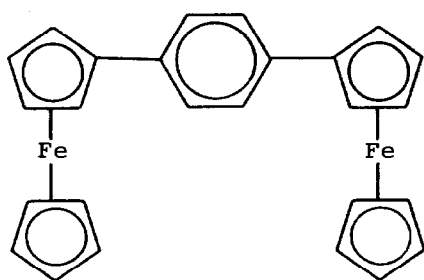
The mechanism of polymerization was discussed [166]. The electrodeposition of polymer films formed by oxidation of poly(vinylferrocene), polybipyrazine and polyaniline has been studied by ellipsometry. Poly(vinylferrocene) films in 0.1M  $(C_4H_9)_4NBF_4/CH_3CN$  were 15% thicker in the oxidized form than in the reduced form [167]. Variable temperature  $^{57}Fe$  Moessbauer studies have been carried out on polymers prepared from vinylferrocene and 1,1'-divinylferrocene (12.5). Nonlinear temperature dependence of Moessbauer absorption line area was found with all the polymers [168].

### 13. APPLICATIONS OF FERROCENE

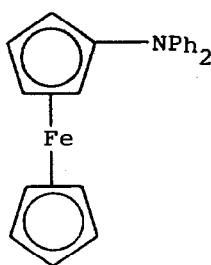
#### (i) Ferrocene catalysts and photosensitizers

Solar irradiation of *p*-differrocenylbenzene (13.1) methylviologen and triethanolamine in the presence of colloidal platinum caused the evolution of hydrogen. When *m*-differrocenylbenzene was used then the reaction was less efficient because of the weaker electron-donating power of the *m*-isomer [169]. Photolysis of a mixture of tetrabromomethane-ferrocene and tetrabromomethane-dibenzylaniline charge transfer complexes produced the ferrocenium ion and a dye. Slower radical reactions also produced the tetrabromoferrate(III) ion [170]. A mathematical model was constructed of the characteristic curve obtained from a tetrabromomethane-ferrocene photosensitive layer. A differential equation was used which related the concentration charges of a coloured reaction product with the intensity of the ultraviolet radiation. A good agreement was obtained between the calculated and experimental curves [171]. In related work the halographic characteristics of light-sensitive layers prepared from tetrabromomethane-ferrocene were investigated [172]. The ferrocene-tetrabromomethane charge-transfer complex has been used as a photoimaging material when placed as a thin layer within a polymer matrix. Photosensitivity of the layer and its maximum optical density were dependent on the concentration of tetrabromomethane. The intensity of the image was enhanced by thermal processing and the rate of intensification was dependant on the nature of the polymer matrix and the processing temperature [173].

The ferrocene-tetrabromomethane charge transfer complex has been incorporated into a poly(vinyl acetate) binder to give a



13.1



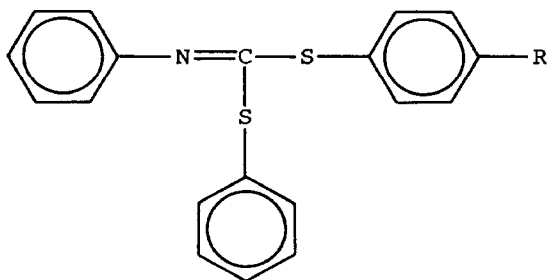
13.2

photosensitive material suitable for holographic recording [174]. The same charge transfer complex has been used as the basis of a photoimaging film for making relief and offset printing plates [175]. It has also been applied to the preparation of photo-thermographic films on plates for lithography. An incandescent lamp was used to expose the film [176].

