FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1984*

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CONTENTS

1. REVIEWS

A special issue of the Journal of Organometallic Chemistry dedicated to Professor Makoto Kumada includes an introduction by Sakurai in which the contribution to ferrocene chemistry by Kumada is outlined [1].

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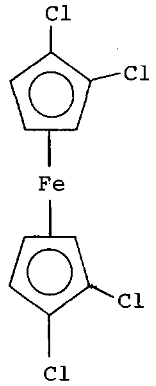
* Annual Survey covering the year 1983 see J. Organometal. Chem., 278 (1984) 255.

The chemistry of ferrocene has been the subject of a detailed survey by Perevalova, Reshetova and Grandberg [2].

2. STRUCTURAL DETERMINATIONS

The crystal and molecular structure of benzoylferrocene has been determined by X-ray crystallography [3]. The crystal structure of the chloro-ferrocene (2.1) was determined by X-ray analysis. The η-cyclopentadienyl rings were displaced by 2.5° from an eclipsed configuration [4].



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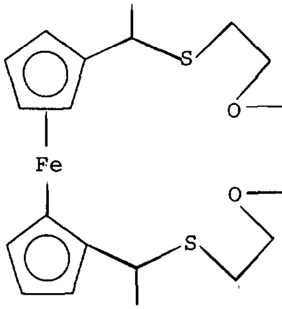

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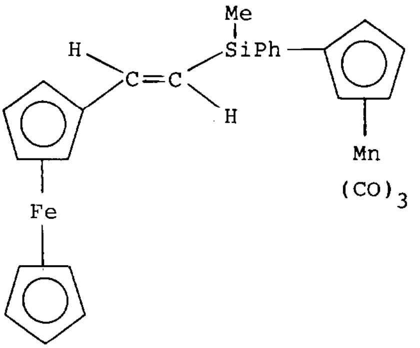
The structure and dynamics in the three crystal phases of 1,1',2,2'-tetrachloroferrocene (2.1) have been studied by X-ray diffraction, incoherent neutron scattering and dielectric permittivity measurements. In the low-temperature ordered phase the two η-cyclopentadienyl rings were in an eclipsed configuration. The intermediate phase had hexagonal symmetry and the high-temperature phase was body-centred cubic [5].

The structure of the meso-diastereoisomer of the ferrocenophane (2.2) has been determined by X-ray analysis. The η-cyclopentadienyl rings were eclipsed [6].

The addition of cymantrenylmethylphenylsilane to ferrocenylacetylene produced the trans-complex (2.3). The crystal structure of this complex was determined by X-ray analysis. The iron and manganese atoms were on the same side of the SiCH=CHC plane [7].

The plastic phase of formylferrocene has been examined by X-ray diffraction and Moessbauer spectroscopy [8].



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Studies have been carried out on the phase transition near the melting point in acetylferrocene. The X-ray crystal structure was determined at room temperature. Weissenberg and oscillation photographs taken up to the melting point were consistent with the acetylferrocene molecules rotating around the crystallographic axes formed by the iron atoms [9].

The crystal and molecular structure of the dimethylaminomethylferrocene-borane salt, $2[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2NHMe_2)]^+\text{-}[B_{12}H_{12}]^{2-}$, has been determined by X-ray crystallography [10].

The structure of diferrocenium μ-oxo-bis[trichloroferrate(III)] has been determined by X-ray analysis. The anion possessed two iron atoms bridged by oxygen with each iron atom also bound to three equivalent chlorines [11].

3. THEORETICAL STUDIES

Ab initio molecular orbital calculations have been carried out for ferrocene and poly-chlorinated ferrocenes and the electric field gradients at the iron atoms were determined. An anomalously large quadrupole splitting in polychlorinated ferrocenes was explained in terms of a decrease in electron donation from the η-cyclopentadienyl ring to e_{1g}3d orbitals [12].

A semiempirical crystal orbital investigation has been carried out on the one-dimensional poly(ferrocenylene) system. The calculations predicted that the highest filled band was a ligand π band with iron 3d bands at lower energies [13].

The band structures of a series of one-dimensional polydecker sandwich compounds have been studied by a semiempirical crystal-orbital procedure based on the INDO approximation [14].

Structure-resonance valence bond theory has been used to derive charge distributions and bond orders in a series of ferrocenes and α-ferrocenylalkyl cations. The charges and bond orders derived were compared with NMR chemical shift and X-ray data. The high stability of ferrocenylcarbenium ions and the role of the metal in stabilizing these ions was explained within the conventional ideas of structural organic chemistry and resonance theory [15].

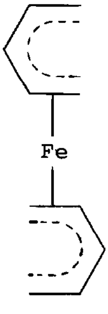
The Polya method has been used to calculate the total number of chiral and achiral configurations of C_{1-14} alkyl derivatives of ferrocene and compared with an earlier method by Coffman [16].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

A radiation chemical study has been carried out on aqueous solutions of ferrocenyl-substituted carboxylic acids saturated with N_2O. It was demonstrated that the hydroxyl radical underwent an oxidation reaction with the carboxylic acids [17].

The He(I) photoelectron spectrum of bis(η-pentadienyl)iron (4.1) has been recorded, interpreted and compared with the ferrocene spectrum. The spectra of the two compounds were similar in appearance but could not be correlated directly [18].

The He(I) photoelectron spectra for chloroferrocene, 1,1'-dichloro- and 1,1'-dibromo- ferrocene (4.2; X = Cl, Br)



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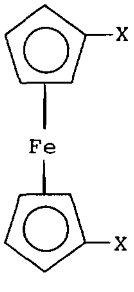

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have been recorded and interpreted. The difference between the ionization potentials of the $e_{2g}(\underline{d})$ and $a_{1g}(d)$ level was not affected by the ring substitution. Only the splitting of the $e_{1u}(\pi)$ level of the ligand was observed in the spectra. It was concluded that there was significant mixing of the iron p orbitals with the $e_{1u}(\pi)$ level [19].

Electron transmission spectroscopy has been used to determine the electron affinities of vanadocene, chromocene and ferrocene. The electrons were captured to form transient anions and the electronic structures of these species were discussed [20].

Inelastic neutron scattering spectroscopy has been used to determine the splitting of the two lowest orbitally degenerate Kramers doublets in the perdeuteroferrocenium cation. A value of 515 cm^{-1} was obtained [21].

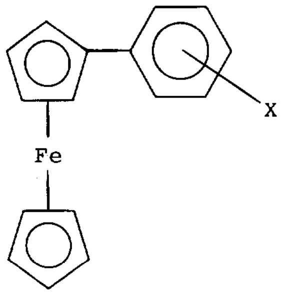
Moessbauer spectroscopy has been used to investigate the structures of the diferrocenyl methyl cation and protonated diferrocenyl ketone. Evidence was obtained to support the involvement of $\underline{e}_1$ rather $\underline{e}_2$ orbitals in the stabilization of the cation. The reactions of diferrocenylketone and diferrocenylmethanol with iron(III) chloride were investigated using frozen solutions [22].

Moessbauer spectroscopy has been used to investigate a solution of 1,1'-diacetylferrocene in the cold smectic C liquid crystal 4-pentylphenyl-4'-heptyloxythiobenzoate (7δ5). Linear Debye behaviour was observed over the temperature range 110-300 K and the smectic glass-supercooled smectic transition (Tg) was determined as Tg = 215 K [23].

A Moessbauer study has been carried out on a series of mono- and di- substituted ferrocenes. A linear relationship was found between the ^{57}Fe Moessbauer quadrupole splittings and the oxidation potentials which were measured chronopotentiometrically as quarter-wave potentials [24].

Substituent and conformational effects in a series of arylferrocenes (4.3; X = $\underline{o}$-, $\underline{m}$-, $\underline{p}$-Me, $\underline{o}$-, $\underline{m}$-, $\underline{p}$-NO_2, $\underline{o}$-, $\underline{m}$-, $\underline{p}$-OMe, H) have been investigated by ^{1}H and ^{13}C NMR spectroscopy and by ^{57}Fe Moessbauer spectroscopy. Substituent constants for the ferrocenyl group were obtained, $\sigma = -0.01$ and $\sigma^+ = -0.19$ [25].

The reaction of biferrocene and biferrocenylene with mercury(II) chloride produced the corresponding $HgCl_2$ adducts.



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The ^{57}Fe-Moessbauer spectrum of the biferrocene adduct exhibited a large quadrupole splitting value which suggested the presence of a Fe-Hg bond. The quadrupole splitting value for the biferrocenylene adduct was much smaller and this was taken to indicate the presence of the averaged-valence state of Fe(II) and Fe(III) [26].

A comparative Moessbauer study has been carried out on $FeCl_3$-graphite and the ferrocene-iron oxide chloride (FeOCl) intercalation compounds. At room temperature the spectra consisted of resonance lines which were characteristic of iron(II) only [27].

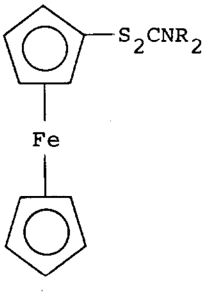
The ^{57}Fe Moessbauer spectra of five bis(η-pentadienyl)iron compounds have been recorded and compared with the corresponding spectra for ferrocene and azaferrocene. A decrease in the isomer shift parameter on going from ferrocene to bis(η-pentadienyl)iron was accounted for by a change in the orbital population around the metal atom resulting in an increase in the electron density at the iron nucleus [28].

A detailed analysis of the IR spectra of substituted 2-(3-phenylferrocenylmethylene)- and 2-(1'-phenylferrocenylmethylene)-1,3-indanones recorded in chloroform and tetrachloromethane enabled the transmissive factors for 1,3- and 1,1'-ferrocenylene groups to be determined. Evidence for vibrational coupling in1,3-indanones was obtained [29].

The preparation and electronic absorption spectra of potassium tris(1,1'-ferrocenedicarboxylato)ferrate(III) have been reported [30].

Several alkyl- and dialkyl-ferrocenophanes have been protonated in HBF_3OH. Long-lived protonated ferrocenophanes were observed by ^1H NMR spectroscopy and were stable to decomposition. For those complexes where the conformation was determined only a single conformation was observed. Spin-spin coupling was detected between hydrogen bound to iron and cyclopentadienyl ring hydrogens [31].

Lithioferrocenes have been treated with bis(dialkyldithiocarbonates), $R_2NCS_2S_2CNR_2$ to form the corresponding mono- and di-substituted ferrocenes (4.4 and 4.5; R = Me, Et, $CHMe_2$) respectively. Rotation about the C-N carbamate bond was examined by ^1H NMR spectroscopy and the barrier to rotation in the complexes (4.4 and 4.5; R = Me, Et) was determined as $\sim$16 kcal mol^{-1} [32].



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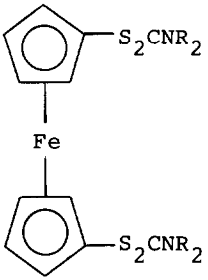

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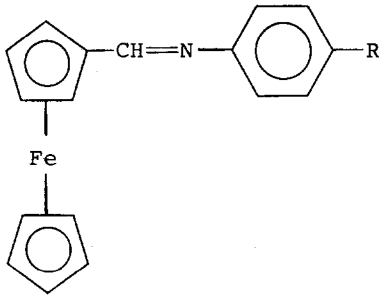
The ferrocenylazomethines (4.6; R = Me, OMe) interacted with electron acceptors such as CBr_4 and CBr_3CO_2H and formed immonium salts in the case of CBr_4. NMR and UV spectroscopy were used to study the interaction [33].

^{13}C NMR chemical shifts [δ(CO)] and carbonyl stretching frequencies [ν(CO)] have been measured for a series of ferrocenylketones (4.7; X = H, o-, m-, p-Me, Cl; p-OMe, o-, m-Br; p-CN: 4.8; R = H, t-Bu, 1- adamantyl, 9-anthracyl), The δ(CO) values were used to estimate the interplanar angle between the η-cyclopentadienyl ring plane and the carbonyl plane. The ν(CO) and δ(CO) values were found to correlate approximately [34].



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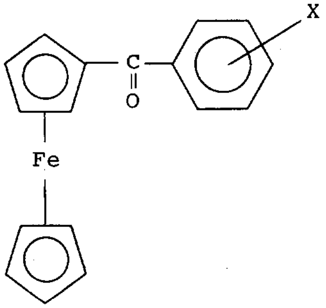
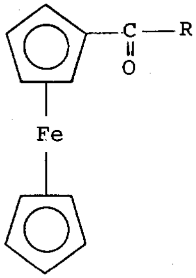
The same ferrocenylketones were reduced to give the corresponding alcohols. The ^1H NMR spectra of the carbenium ions derived from these alcohols have been measured and discussed, together with those of the ketone precursors in CF_3CO_2H [35].

Polarisation transfer sequence in conjunction with 2-D NMR have been used to assign resonance signals in the ^{13}C NMR spectra of the ferrocene and ruthenocene containing cryptands (4.9; M = Fe, Ru; m, n = 1, 2 or 3). The results indicated a <u>trans</u> disposition of the carbonyl groups [36].

The ^{57}Fe NMR spectra of eight ferrocenes have been recorded and the chemical shifts correlated well with Hammett σp parameters [37].





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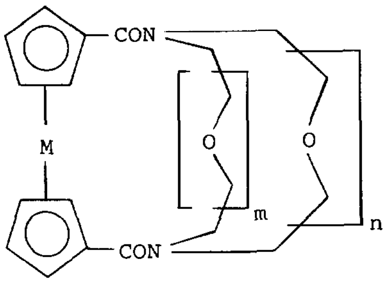

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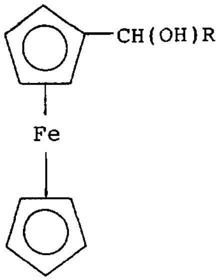

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^{57}Fe spin lattice relaxation times have been determined by the inversion recovery method for ferrocene and pentacarbonyliron [38].

The vapour pressure of ferrocene has been measured by a static method (diaphragm manometer) and dynamic methods (torsion and mass-loss effusion). The free energy and the heat capacity of sublimation were calculated [39].

Adiabatic calorimetry has been used to determine the heat capacity of ferrocene-$\underline{d}_{10}$ in the temperature range 13-300 K. A λ-type phase transition was detected at 164.1 K between the metastable low temperature phase and the undercooled high temperature phase. A first order transition from the stable low temperature phase to the high temperature phase occurred at 251 K. The temperature of the first order transition was shifted by 9 K compared with ferrocene but the entropy and enthalpy of the two transitions were similar to those for ferrocene. The difference in heat capacity between ferrocene and ferrocene-$\underline{d}_{10}$ for the three phases was interpreted in terms of changes in the frequencies of the normal modes and the (C_p-C_v) correction [40].

