FERROCENE
ANNUAL SURVEY COVERING THE YEAR 1978*

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CONTENTS

1. REVIEWS

Sutherland and co-workers have presented a review on the hydrogenation of aromatic ligands during exchange reactions between ferrocene and arenes in the presence of aluminium chloride. The mechanism of the hydrogenation was discussed and the synthetic applications were considered [1].

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[*] Ferrocene, Annual Survey covering the year 1977 see J. Organometal. Chem., 167 (1979) p. 53-154.

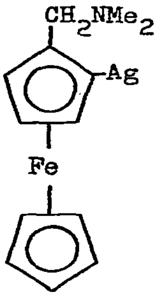
The applications of (η-cyclopentadienyl)transition metal complexes have been discussed by Kochetkova and Krynkina [2]. Solomatin has reviewed the use of ferrocene compounds in analytical chemistry [3]. Ferrocene chemistry has been included in a review of the 1976 literature of η-cyclopentadienyl and η-arene complexes [4]. The chemistry of heterocyclic ferrocenes has been included in a wider review by Volz and Kowarsch [5].

2. STRUCTURAL DETERMINATIONS

The structures of ferrocene and related compounds were discussed and the application of the molecular orbital approach to these compounds was considered [6]. INDO SCF MO calculations have been carried out for several diamagnetic (η-hydrocarbon) transition metal complexes including metallocenes, such as ferrocene, mixed sandwich complexes and half-sandwich complexes. Calculations for the free ligands $C_5H_5^-$, C_6H_6 and $C_7H_7^+$ were also carried out. Reductions in the π-bond order on complex formation were found in each case. The ^{1}H NMR chemical shift for a given ring proton, relative to the shift for the appropriate proton on the free ligand, showed a good linear correlation with the corresponding change in the charge density on that proton. It was concluded that the evidence indicated an appreciable diminution in the aromatic character of the ligand rings on complex formation [7].

The electron structure of ferrocene was studied by ultralong-wave X-ray spectroscopy. There was a high degree of delocalization of electron density for the e_{2g} level and there was an appreciable 3d population in energy levels having ionization energies of approximately 50 kJ mol^{-1} [8]. The crystal and molecular structures of sym-octamethylferrocene and decamethylferrocene were determined by X-ray analysis. In both molecules the η-cyclopentadienyl rings were staggered. The methyl groups in sym-octamethylferrocene deviated from the η-cyclopentadienyl ring plane being inclined away from the iron atom. High thermal motion prevented an accurate determination of the geometry of decamethylferrocene at room temperature [9].

The structure of 2-silver(dimethylaminomethyl)ferrocene (2.1) was investigated by X-ray analysis. The silver atoms formed a planar square with the substituted η-cyclopentadienyl rings acting as bridging ligands through one of the carbon atoms of each ring. The nitrogen atoms did not appear to participate in a distinct



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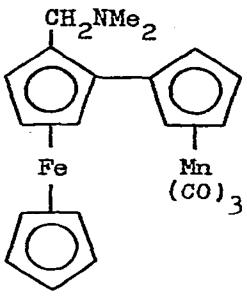


2.2

coordination of the silver atoms. Some reactions of the complex (2.1) were also investigated. Thermal decomposition of a mixture of the complex (2.1) and cymantrenylsilver gave the ferrocenylcymantrenyl derivative (2.2) and the coupling products of symmetrical radicals [10].

The crystal and molecular structure of ferricinium tetrachloroferrate was determined by X-ray diffraction. The η-cyclopentadienyl rings were almost eclipsed and nearly parallel. The inter-ring distance was 3.36 Å which is almost identical to that of ferrocene. It was concluded that the removal of an electron does not seem to affect the Fe—C bond distance [11].

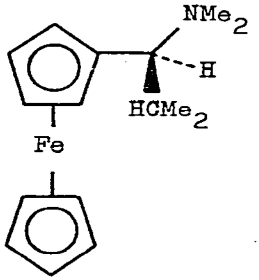
A 3:1 thiourea-ferrocene clathrate was subjected to a single-crystal X-ray diffraction study at 295° K and the changes in reflections that accompanied a reversible phase transition were observed also on cooling down to 100° K. At the higher temperature the structure consisted of thiourea molecules which formed a honeycomb of channels by spiralling with a pitch of 120°. The channels enclosed point symmetries 3, $\bar{3}$ and 32. Within these channels, sites of point symmetry 32 were occupied by the ferrocene iron atoms. The η-cyclopentadienyl rings were disordered and regions of three dimensionally delocalised cyclopentadienyl electron density were observed around the iron atoms [12].

The crystal structures of the ordered (150° K) and disordered (295° K) phases in ferrocene were determined by X-ray crystallography. The structure of the ordered phase was triclinic with eight of the sixteen molecules in the unit cell on noncentred sites. The structure of the disordered phase was found to be different from that proposed in previous models [13].

The structure of the mesophase form of formylferrocene (44-123° C) has been examined by Moessbauer spectroscopy and X-ray diffraction. The phase was found to consist of an orientationally disordered molecular crystal. The molecules were, on average, oriented at random about their centres of mass with a centre of mass-iron distance of 46 pm [14].

3. STEREOCHEMISTRY OF FERROCENES

A new method was developed for the determination of the absolute configuration and optical purity of chiral ferrocene derivatives through stereorelating metallation of α-dimethylaminoalkylferrocenes. The absolute configuration of the aminoferrocene (3.1) was assigned [15].



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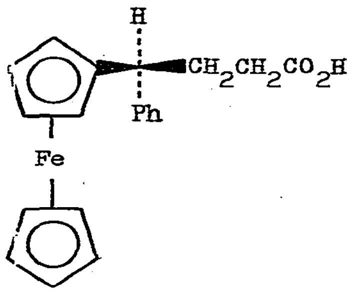
Cyclisation of γ-ferrocenyl-γ-phenylbutanoic acid (3.2) gave the exo- and endo- -phenylferrocenocyclohexenones (3.3 and 3.4). The ketones (3.3 and 3.4) were used to prepare the pseudoasymmetric 1,4-diphenylferrocenocyclohexenes (3.5, 3.6 and 3.7) and the absolute and relative stereochemistries of these compounds were determined [16].

The racemic acid (3.8) was resolved by active α-phenylethylamine and cyclized to give the ketone (3.9). The ketone (3.9) was treated with phenylmagnesium bromide to give the alcohol (3.10) which was reduced to the ferrocenophane (3.11) with retention of configuration. The synthesis, relative and absolute configuration and conformation



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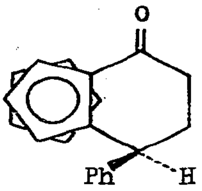

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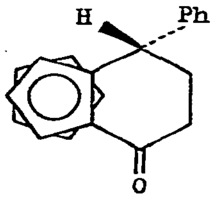

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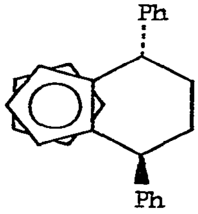

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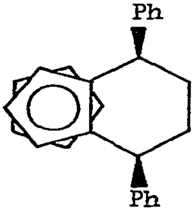

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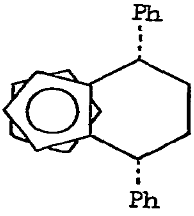

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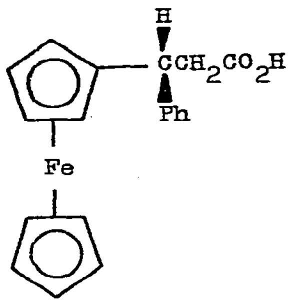
of some methyl substituted [3]-(1,1')-ferrocenophanes was also described. The circular dichroism curves of various metallocene carbocations were reported [17].

Fermentation of ferrocene aldehyde-d with bakers' yeast in glucose solution resulted in stereospecific reduction to give the (+)-alcohol (3.12) together with a small amount of the ether (3.13). Treatment of the alcohol (3.12) with bis(dimethylamino)methane and aluminium chloride gave (+)-N,N-dimethylaminomethyl-1d-ferrocene. This amine readily formed a palladium complex on treatment with sodium tetrachloropalladate [18].

It has been shown that the non-Saytzeff dehydration of α-ferrocenyl-t-carbinols to ferrocenylolefins is subject to stereochemical control in non-acidic media and in acidic media under kinetic control. Specific catalytic effects were not implicated in the determination of product stereochemistry. Thus 2-ferrocenyl-3-methyl-2-butanol had the preferred conformation (3.14) and underwent dehydration with neutral alumina to form predominantly



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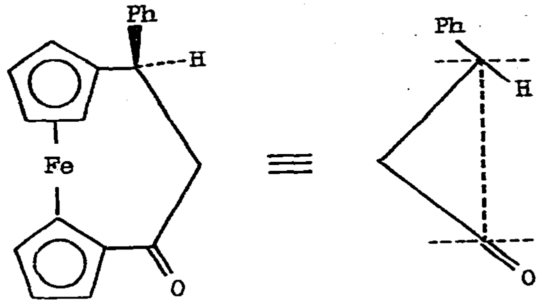

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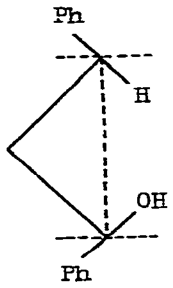

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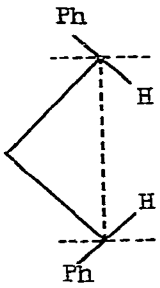

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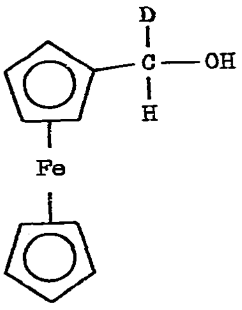

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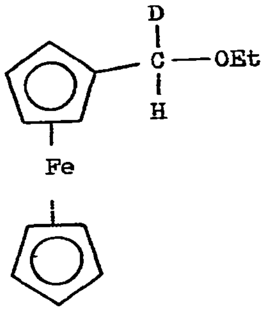

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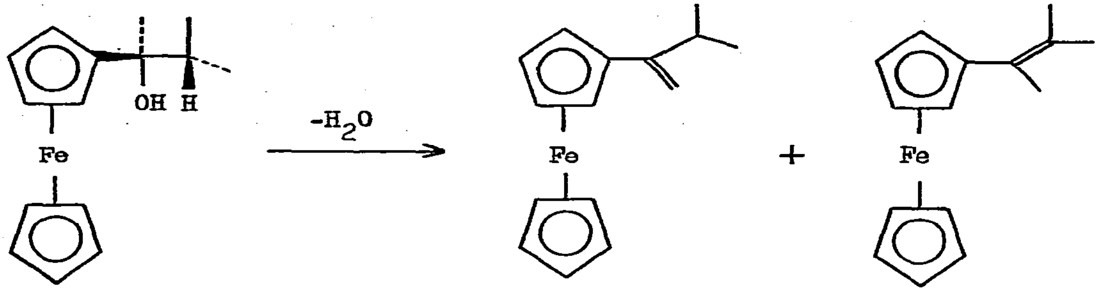
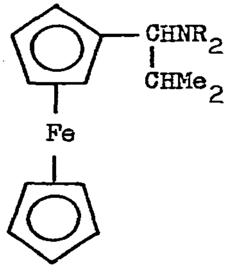


3.14 3.15 3.16

the ferrocenylolefin (3.15) while dehydration with trichloroacetic acid under kinetic control gave a mixture of the olefins (3.15 and 3.16) in which (3.15) predominated. Treatment of the olefin (3.15) with dilute hydrochloric caused rearrangement to the isomer (3.16) [19].

The (dimethylamino)methylferrocene (3.17; R = Me) was converted to the corresponding primary amine (3.17; R = H) by displacement of the dimethylamino group with SCH_2CO_2H using thioglycollic acid and formic acid as the reagent followed by treatment with ammonia, ammonium chloride and mercury(II) chloride to form the product. The ferrocenylbutylamine (3.17; R = H) was used as a chiral template in asymmetrically induced synthesis [20].



3.17

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

A molecular orbital study (CNDO and INDO calculations) was carried out on ferrocene and some substituted ferrocenes. A satisfactory agreement was obtained between calculated and experimental spectra [21].

A semi-empirical molecular orbital method, the PEEL method, was applied to ferrocene. A consistent interpretation of both the photoelectron ionization spectrum and the absorption spectrum were obtained. The calculated order of the highest occupied orbitals, ionization potential (e_{2g}) ionization potential (a_{1g}), agreed with experimental assignments in photoelectron spectra and the calculated energies were close to the observed values [22].

The electronic structures of ferrocenylacetylene, its dimer and trimer were calculated using a Hueckel molecular orbital treatment. The head-to-head structures of the dimer and the trimer were more stable than the corresponding head-to-tail structures [23].

INDO SCF molecular orbital calculations were carried out for a series of metallocenes, including ferrocene, bis(η-benzene) complexes and for some mixed sandwich complexes. In all these compounds the interactions between the metal orbitals and the π-orbitals of the ligand rings made the major contribution to the metal-ligand bonds. There were weaker, but significant interactions between the metal 3d, 4s and 4p orbitals and the carbon 2s and $2p_x 2p_y$ orbitals of the σ-frameworks of the ligands [24].

INDO SCF MO calculations were carried out for a series of d^6 transition metal sandwich complexes including ferrocene and for systems obtained from them by the addition of one extra electron. For all the complexes studied except cobaltocene the extra electron was predicted to reside in a dominantly ligand level and the species generated were less stable than the corresponding d^6 complexes [25].

The self-consistent charge and configuration molecular orbital method was used to compare the electronic structures of (η-cyclopentadienyl)-(3)-1,2-dicarbollyliron and ferrocene. It was concluded that the iron atom could bond to the open near-pentagonal face of the carborane in a similar way that it could bond to a cyclopentadienyl ring except that the interaction involved σ-orbitals of the dicarbollide. However, these σ-orbitals were of the same symmetry type as the π-orbitals of the cyclopentadienyl ring [26].

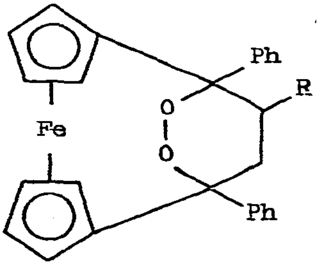
A thermodynamic study of ferrocene was carried out. Equations were obtained for the vapour pressure of ferrocene as a function of temperature [27]. Molecular configurations in the disordered phase of ferrocene have been examined and interpreted in terms of the Willis model. This model permitted only one orientation for an antiprismatic molecule of D_{5d} symmetry. The two orientations permitted for the prismatic molecule of D_{5h} symmetry were independent [28].

Proton radiation effects in ferrocene were investigated. Irradiation of ferrocene at doses of $\leqslant 2 \times 10^{15}$ protons gave only lattice defects but at doses of $2 - 5 \times 10^{15}$ protons polyferrocene was formed. At even higher doses metallic iron and Fe_3C were formed [29].

Ferrocene was suspended in epoxy resin and irradiated, using the Van de Graaff accelerator, with protons. Moessbauer measurements were carried out on the ferrocene sample after irradiation. It was concluded that Fe_3C was formed as ultrafine particles approximately 100 Å in size and these showed superparamagnetic behaviour [30].

Ferrocenyl-4'-methoxyaniline, ferrocenyl-4'-butylaniline, 1,1'-dioctanoylferrocene and dibenzyl-1,1'-ferrocenedicarboxylate were introduced into the smectic B liquid-crystal phase of 4-butoxybenzylidene-4'-octylaniline. These systems were studied by ^{57}Fe Moessbauer spectroscopy at 77° K [31]. The interaction of human serum albumin with ferrocene-^{59}Fe and some iron complexes was investigated by Moessbauer spectroscopy at 85 and 300° K [32].

A Moessbauer study was carried out on tetramethylene bridged ferrocene derivatives [33].



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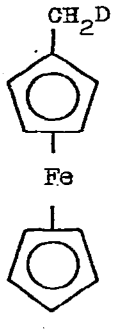

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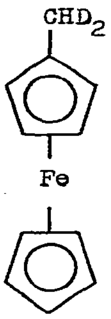

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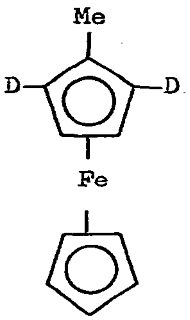
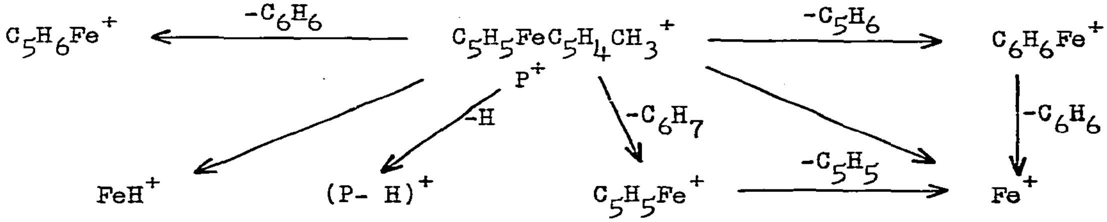


4.4

The ferrocenophane peroxides (4.1; R = H, Me) have been investigated by electron-impact mass spectrometry. Fragments were found to arise by thermal decomposition, rearrangement or loss of ethylene by a retro Diels-Alder reaction. The results obtained were sensitive to the temperature of the inlet system [34].

The mass spectra of methylferrocene and its deutero analogues (4.2, 4.3 and 4.4) were recorded and interpreted. The main fragments in the methylferrocene spectrum were formed by breaking of the metal-ligand bond (Scheme 4.1). It was shown that the ions $C_{11}H_{11}Fe^+$, $C_6H_6Fe^+$, $C_5H_5Fe^+$ and $C_5H_6Fe^+$ originated from an isomerized form of the molecular ion in which all the hydrogen atoms were redistributed among the ligands [35].



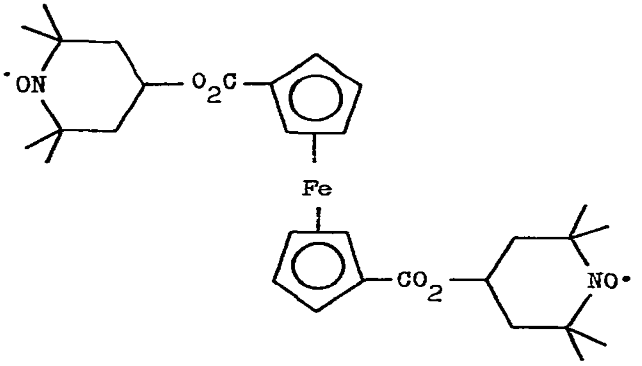
Scheme 4.1

Mass spectrometry was used to analyse the product mixture obtained from the electrochemical alkylation of ferrocene. The results showed that the concentrations of the alkylferrocenes present could be determined semiquantitatively using this technique [36].