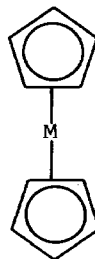
Vinylferrocene and diphenylferrocenylamine (13.2) have been used in electrophotographic systems for reprography [177]. Ionizing radiation induced image formation in poly(vinylethylal) layers containing tetrabromomethane and ferrocene. Latent image centres were based on ferrocenium tetrabromoferrate and the concentration was dependent on the magnitude of the radiation dose [178]. Explosive compounds prepared from mercury(II) nitrate and ferrocene or its derivatives have been tested as primers. They were found to be insensitive to moisture and cyclohexanone and the performance was unaffected at temperatures  $\leq 125^\circ$ . They were sensitive to electrostatic initiation and they were handled wet. These compounds were potentially applicable for high temperature percussion and electrical primers and high-temperature detonators and initiators [179]. The effect of ferrocene as a catalyst was studied in the short reaction time hydrogenation of coal at  $465^\circ\text{C}$  [180]. Ferrocene has been evaluated as a catalyst in the hydroliquefaction of brown coal [181].

Dyeing textiles in the presence of acetylferrocene or 1,1'-diacetylferrocene increased the lightfastness of the dye [182].

Oxidation of polypropylene in the presence of ferrocene (0.005-0.5%) gave high molecular weight ketones [183]. The radical arylation of the thiobenzanilides  $\text{PhCSNHC}_6\text{H}_4\text{R}-4$ , where  $\text{R} = \text{H}, \text{MeO}, \text{NO}_2$ , by the aryldiazonium salt  $4\text{-RC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ , where  $\text{R} = \text{H}, \text{MeO}, \text{NO}_2$ , to give  $\text{PhC}(\text{SC}_6\text{H}_4\text{R}-4)=\text{NC}_6\text{H}_4\text{R}-4$  was catalysed by ferrocene [184]. Similar radical arylation of the dithio-urethane  $\text{PhNHCS}_2\text{Ph}$  with the aryldiazonium borofluorides  $p\text{-RC}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$  in the presence of ferrocene produced the corresponding unsaturated compounds (13.3;  $\text{R} = \text{H}, \text{NO}_2, \text{Me}, \text{OMe}$ ) [185].



13.3



13.4

Photodegradable polyethylene films containing a photosensitizer, which was a ferrocene derivative and phthalocyanine green were prepared and used in agriculture for covering soil [186].

Fine carbon fibres have been obtained by the gas phase reaction of ferrocene with benzene in hydrogen containing 3%  $\text{H}_2\text{S}$  at  $1095^\circ\text{C}$  [187]. Ferrocene has been used as a source of gaseous catalytic iron particles on which benzene decomposed to give carbon fibres. The morphology of fibres obtained under different conditions was examined [188]. Carbon fibre has been produced by vapour deposition of carbon obtained by thermal decomposition of gaseous hydrocarbons in the presence of metallic particles. Metallocenes (13.4;  $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{Ru}, \text{Os}, \text{Pd}$ , were degraded to provide the metal particles [189]. A film dosimeter of ionizing radiations with an expanded working temperature range contained polyphenol quinoxaline as the polymer and ferrocene as the radiochromic additive [190]. Ferrocene has been used as one of the components in a flame



retardent for polyethylene [191].

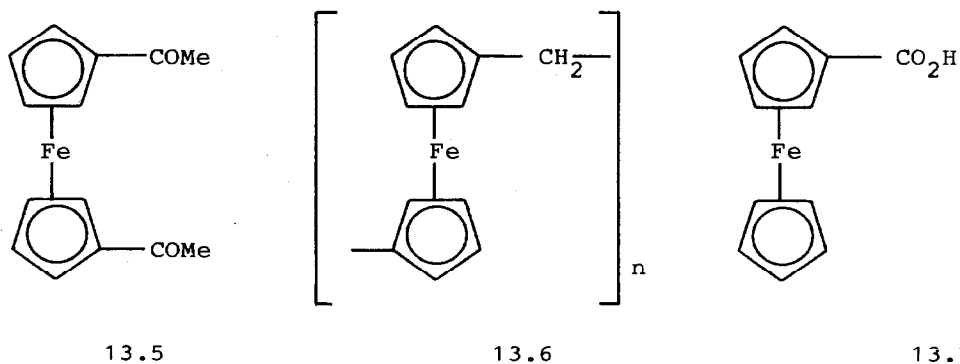
(ii) Ferrocene stabilizers and improvers