The heat capacity of azaferrocene has been measured in the temperature range 10-300 K. Phase transitions were observed at 200, 278.5 and 289.5 K with associated enthalpy changes of 3000, 650 and 6750 J mol^{-1} respectively. Phosphaferrocene showed similar thermal behaviour [41].

Thermal decomposition rates of ferrocene have been measured by very low-pressure pyrolysis and the first and second bond energies determined as 91.4 and 51 kcal mol^{-1} [42].

Pulsed gas chromatography has been used in a kinetic investigation of the thermal decomposition of ethylferrocene, diethylferrocene, t-butylferrocene and (η-diethylbenzene)(η-ethylbenzene)chromium [43].

The ferrocenyl-ketones (4.8; R = H, Me, Et, Pr, Ph) were estimated via capillary gas chromatography and no decomposition of the molecules occurred. However, the corresponding alcohols (4.10) decomposed in the injector. Initial decomposition was avoided by on-column injection but some decomposition of the alcohols occurred in the capillary column [44].

A method has been developed for the separation of two or more components in solution by dynamic-column liquid chromatography. A mixture of ferrocene and formylferrocene was used to demonstrate the method [45].

Partition thin-layer chromatography and high-performance thin-layer chromatography have been used to separate a series of hetero[n](1,1')-ferroceno- and -ruthenocenophanes. These compounds were prepared from ferrocene and ruthenocene diols and α,ω-dithiols in dilute solution in the presence of trifluoroacetic acid as the catalyst [46].

5. ELECTROCHEMISTRY AND PHOTOSENSITIVE ELECTRODES

A photoelectrochemical cell has been constructed using cadmium telluride thin fims in a nonaqueous electrolyte containing the ferrocene-ferrocenium couple [47].

A photoelectrochemical cell containing a semiconductor photoactive electrode, such as Si or GaAs, an electrolyte such as $LiClO_4$ dissolved in MeCN, and a redox couple, such as (1-hydroxy)ethylferrocene-(1-hydroxy)ethylferrocenium ion, has shown a solar energy conversion efficiency of $\gtrsim$ 10% [48].

The IUPAC Commission on Electrochemistry has recommended that the redox couples ferrocene/ferrocenium ion and bis(η-biphenyl)chromium(I)/bis(η-biphenyl)chromium(O) be used as reference redox systems. The recommended procedures for measuring and reporting electrode potentials in nonaqueous solvents using these reference electrodes were presented [49].

The electrode potentials have been measured for the ferrocene-ferrocenium electrode in aqueous-organic solvents containing hydrogen chloride at different concentrations of ferrocene and ferrocenium picrate. The potentials were relatively unaffected by the nature of the organic solvent [50].

Cyclic voltammetry has been used to determine the heterogeneous electron transfer rate constant (k_o) of the ferrocene-ferrocenium ion couple at a platinum electrode in 18 nonaqueous solvents. Specific solution resistance was determined in 118 combinations of solvent and supporting electrolyte and values of k_o fell in the range 0.09-0.04 cm s^{-1} [51].

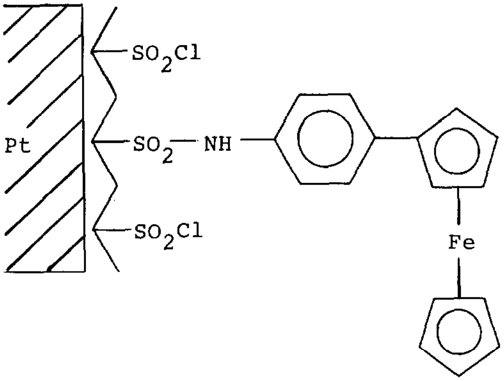
The ferrocene-ferrocenium ion potential was determined in a potentiometric study in propylene carbonate when the proton medium effect was obtained [52].

Cyclic voltammetry and differential pulse voltammetry have been used to examine the electrochemistry of the ferrocene-ferrocenium ion couple in cationic, anionic and nonionic micellar solution. Solubilities of ferrocene were measured by d.c. voltammetry and spectrometry. Reversible half-wave potentials were obtained and the results were explained in terms of micelle solubilization equilibria for the reductant ferrocene and the oxidant ferrocenium ion. In each solution examined, a standard potential for the ferrocene-ferrocenium ion couple in water was determined from the half-wave potentials, the partition coefficients of ferrocene and ferrocenium ion and the ratio of their diffusion coefficients [53].

The use of surface reaction entropies for examining reactant-solvent interactions at electrochemical interfaces has been investigated. The reaction entropies were determined for a surface-attached ferrocene/ferrocenium ion couple in a series of solvents [54].

Ferrocene, acetylferrocene, 1,1'-di(acetyl)ferrocene, α-hydroxyethylferrocene and 1,1'-di(α-hydroxyethyl)ferrocene were electropolymerized onto glassy carbon electrodes. The electrodes exhibited a rapid response to changes in hydrogen ion concentration [55].

Films of p-chlorosulphonated polystyrene were deposited on glassy carbon and platinum electrodes. These electrodes were treated with p-ferrocenylaniline to give the ferrocene



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containing electrodes (5.1) which were studied by cyclic voltammetry [56].

Plasma-polymerized vinylferrocene (PPVF) has been obtained as a film on glassy carbon electrodes. The electrode characteristics and composition of the PPVF film were shown by cyclic voltammetry and XPS to be determined by the conditions used in preparation. The ferrocene-ferrocenium ion redox reaction in the PPVF film was charaterized as fast electrochemical charge transport [57].

Sulphonyl compounds have been used to bind hydroxymethylferrocene chemically to tin oxide glass film electrodes. The electrode response was as expected for surface bound electrochemistry although some nonideal characteristics were observed. The electrode was an effective catalyst for the oxidation of ferrocytochrome c and nicotinamide adenine dinucleotide reduced form [58].

An electroactive layer was formed on platinum electrodes by droplet evaporation of a copolymer of vinylferrocene and S(methacrylpropyltrimethoxysilane) followed by siloxane crosslinking. Different copolymer layers were formed by changing the concentration of vinylferrocene present. The electrochemical behaviour of the coated electrodes was investigated via cyclic voltammetry [59].

An electrochemical study has been carried out on plasma polymerized films of vinylferrocene deposited on titanium, thermally oxidized titanium and single-crystal titanium(IV) oxide. Oxidation of the ferrocenyl groups in the polymer coatings occurred at potentials 1.5 V positive of the flatband potential for titanium(IV) oxide in methyl cyanide. The ease of oxidation decreased as the thickness of the oxide phase increased [60].

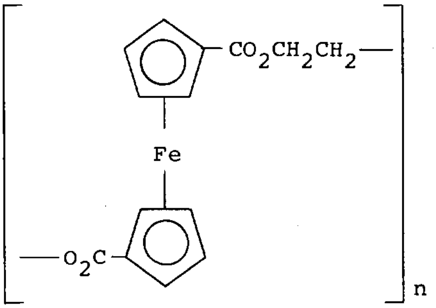
The spontaneous adsorption of ferrocenes on highly ordered pyrolytic graphite edges has been investigated electrochemically. Surface coverages of approximately 2×10^{-8} mol cm^{-2} were found and three of the adsorbed compounds had oxidation waves more negative than their solution counterparts [61].

The ferrocenyltrimethylammonium cation has been used to enhance the rate of charge transfer by the $[\mathrm{Co}(2,2',2''\text{-terpyridine})_2]^{3+}$ ion in Nafion coated electrodes [62].

Unusual electrochemical behaviour was exhibited by the ferrocene-ferrocenium ion couple in Nafion films on a Nafion coated gold electrode [63].

Transmembrane electron transport has been studied using t-amylferrocene as a one-electron carrier [64].

Batteries containing either polyferrocene [65] or the ferrocenylene polymers (5.2) [66], (5.3 or 5.4) [67] as the cathode and which could reversibly take up either cations or anions have been constructed. The electrolyte was a lithium perchlorate polypropylene carbonate mixture and the anode was lithium. The batteries showed improved charge and discharge



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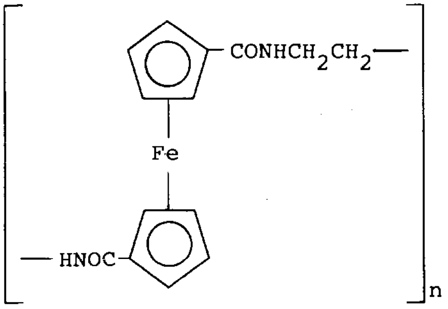

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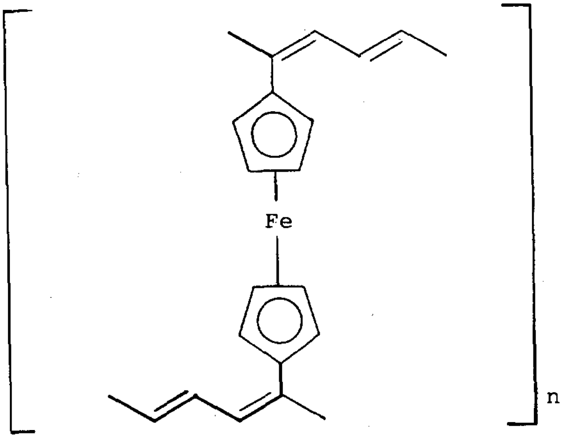

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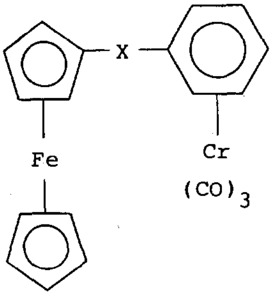
capacities by comparison with lithium-polyacetylene batteries [68].

The mixed ferrocenyl-(η^6-phenyl)tricarbonylchromium complexes [5.5; X = CH=CH, CO, CH_2, $CH_2CH(OH)$, CH_2CO and 5.6] have been the subjects of an electrochemical investigation. An induced electrooxidation of the (η^6-phenyl)tricarbonylchromium moiety occurred in the compounds (5.5; X = CH=CH, CO and 5.6) where the ferrocenyl group was in conjugation [69].

Cyclic voltammetry studies have been carried out on a series of arylferrocenes (5.7; for example X = H, *m*-, *p*-OMe, *m*-, *p*-COMe, *m*-, *p*-CHO, *p*-NO_2, *p*-CF_3) and two series of ferrocene analogues of chalcone (5.8; for example X = H, *p*-Br, *m*-, *p*-NO_2, *p*-OMe, *m*-Cl and 5.9: for example X = H, *p*-OMe, *p*-Cl, *p*-CN, *p*-NO_2, *m*-Cl,



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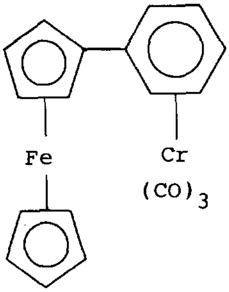

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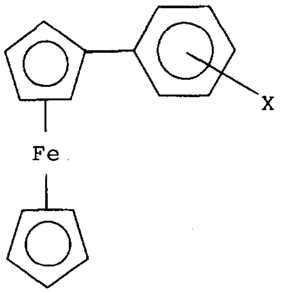

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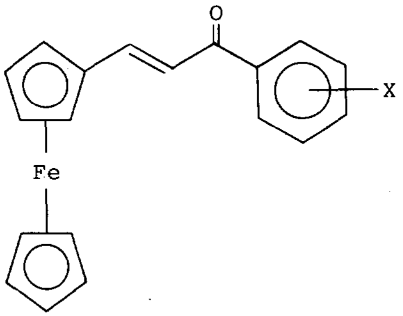

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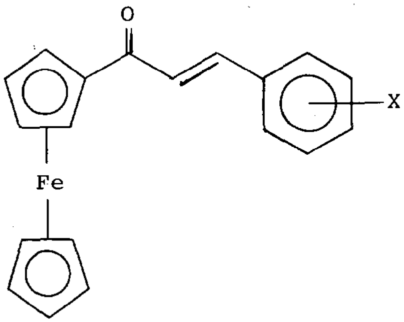

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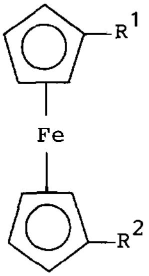

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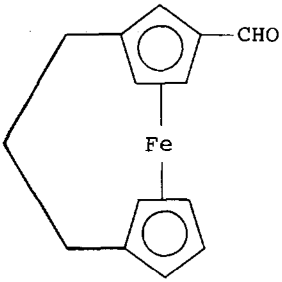
m-NO_2). Good correlations were found between the oxidation potentials and the Hammett σ constants and the ^{13}C NMR chemical shifts for several carbon atoms in the ferrocenyl group [70].

The substituted ferrocenes [5.10; R^1 = PhCO, *p*-NCC_6H_4CO, R^2 = H; R^1 = R^2 = $PhCH_2CO$, *p*-ClC_6H_4CO, $Me(CH_2)_9CO$] have been prepared and their redox potentials determined by cyclic voltammetry [71].

A comparative study of the electrochemical reduction of acetylferrocene and the ferrocenophane (5.11) has been carried out. In nonaqueous solvents the anion radical of the ferrocenophane (5.11) retained the ferrocene structure whilst that of acetylferrocene decomposed by iron-cyclopentadienyl ring cleavage [72].



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The outer-sphere electron-transfer reaction between the clathrochelate $[Co(dimethylglyoximate)_3(BF)_2]^+$ and ferrocene was first order in each reactant. The self-exchange and cross reaction rate constants did not accord well with Marcus theory predictions [73].

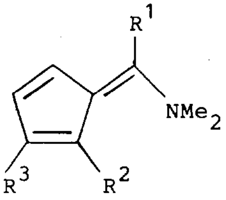
The diffusion coefficients of ferrocene in acetone and aqueous acetone have been determined by the rotating disc method [74].

Cyclic voltammetry and coulometry have been used to study the electrochemical oxidation of ferrocene in two-phase media. In micellar solutions the oxidation of micelle solubilized ferrocene was reversible and involved an electron transfer mechanism with diffusion of the micelles. In a dodecane in water emulsion the mechanism was found to be different [75].

Voltammetry has been used to show that methylferrocene was principally in the micelle phase in a dodecyltrimethylammonium bromide micellar solution [76].