The electronic spectra of two series of metallocenes $(\eta\text{-}C_5H_5)_2M$ and $(\eta\text{-}C_5H_4Me)_2M$ (M = V, Cr, Mn, Fe, Co, Ni) were recorded between 10 and 50×10^3 cm^{-1}. For the V, Cr, Mn and Fe derivatives the charge-transfer bonds corresponded only to ligand → metal excitations ($e_{2u} \rightarrow e_{2g}, a_{1g}, e_{1g}$) and for the Co derivatives evidence was also found for metal → ligand ($e_{1g} \rightarrow e_{2u}$) transitions. The paramagnetic susceptibilities of these compounds were also determined and discussed [37].

1,1'-Di(chlorocarbonyl)ferrocene was condensed with 2,2,6,6-tetramethylpiperidin-4-ol N-oxide to form the ferrocenedicarboxylate (4.5) which was the subject of an ESR investigation. The results were consistent with a species with an activation energy for internal movement <2 kcal mol^{-1} and with a conformation in which the two nitroxide groups were twisted slightly out of the line joining the two groups in the molecule [38].

The detection of a low frequency vibrational mode coupled to the ground and first excited electronic states has been reported for the complexes $[\text{Ferricinium}]^+X^-$, where X = tetrafluoroborate and hexachloroferrate. The frequency of the mode in the ground state was ~ 84 cm^{-1} and it was assigned to the ν_6 Raman inactive ring torsional vibration. Intensities were discussed in terms of the



4.5

Frank-Condon factor in the relationship for the Raman process [39].

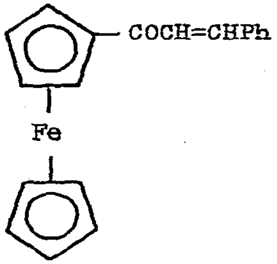
The π-electron density at the β-carbon atom in the ferrocenylchalcone (4.6) was determined from the ^{13}C NMR shielding constants and the value obtained was 0.9297 [40]. NMR data for a series of ferrocenes and α-ferrocenylcarbenium ions were discussed. It was suggested that in an α-ferrocenylcarbenium ion the cyclopentadienyl ring formed a fulvalene with the α-carbon atom which in turn was bonded to the iron atom via all six carbon atoms [41].

Ferrocenes bearing electron withdrawing groups such as CO_2H, CO_2Me, CHO, COMe underwent polarographic reduction in two steps, the first one-electron step gave a radical anion while the second two-electron step gave a dianion. Controlled potential electrolysis at the potential of either the first wave or the second wave caused cleavage of the metallocene group to cyclopentadienide anions and iron. The cyclopentadienide anions combined with transition metal salts to form (η-cyclopentadienyl)metal compounds and the reaction was of general applicability [42].

The kinetics and mechanism of the protodeboronation of ferroceneboronic acid in moderately concentrated sulphuric acid were investigated. It was concluded that the reaction probably proceeded by an $\underline{A}$ - $\underline{S}_E$ 2 - type mechanism and that there was no indication that the iron atom participated in the electrophilic attack by a proton in the early stages of the protodeboronation [43].

A cell has been described which employed an n-type silicon-based semiconductor in an ethanol solution of ferrocene. Conversion of light (633 nm) to electricity with an output of 0.25 V and an efficiency of 2% was achieved [44]. Ferrocenyltrichlorosilane (4.7) was prepared by the addition of lithioferrocene to an excess of silicon tetrachloride. The ferrocenyl-silane (4.7) was attached directly to a pretreated platinum electrode. The derivatized platinum electrodes were characterised by cyclic voltammetry and it was concluded that the electroactive ferrocene was attached via hydrolysis of one or more of the silicon-chlorine bonds. The derivatized electrodes were very durable and in one experiment over three thousand five hundred cyclic voltammograms were run at 100 mVs^{-1} with only approximately 30% loss of the electroactive material [45].

The ferrocenyl-silane (4.8) was prepared by the addition of 1,1'-dilithioferrocene to silicon tetrachloride. An n-type silicon



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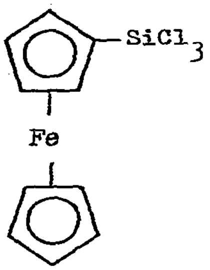

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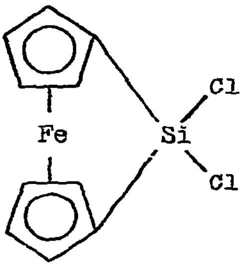
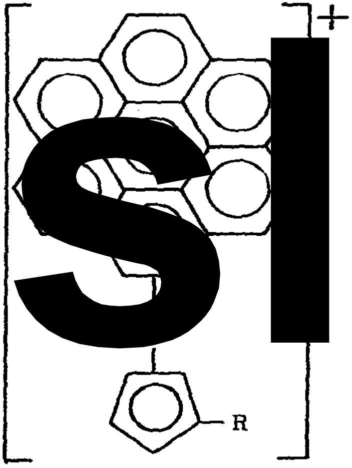


4.8

electrode was dipped into aqueous sodium hydroxide, washed, dried and treated with the silane (4.8) which became covalently linked to the silicon surface. The surface attached ferrocene was cycled photoelectrochemically between reduced and oxidized forms repeatedly without any substantial deterioration. Whereas nonderivatized electrodes showed no cyclic waves and a build up of silicon dioxide which led to a rapid decline of the photocurrents [46].

5. REACTIONS OF FERROCENE

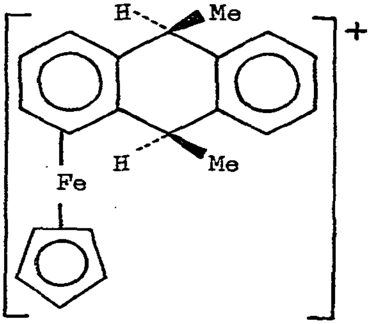
Electrolysis of a solution containing dimethylformamide, cyclopentadiene and lithium bromide between an iron anode and a



5.1

nickel cathode gave ferrocene in a current yield of 88% [47]. A series of labelled ruthenocenes was prepared by heating substituted ferrocenes with ^{103}RuCl$_3$. For example, benzoylferrocene and ^{103}RuCl$_3$ were heated at 180° for approximately half an hour to give benzoylruthenocene, ruthenocene and 1,1'-dibenzoylruthenocene. When a mixture of acetylferrocene-^{59}Fe and ferrocene methylcarboxylate was heated in the presence of iron(III) chloride a variety of labelled ferrocene derivatives was obtained [48].

The ligand exchange reactions of ferrocene and some substituted ferrocenes with coronene were investigated. Ferrocene and 1,1'-dimethylferrocene underwent exchange to give the η-coronene derivatives (5.1; R = H) and (5.1; R = Me) respectively which were isolated as their hexafluorophosphate salts [49].



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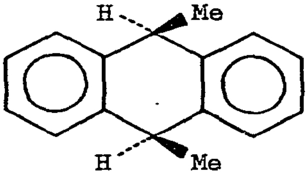

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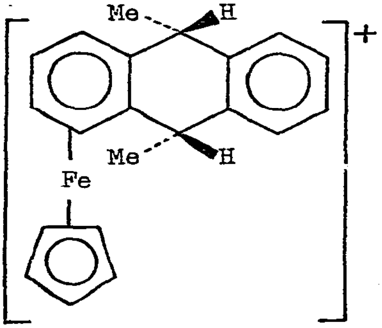

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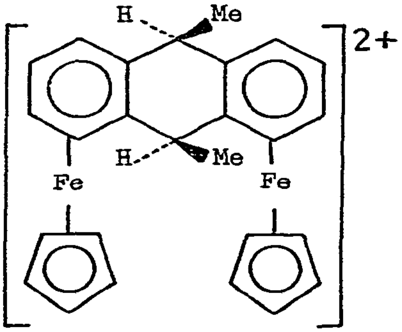
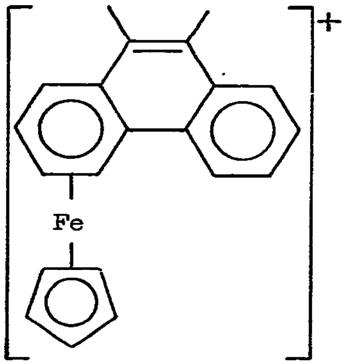


5.5

Ferrocene underwent a ligand exchange reaction with 9,10-dimethylanthracene in the presence of an aluminium chloride-aluminium mixture in decalin to form the stereospecifically hydrogenated product (5.2) where the hydrogen had been added cis and endo. When cis-9,10-dihydro-9,10-dimethylanthracene (5.3) was used in the ligand exchange reaction, two isomeric products (5.2 and 5.4) were obtained. The dication (5.5) was formed by ligand exchange between the cation (5.2) and ferrocene or directly from 9,10-dimethylanthracene and excess ferrocene [50].

Ferrocene underwent ligand exchange with phenanthrene and 9,10-dimethylphenanthrene in the presence of aluminium chloride and aluminium. The reaction with 9,10-dimethylphenanthrene in cyclohexane at reflux temperature gave the mononuclear cation (5.6)



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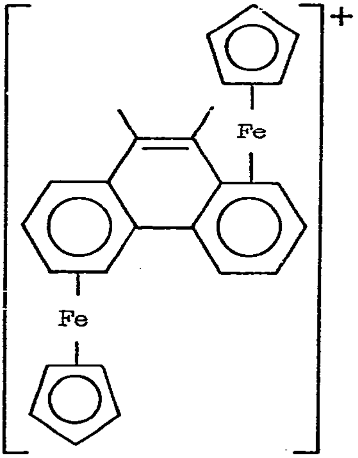

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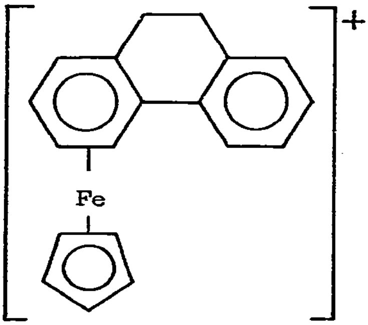

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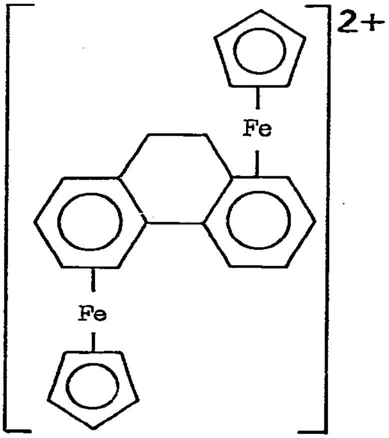

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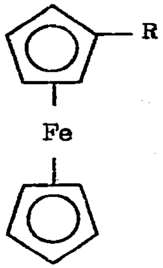

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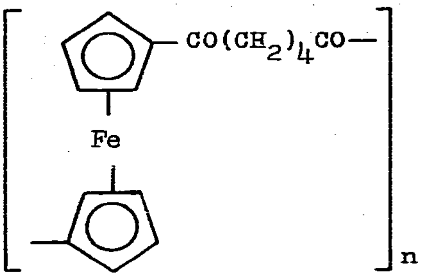

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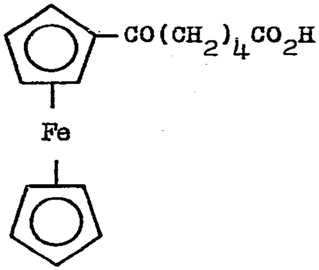

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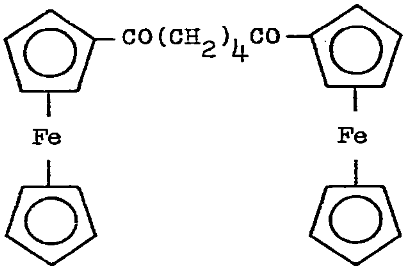

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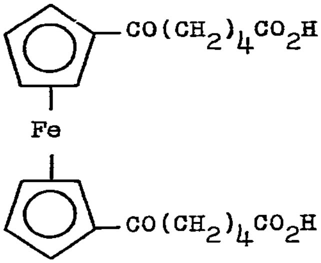

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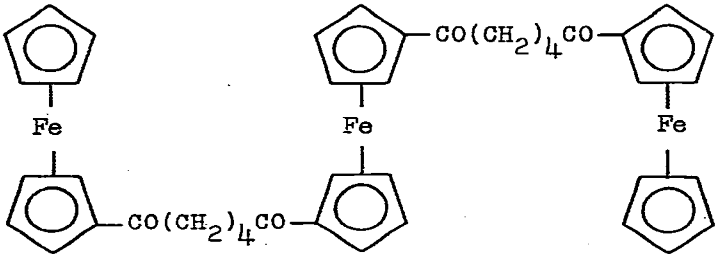
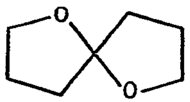


5.15

and the binuclear cation (5.7). Exchange with phenanthrene gave products analogous to those obtained with phenanthrene but gave, in addition, products where hydrogenation accompanied exchange, these were the mononuclear cation (5.8) and the binuclear dication (5.9) [51].

A series of acylferrocenes (5.10; R = C_{5-7} cycloalkenyl possibly substituted with C_{1-4} alkyl, Ph, CH_2Ph, Cl) was prepared by treating ferrocene with the appropriate acid chloride in the presence of a catalyst. Some of the acylferrocenes were administered to rats [52].

Ferrocene was acylated with isononanoyl chloride in the presence of aluminium chloride to give (trimethylhexanoyl)ferrocene [53].



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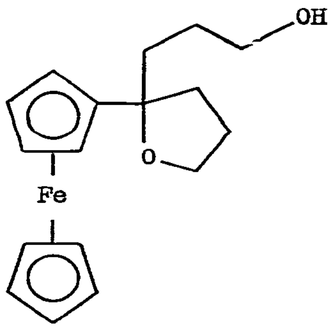

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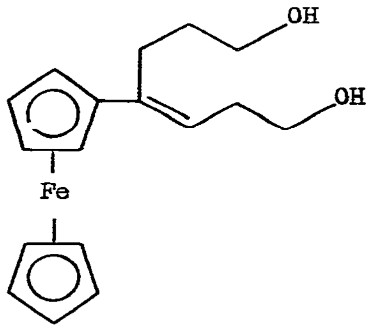

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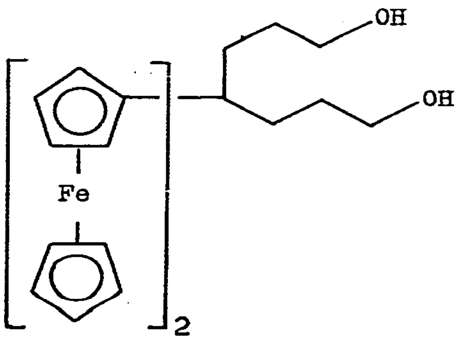

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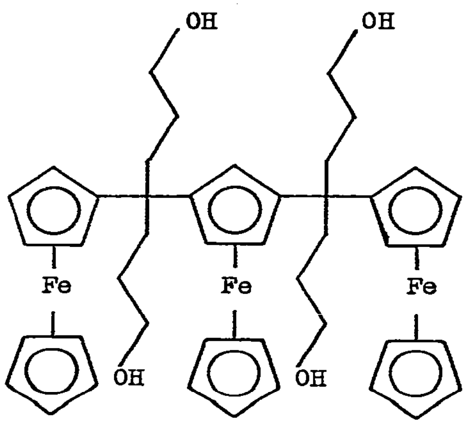

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Ferrocene was alkylated with methyl monochloroacetate in the presence of aluminium chloride to give methyl ferrocenylacetate [54]. The acetylation of ferrocene with acetic anhydride has been reported using as catalyst magnesium halides (chloride, bromide and iodide) in the form of the etherates in benzene [55].

The Friedel-Crafts acylation of ferrocene with adipoyl chloride has been reinvestigated using aluminium chloride as catalyst and methylenedichloride as solvent. In addition to the previously reported polymeric product (5.11), both monoacylated (5.12 and 5.13) and diacylated (5.14 and 5.15) ferrocenes were obtained together with four secondary products which arose by transformations of the first formed compounds [56].

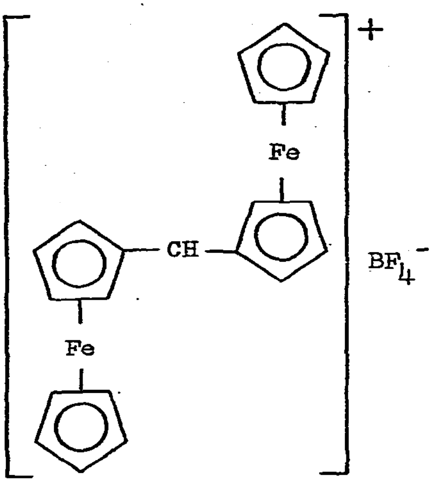
The reaction of ferrocene with 1,6-dioxaspiro[4.4]nonane (5.16) in the presence of trifluoroacetic acid gave a mixture of ferrocenylalcohols (5.17 - 5.20) in which the binuclear diol (5.19) was predominant, the mechanism of the reaction was discussed [57].

6. FERRICINIUM SALTS

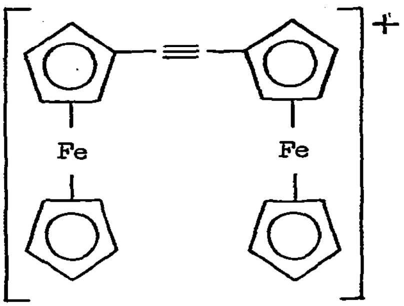
The crystal and molecular structure of α,α-diferrocenylmethylium tetrafluoroborate (6.1) has been determined by X-ray crystallography. The diferrocenyl cation has a transoid conformation similar to that determined for diferrocenyl ketone. The substituted ferrocenyl rings were found to be bent at the α-carbon atoms so that distances between the two iron atoms and the exocyclic carbon were reduced to 2.69 and 2.81 Å respectively. It was concluded that the distorted structure resulted from metal-exocyclic carbon interaction and that stabilization of α-ferrocenylcarbenium ions was attributable to such interaction and to delocalization of positive charge [58].