The utilization of ferrocenes as tribological additives and special synthetic lubricants has been the subject of a review [192]. Poly(ethylene terephthalate) was modified by the addition of  $\leq 0.5\%$  1,1'-diacetylferrocene (13.5) and the transition temperatures were investigated. The three main transitions were glass transition, cold crystallization and melting and they were monitored via inverse gas chromatography and differential thermal analysis. All the transitions were changed by the addition of 1,1'-diacetylferrocene (13.5) [193]. A binuclear ferrocene has been used as a UV stabilizer for polyethylene at concentrations of  $\geq 0.1 \text{ mol kg}^{-1}$ . It was more effective than hydrated iron(III)oxide [194]. Some linear polymeric ferrocene compounds have been compounded with cable-grade plasticized poly(vinyl chloride) and the compatibility of these compounds was investigated. Poly(ferrocenylenemethylene) (13.6) exhibited good compatibility up to a loading of 9%. It was suggested that these compounds were potentially useful for poly(vinyl chloride) based engineering and biomedical materials [195].

Adhesive compositions activated by acids have been prepared from an acrylic monomer, a peroxy initiator, a ferrocene compound and a vinyl ether [196]. Ferrocenium salts with complex anions were mixed with peroxides and used as initiators for the polymerization of acrylates. The gel time of the acrylate adhesive increased with increasing ferrocenium ion concentration and this enabled the pot life to be controlled [197]. Ferrocene has been incorporated into semiinsulating epitaxial layers of In-P based compounds using an MOCVD process. The devices were used in lasers, field effect transistors and integrated optoelectronic circuits [198]. Ferrocene was included in a series of compounds that was mixed with olive oil, castor oil and lithium tetrahydroborate for use as combustion improvers in gasoline and diesel fuels. Exhaust pollution was reduced [199].

(iii) Clathrate complexes

The oxidation of ferrocenecarboxylic acid (13.7) in the presence of  $\beta$ -cyclodextrin has been studied electrochemically in



pH 9.2 aqueous buffer solution where the ferrocenecarboxylic acid was present as the anion. Induced circular dichroism and ultraviolet-visible absorption spectra indicated that the anion was complexed with the  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4)$  axis parallel to the axis of the  $\beta$ -cyclodextrin cavity. Cyclic voltammetry was used to determine the formation constant of the guest-host complex and it also indicated that the oxidation of the ferrocenecarboxylic acid proceeded via prior dissociation of the complex. No binding of the oxidized form of the ferrocenecarboxylic acid (13.7) and the  $\beta$ -cyclodextrin was detected [200]. Complex formation of cyclodextrins was investigated in alcohols and other solutions. The binding of ferrocene by  $\beta$ -cyclodextrin was stronger in ethylene glycol than in dimethylformamide or dimethylsulphoxide [201]. Ferrocenecarboxylic acid (13.7) in dimethylsulphoxide was taken up by  $\beta$ -cyclodextrin through interaction with amino groups to form a clathrate complex. The interaction was investigated by circular dichroism [202].

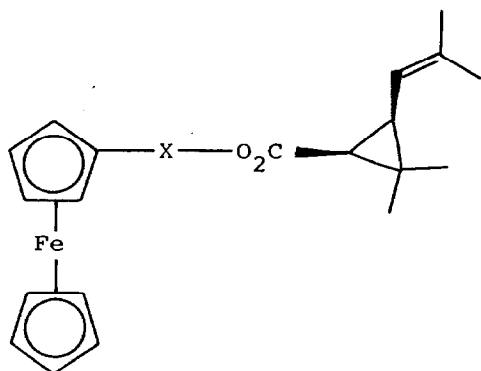
Ferrocene and substituted ferrocenes formed inclusion compounds with cyclodextrins. Crystalline products were obtained with cyclodextrin:ferrocene ratios of 1:1 and 2:1, they showed good thermal stability and did not liberate ferrocene at 100°C in vacuo. Inclusion compounds were not formed between cyclodextrin and 1,1'-disubstituted ferrocenes [203]. Moessbauer spectroscopy has been used to investigate the behaviour of an  $\alpha$ -cyclodextrin-ethylferrocene clathrate complex. Changes in

the Moessbauer spectrum were interpreted in terms of increasing rotation of the ferrocene molecule within the clathrate cavity as the temperature increased. The barrier to rotation was determined as  $8.8\text{kJ mol}^{-1}$  [204]. Cyclic voltammetry has been used to determine the formation constant of the complex formed between ferrocene and  $\beta$ -cyclodextrin in dimethyl sulphoxide [205].