6. PREPARATIONS OF FERROCENE

Reaction of the electron-rich 6-dimethylaminopentafulvenes (6.1, R^1 = H, Me, NMe_2; R^2 = H; R^1R^2 = CH_2CH_2, R^3 = H, CO_2Et, Me_3C, $CONMe_2$) with $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}\underline{p}\text{-xylene})]^+PF_6^-$ or $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)]^+PF_6$ gave the corresponding ferrocenyl or ruthenocenyl salts (6.2; M = Fe, Ru). Treatment of these salts with ethanol and aqueous sodium hydroxide produced the corresponding carbonyl derivatives (6.3). The presence of strong



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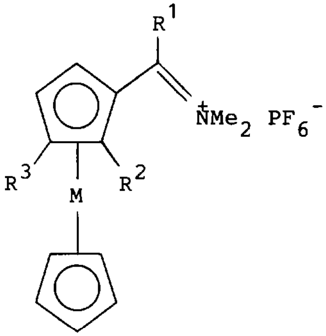

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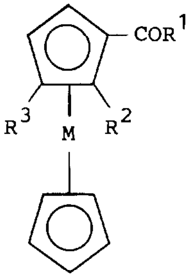
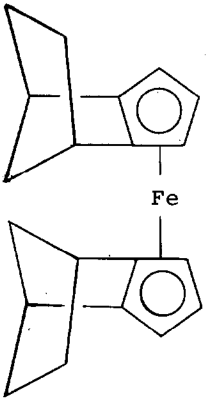


6.3

electron-withdrawing groups on the pentafulvene molecules inhibited the reaction [77].

Metal chlorides have been treated with N,N-dimethylaminocyclopentadienyllithium in THF at -30°C to give the corresponding metallocenes. Thus 1,1'-bis(dimethylamino)ferrocene was prepared in 33 % yield and was studied by cyclic voltammetry. The redox potential was -0.23 V vs. SCE [78].

Treatment of the isodicyclopentadienide anion and the corresponding dehydrocongener with iron(II) produced the stereochemically homogeneous ferrocenes (6.4 and 6.5) respectively. The structure of the latter compound was determined by X-ray analysis [79].



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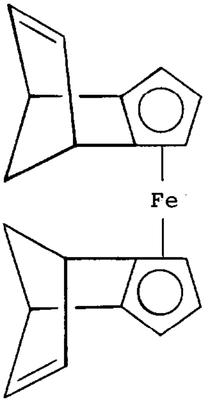


6.5

Controlled potential electrolysis of cyclopentadienylthallium in dimethylformamide using an iron anode gave ferrocene in 92% yield [80].

The gas phase reactions of $FeCH_3^+$ and $CoCH_3^+$ with cyclic hydrocarbons have been studied. Protonated ferrocene was obtained when cyclopentene was the reagent [81].

High purity ferrocene has been obtained by crystallization from benzene, sublimation and vapour zone purification [82].

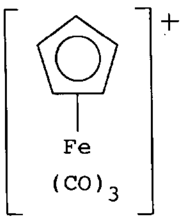
7. REACTIONS OF FERROCENE

The formation of electron-donor acceptor complexes between ferrocene, tetrachloromethane and tetranitromethane has been examined spectroscopically in the range 290-800 nm. Formation of the ferrocenium ion increased with time and with the concentration of tetranitromethane [83].

The easy conversion of ferrocene into the tricarbonyl(η-cyclopentadienyl)iron cation (7.1) with aluminium chloride and carbon monoxide has been exploited to form a range of (η-cyclopentadienyl)iron complexes. Similar ligand exchange reactions of ferrocene with arenes have also been used as the starting point in the preparation of these complexes [84].

Quinoline has been treated with $PhSO_2N{=}CClPh$ and ferrocene to form the heterocycle (7.2). Similar reactions were carried out with isoquinoline and imidazole [85].

Crystalline one-to-one inclusion complexes have been formed by the addition of ferrocene, acetylferrocene and α-hydroxyethyl-



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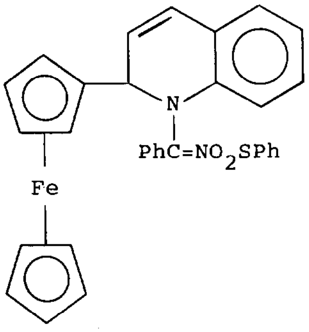


7.2

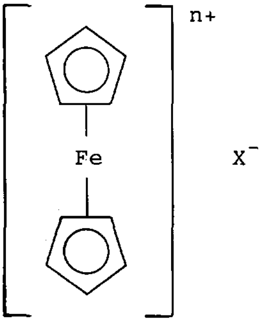
ferrocene to β- and γ-cyclodextrin. Two-to-one complexes were formed by the treatment of α-cyclodextrin with ferrocenes [86].

8. FERROCENIUM SALTS AND MIXED-VALENCE SALTS

Correlation effects in the metallocenes $(\eta\text{-}C_5H_5)_2M$, where M = Mg, Ge, V, Mn, Fe, Co, and the metallocenium cations $[(\eta\text{-}C_5H_5)_2M]^+$, where M = Fe, Co, have been studied by ab initio Hartree-Fock calculations. Comparisons of computed metal-cyclopentadienyl ring distances were used to show that charge-transfer effects were more important than ring-ring dispersion forces in bonding [87].

Ferrocene has been oxidized by iron(III) chloride to give the ferrocenium salts [8.1; n = 1, X = $FeCl_4^-$; n = 2, X = $O(FeCl_3)_2$] which were characterized by X-ray powder diffraction, Moessbauer and IR spectroscopy. The salt had been previously identified as $[(\eta\text{-}C_5H_5)_2Fe]^+FeCl_3^-$ [88].

Ion pair formation between iodine and substituted ferrocenes in benzene has been investigated. The equilibrium constants (K) for the formation of the ferrocenium salts (8.2; R = H, Me, Et, Ph) from the corresponding ferrocene and iodine increased with electron donating substituents and decreased with electron withdrawing substituents. Correlation of polarographic half-wave potentials with K showed that the major influenece on K was the effect of the substituent on the ease of oxidation of the parent ferrocene [89].



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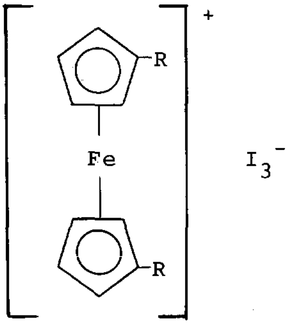

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Treatment of ferrocene with trichloroacetic acid in the presence of air produced ferrocenium trichloroacetate with two trichloroacetic acid molecules attached. Controlled recrystallization of this di-solvate from water produced the corresponding mono-solvate [90].

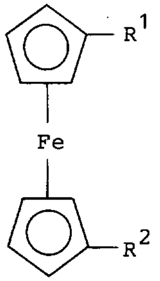
Treatment of the ferrocenes (8.3; $R^1 = R^2$ = H, Et; $R^1 = Me_3C$, isopentyl, isooctyl, R^2 = H; R^1 = H, $R^2 = CMe_2CN$) with concentrated sulphuric acid at 0°C generated the corresponding ferrocenium ions. Reaction of these ions with the free radical $NCMe_2C^{\bullet}$, generated from azobisisobutyronitrile, afforded the substituted ferrocenes (8.4) [91].

The reduction of the ferrocenium cation on zirconium tungstate has been investigated. The electron-exchange capacity of the zirconium tungstate was increased by lowering the acidity of the medium [92].

Metallocenium cations, including the ferrocenium ion, have been used to prepare metallocenylboranes [93].

The ferrocene-ferrocenium cation system has been used for initiating radical reactions of aryldiazonium salts. The reaction of the salts $[4\text{-}R^1C_6H_4N_2]BF_4$ with ferrocene gave $4\text{-}R^1C_6H_4^{\bullet}$ radicals which were treated with $R^2CSNHPh$ (R^2 = Ph, PhNH) to give $R^1C_6H_4SCR^2{=}NPh$ [94].

Polymer-coated microelectrodes and twin electrode thin layer cells have been used to study polymer-solution interfacial electron transfer mediation kinetics and the rates of permeation of ferrocene and the ferrocenium ion through the polymer films.



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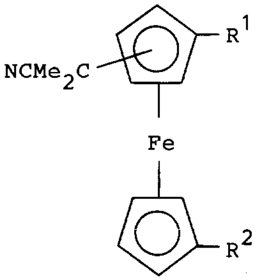
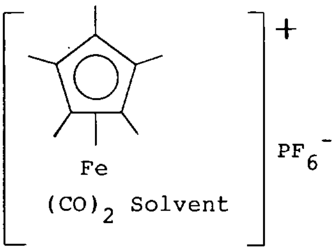


8.4

Ferrocene had a three-fold greater rate of permeation than did the ferrocenium ion [95].

The oxidative cleavage of $[(\eta\text{-}C_5Me_5)Fe(CO)_2]_2$ has been carried out with ferrocenium hexafluorophosphate in a variety of solvents to give the salts (8.5; solvent = THF, acetone, methyl cyanide, pyridine) [96].



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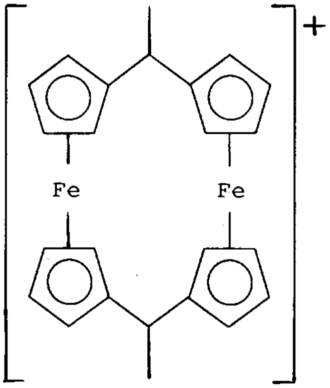

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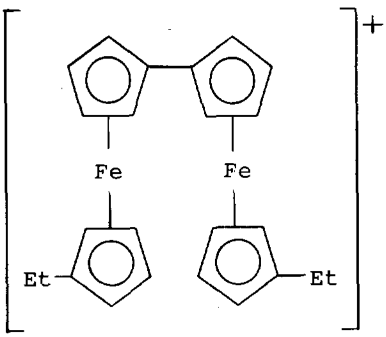
The crystal and molecular structure of the 1,12-dimethyl-[1.1]ferrocenophanium ion (8.6) has been determined by X-ray crystallography. The cation assumed a syn-conformation with non-equivalent metallocene units, one corresponding to iron(II) and the other to iron(III). Moessbauer spectroscopy indicated a mixed-valence rather than a valence-delocalized cation [97].

Moessbauer spectroscopy has been used to investigate the electronic structure of several mixed valence biferrocenium and mononuclear ferrocenium cations in high magnetic fields. Spin-lattice relaxation effects were detected in ferrocenium hexaflurophosphate. Spin relaxation was found to affect the magnitude of the internal magnetic field at the iron nucleus in the mixed-valence biferrocene cation invalidating the previous proposal that the field arose from the presence of the unpaired electron in an orbital with essentially ligand character [98].

Electrical conductivity measurements on the mixed valence biferrocene salt (8.7) indicated a change from a trapped-valence



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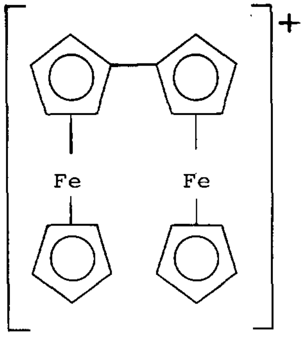


8.8

state to an average-valence state over the temperature range 230-275 K [99].

Vibronic coupling in the mixed valence ion of biferrocene (8.8) has been studied using the Peipho-Krausz-Schatz model. Strong interaction was predicted approaching the Robin and Day class II-III borderline [100].

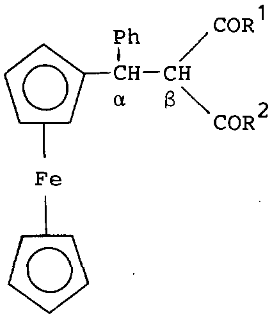
9. FERROCENYL CARBENIUM IONS

Treatment of the β-dicarbonyl compounds (9.1; $R^1 = R^2 =$ Ph, OEt; $R^1 =$ Me, $R^2 =$ OEt) with Lewis acids, for example aluminium chloride, resulted in C_α-C_β bond cleavage to give the corresponding ferrocenylcarbocation [101].

The ferrocenyldicarbonyl compounds (9.2; $R^1 = R^2 =$ Me, OEt, $R^1 =$ Me, $R^2 =$ OEt) have been protonated with trifluoroacetic acid to form diastereomeric carbocations. Thus the ester (9.2; $R^1 =$ Me, $R^2 =$ OEt) gave the carbocations (9.3 and 9.4) which were characterized by NMR spectroscopy [102].

Treatment of 1-methyl-1,3-diferrocenylallyl alcohol with tetrafluoroboric acid and acetic anhydride gave the diferrocenylallyl cation (9.5) which underwent facile dimerization in the presence of dimethylaniline or pyridine to form the tetraferrocenylcyclohexene (9.6). This product was obtained as a mixture of two diastereoisomers [103].

NMR spectroscopy has been used to investigate the protonation of the α,β-unstaurated ketones (9.7; R = Me, Ph, cymantrenyl, ferrocenyl) in trifluoroacetic acid [104].



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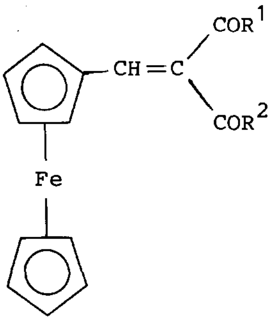

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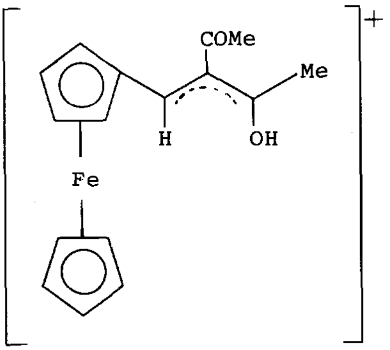

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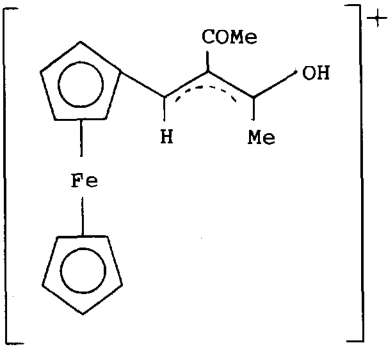
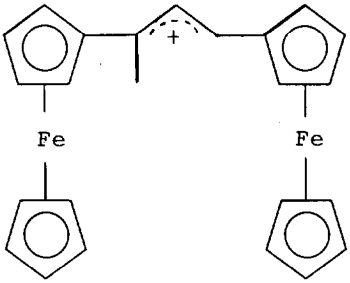


9.4

Several ferrocenylmethylcarbenium ions have been prepared as the tetrafluoroborate salts [9.8; R^1 = H, Me, Ph, 2-(2-furyl)-vinyl; R^2 = 3-indolyl, ferrocenyl, 1-methyl-2-pyrrolyl] by treatment of the ketones $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4COR^1)$ with R^2H and $Ph_3C^+BF_4^-$ in acetic acid or $POCl_3$ [105].

A spectroscopic technique has been used to investigate the equilibrium between ferrocenylarylmethanols (9.9; X = H, Me, OMe, Ph, F, Cl, Br, NO_2) and the corresponding ferrocenylmethyl carbenium ions in aqueous sulphuric acid. A Hammett ρ value of -1.44 was obtained from the Hammett plot of pK_{R^+} vs. σ^+ substituent constant demonstrating the powerful electron releasing character of the ferrocene nucleus [106].