Isotope shifts in paramagnetic perdeuterometallocenes including the perdeuteroferricinium ion have been determined by ^{13}C NMR spectroscopy. Shifts of both positive and negative sign were observed and a large dipolar shift was observed for the perdeuteroferricinium ion. The isotope shift increased with the number of unpaired electrons and with the efficiency of electron delocalisation [59].

The mixed valence cations of biferrocene and biferrocenylacetylene (6.2) were formed from the neutral ferrocenes using $[(2,2'\text{-bipyridine})_2Ru.PPh_3.Cl](PF_6)_2$ as the oxidising agent. The cations displayed near-infrared absorption bands which were assigned to intervalence transfer transitions between isolated Fe(II) and

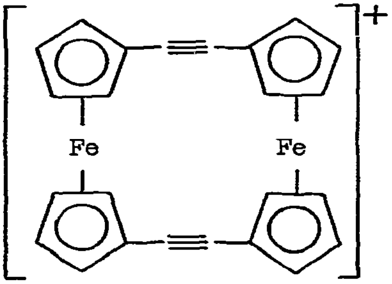


6.1



6.2

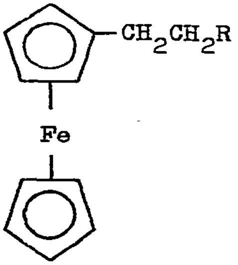
Fe(III) sites. The energies of these bands were correlated with functions of the dielectric constant of the medium used in accordance with Hush theory. The energies were also correlated with the iron-iron separation in the cation. It was concluded that the mixed-valence cations have localized valence sites and the intervalence transfer properties were consistent with the Hush treatment for optical electron transfer [60].



6.3

Oxidation of the neutral ferrocenylacetylenes with iodine in benzene gave the mixed valence cation (6.2) and the averaged-valence cation (6.3). Moessbauer spectroscopy indicated that the two iron atoms in the cation (6.2) were involved in intramolecular electron transfer while, in contrast, the two iron atoms in the cation (6.3) were both in the same oxidation state. The magnitude of the quadrupole splitting indicated strong interactions between the iron atoms through the conjugated π-system [61].

The enzyme catalysed oxidation of ferrocene and some substituted ferrocenes to the corresponding ferricinium ions by hydrogen peroxide in the presence of native or immobilized horseradish peroxidase was studied. The initial and maximum rates of oxidation were determined



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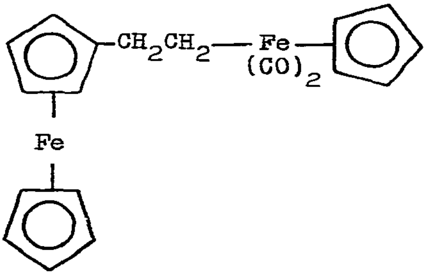

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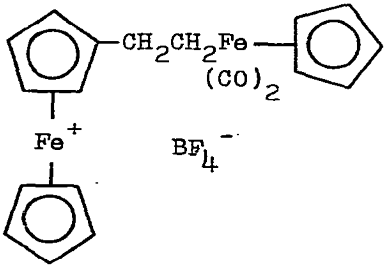


6.6

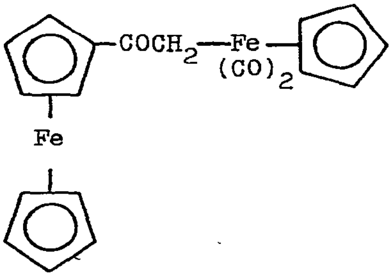
and it was found that the rate of oxidation was independent of the hydrogen peroxide concentration. Ferrocene was also oxidized by horseradish peroxidase in a coupled system with glucose oxidase in the absence of any added hydrogen peroxide [62].

A series of sym-polymethylferricinium hexafluorophosphates, $(Me_nC_5H_{5-n})_2Fe^+PF_6^-$ (n = 0 - 5), was prepared and their infrared spectra were recorded. Compared to the analogous sym-polymethylferrocenes the infrared spectra of the salts displayed a marked decrease in band intensity for C—H stretching modes of the methyl groups. Whereas, the intensities and the frequencies of the corresponding bands for the ring C—H stretching modes were higher [63].

The reaction of sodium(dicarbonyl)(η-cyclopentadienyl)ferrate(-1) with the ferrocene derivatives (6.4; R = p-$MeC_6H_4SO_3$, Cl) gave 2-ferrocenylethyldicarbonyl(η-cyclopentadienyl)iron (6.5). Treatment of the latter compound with trityl tetrafluoroborate gave the ferricinium salt (6.5) [64].

Reaction of the ferrocenyl-ketone (6.7) with HBF_4 or Et_3OBF_4 gave the tetrafluoroborate salts (6.8; R = H and Et) respectively. Treatment of the salt (6.8; R = H) with diazomethane gave the corresponding methylated derivative (6.8; R = Me) [65].

Reaction of the dicarbonyliron complex (6.9) with ferrocenylethylene gave the cationic complex (6.10). Ferrocenylethylene was released from the complex (6.10) on treatment with triphenylphosphine, sodium iodide, sodium trifluoroacetate, sodium cyanide, sodium hydroxide or sodium borohydride [66].



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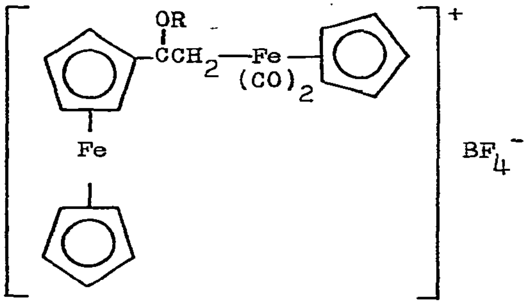

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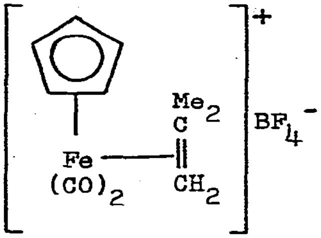

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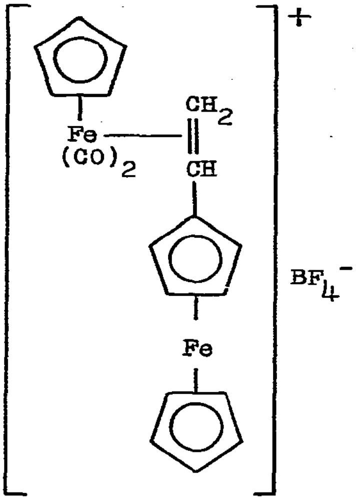

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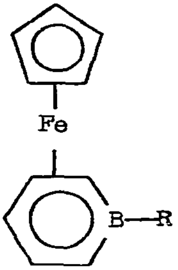
Oxidation of the borinato-iron complexes (6.11; R = Me, Ph) gave the corresponding ferricinium derivatives (6.12) [67]. The reaction of the ferricinium ion with hydroxide ion in the presence of potassium hexacyanoferrate gave potassium hexacyanoferrate(II) and the ferricinium ion decomposed without any ferrocene being formed [68].



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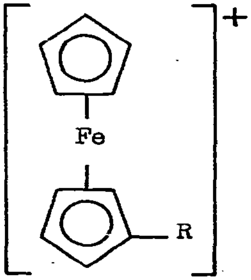

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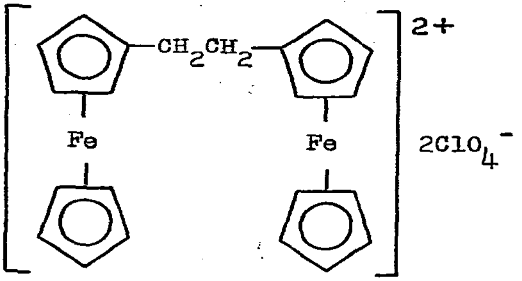


6.13

The thermal decompositions of (ferrocenylmethyl)dimethylammonium perchlorate and picrate [69] and 1,1'-diethylferricinium and ethylenediferricinium perchlorates (6.13) [70] were studied. The mechanisms of the decompositions were discussed.

Complexes have been formed between the ferricinium cation and transition metal β-diketonate and isopolyacid anions. Aminoferrocenes also took part in complex formation with transition metal thiocyanates [71]. The electrode potentials of the ferricinium ion-ferrocene system were determined in some acidic aqueous-organic solutions. The potential varied between +0.1 - +0.66 V as the concentration of the acid (hydrochloric, sulphuric and perchloric) changed and the quantity of the organic solvent (acetic acid, methyl cyanide, acetone, alcohol, dimethylformamide and dimethylsulphoxide) changed [72].

Cyclic voltammetry has been used to investigate the mechanism of oxidation of ferrocene to the ferricinium ion in aqueous acid-organic solvent mixtures containing 0.02 M tetraethylammonium perchlorate. Rate constants for the oxidation were obtained and the reaction was found to involve a fast protonation step followed by a change from solvated ferrocene to hydrated ferricinium ion. The instability of the ferricinium ion caused the reaction to be quasi-irreversible. Changes in the nature and concentration of the mineral acid and the organic solvent caused the redox properties of the ferrocene-ferricinium ion couple to change in a controllable manner. These controlled changes together with complexation of metal cations formed the basis of a method for determining one oxidant in the presence of a second [73].

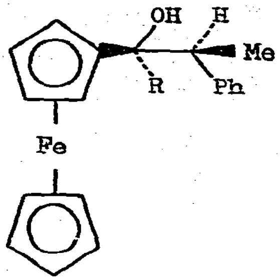
Denisovich and co-workers found that the interaction of radicals formed in anode decarboxylation of carboxylate anions with the ferricinium ion generated at the same electrode led to the formation of alkylferrocenes. For example, the electrolysis of a mixture of potassium acetate, acetic acid and ferrocene gave a mixture of methylated ferrocenes. A similar reaction of the ferricinium ion with radicals generated from dibasic acids or their half esters gave esters of ferrocenyl containing carboxylic acids. It was shown that the orientating effects of the substituents were the same for radical substitution in the ferricinium ion as for electrophilic substitution of the corresponding neutral ferrocene derivative [74].

The ferrocene-ferricinium cation system has been used to determine Hammet and Pleskov redox functions in propanol-water and iso-propanol-water mixtures containing perchloric acid. The Pleskov function was a better measure of the acidity of the solution [75]. The standard proton affinities of water-alcohol and water-ketone mixtures have been determined from acidity function measurements of galvanic cells with platinum-ferrocene-ferricinium electrodes. Changes in the water-alcohol ratio or in the hydrocarbon group on the alcohol had little effect on the proton affinity [76].

7. FERROCENYL CARBENIUM IONS

The alcohols (7.1; R = H, Me, Ph) underwent stereospecific heterolysis (exo-departure of the protonated OH) in trifluoroacetic acid to give the corresponding cation which equilibrated with its diastereoisomer by rotation about the ferrocenyl—C^+ bond. When the equilibrium mixture of the cations was quenched with aqueous sodium carbonate the alkenes (7.2 and 7.3) were obtained. It was shown that the alkenyl-ferrocenes (7.2 and 7.3) underwent preferential exo-protonation in trifluoroacetic acid to give ferrocenylalkylium ions which underwent exo-deprotonation in the presence of base [77].

Ferrocene was treated with isobutyraldehyde and trifluoroacetic acid to form 1-ferrocenylisobutanol which gave the ferrocenylisobutyl carbenium ion (7.4) under the reaction conditions used [78]. The ferrocenylbenchrotrenylcarbenium ion (7.5) was obtained as a stable violet-blue fluoroborate by treatment of the appropriate



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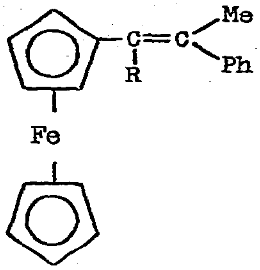

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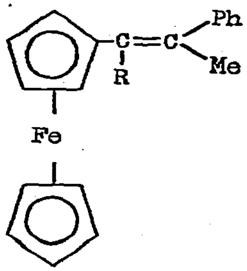

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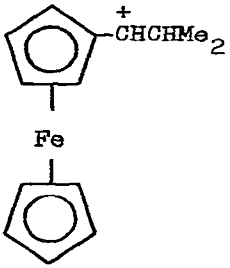

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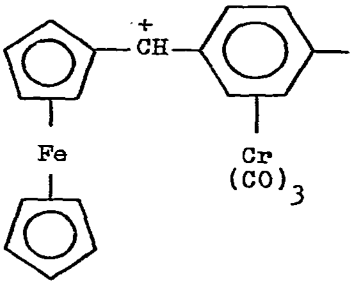
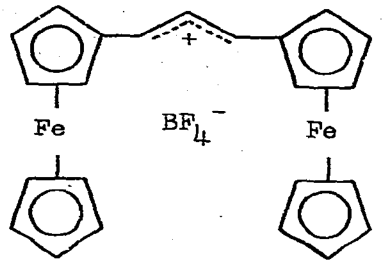


7.5

carbinol with fluoroboric acid in propionic anhydride [79]. Treatment of 1,3-diferrocenylallyl alcohol and 1-methyl-1-cymantrenyl-3-ferrocenylallyl alcohol with fluoroboric acid in acetic anhydride gave the cations (7.6 and 7.7) respectively. Treatment of the cation (7.6) with N,N-dimethylaniline gave the olefin (7.8), the cation (7.7) underwent a similar reaction [80].

A mechanistic study was carried out on the fragmentation of ferrocenyldiarylmethylium ions in aqueous acidic methyl cyanide. For example, the cations (7.9; Ar = Ph, p-anisyl) fragmented to give the corresponding fulvenes (7.10) together with repeated reversible formation of the alcohol precursors (7.11). Changes in acid strength



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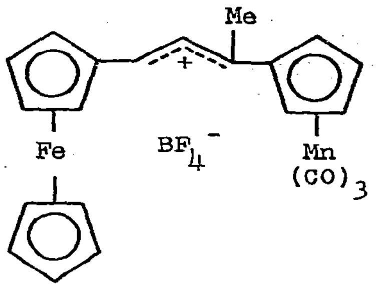

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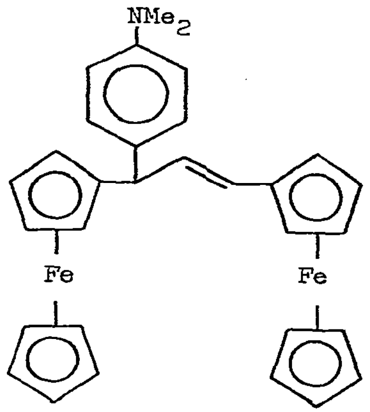
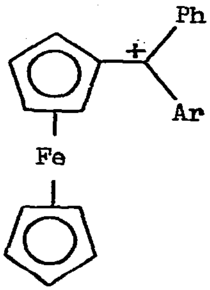


7.8

and substituent effects were investigated [81]. 5,6-Bis(diisopropylamino)calicene (7.12) was heated with iron(III) chloride in THF to form the dicyclopropenium complex (7.13) after the addition of potassium perchlorate [82].

The acid-catalyzed hydration of ferrocenylacetylenes with alkyl substituents in the 2-, 3- or 1'-positions has been subjected to a kinetic study. The reaction involved the formation of an intermediate vinylcarbenium ion (7.14) and gave acetylferrocenes as the products [83].

Comparison of the pK_R values for the carbenium ions derived from the ferrocenylcarbinols (7.15; R = H, Me) with those for the



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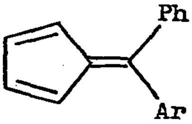

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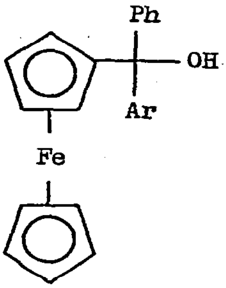

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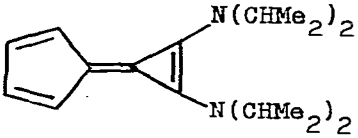

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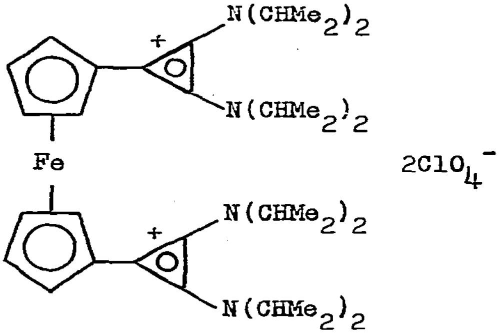

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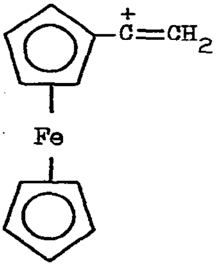

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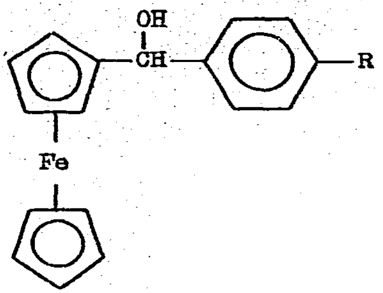

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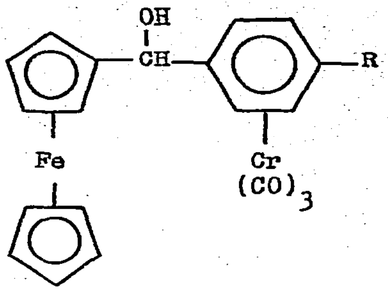


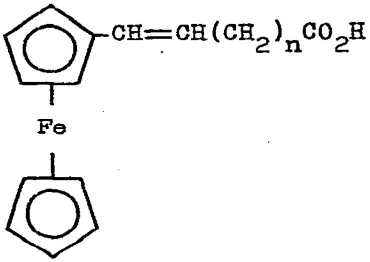
7.16

chromiumtricarbonyl complexes of the carbinols (7.16; R = H, Me) demonstrated that the ferrocenyl group was much more efficient than the chromiumtricarbonyl group in stabilizing the adjacent carbenium ion [84].