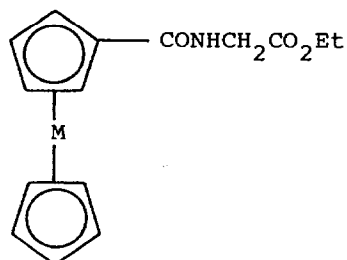
$\beta$ -Cyclodextrin-6-ferrocenecarboxylate behaved as a host towards cyclohexanol or adamantanecarboxylic acid as guests to form complexes in polar solvents. The interaction was studied by circular dichroism [206]. Liquid chromatography on  $\beta$ -cyclodextrin columns has been used to separate thirteen enantiomeric pairs of ferrocene, ruthenocene and osmocene derivatives [207]. The ferrocene-ferrocenium couple has been used as the reference standard in an electrochemical investigation of iron(II) clathrochelate complexes [208].

(iv) Biochemical and biological applications

Several ferrocenylpyrethroids [13.8;  $X = \text{CH}_2\text{S}(\text{CH}_2)_2$ ,  $2\text{-CHMeS}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ ,  $(\text{CH}_2)_2$ ,  $\text{CH}=\text{CHCH}_2$ ] have been evaluated as insecticides. The two sulphur containing compounds were the

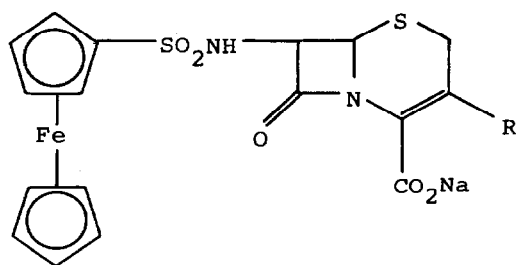


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13.9

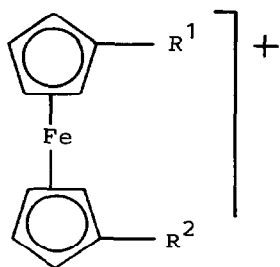
most effective [209]. The ferrocenoylglycine ester (13.9;  $M = \text{Fe}$ ) underwent metal-exchange with radioactive  $\text{RuCl}_3$  ( $^{97}\text{Ru}$ ,  $^{103}\text{Ru}$ ) to form the ruthenocene analogue (13.9;  $M = \text{Ru}$ ) which was a potential radiopharmaceutical with a clearance similar to Hippuran [210]. Several ferrocene derivatives of  $\beta$ -lactam



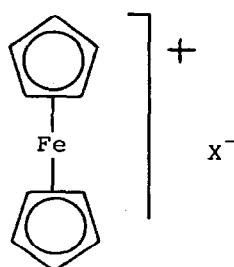
13.10

antibodies have been prepared from ferrocene mono- and di-sulphonyl chlorides. For example the cephalosporanic acids (13.10;  $R = \text{Me}, \text{CH}_2\text{OCOMe}$ ) were obtained in yields of 89 and 70% respectively and were characterized by IR spectroscopy and TLC [211].