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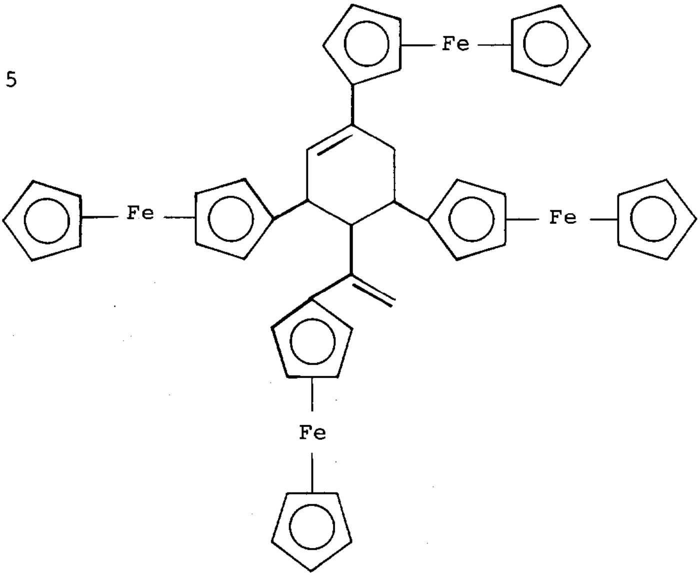

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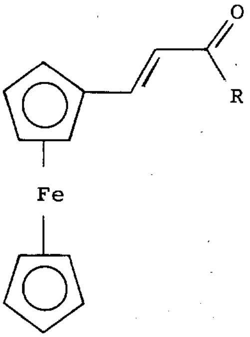

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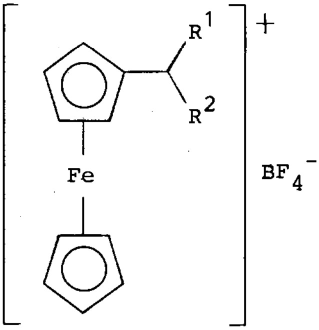

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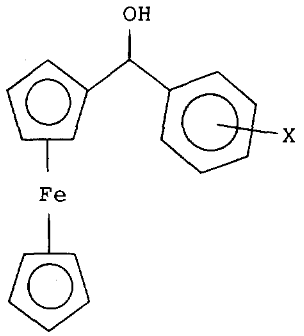

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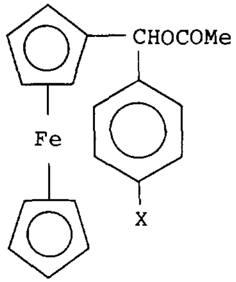
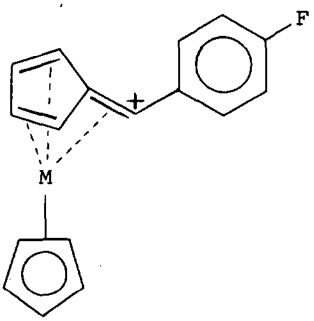


9.10

Several ferrocenylarylmethyl acetates (9.10; X = H, Me, Cl, Br, NO_2, MeO) have been hydrolyzed in acetone-water mixtures. A correlation was obtained between the first-order rate constants obtained and the $\sigma+$ substituent constants or the $E_{\frac{1}{4}}$ chronopotentiometric potentials. The powerful electron releasing character of the ferrocenyl group was confirmed and ferrocenylcarbenium ions were suggested as reaction intermediates [107].

Ferrocene- and ruthenocene-carboxaldehyde were each treated with *p*-fluorophenylmagnesium bromide to form the corresponding metallocenyl-*p*-fluorophenylmethanols which gave the metallocenylcarbenium ions (9.11; M = Fe, Ru) in trifluoroacetic acid. Evidence from ^{19}F NMR spectroscopy indicated that the ruthenocenyl group was more efficient in charge delocalization than the ferrocenyl group [108].

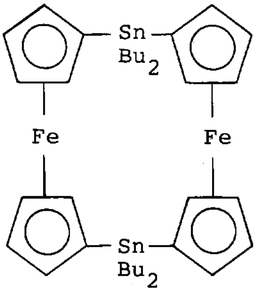


9.11

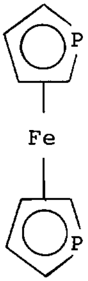
10. FERROCENE CHEMISTRY

(i) Derivatives containing other metals (metalloids)

Reaction of 1,1'-dilithioferrocene with dibutyldichlorotin produced the ferrocenophane (10.1). The crystal and molecular structure of this ferrocenophane was determined by X-ray analysis. The bond distances and angles were regular with one butyl group on each tin atom disordered [109].



10.1

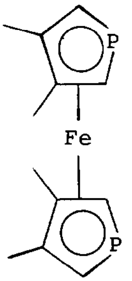


10.2

The electronic structure of 1,1'-diphosphaferrocene (10.2) has been investigated by photoelectron spectroscopy and by EHT and MS X_α calculations [110].

Tetramethyldiphosphaferrocene (10.3) has been evaluated as a ligand for the preparation of transition metal complexes. Both mononuclear (10.4; M = Cr, Mo, W) and binuclear (10.5) complexes were obtained and one of them (10.5) was characterized by X-ray crystallography [111].

The electrochemical behaviour of the phosphaferrocenes (10.6; 10.7; R = H, Me) have been compared with ferrocene using several types of electrodes and several solvents. Reversible one-electron reduction in propylene carbonate was observed at -2.55 V, -2.15 V and -2.33 V for the phosphaferrocenes (10.6; 10.7; R = H, Me) respectively, compared with -2.93 V for ferrocene. One-electron oxidations were observed at potentials near to that of ferrocene. The phosphaferrocene cations were less stable than the ferrocenium cation. ESR spectroscopy of the radical cation derived from the tetramethyl compound (10.7; R = Me)



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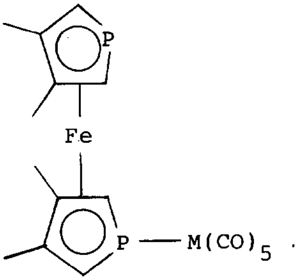

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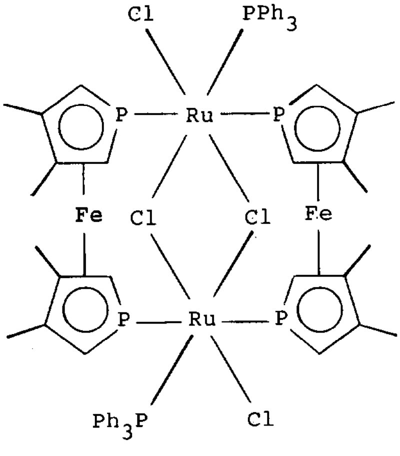
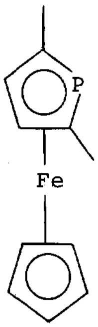
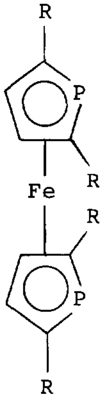


10.5

indicated that the electron was localized on iron. HOMO and LUMO levels were used to interpret the results [112].

The reaction of monolithioferrocene with octachlorocyclotetraphosphazene produced the cyclotriphosphazene (10.8). X-ray analysis confirmed the structure of this molecule and the single bond between the nitrogen atom and the cyclotriphosphazene group was shorter than the proposed double bond to the terminal phosphorus atom due to delocalization within the P-N skeleton. Treatment of lithioferrocene with a 1:1 mixture of octachlorotetraphosphazene and hexachlorocyclotriphosphazene produced the trimer-tetramer bi(cyclophosphazenes) (10.9; R = H, Cl) [113].



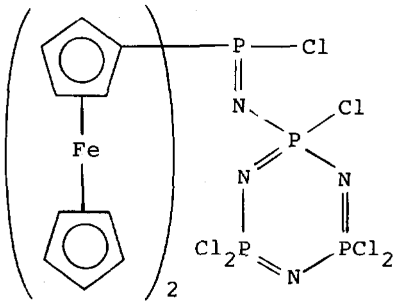


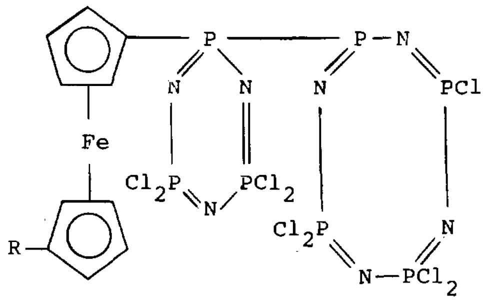
10.6

10.7

The metalladiselenaferrocenophanes (10.10; M = Zr, Hf; R = H, t-Bu) have been prepared by the reaction of the selenol (10.11) with the corresponding dichlorobis(η-cyclopentadienyl)-metal complex in the presence of triethylamine. The ferrocenophanes (10.10) were studied by variable temperature ^{1}H NMR. At room temperature the complexes appeared to be non-fluxional and the ferrocene moiety had a staggered conformation [114].

The interaction of diferrocenylmercury with ytterbium produced the ferrocene derivative of divalent ytterbium (10.12) [115].





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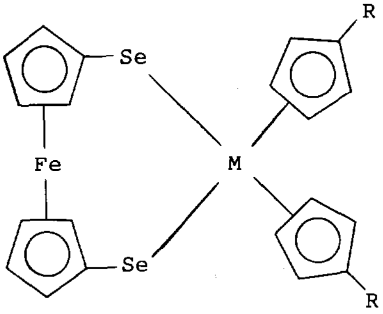

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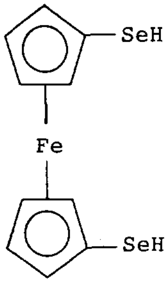
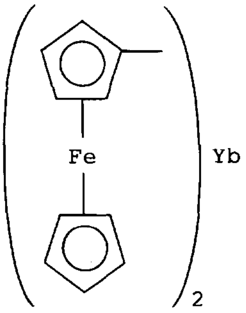


10.11

Diferrocenylmercury has been treated with the mercury amalgams of several lanthanide elements in THF to form bivalent lanthanide derivatives of metallocenes (10.13; M = Sm, Eu, Yb, n = 0, 1) which were characterized by ^{1}H NMR spectroscopy [116].

The cations (10.14; n = 1, 2) have been prepared by oxidation of the parent ferrocenophane with ferrocenium and substituted ferrocenium salts or 7,7,8,8-tetracyanoquinodimethane [117].

Paramagnetic vanadocene units have been linked by ferrocene to yield the mixed metallocene species (10.15; R = H, Me).



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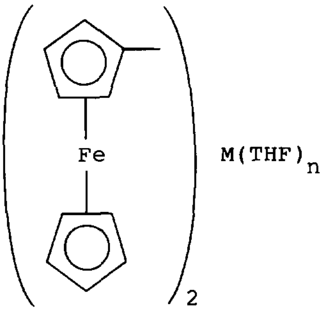

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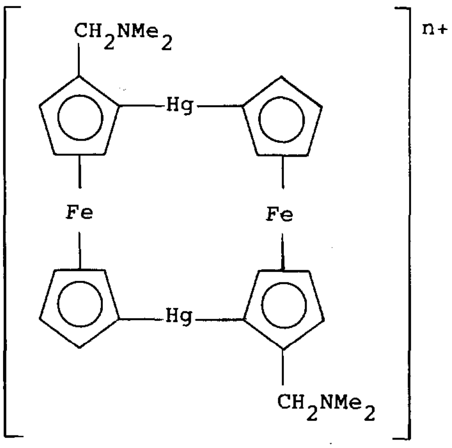
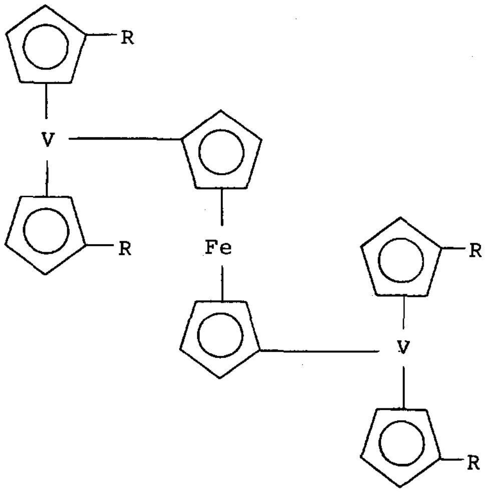


10.14

X-ray analysis of the tetramethyl derivative (10.15; R = Me) indicated that the cyclopentadienyl rings on ferrocene were distorted to an η^4- situation [118].

Radiopharmaceuticals have been prepared containing ferrocene or ruthenocene and glycine or alanine. Thus ferrocenyl-CO-Gly-OEt has been treated with $^{103}RuCl_3$ in ethanol to form



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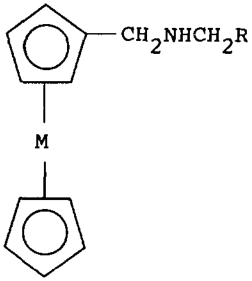


10.16

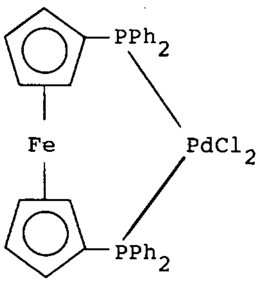
[^{103}Ru]-ruthenocenyl-CO-Gly-OEt which was then saponified to give [^{103}Ru]-ruthenocenyl-CO-Gly-OH. This product was injected into rats and mice and the organ distribution determined. Related reactions were reported [119].

The condensation of formylferrocene with the amines RCH_2NH_2, where R = p-$HOC_6H_4CH_2$, Ph, $PhCH_2$, 4-imidazolylmethyl, produced the corresponding secondary amines (10.16; M = Fe). A similar series of radioactive ruthenocenes (10.16; M = ^{103}Ru) was prepared and these compounds were tested as radiopharmaceuticals [120].

The exchange reaction of ferrocene with $^{103}RuCl_3$ at 180° for 30 minutes gave a good yield of ^{103}Ru labelled ruthenocene. Labelled formylruthenocene was used to prepare a series of amines [121].

Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (10.17) has been shown to be an effective catalyst for cross-coupling of sec-butylmagnesium chloride with bromobenzene, (E)-β-bromostyrene, 4-bromoanisole and 2-bromotoluene. The complex (10.17) was also found to be a good catalyst for the cross-coupling of n-butylmagnesium chloride and sec- and n-butylzinc chloride with organic bromides. The structure of the complex (10.17) was determined by X-ray analysis [122].