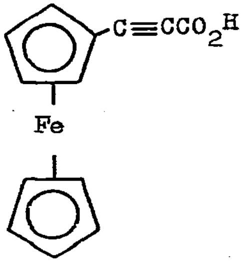
8. FERROCENE CHEMISTRY

(i) Photochemistry

The unsaturated acids (8.1; n = 0.1 and 8.2) were irradiated with ultraviolet light of wavelength 240-250 nm in aqueous solution at pH 9 in the presence of nitrous oxide. Photo-oxidation occurred and the corresponding ferricinium ions were produced which could be chemically reduced back to the original acids. It was thought that



8.1



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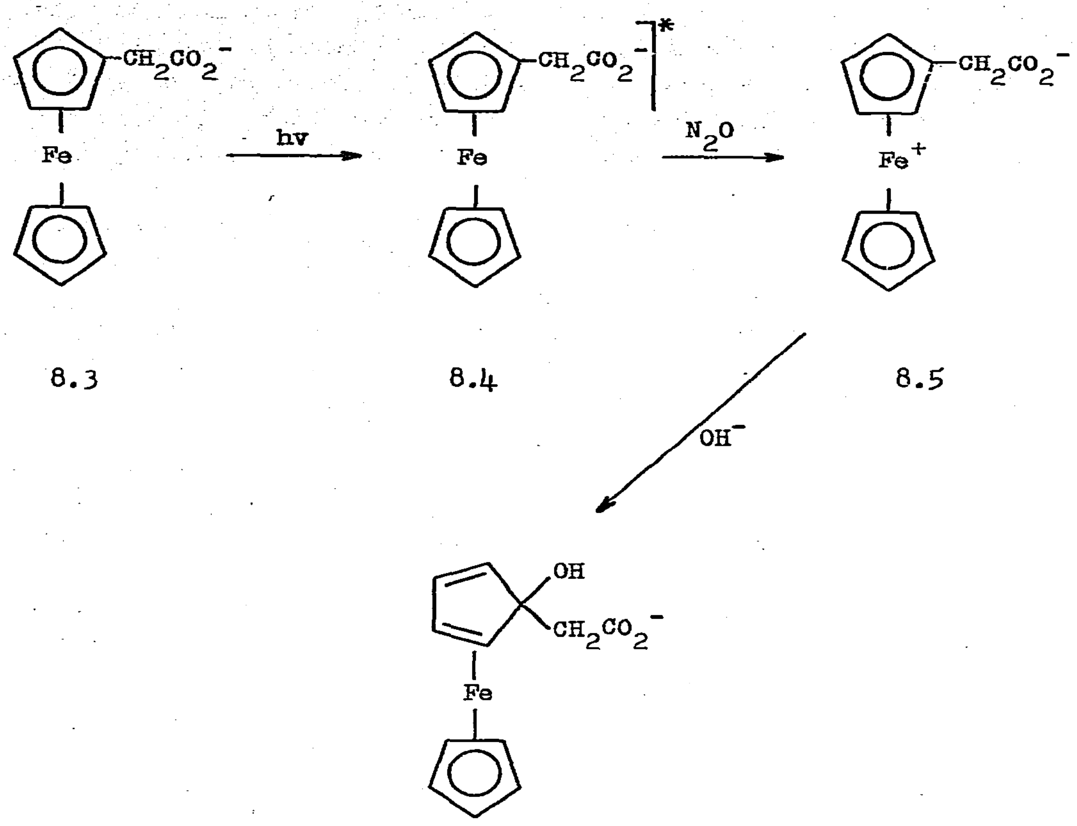


8.3

8.4

8.5

8.6

oxidation occurred by electron transfer to nitrous oxide from a photo-excited state of the acid [85].

The photochemical excitation of the ferrocenylacetate (8.3) and ferrocenoate anions gave, in each case, an excited state (8.4) which transferred an electron to nitrous oxide which acted as an electron acceptor. The lifetimes of the excited states were 2 μs and 0.07 μs respectively. The product of electron transfer from the excited state of the acetate (8.3) was the zwitterion (8.5) which with base was thought to form the (η-cyclopentadiene)-(η-cyclopentadienyl)iron complex (8.6) [86].

Ethanol solutions of octamethylferrocene and octamethylferricinium hexafluorophosphate were irradiated with incandescent

40-500 W lamps. A periodical variation in the optical density of the solutions was observed throughout the range of electron absorption spectra studied (210-800 nm). The period of variation increased with the concentration of the solution. It was suggested that an oscillating photochemical redox process was being observed [87].

Carbon tetrachloride and other halogeno compounds with a similar or higher electron affinity underwent photoinduced dehalogenation in alcohol in the presence of ferrocene or iron(III) chloride. A chain propagation mechanism was used to explain the high quantum yield obtained which was >6 for carbon tetrachloride. Methyl trichloroacetate was monodehalogenated in low quantum yield even though it had a high electron affinity [88].

Copolymers of methyl methacrylate or styrene with 1-ferrocenylethyl methacrylate have been synthesized and their efficiencies as photosensitizers evaluated for the redox reaction between L-ascorbic acid and Fast Red A. High proportions of 1-ferrocenylethyl methacrylate in the copolymers caused low quantum yields for sensitization. The quantum yield changes were discussed in terms of Perrin's model for static quenching interaction between adjacent excited and ground-state ferrocene groups. It was considered that both quenching interaction and energy migration occurred between nearest-neighbour ferrocene groups with the former assuming more importance than the latter [89].

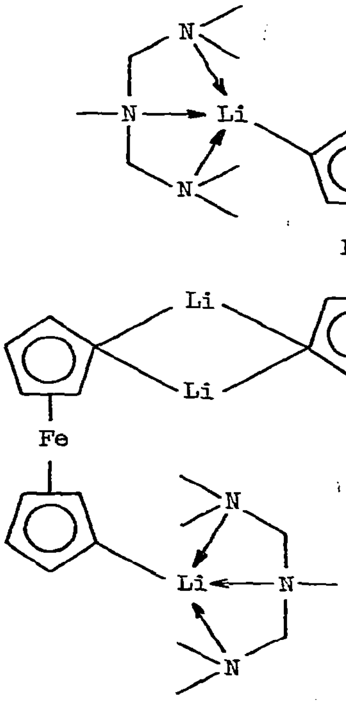
The quenching of $[UO_2]^{2+}$ emission by ferrocene, some substituted ferrocenes, ruthenocene, some substituted ruthenocenes and osmocene has been investigated. All of these metallocenes were strong quenchers of the excited state $(UO_2^{2+})^*$ and the quenching constants $\underline{k}_Q$ were obtained both from luminescence intensity and lifetime measurements. The values of $\log_{10}\underline{k}_Q$ were correlated with the oxidation potentials of the metallocenes and this supported an electron transfer mechanism between $(UO_2^{2+})^*$ and the metallocenes [90].

The photochemical reduction of benzophenone and poly(vinylbenzophenone) by <u>iso</u>-propanol in the presence and absence of ferrocene and of vinylferrocene-vinylbenzophenone copolymer was studied. In the presence of local concentrations of ferrocene, which behaved as a quencher, it was concluded that energy migration along the polymer chain was negligible within the triplet lifetime (approximately 10^{-7}s) [91].

(ii) Derivatives containing other metals (metalloids)

Ferrocene was metallated by n-pentylsodium in the presence of tetramethylethanediamine (TMEDA) to give 1,1'-disodioferrocene and sodioferrocene in the ratio 9:1. The reaction gave near quantitative yields after 1 hour at room temperature. In the absence of TMEDA yields were lower and polymetallation products were also obtained [92].

The reaction between n-butyllithium and potassium(-)(1R)-menthoxide gave n-butylpotassium which was used to metallate ferrocene. The 1,1'-dimetallated ferrocene was the predominant product and was obtained in 74% yield [93]. The metallation of ferrocene with n-butyllithium in the presence of pentamethyldiethylenetriamine (PMDT) in the molar ratio 1:3 gave a dilithioferrocene which was investigated by ^{1}H NMR spectroscopy and X-ray analysis. The ^{1}H NMR spectrum was temperature dependent in benzene and toluene solution with both cyclopentadienyl and base exchange taking place. The solid



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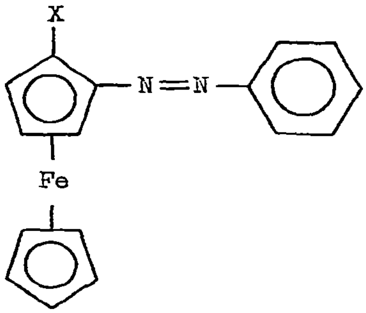
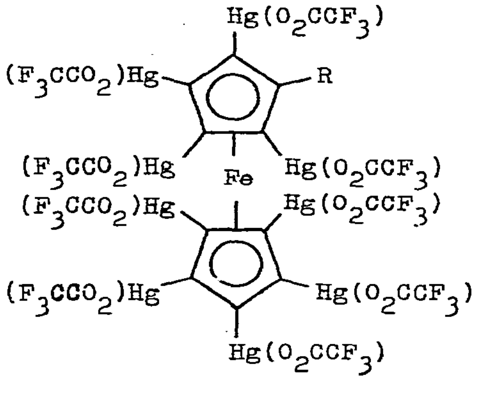


8.8

complex $[(\eta-C_5H_4)_2Fe.PMDT.Li_2]_2$ (8.7) had two types of lithium atoms solvated and unsolvated. The solvated lithium atoms were each bound to the three nitrogen atoms of the PMDT while the unsolvated lithiums participated in a four-centre electron deficient bridge between the two ferrocene groups. The lithium-iron distance was short (2.667 Å) which indicated bonding between the lithium and a ferrocene e_g molecular orbital [94].

Phenylazoferrocene was mercurated to give a mixture of 2-chloromercuri(phenylazo)ferrocene (8.8; X = HgCl) and bis(2-phenylazoferrocenyl)mercury. Both of the compounds were converted by iodine to the 2-substituted iodoferrocene (8.8; X = I) in high yield [95].

Treatment of the ferrocene derivatives (8.10; R = Me, Et, CN, COMe, CHO; X = H) with mercury(II) trifluoroacetate gave high yields of the corresponding mercurated derivatives (8. 9). The mercurated compounds (8. 9) were converted to the haloferrocenes (8.10; X = Br, I) by reaction with potassium tribromide and potassium triiodide respectively [96].



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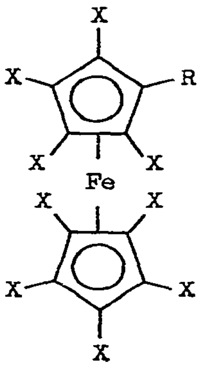
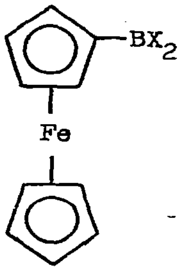


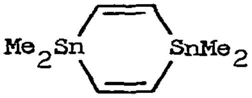
8.10

The ferrocenyldihaloboranes (8.11; X = Cl, Br, I) were prepared by the reaction of ferrocenylmercurichloride with the corresponding boron trihalide. The infrared spectra of the ferrocenyl-boranes (8.11; X = Cl, Br, I) were recorded and the $^{10}B—X$ and $^{11}B—X$ stretching frequencies were assigned [97].

Ferrocenyldibromoborane combined with the distannacyclohexadiene (8.12) to give the diferrocenyldiboracyclohexadiene (8.13) which was characterized as the nickel complex (8.14) [98].



8.11

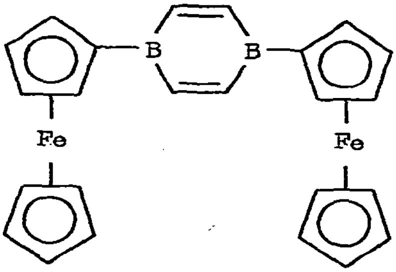


8.12

The thiodiborolene (8.15) was treated with manganese carbonyl and bis[dicarbonyl(η-cyclopentadienyl)iron] to form the triple-decker mixed metal complex (8.16). This product (8.16) gave a cationic complex with aluminium chloride which was in turn pyrolyzed to yield the neutral tetra-decker complex (8.17) [99].

The hydrosilylation of silylacetylenes, $R^1R^2Si(C\equiv CH)_2$, where $R^1 = R^2$ = Et, Ph, R^1 = Me, R^2 = Ph, with the ferrocenylsilane (8.18) using a Speier's catalyst gave the products (8.19; $R^1 = R^2$ = Et, Ph, R^1 = Me, R^2 = Ph) which were formed according to Farmer's rule [100].

Reaction of α-naphthylferrocenylmenthoxysilane with boron trifluoride etherate gave the bifunctional enantiomeric silane (8.20). Treatment of the ferrocenylsilane (8.20) with palladium(II) chloride gave the fluorochlorosilane (8.21). Treatment of the



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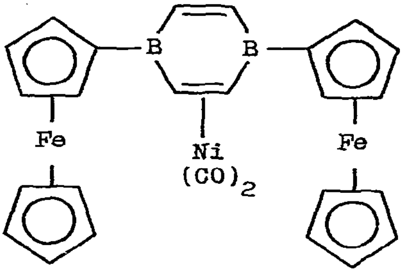

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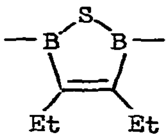

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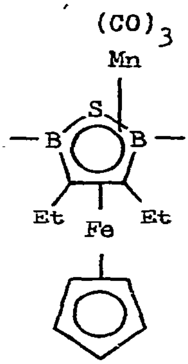

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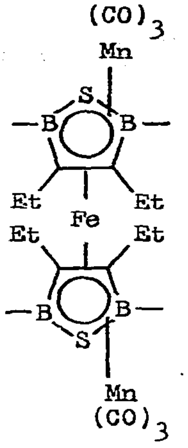
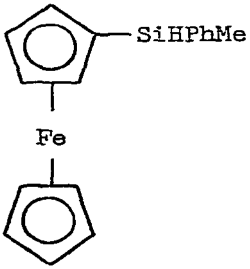


8.17

fluorosilane (8.20) with Grignard reagents and organolithium compounds resulted in selective replacement of the fluorine atom. In these reactions there was retention of configuration with the organolithium compounds and a mixed stereochemistry was found with Grignard reagents. When Grignard reagent was used in solvents with increasing basicity the stereochemistry changed from inversion



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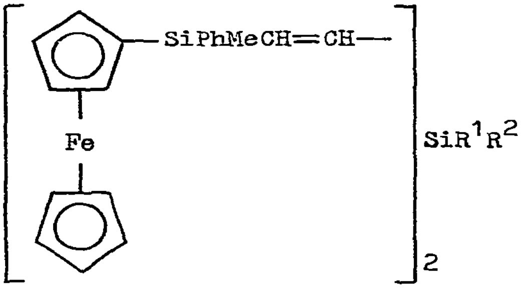

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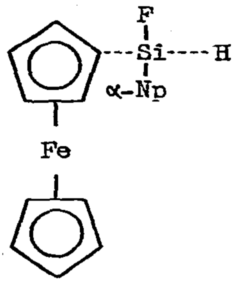
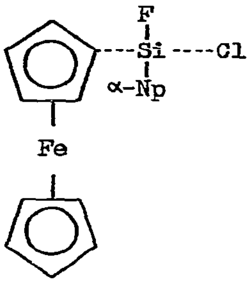




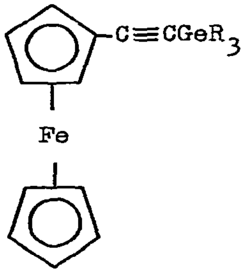
α–Np = α-naphthyl

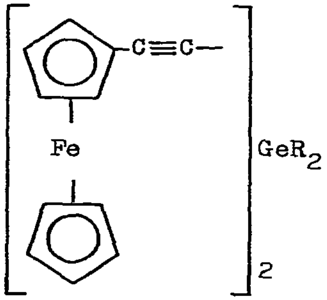
8.20

8.21

to retention. Inversion was the result of axial attack of the reagent whilst retention was explained in terms of an equatorial attack [101]. Monosubstituted acetylenes including ferrocenylacetylene combined with trisubstituted silanes MePhSiHR in the presence of Speier's catalyst to give one of two possible regioselective products $MePhR^1SiCH{=}CHR^2$ and $MePhR^1SiCR^2{=}CH_2$, where $R^1 = R^2$ = ferrocenyl, R^1 = cymantrenyl, R^2 = Ph, $SiPh_3$ [102].

Ferrocenylacetylene was lithiated and the β-lithio intermediate treated with trialkylchlorogermanes to form the germylferrocenes (8.22; R = Me, Et, Ph) and with dialkyldichlorogermanes to form the diferrocenylgermanes (8.23; R = Me, Et, Ph). These products (8.22 and 8.23) were hydrogenated over Raney nickel but were not





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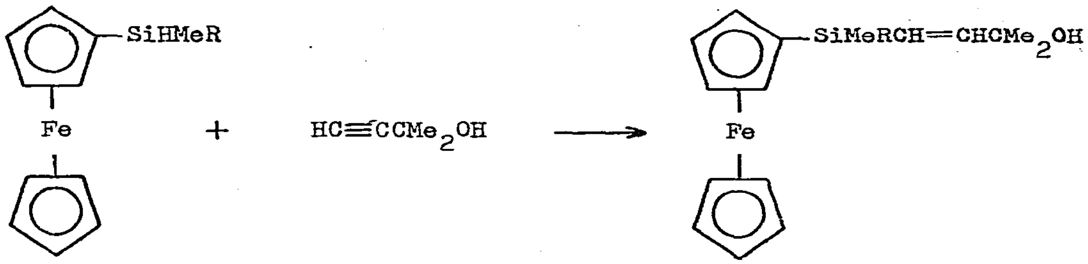
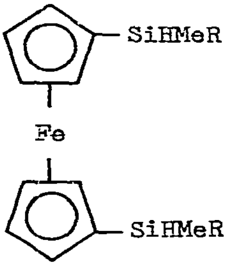


8.24 8.25 8.26

reduced by palladium on calcium carbonate, a reagent which is powerful enough to reduce silylacetylenes [103].

α-Hydroxyacetylenes underwent hydrosilation with ferrocenylsilanes to form vinyl silanes. In a typical reaction the dimethylsilane (8.24; R = Me) combined with the hydroxyacetylene (8.25) to give the product (8.26; R = Me). Similar reactions were carried out with 1,1-disilylferrocenes. The relative rate of the reaction was determined by the nature of the ferrocenylsilane and the presence of H_2PtCl_6; the following order of reactivity was observed:

(8.27; R = Me) $>$ (8.24; R = Me) $\gg$ (8.24; R = Ph) $>$ (8.27; R = Ph) [104].