(Ferrocenylmethyl)cetyldimethylammonium chloride has been used to demonstrate the presence of electron-dense material in clear synaptic vesicles in rat cerebral cortex and neuromuscular junctions of frog cutaneous pectoris muscle [212]. The kinetics and mechanism of the oxidation of NADH by ferrocenium ions and quinones has been investigated. The rate of oxidation by the ferrocenium ion was independent of pH and buffer salt concentration and showed no deuterium isotope effect [213]. The oxidation of reduced spinach plastocyanin by the ferrocenium ions (13.11;  $R^1 = R^2 = \text{H}, \text{Me}$ ;  $R^1 = \text{H}, R^2 = \text{HgCl}, \text{Ph}$ ) has been investigated. The oxidations obeyed a second order rate law that was first order with respect to the ferrocenium ion and protein concentrations. The possible mechanisms of electron transfer were discussed [214]. A series of ferrocenium salts (13.12;  $X^- = [\text{FeCl}_4]^-$ ,  $1/2 [\text{Cl}_3\text{FeOFeCl}_3]^{2-}$ ,  $[\text{H}_5\text{Mo}_7\text{O}_{24}]^-$ ,  $[2,4,6-(\text{NO}_2)_3\text{C}_6\text{H}_2\text{O}]^-$  and  $[\text{CCl}_3\text{CO}_2]^- \cdot 2\text{CCl}_3\text{CO}_2\text{H}$ ) were found to exhibit tumor-inhibiting activity when tested against Ehrlich ascite tumors in CF1 mice. The best antineoplastic properties, with optimum cure rates of 100%, were found with ferrocenium trichloroacetate and ferrocenium picrate [215, 216]. The

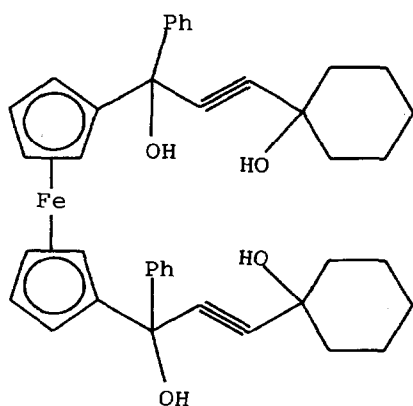


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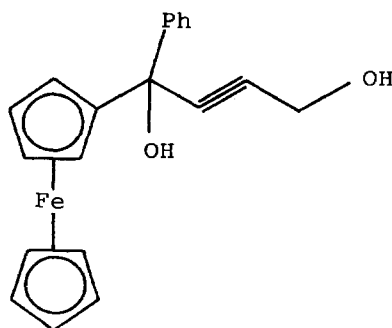


13.12

ferrocenyl-alcohols (13.13 and 13.14) have been prepared from benzoyl- and 1,1'-dibenzoylferrocene and the corresponding lithiated alkynes. The bactericidal activity of these compounds was investigated [217].



13.13



13.14

#### (v) Ferrocene in analysis

Substituent effects in para-substituted poly-N-phenyl pyrrole film electrodes have been investigated by cyclic voltammetry using the ferrocene-ferrocenium couple [218]. Enzyme electrodes have been developed for blood glucose monitoring in diabetes control. These electrodes included a mediator compound

to transfer electrons between the enzyme and one of the conductive surfaces. The mediators used included chloroferrocene and ferrocene carboxylic acid [219]. Silver was determined in copper-zinc ores by titration with a standard ferrocene solution in ethanol using a platinum indicator electrode at 0.8V against a mercury sulphate reference electrode. Before the titration the silver was extracted from 2M nitric acid solution into dihexylsulphide in chloroform and this latter solution was diluted with ethanol and sulphuric acid was added. The relative standard deviation for the determination was 0.02-0.03 for 16-33% silver [220].

Ferrocene has been determined by amperometric or potentiometric titration with cerium(IV). The redox potential of the ferrocene-ferrocenium ion couple varied with the composition of the aqueous-organic solvent mixture [221]. Square wave voltammetry on platinum microdisc electrodes using synchronous demodulation has been used to estimate ferrocene. A detection limit of  $2 \times 10^{-7}$  M was obtained for ferrocene in methyl cyanide [222]. Iron has been determined in several ferrocene compounds by flameless atomic absorption spectrometry [223]. The quaternary ammonium salts of ferrocene-borane anions have been separated by thin-layer chromatography on silica gel [224].

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