2-(Dimethylaminomethyl)-1-iodoferrocene has been prepared in good yield from the cyclopalladated complex of dimethylaminomethylferrocene by treatment with iodine. Reaction of the iodo derivative with copper(I) oxide and acetic acid followed by pyridine gave the ferrocenyl-acetate (10.18). Base hydrolysis



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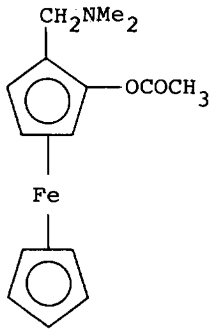

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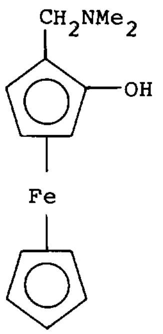

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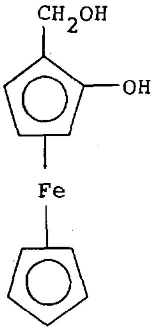

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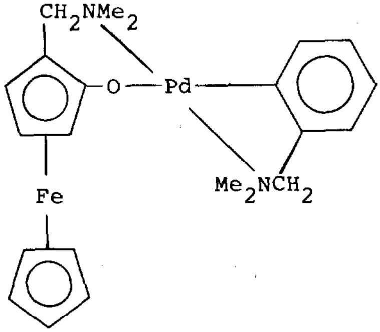
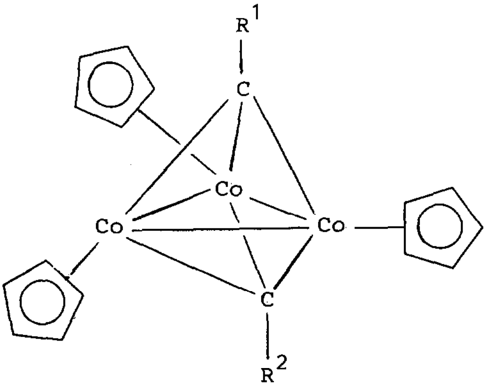


10.21

of this acetate produced the 2-substituted hydroxyferrocene (10.19) which was used to prepare the alcohol (10.20) and the palladium complex (10.21) [123].

The ferrocenyl bis(carbyne)cobalt capped cluster complexes (10.22; R^1 = ferrocenyl, R^2 = H, ferrocenyl) have been synthesized. The electrochemistry of these and several other capped cluster complexes (10.22; R^1 = Ph, R^2 = H, Ph; R^1 = Me_3Si, R^2 = H, I)



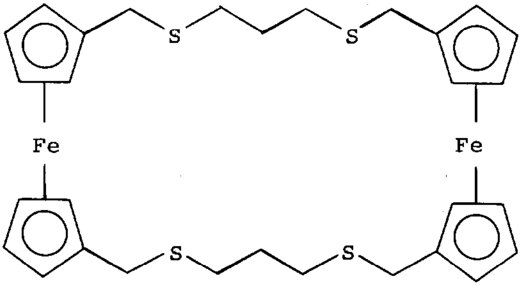
10.22

has been investigated. The complexes (10.22) underwent chemically and electrochemically reversible one-electron oxidation at ≈0.6 V vs. Ag/AgCl; irreversible reduction at ≈-1.55 V at Pt and irreversible oxidation at high positive potentials. The redox series for the ferrocenyl complex (10.22; R^1 = ferrocenyl, R^2 = H) was 2+/1+/0/1- and for the diferrocenyl complex (10.22; $R^1 = R^2$ = ferrocenyl) was 3+/2+/1+/0/1-. Monocations derived from the complexes (10.22) were reduced by nucleophiles such as Ph_3P, I^-, MeO^- to the neutral cluster complexes. Spectroscopic and electrochemical evidence collected for these complexes (10.22) suggested that π interaction between RC and Co_3 dominated the redox chemistry [124].

10. (ii) General chemistry

The reaction of 1,1'-bis(hydroxymethyl)ferrocene with 1,3-propanedithiol in the presence of trifluoroacetic acid produced the binuclear 2,6,19,23-tetrathia[7.7]ferrocenophane (10.23) [125].

Barborak and Chance have described a method for the direct synthesis of ferrocenyl alcohols from aldehydes and ketones. The carbonyl compound was dissolved in cold concentrated sulphuric acid to which ferrocene was added. After a short reaction time the mixture was worked up. The aldehydes produced alcohols and the ketones usually provided the olefin derived from the alcohol. For example, the reaction of ferrocene with acetaldehyde in sulphuric acid for one minute afforded the alcohol (10.24) in 54% yield [126].



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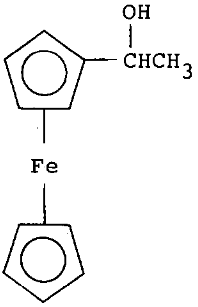
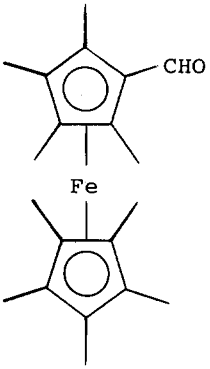


10.24

The Cannizzaro reaction of aromatic aldehydes in the presence of sodium hydroxide was promoted by ultrasound. When p-chlorobenzaldehyde and acetylferrocene were reactants and competition between the Cannizzaro and Claisen-Schmidt reactions was possible then ultrasound facilitated the Cannizzaro reaction only when the ketone was too unreactive to give the Claisen-Schmidt reaction [127].

Oxidation of decamethylferrocene with barium permanganate produced the aldehyde (10.25) which was reduced to give the alcohol (10.26; R = H). Treatment of the aldehyde (10.25) with methyllithium, phenylmagnesium bromide or ferrocenyllithium produced the corresponding alcohols (10.26, R = Me, Ph, ferrocenyl) [128].



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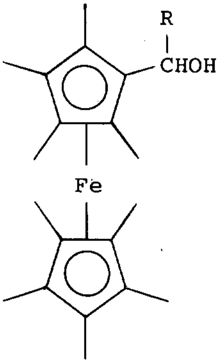

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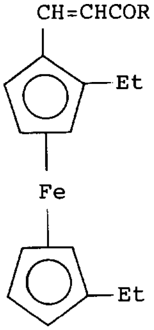
The aldol condensation of 1,1'-diethylferrocenecarboxaldehyde with ketones and the reaction of acetyl-1,1'-diethylferrocene with m-IC_6H_4CHO produced the corresponding unsaturated ketones (10.27; R = Me, Et, Bu, ferrocenyl) and (10.28). The physicochemical properties of these compounds were studied [129].

Treatment of 1,1'-diacetylferrocene with ethyl acetate in the presence of sodium amide produced the carbonyl compound (10.29) which was a good ligand for lead and cerium [130].

Acetylferrocene has been treated with dimethylformamide and phosphorus oxychloride followed by sodium perchlorate or sodium iodide to give the salt (10.30; X = I, ClO_4) which was hydrolyzed to form the aldehyde (10.31). Some reactions of this aldehyde were explored, thus with $HP(O)(OEt)_2$ and aniline



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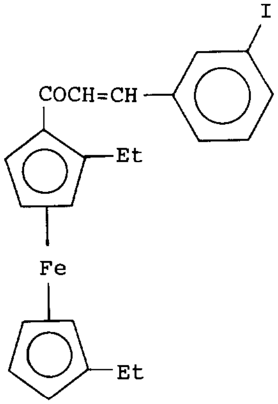


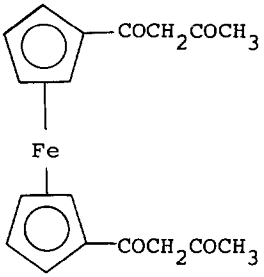
10.28

the product (10.32) was obtained [131].

The formylvinylferrocene (10.31) combined with the nitriles, RCH_2CN where R = CN, CO_2Me, CO_2Et, $CONH_2$, to form the ferrocenylbutadienes (10.33; X = CN, CO_2Me, CO_2Et, $CONH_2$). 1,1'-Bis(formylvinyl)ferrocene (10.34) underwent the same reaction [132].

Ferrocenecarbaldehyde has been treated with n-butyllithium and N-phenylbenzanilides to give ferrocene, ferrocenylmethanols, ferrocenylmethylether and amylferrocene [133].

The ferrocenylcarboxylic acids (10.35; n = 1, 2) have been reduced under Clemmensen conditions to give good yields of the



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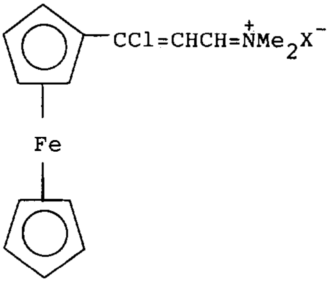

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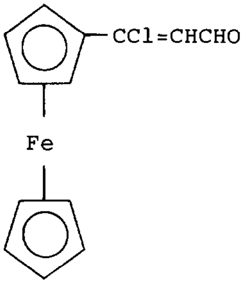

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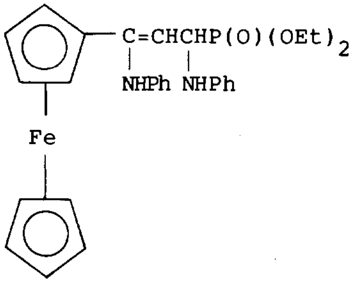

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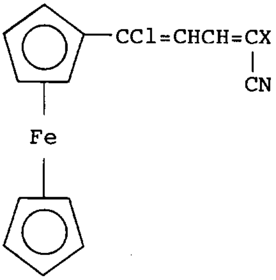

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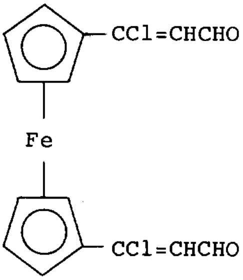

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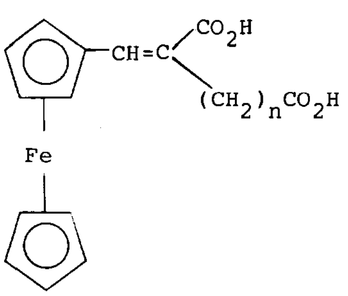

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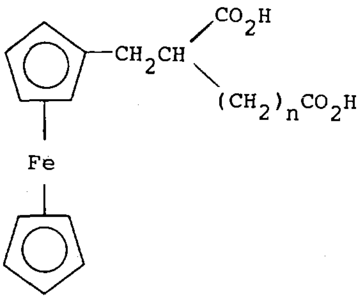

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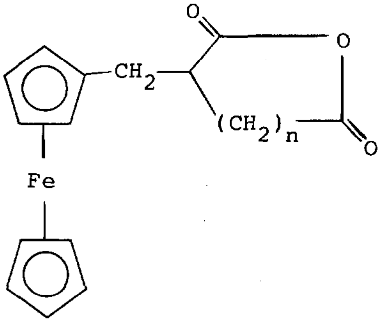


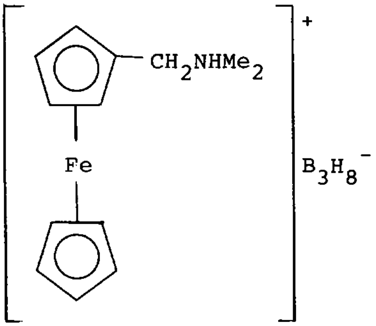
10.37

corresponding saturated compounds (10.36). Treatment of the acids (10.36) with trifluoroacetic anhydride produced the cyclic anhydrides (10.37) [134].

The reaction of dimethylaminomethylferrocene hydrochloride and 1,1'-bis(dimethylaminomethyl)ferrocene with $B_3H_8^-$ and $B_nH_n^{2-}$ produced the corresponding salts (10.38 and 10.39; n = 9,10,12) [135].

The ferrocenylmethylation of aniline has been used as the basis of an undergraduate experiment. The aniline derivatives (10.40, 10.41 and 10.42) were prepared and characterised [136].

Prostoglandin analogues including the ferroceneheptanoate (10.43) have been prepared through an intermediate cyclopalladated



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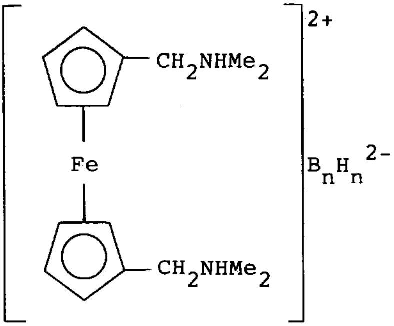

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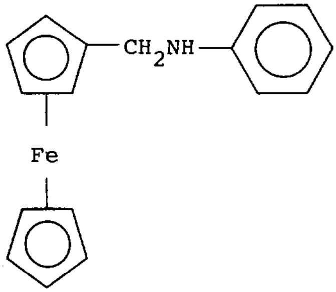

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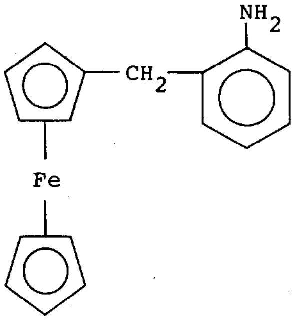

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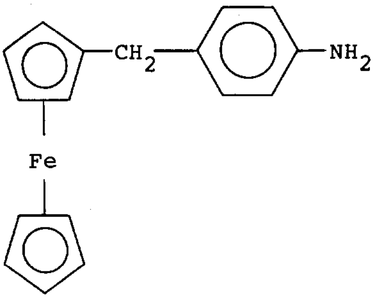

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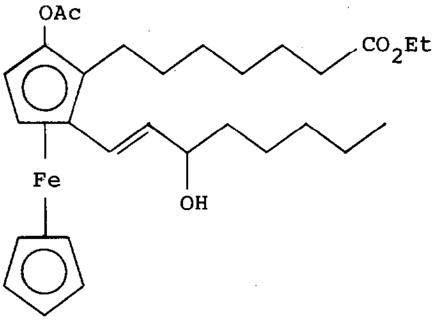

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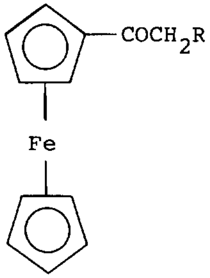

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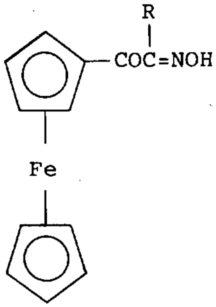


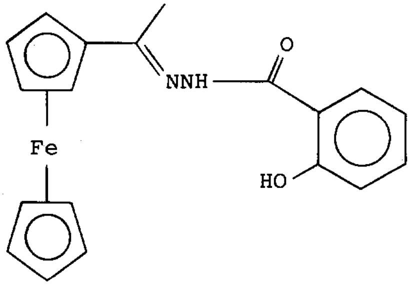
10.45

aminomethylferrocene [137].