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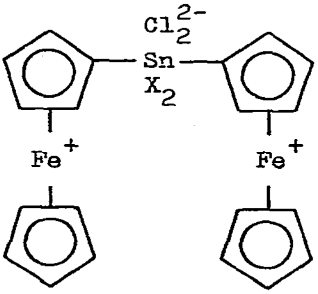
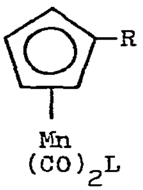


8.28

Complex formation by diferrocenyltin dichloride has been investigated. The dichloride combined with chloride, bromide and iodide ions in ether at -40° to form the ferricinium salts (8.28; X = Cl, Br, I). A 1:1 complex was formed with dimethylformamide while a 1:2 complex was formed with dimethylsulphoxide [105].

Diphenylchlorophosphine was treated with ferrocene in the presence of aluminium(III) chloride to form ferrocenyldiphenylphosphine [106]. Ferrocenylphosphine derivatives of benchrotrene and substituted cymantrenes have been obtained by direct reaction between the phosphine and the complex with the loss of carbon monoxide. The monosubstituted cymantrene analogues (8.29; R = H, Et, C_5H_{11}, COMe, COBu) were prepared together with the benchrotrenes (8.30) where the ligand L was triphenylphosphine, ferrocenyldiphenylphosphine, diferrocenylphenylphosphine or triferrocenylphosphine [107].



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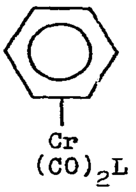

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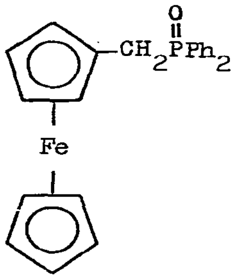
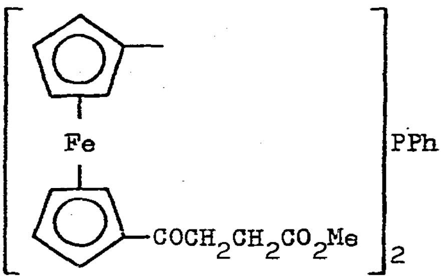


8.31

A mixture of two isomeric diphenyl(cyclopentadienylmethyl)phosphine oxide complexes was treated with dicarbonyl(η-cyclopentadienyl)iron dimer to give the ferrocenylmethylphosphine oxide (8.31) [108].

The preparation of a number of ferrocenylphosphines and ferrocenylphosphine oxides has been reported. A typical synthesis involved the treatment of diferrocenylphenylphosphine oxide with $MeO_2CCH_2CH_2COCl$ in methylene chloride using aluminium chloride as catalyst to give the diferrocenylphosphine (8.32) in 70% yield. This product gave two reduction products with zinc and hydrochloric acid and a third reduction product with sodium borohydride [109].



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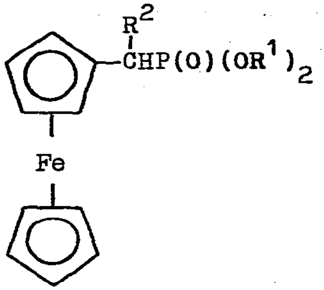
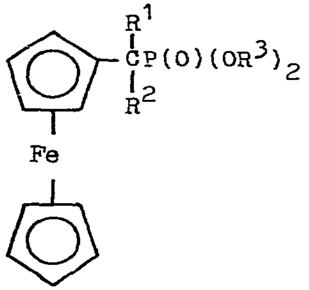


8.33

The condensation of formylferrocene with the phosphonates $HP(O)(OR^1)_2$ (R^1 = Me, Et, $CHMe_2$) gave the corresponding ferrocenylhydroxymethylphosphonates (8.33; R^2 = OH). These phosphonates (8.33; R^2 = OH) were treated with dimethyl sulphate and acetic anhydride to give the corresponding ethers (8.33; R^2 = Me) and esters (8.33; R^2 = COMe) [110].

Treatment of either formylferrocene or acetylferrocene with an amine in the presence of a dialkylphosphonate gave the corresponding ferrocenylaminomethyl phosphonate (8.34; R^1 = H, Me; R^2 = PhNH, p-MeC_6H_4NH, p-$O_2NC_6H_4NH$, morpholino, piperidino; R^3 = Me, Et, Pr, Me_2CH, Bu, Me_2CHCH_2). The antimicrobial activity of all these compounds was investigated [111].



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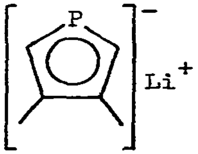

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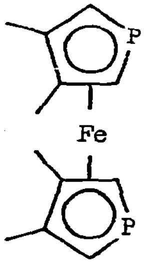

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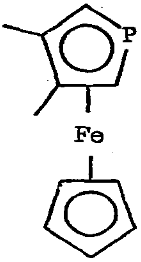

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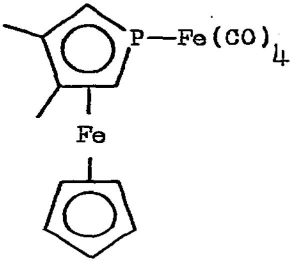
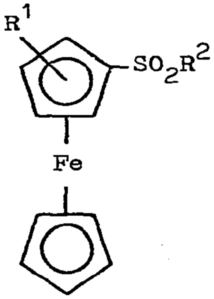


8.38

Dimethyl-3,4-phospholyl-lithium (8.35) was heated with iron(II) chloride to form the 1,1'-diphosphaferrocene (8.36) as a stable red solid. A tetraphenyl-1,1'-diphosphaferrocene was formed in the same way [112].

A convenient synthesis of dimethyl-3,4-phosphaferrocene has been reported. (η-Cyclopentadienyl)dicarbonyliron dimer was heated with 1-t-butyl-3,4-dimethylphosphole to give the phosphaferrocene (8.37) in 38% yield. Treatment of the product with diiron nonacarbonyl gave the phosphorus complex (8.38) [113].

The ferrocene sulphones [8.39; R^1 = H, Me; R^2 = H, Na, NEt_2, (η-$C_5H_4CH_2$)Fe(η-C_5H_5), CH_2CH_2CN, $CH_2CH_2CO_2H$, $CH(OH)C_6H_4NMe_2$] were prepared from the corresponding sulphonic acids. Sulphonation of



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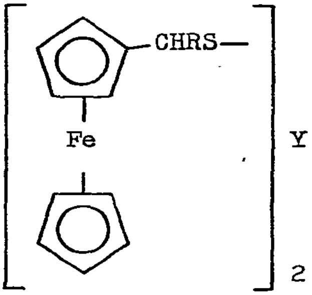

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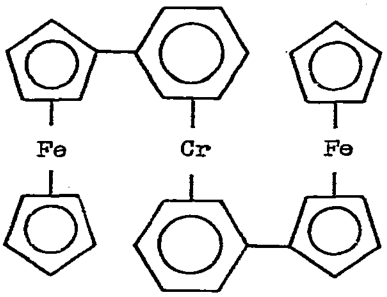
methylferrocene with sulphur trioxide in dioxane gave a mixture of mono- and di-sulphonic acids which were separated as their lead salts [114]. Ferrocenylmethanol and 1-ferrocenylethanol combined with difunctional mercaptans HSYSH, where Y = CH_2CH_2, $CH_2CH_2CH_2$, CH_2CHMe, $(CH_2CH_2)_2O$, $(CH_2CH_2)_2S$ to give the corresponding sulphides (8.40; R = H, Me) [115].

Phenylferrocene was treated with chromium(III) chloride followed by aluminium(III) chloride and aluminium to form the bis(η-benzene)-chromium complex (8.41) which was characterized as the iodide [116].



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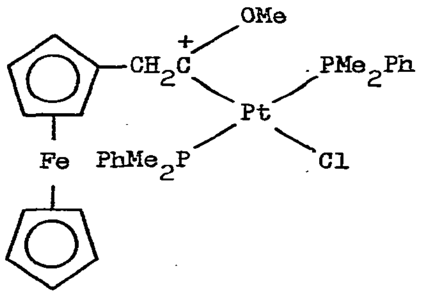


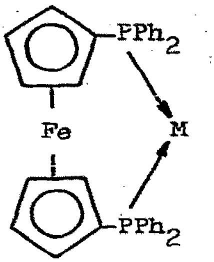
8.42

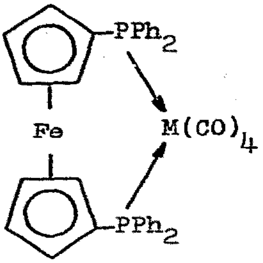
Ethynylferrocene was treated with cis-$PtCl_2(PMe_2Ph)_2$ to form the complex trans-$PtCl[C{\equiv}C(C_5H_4)Fe(C_5H_5)](PMe_2Ph)_2$ which underwent protonation in methanol to give a platinum stabilized carbenium ion (8.42) rather than the alternative ferrocenyl stabilized carbenium ion [117].

Diferrocenylmercury was treated with $MeAuPPh_3$ and fluoroboric acid in THF to form the ferrocenylgold complex $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)(AuPPh_3)_2]BF_4$ [118].

8. (iii) Complexes of ferrocene-containing ligands

1,1'-Bis(diphenylphosphino)ferrocene has been evaluated as a bidentate ligand towards transition metals. Complexes containing cobalt, nickel and copper halides were obtained (8.43; M = $CoCl_2$, $CoBr_2$, CoI_2, $NiCl_2$, $NiBr_2$, NiI_2, CuI) together with three tetracarbonyl complexes (8.44; M = Cr, Mo, W). The ferrocene ligand was found to behave in much the same way as bis(diphenylphosphino)-ethane [119].

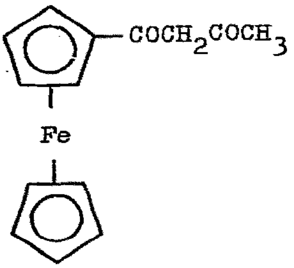




8.43 8.44

Ferrocenoylacetone (8.45), HL, has been used as a bidentate ligand to form the complexes VOL_2, CrL_3, MnL_2, CoL_2, NiL_2, CuL_2. The complexes were characterized by spectroscopy and the ML_2 complexes underwent thermal degradation in a single stage reaction with the exception of $CuL_2.H_2O$ which was degraded by a two-stage process [120].

Titanium polyferrocene oximes (8.46; R = Ph, Me) were prepared by the reaction of bis(η-cyclopentadienyl)titanium dichloride with the appropriate oxime in the presence of excess base. The polymers (8.46; R = Ph, Me) were analysed thermogravimetrically and by



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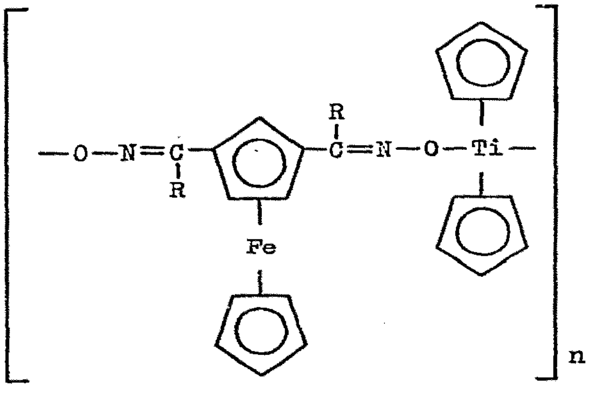

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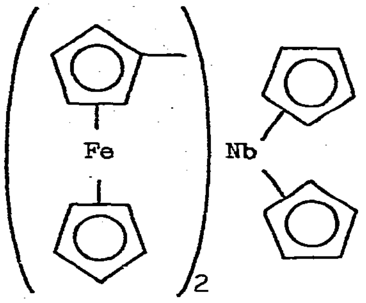
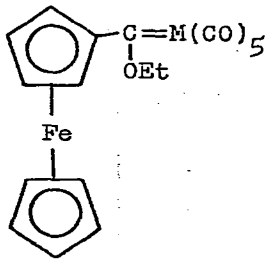


8.47

differential scanning calorimetry. Thermal transitions occurred by similar exothermic routes in nitrogen and air up to approximately 180° and above this temperature they occurred by different paths. The polymers began to degrade at about 250° but they retained 50% of their weight up to 600° [121].

Reaction of dichlorobis(η-cyclopentadienyl)niobium with ferrocenyllithium gave the ferrocenyl-niobium complex (8.47) [122]. Treatment of the ferrocenyl derivatives (8.48; M = Cr, Mo, W) with BX_3 gave the carbynes (8.49; M = Cr, Mo, W; X = Cl, Br, I) [123].

Acetylferrocene thiosemicarbazone has been treated with iron(II) chloride to form the complex (8.50) which was characterized by Moessbauer spectroscopy. In the same way 1,1'-diacetylferrocene



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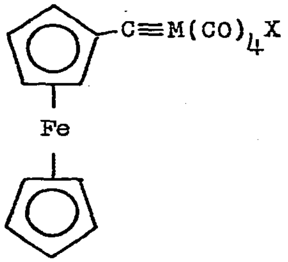

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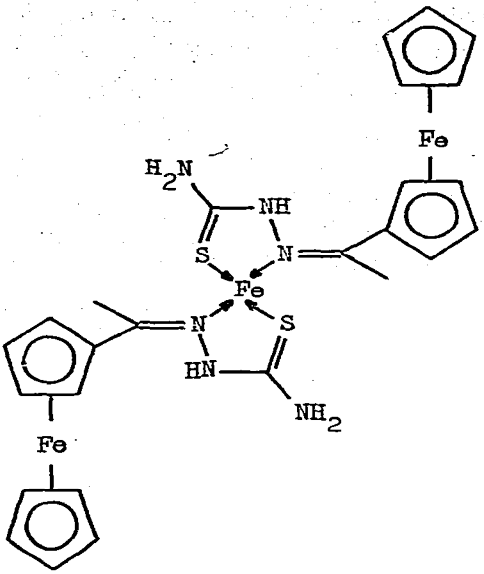

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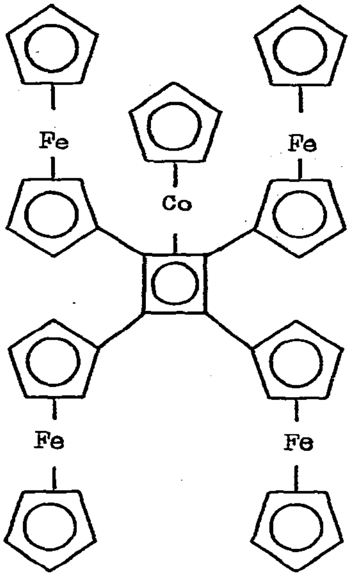

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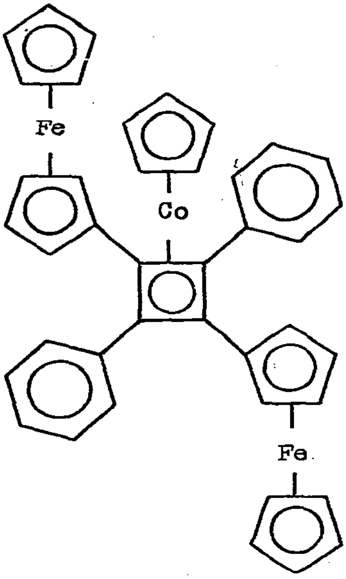

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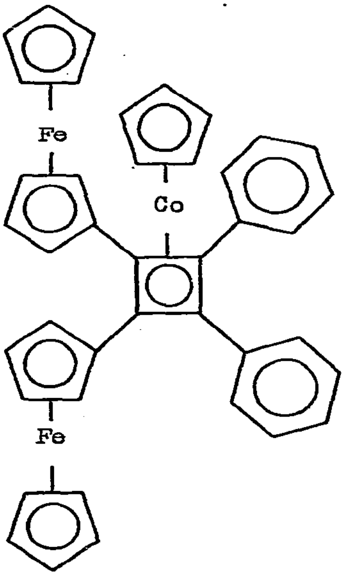


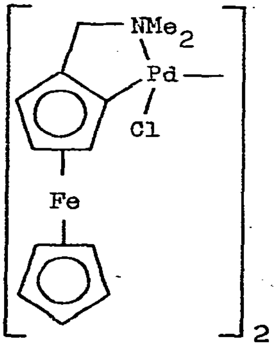
8.53

thiosemicarbazone gave a polymeric complex with iron(II) chloride [124]. The reaction of dicarbonyl(η-cyclopentadienyl)cobalt with diferrocenylacetylene gave the mixed sandwich complex (8.51). A similar reaction between dicarbonyl(η-cyclopentadienyl)cobalt and ferrocenylphenylacetylene gave the two isomers (8.52 and 8.53). The structure of the latter isomer (8.53) was determined by X-ray analysis. The η-cyclobutadiene ring was square with average bond length of 1.462 Å but it was not quite planar with one of the carbon atoms being 0.035 Å out of the plane formed by the other three atoms. The η-cyclopentadienyl rings of ferrocene were in the eclipsed conformation [125].

An optically active cyclopalladated ferrocene (8.54) was obtained by treating (N,N-dimethylamino)methylferrocene (8.55) with salts of optically active acids and sodium tetrachloropalladate(II) in methanol. Typical acids used were N-acetyl-L-valine, mandelic acid and lactic acid. The cyclopalladated product (8.54) was obtained in 70% yield with an enantiomeric excess of 12% [126].

The ferrocene-palladium complexes (8.54 and 8.56) were treated with olefins under mild conditions to give the corresponding 1,2-disubstituted ferrocenes (8.57; R^1 = H, Me, R^2 = Ph, CO_2Et, CO_2Me, CN, COMe, COPh and 8.58; R = COMe, COPh) [127].