Treatment of the ferrocenyl-ketones (10.44; R = H, $COCH_3$) with butyl nitrite and a sodium alkoxide produced the corresponding oxime (10.45) [138].

The ferrocenylhydrazide (10.46) = HL has been used to prepare several transition metal complexes $ML_2(H_2O)_n$, where M = Mn, Co, Ni and n = 4, 2, 2. Changes in the arene group of the ligand led to changes in the stoichiometry of the complexes [139].

Ferrocenyliminium cations (10.47, 10.48; R^1 = H, Me, Ph, 4-$MeOC_6H_4$; R^2 = H, Me, Et, $CHMe_2$, CMe_3) have been converted quantitatively to the corresponding acylferrocenes with aqueous base. Nucleophilic addition to the iminium ion was the rate



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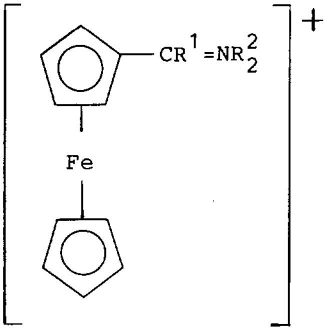

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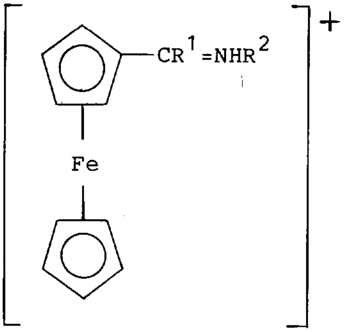

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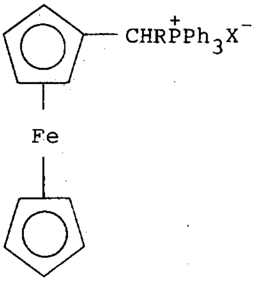

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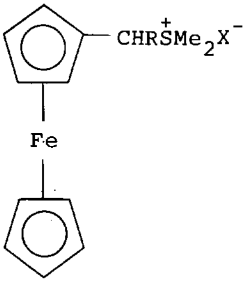

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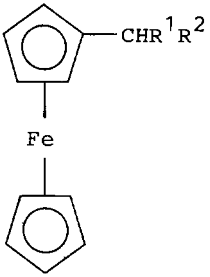

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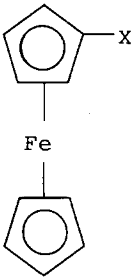


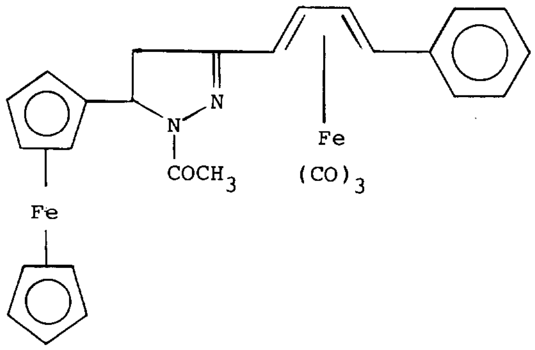
10.52

determining step and steric effects were more important than electronic effects in controlling the rate of reaction [140].

Ferrocenylalkylation of triphenylphosphine and dimethylsulphide with 1-ferrocenylalkanols has been used to prepare a range of ferrocenylonium compounds (10.49 and 10.50; R = H, Me, X = BF_4, ClO_4). These products were treated with sodium cyanide and sodium azide to give the derivatives (10.51; R^1 = H, Me; R^2 = CN, N_3) [141]. Several C- and N-α-ferrocenylalkyl compounds have been prepared in the same way [142].

Treatment of ferrocenyllithium with $(\eta\text{-}C_5H_5)Cr(NO)_2Cl$ and decomposition of the intermediate formed with hydrogen peroxide gave nitrosoferrocene (10.52; X = NO) and nitroferrocene (10.52; X = NO_2). Nitrosoferrocene was attacked by $CH_2(CN)_2$ and by PEt_3 to give the derivatives [10.52; X = $N{=}C(CN)_2$, $N{=}PEt_3$] [143].

Asymmetric induction in the synthesis of pyrazolines with ferrocenyl and phenylbutadieneiron tricarbonyl substituents has been estimated. Diastereomeric selectivity was shown to be sufficiently high both by the induction of a chiral centre and by a chirality plane and vice versa. An X-ray diffraction study was carried out on the diastereomeric 1-acetyl-3-[4-phenylbutadieneiron tricarbonyl]-5-ferrocenylpyrazolines (10.53) [144].



10.53

11. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

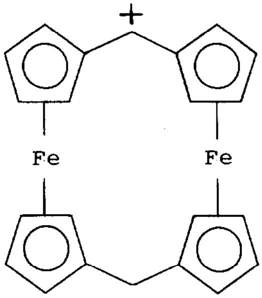
The syntheses of ferrocenophanes and crown ethers containing ferrocene have been reviewed [145].

The Moessbauer spectra of 34 mono- di- and tri-bridged ferrocenophanes and keto derivatives have been measured and interpreted. The influence of ring-tilt and bond shortness on the electron withdrawing effect of the carbonyl group was observed in some trimethylene-bridged compounds. These findings were interpreted in terms of a change of electron population in cyclopentadienyl-ring based orbitals and the absence of coplananity of the carbonyl group with the ring [146].

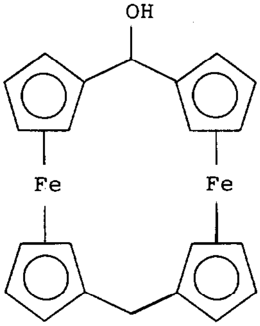
In a US Government Report Seyferth gave details of the preparation of phosphorus- and arsenic-bridged ferrocenophanes and their reactions with organolithium reagents. Some ferrocenylenephenylphosphine polymers were prepared and their cobalt complexes were active as hydroformylation catalysts [147].

The interconversion of the [1.1]ferrocenophan-1-yl cation (11.1) and [1.1]ferrocenophan-1-ol (11.2) has been studied and compared with the interconversion of the diferrocenylmethyl cation and diferrocenylmethanol in aqueous methyl cyanide. It was concluded that the conformations of the ferrocenophanes (11.1 and 11.2) permitted unhindered exo-addition and departure of a water molecule [148].

[1.1]Ferrocenophane (11.3; R = H) dissolved in HBF_3OH with the liberation of 1 mol of hydrogen for each mol of the ferrocenophane and the formation of the corresponding dication of the



11.1



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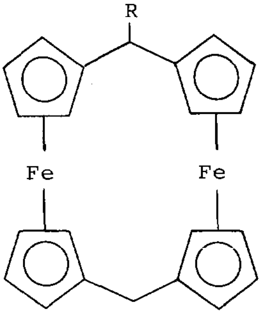


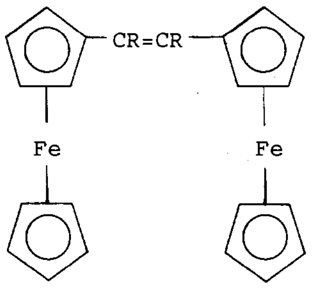
11.3

ferrocenophane. The complex (11.3; R = H) has been used in a photoelectrochemical cell with a p-type silicon cathode to generate hydrogen. A more efficient process for hydrogen generation in such a cell involved the use of an electrode coated with a polymer containing the 1-methylferrocenophane (11.3; R = Me) bound to poly(chloromethylstyrene) [149].

The bridge geometries in [1.1]ferrocenophane (11.3; R = H) and the carbocation and the carbanion derived from it have been the subject of a theoretical study using INDO-SCF calculations. The possibility of C-H-C hydrogen bonding in the carbanion was considered but was unlikely in view of the large calculated distance between the two bridge carbon atoms. The ^{1}H NMR spectrum of this species was best interpreted in terms of rapid proton exchange between two bridge carbons. Calculations of the ground state charge distribution for the carbocation and carbanion indicated that the ionic bridges were highly conjugated and the ionic charge was distributed over the ferrocene groups in each case [150].

The liberation of hydrogen gas from solutions of [1.1]-ferrocenophane (11.3; R = H) in acids has been the subject of an INDO-SCF investigation. It was concluded that hydrogen was formed by homolytic cleavage of metal-hydrogen bonds from a high energy twisted conformation which gave a stable dication and hydrogen [151].

Cyclic voltammetry of the biferrocenes (11.4; R = H, Me)



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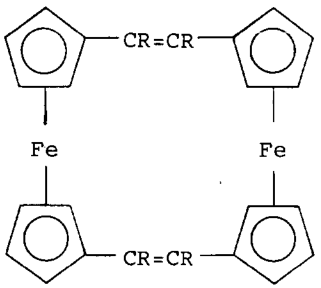
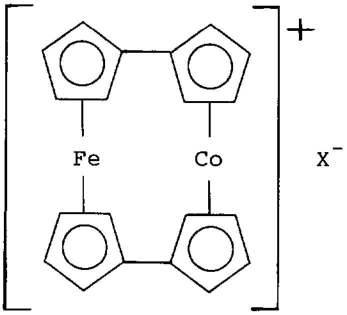


11.5

and the biferrocenylenes (11.5; R = H, Me) indicated a small first oxidation potential and a large second potential for (11.4) while the biferrocenylenes (11.5) showed the reverse. The mono-oxidized form of the biferrocene (11.4) was shown by Moessbauer spectroscopy to be a mixed valence species while the dioxidized form of the biferrocenylene (11.5) contained only Fe(III) [152].

Ferrocenylenecobaltocenylenium chloride and hexafluorophosphate (11.6; X = Cl, PF_6^-) have been prepared and their magnetic properties examined [153].

The 2,2'- and 3,3'-trimethylene[1.1]ferrocenophanes (11.7 and 11.8) respectively have been prepared and characterized. NMR spectroscopy demonstrated that the 2,2'-bridged ferrocenophane



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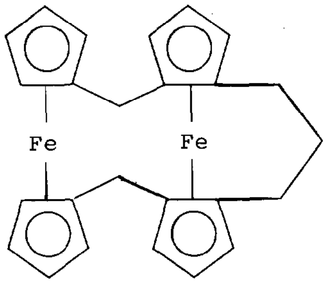

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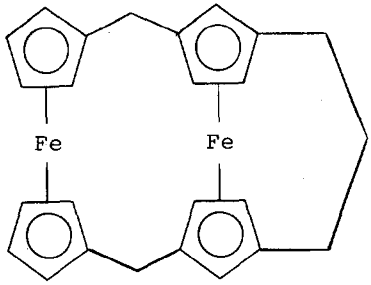


11.8

(11.7) had rigid [1.1] methylene groups while the 3,3'-bridged compound (11.8) showed rapid interconversion of the [1.1]methylene protons. Ring tilting in these compounds was discussed and the redox potentials were determined [154]

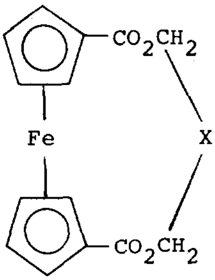
The crystal and molecular structure of the dimercurioferrocenophane dication (10.14; n = 2) has been determined by X-ray crystallography. The Hg...N distance indicated secondary interaction [155].

The reaction of 1,1'-bis(chloroformyl)ferrocene with the diols $HOCH_2XCH_2OH$, where X = $(CH_2OCH_2)_n$, 2,6-pyridinylene, 2,5-furanylene, 2,5-thiophenylene, 1,3-phenylene, CH_2SCH_2, n = 0 - 3, afforded the ferrocenophanes (11.9) together with the diols (11.10). Further reaction of the diols (11.10) with 1,1'-bis(chloroformyl)ferrocene produced the crown ethers (11.11). The ability of the cyclic molecules (11.9 and 11.11) to complex with metal ions was investigated [156].

The ferrocenophane (11.12) has been prepared by reaction of hydroquinone with 1,1'-bis(chloroformyl)ferrocene [157].

Ring expansion of the [1]ferrocenophane (11.13) was achieved by treatment with phenyllithium and then $(\eta\text{-}C_5H_5)Fe(CO)_2I$ to form the [2]ferrocenophane (11.14) and its carbonyl insertion product (11.15) in addition to acyclic products. The crystal and molecular structure of [2]ferrocenophane (11.14) was determined by X-ray crystallography [158].

[2]Ferrocenophanes were oxidized with iodine in benzene and the resultant polyiodides were studied by Moessbauer



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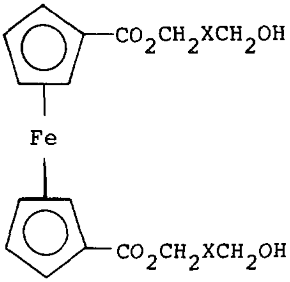

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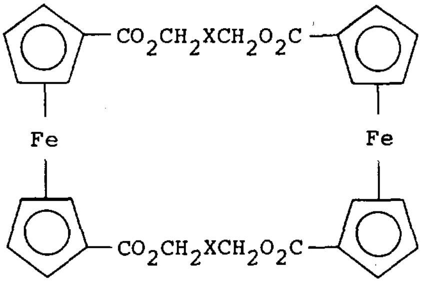

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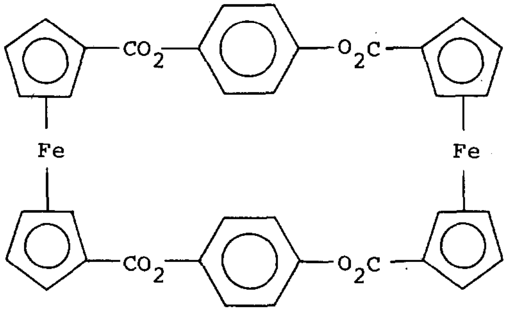

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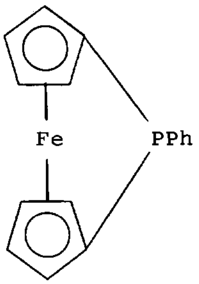

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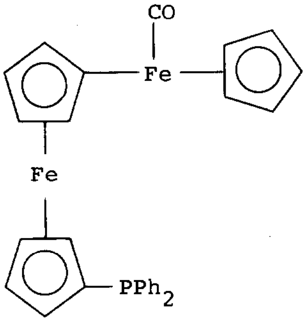

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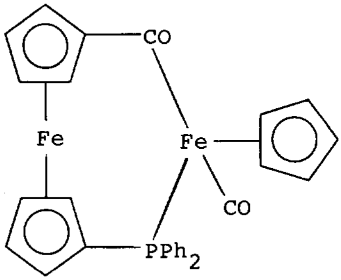

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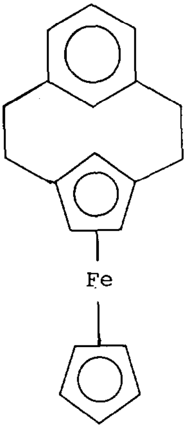
spectroscopy. A high quadrupole splitting value of 3.70 mm s^{-1} was obtained and it was concluded that there was strong direct interaction between the iron and iodine atoms [159].

Reaction of 1,3-di(hydroxymethyl)ferrocene with m- and p-di(mercaptomethyl)benzene in the presence of trifluoroacetic acid gave the corresponding sulphides. Desulphurization of these sulphides produced the ferrocenophanes (11.16 and 11.17) respectively. The structures of the ferrocenophanes (11.16 and 11.17) were determined by X-ray analysis [160].

1-Dimethylaminomethyl-2-iodoferrocene was used as the starting material in an eight-step synthesis of the ferrocenophane (11.18;



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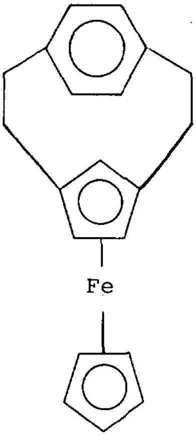
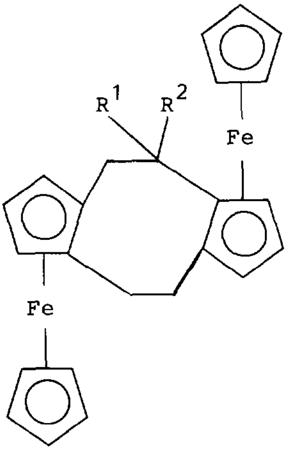


11.17

$R^1 = R^2 = H$). X-ray analysis indicated that this molecule had a centrosymmetrical chair conformation. The ketone (11.19) was reduced to a mixture of the endo- and exo-alcohols (11.18; $R^1 = H$, $R^2 = OH$; $R^1 = OH$; $R^2 = H$) [161].



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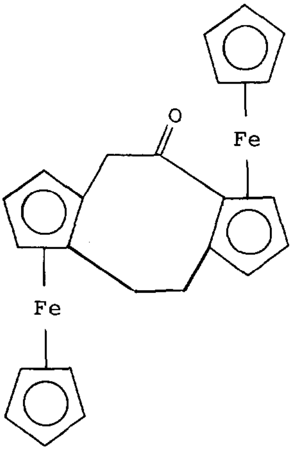
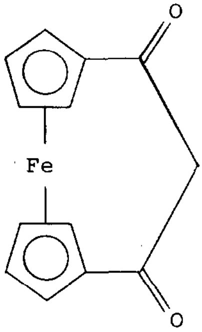


11.19

The crystal and molecular structure of [3]ferrocenophane-1,3-dione (11.20) has been determined by X-ray crystallography. The two cyclopentadienyl rings were tilted by 9.8° with respect to each other and the bond angles in the bridge were 3-6° less than normal [162].



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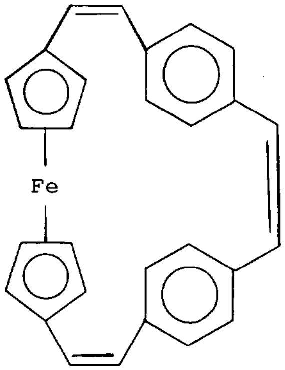
The ferrocenophane (11.21) has been prepared from the bis-phosphonium salt (11.22) by a two-fold Wittig reaction followed by a titanium mediated coupling of the resultant dialdehyde (11.23). The ferrocenophane (11.21) was examined by ^{1}H NMR spectroscopy and was found to exist as two mirror images with opposite helicity [163].

Methylmagnesium iodide attacked 3-phenyl[5]ferrocenophane-1,5-dione to give the 1,1,5,5-tetramethyl derivative which was in turn subjected to Friedel-Crafts acetylation to form the 3-(p-acetylphenyl) derivative in 12% yield. In this last reaction the two methyl groups on the terminal-bridge carbon atom inhibited α-acylation of the ferrocenophane. NMR evidence was used to discuss the conformations of the ferrocenophanes [164, 165].

The structural features of several di- and tri-bridged ferrocenophanes have been determined and compared. Thus the structures of the bis(tetramethylene) (11.24), tris(tetramethylene) and tris(pentamethylene) (11.25; n = 4, 5) compounds have been obtained and compared with the previously determined structure of the tris(trimethylene) compound (11.25; n = 3). The metal to cyclopentadienyl ring distances were found to be consistent



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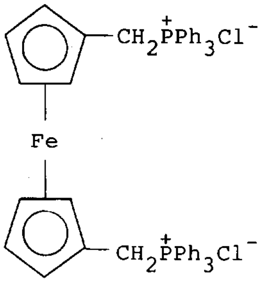

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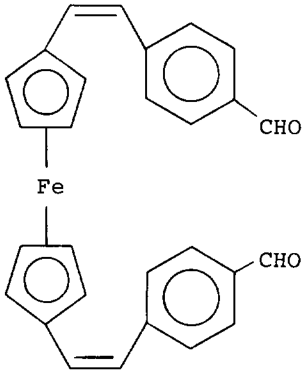

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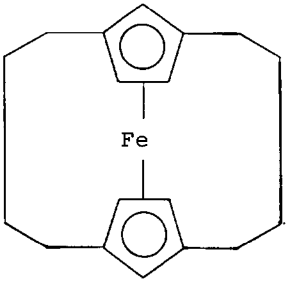

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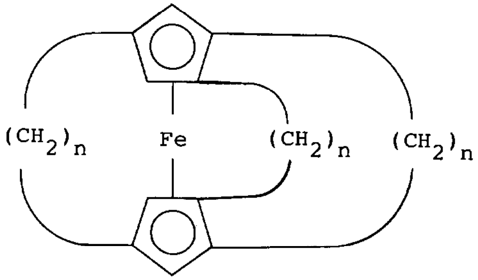
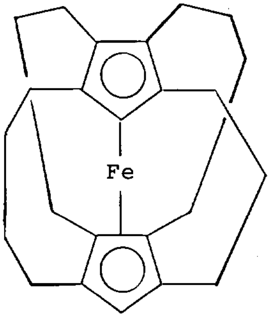


11.25

with the Moessbauer spectra and redox potentials of the compounds. The compounds (11.25; n = 3, 5) had eclipsed cyclopentadienyl rings while the compounds (11.24; 11.25; n = 4) showed rings staggered by 12-14°. The shortness of the bridges was the dominant factor in determining the structure of the tris(trimethylene) compound (11.25; n = 3) while the requirement to avoid eclipsed bridge hydrogens was dominant for the compounds (11.24; 11.25; n = 4, 5) [166].

The ferrocenophane (11.26) and some related tetrabridged ferrocenophanes have been prepared by cyclization of 2-[4][4][3]-(1,3,4)ferrocenophanepropanoic acid with polyphosphate ester. The crystal structure of the ferrocenophane (11.26) was determined by X-ray diffraction. The two η-cyclopentadienyl rings were eclipsed and almost parallel and the distances between the rings and the iron atom were unusually short at 1.589 and 1.591 Å [167].

Aluminium chloride has been found to promote bridge rearrangements in multibridged ferrocenophanes. The cyclization of the butanoic acids (11.27 and 11.28) with $AlCl_3/NEt_3/ClCO_2Et$ gave no tetrabridged ferrocenophane but three dibridged ferrocenophanes (11.29, 11.30 and 11.31) each containing two six-membered rings which were formed via homoannular cyclization of the side chains followed by rearrangement of the existing tetramethylene bridges [168].



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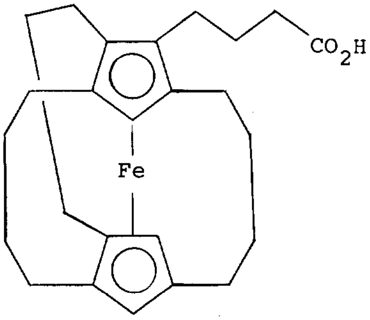

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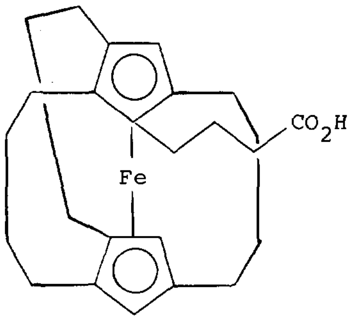

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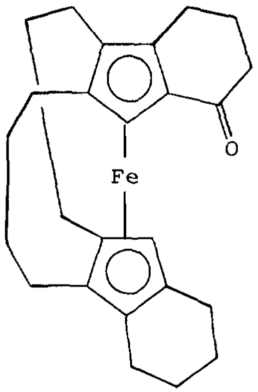

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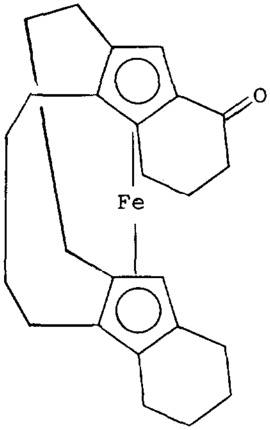

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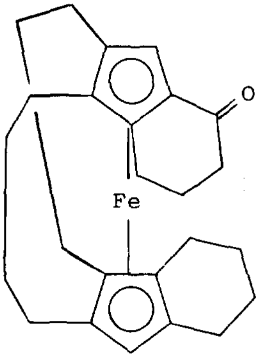
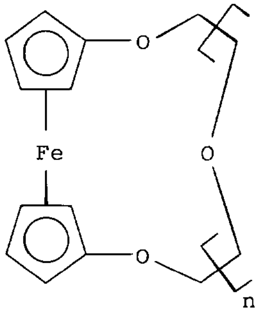


11.31

The NMR spectra of the ferrocenophanes (11.29, 11.30 and 11.31) and related compounds were discussed [169].

Complexation of the crown ether ferrocenophanes (11.32; n = 3, 4) with alkali metal cations caused ^1H and ^{13}C NMR chemical shift changes which arose from conformational changes and electronic field effects. The crystal and molecular structure of one complex, (11.32; n = 3) with NaSCN, was determined by X-ray crystallography. The iron atom was not involved in complex



11.32

formation [170].

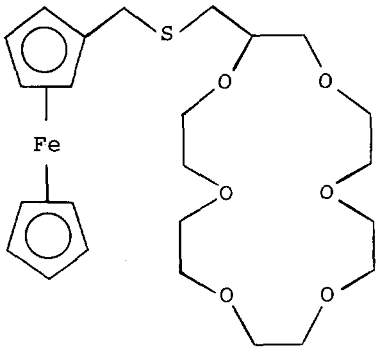
Two ferrocene containing crown ethers (11.33 and 11.34) have been prepared and their ability to complex with alkali metal cations was examined. The crown ether (11.34) exhibited selectivity for K^+ and Rb^+ ions in competitive extraction [171].

Several polythia[n]ruthenocenophanes have been prepared and some comparisons made with the corresponding polythia[n]-ferrocenophanes [172].

The dioxathiaferrocenophanes [11.35; X = $S(CH_2CH_2S)_{1,2,3}$] have been obtained by treatment of 1,1'-bis(2-chloroethoxy)-ferrocene with $NaSCH_2CH_2SNa$. The binuclear tetrathiaferrocenophane (11.36) was formed in the same reaction. The ferrocenophanes [11.35; X = $S(CH_2CH_2S)_{1,2}$] were effective in selectively extracting Hg^{2+} and Cu^{2+} ions from the aqueous metal picrates. The extraction of alkali metal, alkaline earth and transition metal cations was examined [173].

Alkylation of disodium ferrocenedithiolate (11.37) with 1,2-dibromoethane gave the [4]ferrocenophane (11.38) while treatment with the mixed halides $Br(CH_2)_nCl$, where n = 2, 3 gave the dichloro compounds (11.39; n = 1, 2). Cyclization of one of these compounds (11.39; n = 2) was achieved with sodium sulphide to form the [7]ferrocenophane (11.40). The large ring compound (11.41) was obtained from the dichloro ferrocene (11.39; n = 2) and $HSCH_2CH_2SH$. Several related reactions were reported [174].

1,1'-Ferrocenedithiol has been treated with α,ω-dibromo-polyethers to form polyoxadithia[n]ferrocenophanes and polyoxa-



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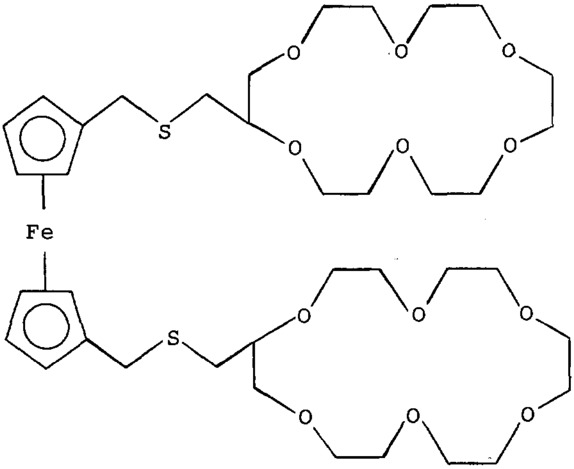
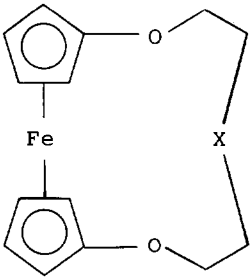


11.34

tetrathia[n.n]ferrocenophanes. These ferrocenophanes were effective in forming complexes with Ag^+ but did not combine with alkali metal or alkaline earth metal cations. The silver complex showed evidence of Fe-Ag electron-transfer interaction [175].