Acetylferrocene was condensed with S-methyldithiocarbazate to give the anil (8.59) which combined with copper(II) ions to give the complex $CuL_2.H_2O$, where LH = the anil (8.59) [128]. Reaction of the ferrocenylphosphine complexes (8.60; R^1 = ferrocenyl



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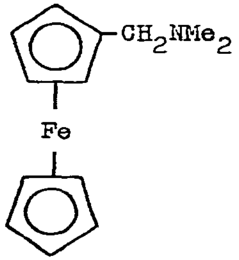

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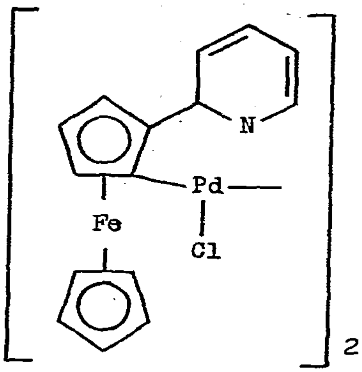

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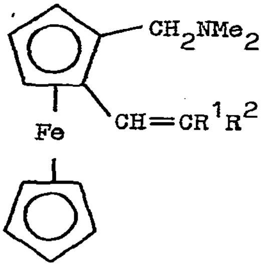

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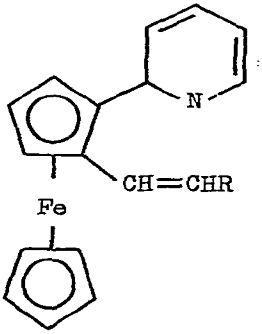

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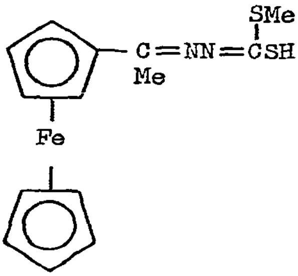

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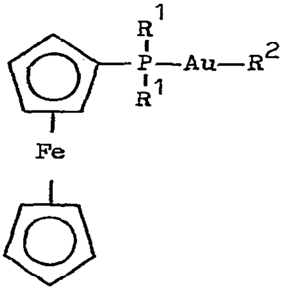

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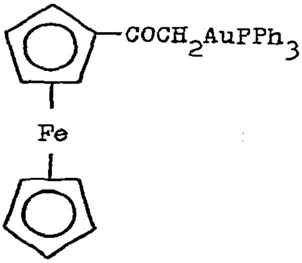

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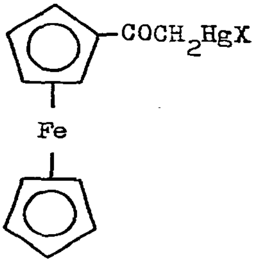


8.62

or phenyl, R^2 = Br) with Grignard reagents gave the corresponding organogold compounds (8.60; R^1 = Ph, R^2 = Me; R^1 = ferrocenyl, R^2 = p-FC_6H_4) [129].

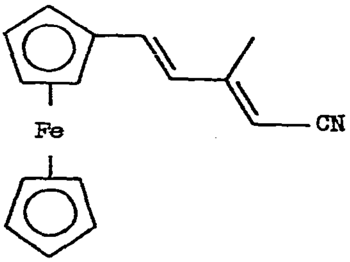
The ferrocene-gold complex (8.61) was prepared by treating acetylferrocene with $(Ph_3PAu)_3O^+BF_4^-$. The ferrocene-mercury complexes (8.62; X = Cl, Br, I) were also prepared [130].

8. (iv) General Chemistry

A general method for the synthesis of ferrocenylalkenes in high yield was reported. This involved the reduction of an acylferrocene with lithium aluminium hydride and direct treatment of the alcoholate with dilute hydrochloric acid, without isolation of the alcohol and gave the ferrocenylalkene. For example, isobutyrylferrocene gave 1-ferrocenyl-2-methylpropene in 92% yield via this route [131].

The cis- and trans-isomers of the ferrocenylbutadiene (8.63) have been characterized and used to form the iron tricarbonyl complex (8.64). The reactivity of the nitrile group in these compounds has been studied using the Pinner, Stefen and Grignard reactions [132].

Treatment of (1-hydroxy-1-arylethyl)ferrocenes (8.65; R = H, Me) or (1-arylvinyl)ferrocenes (8.66; R = H, Me) in hexane with oxygen gas in the presence of silica gel gave the butadiene (8.67), the tetrahydrofuran (8.68) and the butan-1,4-diol (8.69) derivatives formed by oxidative dimerization. A mechanism was suggested for the reaction whereby the dimers were produced via



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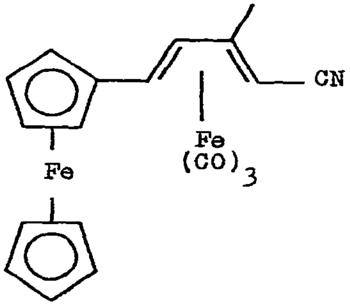

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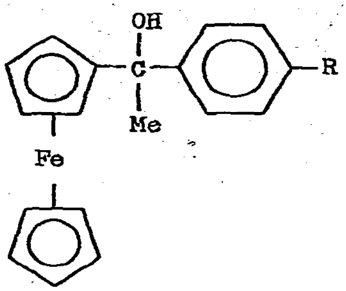

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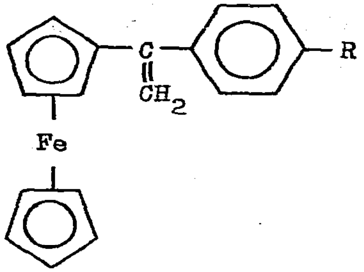

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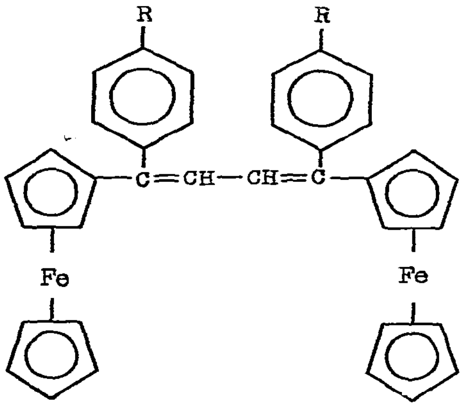

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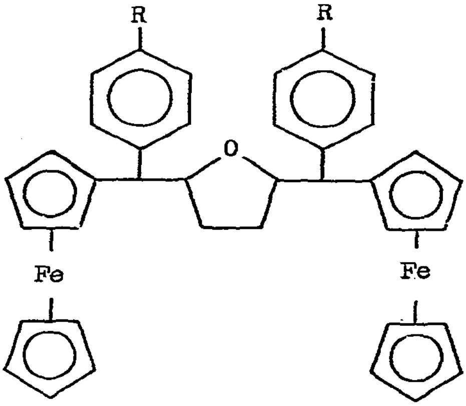

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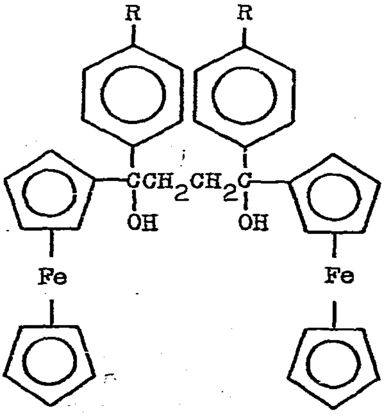

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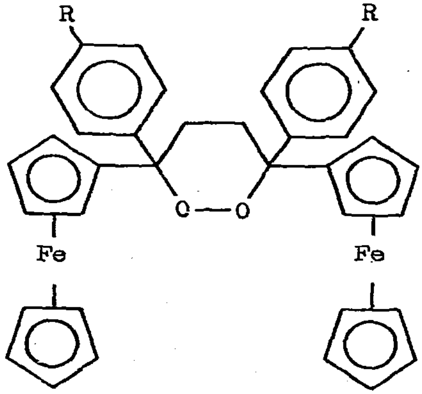

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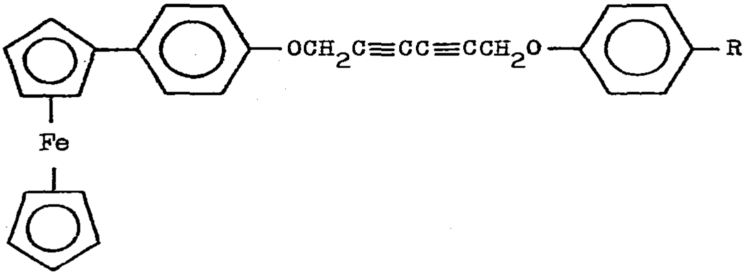

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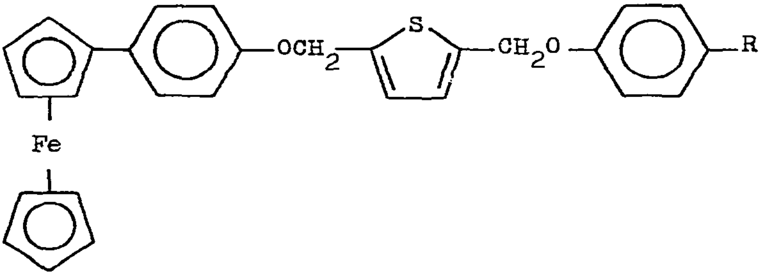
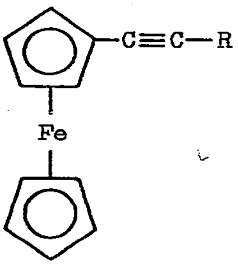


8.72

a six-membered cyclic peroxide (8.70) formed by incorporation of molecular oxygen into two olefin molecules [133].

Cyclization of the ferrocenyl-acetylenes (8.71; R = Br, I) with hydrogen sulphide or sodium hydrogen sulphide in a weakly basic medium gave the corresponding thiophene derivatives (8.72) [134].

The addition of hydrogen chloride, water and butyllithium to ferrocenylacetylenes (8.73; R = Ph, ferrocenyl, 2-thienyl) has been investigated. In a typical reaction the acetylene (8.73; R = Ph) underwent addition of hydrogen chloride when acetyl chloride and aluminium chloride were used as the reagents. The product was a mixture of the cis- and trans-isomers of the olefin



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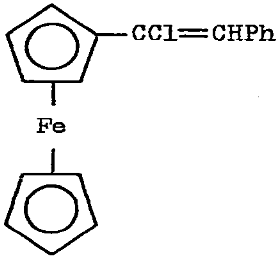


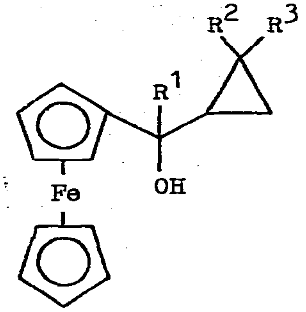
8.74

(8.74) [135]. The cyclopropyl-substituted alcohols (8.75 ; $R^1 = R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = H$; $R^1 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = H$, $R^3 = Ph$; $R^1 = Me$, $R^2 = H$, $R^3 = Ph$) were prepared from the corresponding ketones. The alcohols (8.75; $R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$, $R^3 = Ph$) were converted to the methyl-ethers (8.76; R = H, Ph) respectively by methyl alcohol and silica gel. The alcohol (8.75; $R^1 = Me$, $R^2 = H$, $R^3 = Ph$) was converted to the corresponding olefin (8.77) and the ring opened product (8.78) by chromatography on silica gel. Similar reactions were studied with the other ferrocenyl-alcohols listed [136].

The ferrocenylchalcone (8.79) was cyclized with hydrazine to form the pyrazoline (8.80; R = H) which was acetylated to give the derivative (8.80; R = COMe) and underwent thermal degradation in the presence of platinum, carbon and potassium hydroxide to the <u>trans</u>-diferrocenylcyclopropane (8.81) [137].

Hydrogen-deuterium exchange of the substituted cyclopentadienyl ring protons in cyano-, acetyl- and benzoyl-ferrocene took place in pyridine containing 10% deuterium oxide. Carboethoxy-, formyl-, nitro- and methyl-ferrocene did not undergo exchange under these conditions. However, 1,1'-diacetyl- and 1,1'-dibenzoyl-ferrocene underwent exchange in either pyridine or diglyme [138].

The reactions of 1,2- and 1,3-diacetylferrocene and 1,2-diformylferrocene with aromatic aldehydes were investigated. On condensation with acetophenone the products from both 1,3-diacetylferrocene and 1,2-diformylferrocene were stable but those of 1,2-diacetylferrocene (8.82 and 8.83) underwent decomposition to



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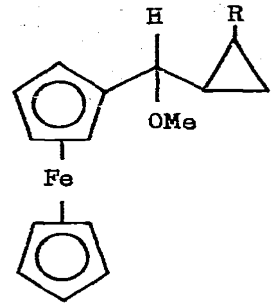

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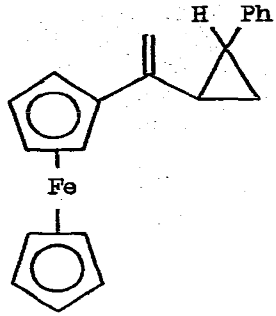

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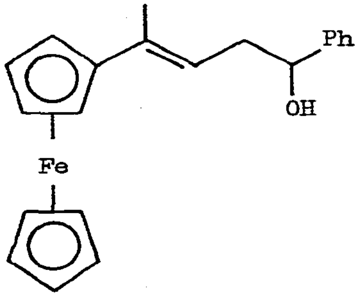

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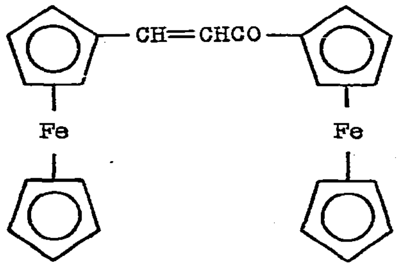

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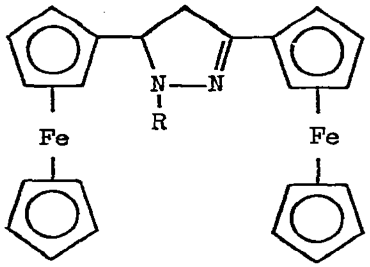

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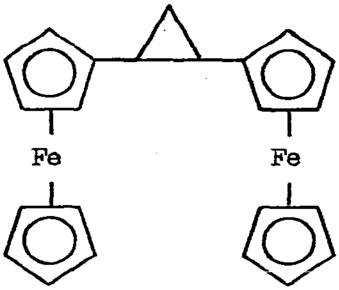

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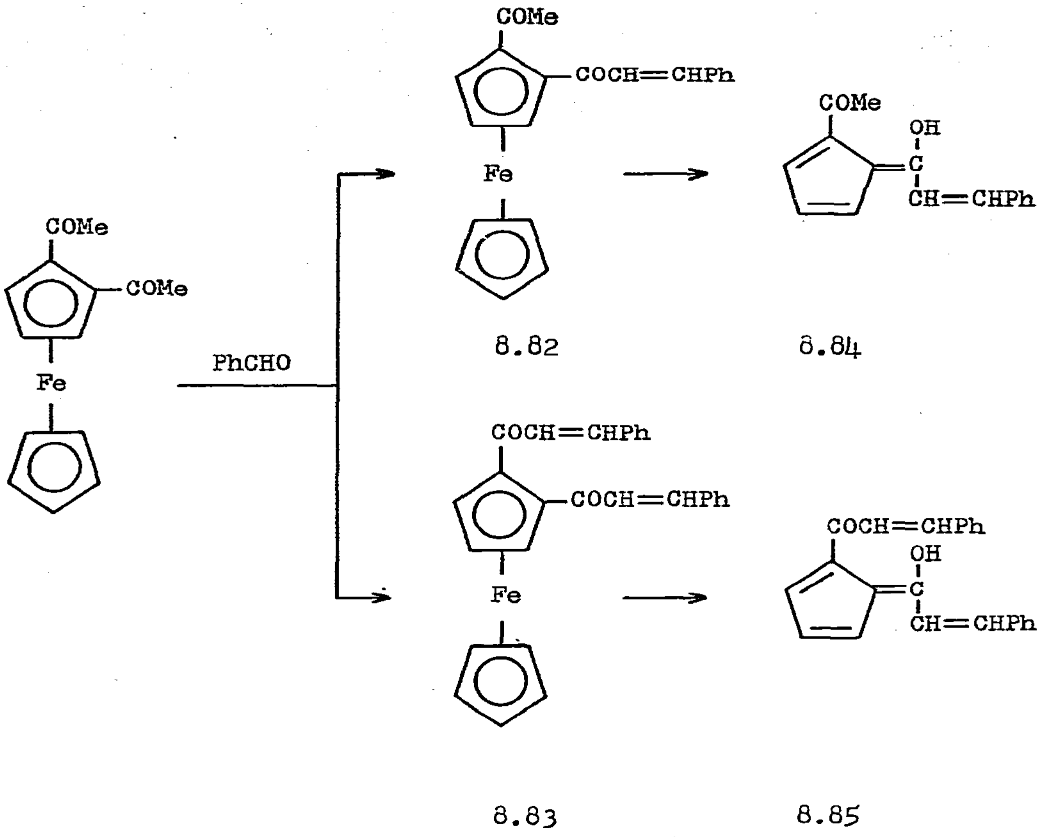
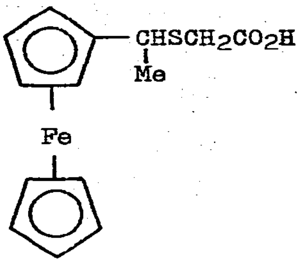


Scheme 8.1

give derivatives of 2-acyl-6-hydroxyfulvene (8.84 and 8.85) (Scheme 8.1) [139].

The reaction of Grignard reagents of acetylenic alcohols with acylferrocenes and acylcymantrenes was investigated [140]. Ferrocenylalcohols were resolved into enantiomers by treatment with optically active thiols. Thus 1-ferrocenylethanol was treated with thioglycollic acid in the presence of trifluoroacetic acid and acetone to form (±)-S-(1-ferrocenylethyl)thioglycollic acid (8.86). This intermediate was added to optically active ephedrine in methanol to form a salt which liberated (−)-S-(1-ferrocenylethyl)-thioglycollic acid which on treatment with mercury(II) chloride in aqueous acetone gave optically active 1-ferrocenylethanol [141].



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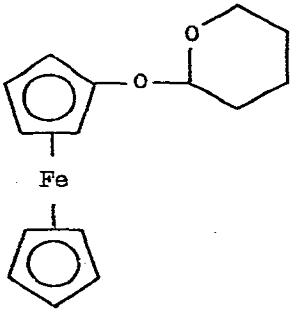
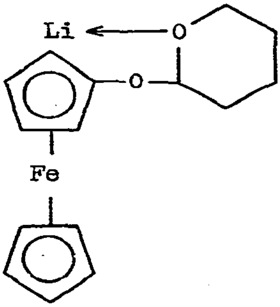
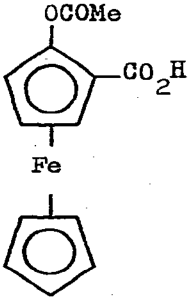
Ferrocenylboronic acid was prepared in good yield via the base hydrolysis of ferrocenylboron dibromide. The ferrocenylboronic acid was converted into hydroxyferrocene and this was treated with 2,3-dihydropyran to give the ferrocenylacetal (8.87). Lithiation of this acetal (8.87) with n-butyllithium gave the corresponding 2-lithiated ferrocene (8.88), which was used to prepare some 1,2-disubstituted ferrocenes including 1-carboxy-2-acetoferrocene ("ferrocenyl-aspirin") (8.89) [142].

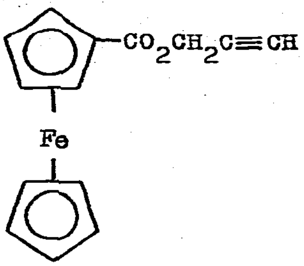
The propargyl ester (8.90) was obtained by esterification of ferrocenylcarboxylic acid with propargyl alcohol, the diester of 1,1'-ferrocenedicarboxylic acid was obtained in the same way [143].







8.87 8.88 8.89



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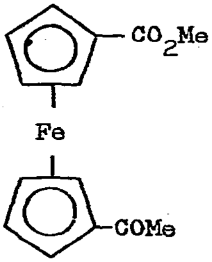
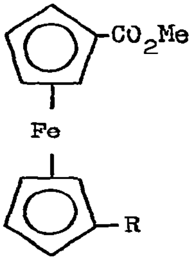


8.91

Acetylation of ferrocenecarboxylic acid methyl ester with acetic anhydride-boron trifluoride etherate or acetyl chloride gave mainly the heteroannularly substituted derivative (8.91) but some 1-carbomethoxy-2-acetylferrocene was also isolated [144].

The ferrocenyl-esters (8.92; R = H, CO_2Me) were prepared by the electrolysis of ferrocene and oxalic acid in methanol on a platinum electrode. Mono, bis- and tris-(3-methoxycarbonylpropyl)-ferrocene were prepared by the electrolysis of ferrocene in the presence of $MeO_2C(CH_2)_3CO_2H$ [145].

The N-ferrocenylmethylpyridinium salt (8.93) was converted to azidomethylferrocene (8.94) on heating with sodium azide in water. 1'-Substituted ferrocenylethylazides were obtained by similar reactions [146].



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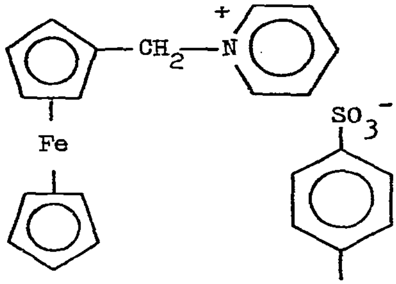

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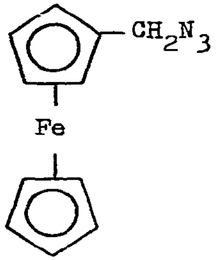
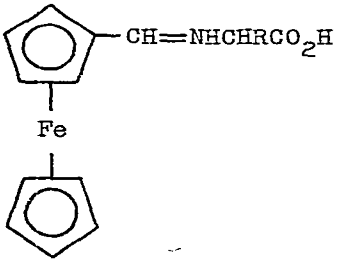


8.94

A number of Schiff bases have been prepared by treating ferrocenecarbaldehyde with amino acids. Yields in the range 87-95% were obtained and the compounds were used as haematinic agents. Typical products were the carboxylic acids [8.95; R = H, DL-Me, DL-$CHMe_2$, DL-CH_2CHMe_2, L-$CH_2CH_2CO_2H$, DL-CH_2CO_2H, L-p-$CH_2.C_6H_4.OH$, L-CH_2CH_2SMe, L-$CH_2CH_2CH_2NHC(=NH)NH_2$] and their ethyl esters [147].

Ferrocenylpyrazolones (8.96; R = H, Ph) were formed from ferrocenyldiketones [$(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4COCR_2CO_2Et)$] by condensation. The products underwent alkylation, formylation and coupling with diazo reagents [148].

Formylferrocene was condensed with substituted hydrazines to give hydrazones (8.97; Y = NH, NMe, NBz, NPh, O, S) in yields of 51-97% [149].



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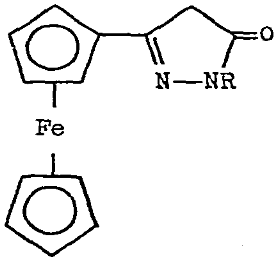

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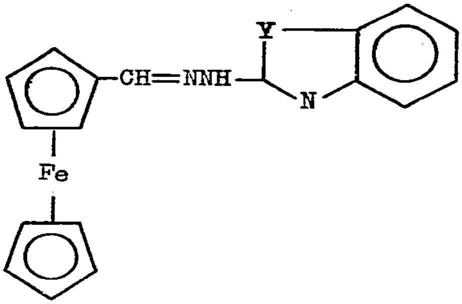

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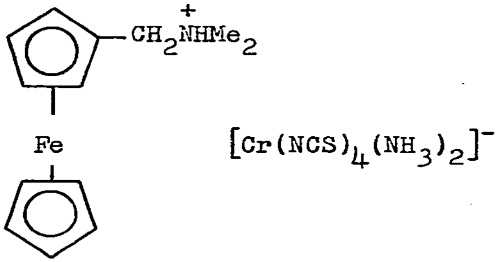


8.98

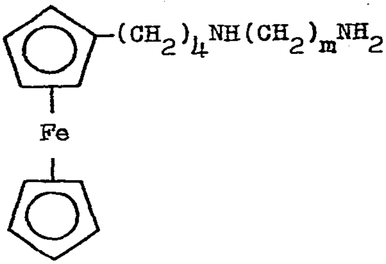
(Dimethylamino)methylferrocene was treated with the Reinecke salt to form the corresponding Reineckate (8.98). An alkyl substituted (dimethylamino)methylferrocene underwent the same reaction [150].

The thermal decomposition of ferrocenylmethyldimethylammonium perchlorate and ethylenediferricinium perchlorate have been the subject of kinetic investigation [151].

(Dimethylamino)methylferrocene was oxidized to the N-oxide in near quantitative yield with hydrogen peroxide [152]. The aminomethylation of 1,1'-diethylferrocene and 2,2-bis(1,1'-diethylferrocenyl)propane with bis(dialkylamino)methanes [$(R_2N)_2CH_2$ where R = Me, Et, Bu] in acetic acid in the presence of phosphoric acid was investigated. The reaction of 1,1'-diethylferrocene with bis(dimethylamino)methane gave a mixture of 1,1'-diethyl-2- and 3-dimethylaminomethylferrocenes [153].

A series of ferrocenyl polyamines (8.99; m = 3, 4, 8.100 and 8.101) was prepared by reduction of the precursor polyamides with diborane in tetrahydrofuran. The polyamines (8.99, 8.100 and 8.101) were subjected to screening for antitumor activity against lymphocytic leukemia P-388. No significant antitumor activity was obtained with any of the polyamines or their corresponding polyhydrobromides. However, the precursor polyamides [8.102; n = 3, R = H; n = 3, R = $(CH_2)_2CONH$; n = 2, R = $(CH_2)_3CONH(CH_2)_2CONH$] did exhibit a low but significant antitumor activity [154].

(Dimethylamino)methylferrocene methiodide has been treated with nucleophiles to give the corresponding ferrocenylmethyl



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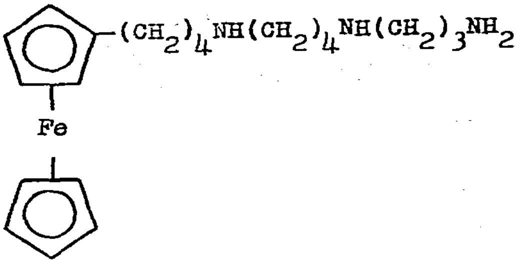

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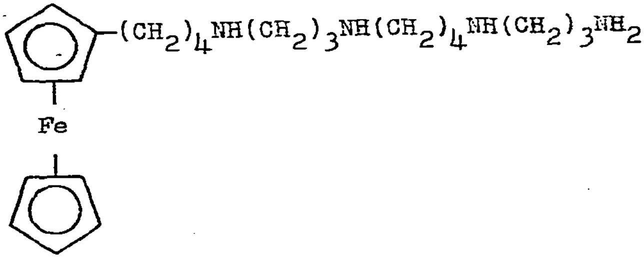

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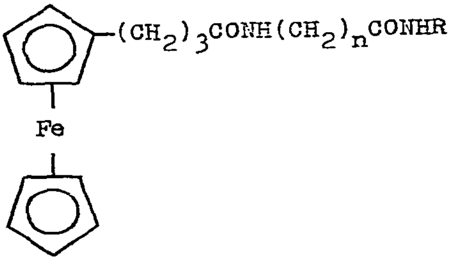

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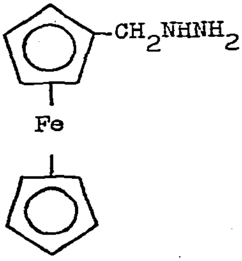
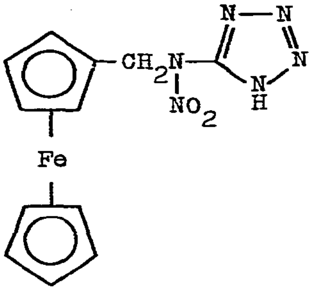


8.103

compounds. Thus reaction with hydrazine gave ferrocenylmethylhydrazine (8.103) in 80% yield [155].

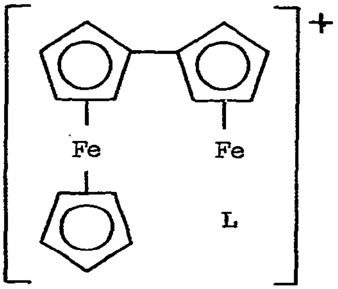
A number of nitrogen heterocycles with ferrocenyl substituents have been prepared by treatment of ferrocenylmethylchloride with the sodium salt of the appropriate heterocyclic anion. A typical product was the ferrocenylmethylaminotetrazole (8.104) [156].

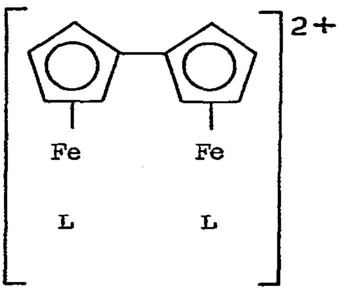


8.104

9. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

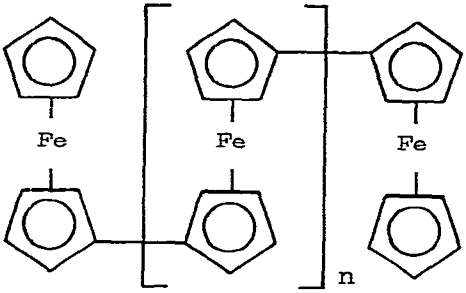
Ligand exchange reactions between biferrocenyl and arenes L (L = benzene, mesitylene, naphthalene and tetralin) were effected in the presence of aluminium chloride. In the presence of one mole of arene the cations (9.1) were formed and with two moles of arene the dications (9.2) were isolated [157].





9.1 9.2

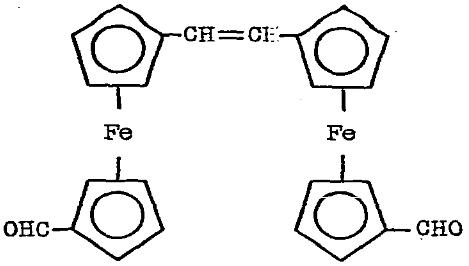
Neuse and co-workers have studied the coupling of 1,1'-dilithioferrocene in the presence of cobalt(II) chloride. In the coupling experiments pure reagents were used and precautions were taken to exclude molecular oxygen and carbon dioxide. A series of polyferrocenylenes (9.3) was obtained and the degree of polymerization was relatively high. It was proposed that the reaction proceeded via the intermediate formation of di- or multi-nuclear cobalt complexes from an oxidative addition step, followed by the reductive elimination of cobalt from the coupled entity [158].



9.3

Intermolecular coupling of 1,1'-diformylferrocene occurred in the presence of a titanium(IV) chloride, lithium aluminium hydride and tributylamine mixture to give 1,2-bis(1'-formylferrocenyl)ethylene (9.4) and the [2,2]ferrocenophane (9.5). Catalytic hydrogenation of the unsaturated derivative (9.5) gave the [2,2]ferrocenophane (9.6). The ferrocenophane (9.6) was also prepared by the reductive coupling of 1,1'-di(hydroxymethyl)ferrocene [159].

The synthesis of [2]orthocyclo[2](1,2)ferrocenophane (9.10) and [2,2](1,2)ferrocenophane (9.11) has been reported. The trimethylammonium salt (9.7; X = $\overset{+}{N}Me_3I^-$) was converted via the phosphorane (9.7; X = $\overset{+}{P}Ph_3I^-$) to the diferrocenylethylene (9.8) and then to the diferrocenylethane (9.9). Cyclization and subsequent reduction gave the ferrocenophane (9.11) as a mixture of two isomers (9.11a and 9.11b) in the ratio 3:1. The orthocycloferrocenophane (9.10) was synthesised by a similar route. The stereochemistry of the ferrocenophanes (9.10 and 9.11) was



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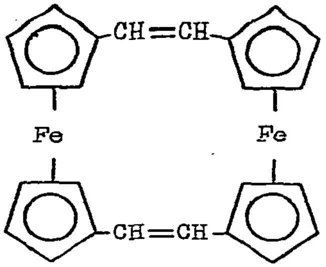

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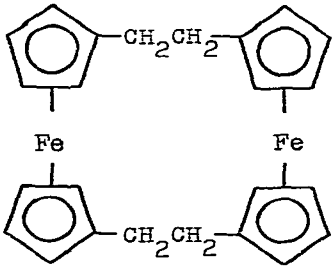
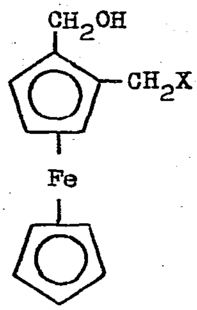


9.6

compared with that of [2,2]orthocyclophane (9.12) which may adopt chair, boat and twist-boat conformations. The four possible conformations for the trans-ferrocenophane (9.11a) are exo-exo chair (9.13), exo-endo (9.14), endo-exo boat (9.15) and endo-endo (9.16). It was considered that the most favourable conformer was the exo-exo chair form (9.13). Similar arguments were developed for the cis-ferrocenophane (9.11b) and for the orthocycloferrocenophane (9.10) [160].

The synthesis of some trimethylene bridged ferrocenes has been reinvestigated. Previous reports that the tribridged compound (9.17) could be converted to the tetrabridged ferrocene (9.18) were shown to be incorrect and the last compound (9.18) has been



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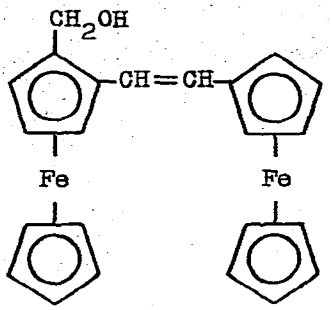

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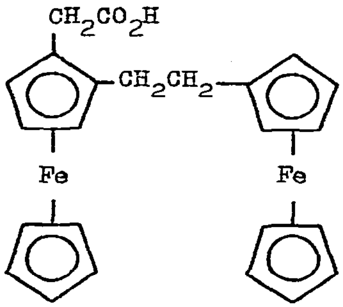

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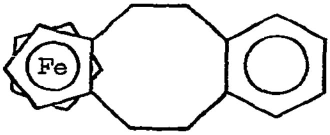

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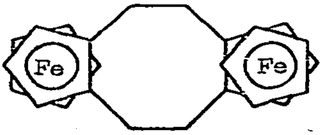
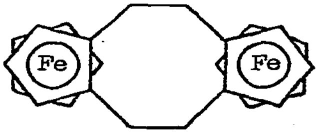
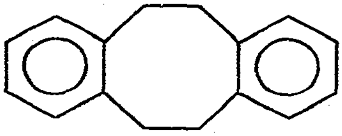


9.11a - trans



9.11b - cis



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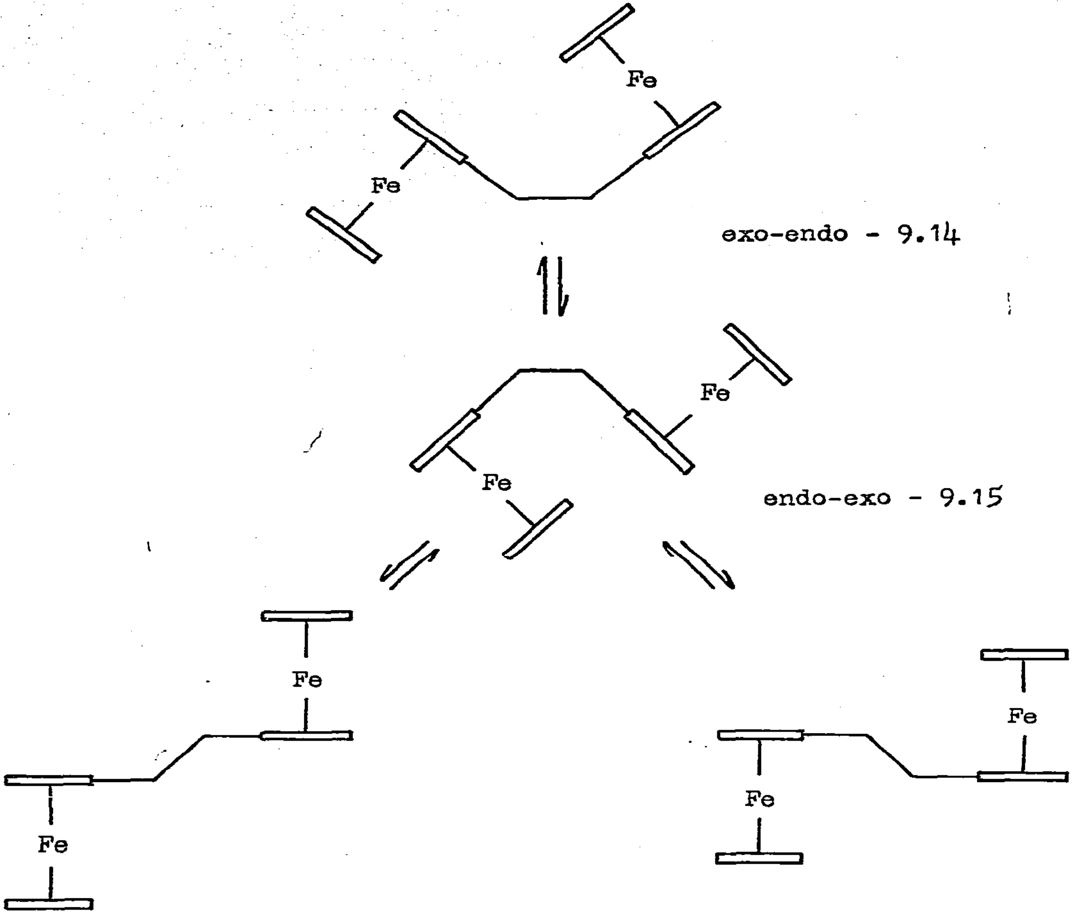


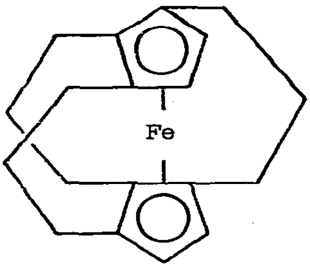
exo-endo - 9.14

endo-exo - 9.15

exo-exo - 9.13

endo-endo - 9.16

reformulated as the homoannular bridged ferrocene (9.19). Attempts to prepare a pentabridged ferrocene were unsuccessful, the product obtained (9.20) contained homoannular bridges. The electrode potentials for ferrocenes bridged with one, two and three trimethylene groups showed a correlation with the angle of ring-tilt. The conformations and configurations of several bridged ferrocenes were discussed and related to previously reported Moessbauer results [161]. The crystal and molecular structures of three multibridged ferrocenes (9.19, 9.20 and 9.21) have been confirmed by X-ray crystallography. One of these structures (9.19) had been claimed previously by Schlögl and Peterlik [162]as the tetrabridged ferrocene (9.18) [163, 164, 165].