Pyramidal inversion of sulphur atoms in ferrocenylsulphide-palladium(II) and -platinum(II) complexes (11.42; M = Pd, Pt; X = Cl, Br; R = i-Pr, i-Bu, Ph) has been investigated by variable temperature NMR spectroscopy. At temperatures down to -100°C



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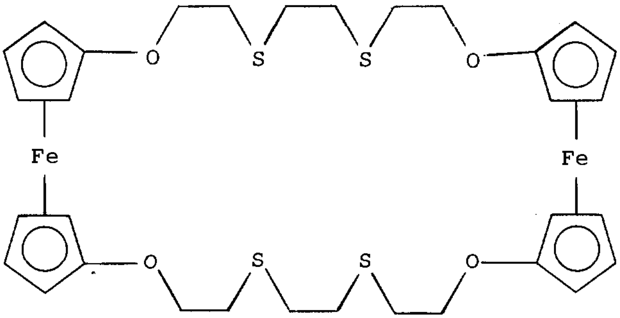

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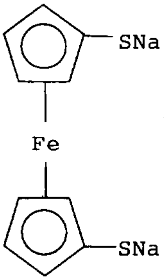

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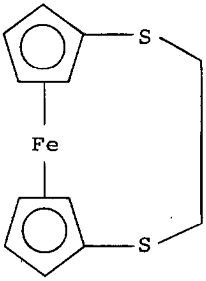

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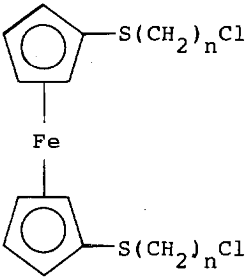

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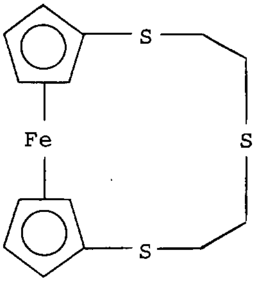

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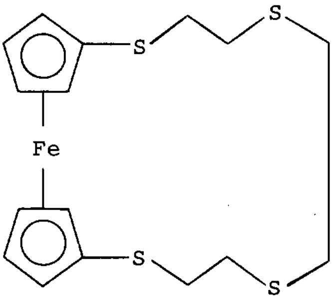

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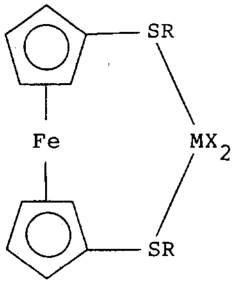

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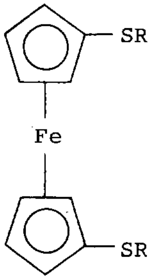
sulphur inversion was slowed sufficiently to give energy data while reversal of the ferrocenophane ring remained fast on the NMR time scale. $\Delta G^{\neq}$ values for the sulphur inversion were in the range 47 to 65 kJ mol^{-1} and were dependent on the nature of the metal, the halogen and the substituent R [176].

Several ferrocenylsulphides (11.43; R = Me, i-Pr, i-Bu, i-pentyl, Ph, $PhCH_2$) have been prepared by treatment of lithiated ferrocene with the appropriate disulphide. The sulphides were effective in forming bimetallic chelate complexes with palladium and platinum halides. Ferrocene dialkyldithiocarbamates (11.44; R = Me, Et, i-Pr) were also reported [177].



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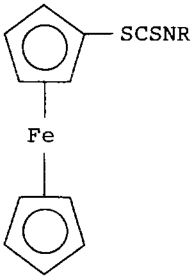
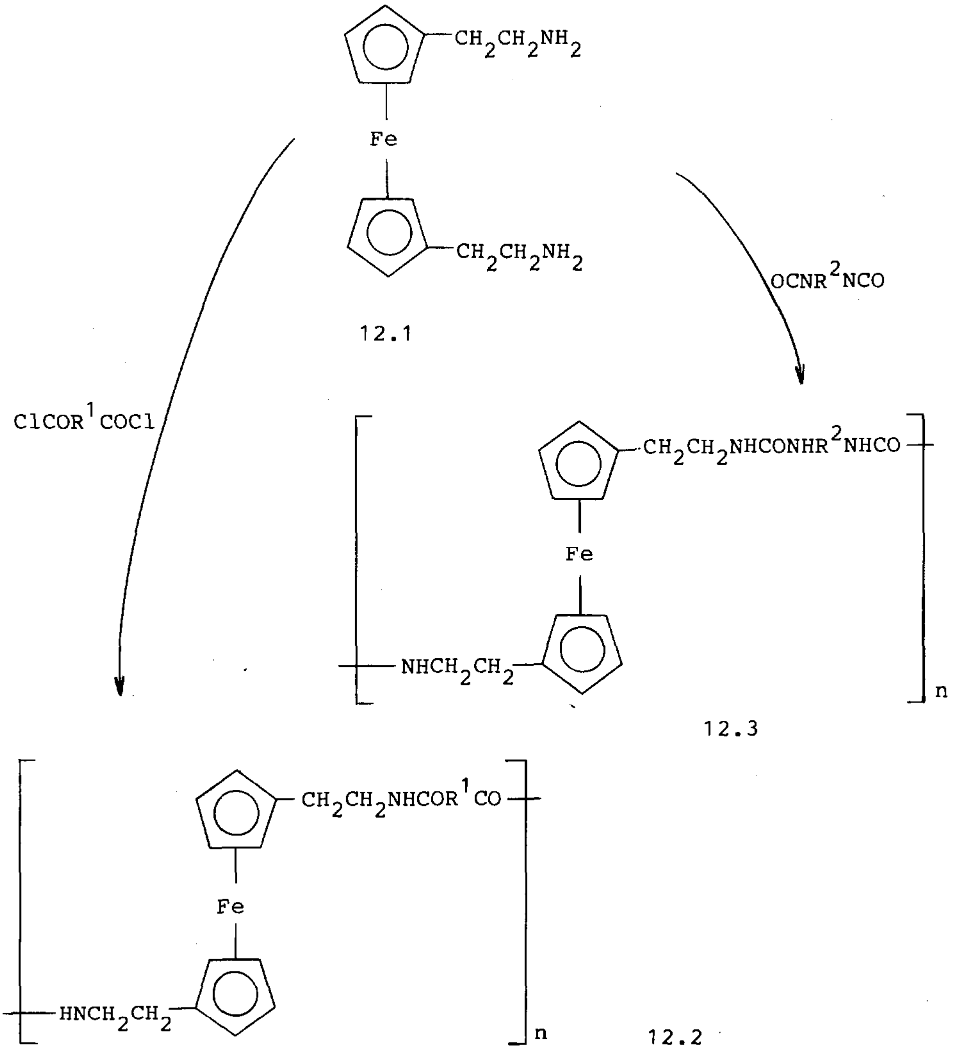


11.44

12. FERROCENE-CONTAINING POLYMERS

A series of vinylferrocene-methyl methacrylate copolymers has been prepared and their absorption from toluene and chloroform onto pyrogenic silicas was measured. The level of absorption depended on the composition of the copolymer, the solvent and the surface area of the silica. High molecular weight copolymer was preferentially absorbed [178].

Copolymers of vinylferrocene with acrylonitrile, maleic anhydride, N-vinylcarbazole, 2-vinylnaphthalene and acenaphthylene were coated on platinum and semiconductor electrodes such as



12.1

12.3

12.2

SnO_2 and In_2O_3. The photochemical properties of these copolymer films were investigated. The photovoltage and the photocurrent were higher on the semiconductor electrodes [179, 180].

Electrically conducting polymers have been obtained from insulating polymers by electrochemical oxidation of a neutral polymer in solution with its concurrent precipitation. Thus anodic oxidation of a solution of poly(vinylferrocene) gave a deep blue polymeric precipitate containing a partially oxidized mixed-valence salt with ferrocene and ferrocenium ion groups [181].

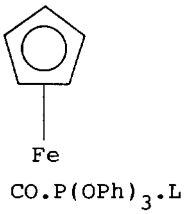
Semiconducting 1,1'-ferrocenylene polymers have been prepared by doping the polymer with, for example, arsenic(V) fluoride [182].

1,1'-Bis(β-aminoethyl)ferrocene (12.1) has been condensed with a variety of diacid chlorides and diisocyanates to give the corresponding ferrocene containing polyamides [12.2; R^1 = p-C_6H_4, $-(CH_2)_4-$, $-(CH_2)_8-$] and polyureas (12.3; R^2 = p-$C_6H_4CH_2C_6H_4$, 2,4-MeC_6H_3) [183].

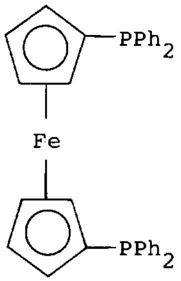
13. APPLICATIONS OF FERROCENE

(i) Ferrocene catalysts and photosensitizers

Ferrocenium tetrafluoroborate has been used as a catalyst for the conversion of the η^1-alkenyl complex [13.1; L = η^1-(E)-CMe=CMePh] to the corresponding acyl complex [13.1; L = η^1-(E)-COCMe=CMePh] at 0°C in the presence of carbon monoxide. The complexes [13.1; L = η^1-(E)-C(CO_2Me)=CHMe, η^1-(E)-CMe=CMeCH-



13.1



13.2

$(CO_2Et)_2$] did not undergo carbonyl insertion under the same conditions [184].

The nickel(II) chloride complex of 1,1'-bis(diphenylphosphino)ferrocene (13.2) has been used as a catalyst for the silylation of (E)-MeCH=$CHCH_2MgBr$ with $HSiMePh_2$ and $HSiMe_2Ph$ to give (E)-MeCH=$CHCH_2SiMePhR$, where R = Me, Ph, with high selectivity [185].

Ferrocene has been used to catalyze the decomposition of aryldiazonium salts, $X.C_6H_4N_2^+BF_4^-$, where X = H, p-MeO, to form the radicals $X.C_6H_4^\bullet$ which were used in organic reactions [186].

Ferrocene-acid anhydride systems have been used as polymerization initiators for vinyl monomers. The rate of polymerization of methyl methacrylate in the presence of ferrocene-benzoic anhydride was proportional to the square concentrations of both compounds of the initiator system [187].

Ethanol and acetaldehyde were prepared from methanol, carbon monoxide and hydrogen under pressure at 50-350°C in the presence of a catalyst system containing cobalt carbonyl and a promoter selected from organosulphur compounds, nitrogen containing compounds, and 1,1'-bis(diphenylphosphino)ferrocene (13.2) [188].

The chemical and physical properties of soot as a function of fuel molecular structure in a swirl-stabilized combustor have been investigated. The fuels used contained 0.05 wt % ferrocene as a smoke suppressant [189].

The electrostatic and imaging properties of an electrophotographic photoreceptor were improved by using ferrocene and dimethylferrocene mixed with a polycarbonate in a protective layer over a selenium light sensitive layer [190]. The importance of charge transfer interaction between the ferrocene and the polycarbonate has been emphasised [199]. The protective layer was not uniform but carried a higher proportion of ferrocene at the face adjacent to the light sensitive layer [192].

Addition of ferrocene to polyphenylquinoxaline enhanced the electrical conductivity which was induced by pulse irradiation with 65 keV electrons [193].

A secondary battery has been developed containing ferrocene. The battery consisted of a polyethylene outer casing, stainless steel current collector and a semipermeable membrane separating the anode and cathode compartments. The anode compartment contained polypyrrole and ferrocene in an electrolyte of lithium perchlorate, methyl cyanide and propylene carbonate [194].

The electrical and physical properties of a silver-iodine battery containing ferrocenium polyiodide have been evaluated [195].

The determination of triphenylhydroxysilane has been carried out by dissolving the sample in acetone containing 0.05-0.07 wt % (octyloxy)silylferrocene followed by gas chromatography on a silicone stationary phase [196].

Ferrocene and a Lewis acid diazonium salt have been used as a catalyst system for the rapid curing of a two-pack epoxy or acrylic resin based adhesive [197].

(ii) Ferrocene stabilizers and improvers

Highly porous, low density spheres based on inorganic materials have been formed for use in the preparation of hygroscopic, flammable or radioactive articles. The spheres were formed from a mixture of powdered copper, polystyrene binding agent and napthalene with ferrocene as a blowing agent. The cold compressed spheres were heated to volatilize the blowing agent and then sintered at 600-700°C to give the product with density 0.4-0.7 g cm^{-3} [198].

The addition of ferrocene to the components used in the manufacture of carbon fibre increased the tensile strength of the carbon fibre [199].

A small quantity of ferrocene was one of the additives in an anaerobic two component adhesive [200].

The addition of 0.5 wt % of α-ferrocenylethanol or diferrocenyldisulphide to oil increased the lubricating properties [201].

(iii) Combustion control

The incorporation of ferrocene compounds as burning rate modifiers into ammonium perchlorate has been regarded as a potentially hazardous operation. Isothermal and dynamic thermogravimetry was used to determine the stability and half-life of a ferrocene additive under processing conditions. Exothermic decomposition peaks were observed at lower temperatures in the mixture than for the pure compounds [202].

The flammability of polystyrene and polypropylene has been studied in the presence of metal chelates, chlorinated hydrocarbons and ferrocene. Flammability was reduced, char was increased and the formation of smoke was suppressed [203].

Addition of a small proportion of ferrocene and t-butylacetate into gasoline gave a difference in octane number requirement increase of 4.5-6 units [204].

(iv) Biochemical and biological applications

The oxidation of ferrocytochrome *c* by six ferrocenium ion derivatives and the reduction of ferricytochrome *c* by decamethylferrocene have been investigated. The rates of these reactions were first order in protein and in ferrocenium ion or ferrocene concentration [205].

The use of carbon monoxide: acceptor oxidoreductase from *Pseudomonas thermocarboxydovorans* strain C2 as a carbon monoxide sensor has been investigated. The enzyme catalysed the oxidation of carbon monoxide to carbon dioxide in the presence of various electron acceptors which included ferrocenium carboxylic acid and 1,1'-dimethylferrocenium ion [206].

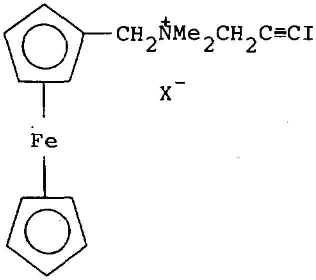
A ferrocene-mediated enzyme electrode has been developed for the amperometric determination of glucose. In the electrode ferrocenium ion was used as the mediator of electron transfer between immobilized glucose oxidase and a graphite electrode. A linear current response proportional to the glucose concentration was found in diabetic blood samples. The effects of oxygen, pH and temperature on the electrode were determined [207].

The growth of Ehrlich ascites tumours in rats was inhibited by ferrocenium salts, $[(\eta\text{-}C_5H_5)_2Fe]^+X^-$, where $X^- = FeCl_4^-$; $2,4,6\text{-}(NO_2)_3C_6H_2O^-$; $CCl_3CO_2^-.2CCl_3CO_2H$. However, ferrocene and tetrachloroferrate salts, $[R_4N]^+[FeCl_4]^-$, showed little activity [208].

Carbamate derivatives of ferrocene have been used as prophylactic agents in the soman poisoning of mice. Administration of the ferrocene carbamate 30 min. before dosing with soman gave a six-fold decrease in acute toxicity. The ferrocene carbamates inhibited the brain acetylcholinesterase [209].

Phenethylamine, tryptamine and other arylalkylamines have been derivatized with N-succinimidyl-3-ferrocenylpropionate and determined by HPLC using electrochemical detection. The technique may be applicable to the determination of amino compounds in body fluids [210].

The iodopropargylammonium salt (13.3; X = halide) has been prepared and tested as a fungicide. It was a better fungicide than 1,2,3,6-tetrahydro-N-[(trichloromethyl)thio]phthalamide [211].



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