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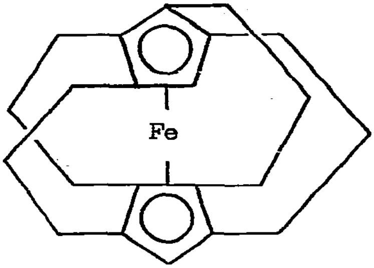

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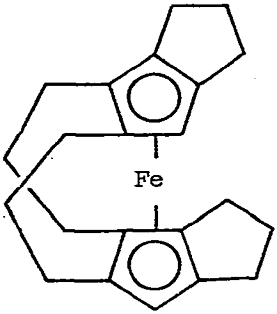

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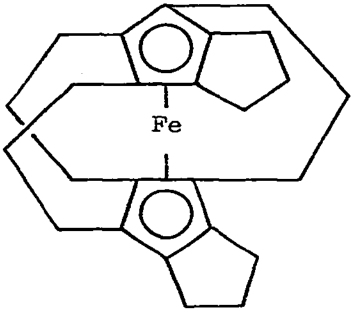

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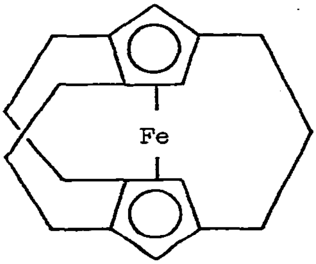
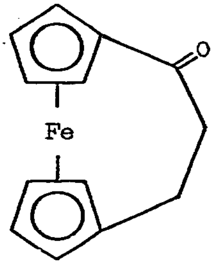


9.21

^{1}H and ^{13}C NMR spectroscopy have been used to investigate the structure of the [3]ferrocenophanes (9.22 and 9.23). Chemical shifts and coupling constants for the bridge hydrogen atoms were obtained and were in agreement with the previously proposed structures [166]. The 4-([3]ferrocenophanyl)butanoic acids (9.24) and (9.25) were dissolved in borax buffer of pH 9 and irradiated with light of approximately 240 nm wavelength in the presence of nitrous oxide. Photo-oxidation occurred to give the corresponding zwitterions (9.26) and (9.27) [167].



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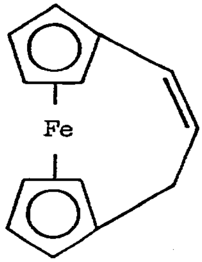

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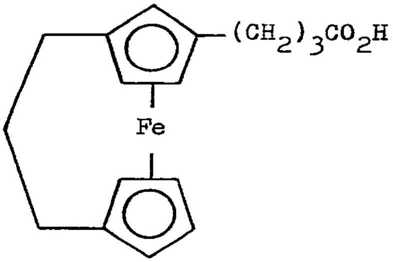

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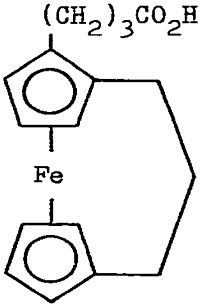

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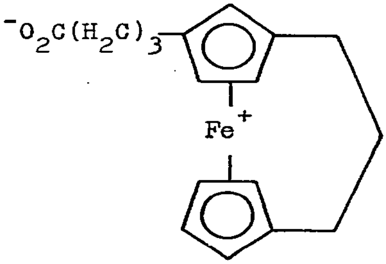

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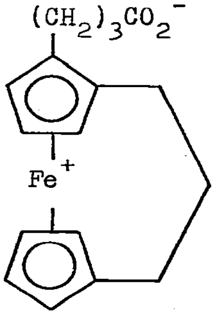
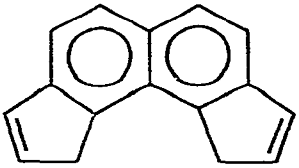


9.27

The dihydrodicyclopentanaphthalene (9.28) was converted to the corresponding dianion with n-butyllithium and then to the binuclear ferrocene (9.29) with iron(II) chloride. The binuclear ferrocenes (9.30 and 9.31) were formed in the same way. In the last case a small proportion of the trinuclear ferrocene (9.32) was obtained from the trianion and iron(II) chloride [168].



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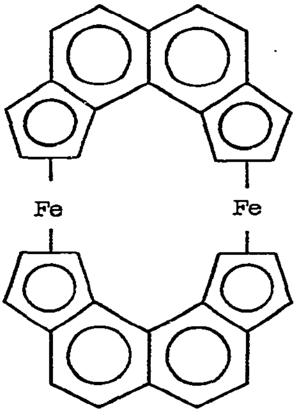

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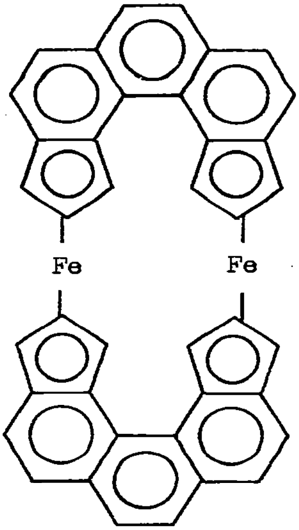

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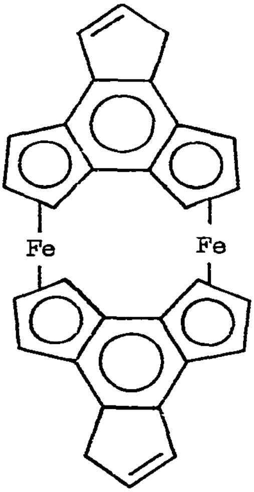

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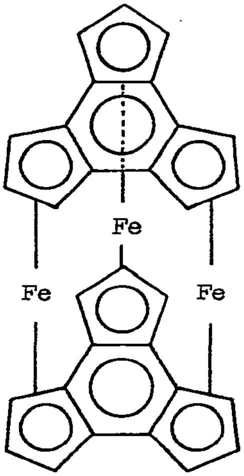


9.32

10. FERROCENE-CONTAINING POLYMERS

The preparation of ferrocene monomers and their polymerization has been discussed by Korshak and Sosin [169]. Ethylene glycol-1,1'-ferrocenedicarboxylic acid-terephthalic acid copolymer gave fibres with good photostability and oxidative thermostability. The crystallinity of these fibres on orientational elongation was higher and the degree of orientation was lower than that of poly(ethylene terephthalate) fibres [170].

The transesterification and polycondensation of 1,1'-diacetylferrocene, dimethyl terephthalate and ethylene glycol gave a modified poly(ethylene terephthalate) containing 1,1'-diacetylferrocene groups. The reaction involved the intermediate formation of dioxolane derivatives of the substituted ferrocene and the subsequent cleavage of these intermediates. The modified polymer formed fibres which showed improved stability to degradation by light and under oxidative thermal conditions when compared with poly(ethylene terephthalate) [171].

Fibre-forming compositions were obtained by the copolymerization of dimethyl terephthalate, ethylene glycol together with a small proportion of 1,1'-diacetylferrocene or 1,1'-dibutyrylferrocene. The metallocene catalyzed the transesterification and was chemically incorporated into the poly(ethylene terephthalate). Fibres obtained from the brown copolymer did not suffer a reduction in mechanical strength or break elongation after UV irradiation for ten days at 40° C [172].

Vinylferrocene was homopolymerized and copolymerized with isoprene, butadiene and 1,6-dibromohexane in the presence of n-butyllithium or lithium metal [173].

Various halogen containing polymers such as chlorinated polyethylenes and poly(vinyl chloride) were treated with ferrocene in the presence of aluminium chloride. Soluble polymers containing up to 62% ferrocene were obtained and in most reactions, substitution was accompanied by dehydrohalogenation [174].

A fire-resistant unsaturated resin has been formed by heating 1,2-polybutadiene with ferrocene in the presence of benzoyl peroxide [175]. Good fire resistance was also achieved by curing an epoxy resin with an amine hardener in the presence of ferrocene [176]. The composition of the oligoester used to form ferrocene-containing unsaturated polyesters has been shown theoretically to determine the Vicat softening point, the Brinell hardness and the stress causing failure during bending of the polyesters. These polymers showed high reactivity and were amenable to hot or cold curing. They were proposed as binders for glass fibre-reinforced plastics and electrical insulators [177].

A fire- and heat-resistant unsaturated polyester or 1,2-polybutadiene composition was obtained by the radical copolymerization of vinylferrocene with suitable organic monomers. A typical composition was based on 1,2-polybutadiene 50 parts, styrene 50 parts, vinylferrocene 30 parts and AIBN 2 parts which were heated for five hours at 100° C to form the cured resin. The resin was heated for 250 hours at 150° C without any change in electrical and mechanical properties and without the evolution of smoke or toxic fumes [178].

Ferrocenylacetylene has been polymerized at 60° C in a mixture of THF and ethanol using bis(triphenylphosphine)nickel(II) halide complexes as catalyst. The polymer was separated by precipitation with ether and had an electrical conductivity of $10^{-10}\Omega^{-1}$ cm^{-1} [179].

Poly(acryloylferrocene) was divided into soluble and insoluble fractions and the thermal stability of each was investigated. The temperature at which 10% weight loss occurred in air and in helium was measured for each fraction. The soluble fraction gave temperatures of 310° C and 350° C while the insoluble fraction gave values of 250° C and 320° C respectively. The thermal stability of polystyrene, poly(acrylonitrile) and poly(vinyl acetate) was enhanced by the incorporation of acryloylferrocene residues but the stability of poly(methyl methacrylate) was decreased by incorporating acryloylferrocene [180].

Acryloylferrocene was copolymerized with vinyl acetate, methyl methacrylate and styrene in benzene using azo-bis-isobutyronitrile as the initiator. The last two copolymers were obtained in 80% yield or better and while some homopolymerization of the organic monomers was detected, acryloylferrocene did not form a homopolymer under these conditions. The ratios of acryloylferrocene units to organic units were 1, 0.59 and 1.37 for vinyl acetate, methyl methacrylate and styrene respectively [181].

Ferrocenylmethyl methacrylate underwent anionic polymerization in a high vacuum system using lithium aluminium hydride-tetramethylethylenediamine as catalyst. The living polymers obtained combined with methyl methacrylate and acrylonitrile to give ferrocenylmethyl methacrylate-methyl methacrylate and ferrocenylmethyl methacrylate-acrylonitrile block copolymers respectively. However, the addition of styrene to the living polymer did not give a block copolymer since the polymer anions were too weak as nucleophiles to initiate the polymerization of styrene. The block copolymer ferrocenylmethyl methacrylate-styrene was obtained by adding the ferrocenyl monomer to living polystyrene [182].

Interfacial condensation has been used to prepare 1,1'-diacetylferrocene dioxime-di(η-cyclopentadienyl)titanium dichloride copolymer in near quantitative yield. The importance of stirring time, stirring rate, monomer ratio and solvent on the reaction was evaluated [183].

Vinylferrocene underwent radical polymerization in benzene with azo-bis-isobutyronitrile as initiator. The rate of polymerization was linear to $\sim$20% conversion and then decreased progressively with time. Aggregation of the polymer at high conversion caused a precipitate to be formed. The ESR spectra of the polymer confirmed the presence of paramagnetic species [184].

p-Vinylbenzophenone-vinylferrocene block copolymer and poly(p-vinylbenzophenone) in iso-propanol were irradiated with ultraviolet light. Photoreduction of the benzoquinone groups occurred and recombination of the radicals located in the polymer chain resulted in intra- and inter-molecular reactions. The presence of the ferrocene group reduced the quantum yields in the photochemical reactions [185].

Copolymers of ethylene with ferrocene and vinylferrocene were irradiated with increasing doses of γ-rays and showed sequential increases and then decreases in tensile strength and elongation at break and decreases in solubility. The detailed form of the changes was dependent on the proportions of comonomers and the radiation dose [186].

The thermochemical properties of polyvinylferrocene, its copolymers with styrene, methyl acrylate and methyl methacrylate; poly(ferrocenylmethyl methacrylate) and its block copolymers with styrene and methyl methacrylate were measured over the temperature range -180° to 250° using thermogravimetry and an automated torsional braid technique. Polyvinylferrocene was found to undergo irreversible changes in the temperature range 220° to 300° so that the glass transition temperature (Tg) was not obtainable directly but extrapolated from the Tg values of its random copolymers.

A low value was obtained by this method but the extrapolated value of Tg for poly(ferrocenylmethyl methacrylate) was equal to that obtained by direct determination. This polymer was plasticized by m-bis(m-phenoxyphenoxy)benzene with a decrease in Tg at low concentrations of plasticizer that was greater than in plasticized polystyrene [187].

Polyferrocene films have been formed by the plasma polymerization method and the electrical conduction measured. Results for several film thicknesses suggested that conduction arose from the space-charge-limited current [188].

The dielectric properties of plasma-polymerized ferrocene thin-films were investigated. The dielectric constant ε and the loss factor tan δ, for aluminium-polyferrocene-aluminium sandwich structures, showed small increases in the temperature range 30-400° [189].

11. APPLICATIONS OF FERROCENE

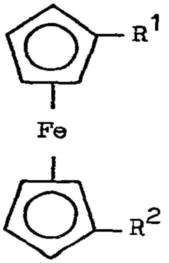
(i) Ferrocene catalysts and photosensitizers

The incorporation of 0.05% α-hydroxyethylferrocene into low density polyethylene gave a photodegradable material suitable for agricultural use when formed into thin film. When used on potato crops the soil temperature was increased by 2.5° C and the yield and nutritional quality of the crop improved [190].

The photodegradation of polyethylene was accelerated by the introduction of a small proportion of acetoxyferrocene or α-hydroxyethylferrocene,2,4-dinitrosoresorcinol and benzophenone into the polymer [191].

Photodegradation of coloured polyethylene was enhanced by up to three-fold when 1-hydroxyethylferrocene and iron(III) oxide were added as photosensitizers [192].

A series of patents was taken out on the use of ferrocene derivatives in positive-working radiation resists. The resists were based on polymers having halocarbonyl and/or carboxylic acid groups together with 0.01-20 wt % of a ferrocene derivative [11.1: $R^1 = R^2 = OH, CH_2OH, (CH_2)_2OH, (CH_2)_3OH, (CH_2)_4OH$] as a sensitizer [193]. Similarly a series of other ferrocene derivatives were used as sensitizers in a range of polymers. The addition of the ferrocene derivatives greatly increased the electron beam sensitivity of the resists [194, 195, 196, 197].



11.1

Radiation resist compositions were prepared that contained 0.1-30 wt % of a metallocene (11.1; $R^1 = R^2$ = H, OH, α-hydroxyalkyl, CHO, CO_2H, alkoxycarbonyl, halogen; M = Fe, Ni, Co, Cr, Mn, Ru). The resists were useful for the fabrication of semiconductors and integrated circuits [198].

A light sensitive composition with an image different in colour from that of the unmodified composition was prepared by mixing ferrocene or a ferrocene derivative with an organic halogen compound and an analytical reagent for iron [199].

Photoimaging compositions were obtained by mixing iodoform, the leuco form of an acid sensitive dye, ferrocene and a binder. A coloured image was obtained on exposure of the composition and this was fixed by heating. Thus, iodoform 4 parts, 3,3-bis-(dimethylaminophenyl)-6-dimethylaminophthalide 4.2 parts, ferrocene 2 parts and polystyrene 10 parts were dissolved in a mixture of toluene and acetone. The solution was coated on a polyester base and gave a clear blue image after exposure and fixing [200].

Photoimaging compositions containing ferrocene were prepared. For example, ferrocene, 3,3-bis-(4'-dimethylaminophenyl)-6-dimethylaminophthalide, trichloroacetamide and polystyrene were dissolved in a mixture of toluene and acetone and coated on a polyester film support. The film was imagewise exposed and fixed at 110° to give clear blue images [201].

Ferrocene formed a charge-transfer complex with carbon tetrabromide which was active photochemically and was used to form photographic images. The formation of ferricinium tetrabromoferrate was implicated in the production of images [202].

A photosensitive composition was prepared by whirl coating an anodized aluminium foil with a mixture of a halogen containing polymer, carboxymethylthioferrocene and a plasticizer in dichloroethane. The plate was exposed imagewise and then developed with a solution of Teepol in aqueous ethanolic sodium hydroxide to give a plate with improved ink receptivity [203].

Dimethylterephthalate and ethylene glycol were polymerized in the presence of 1,1'-diacetylferrocene to give poly(ethylene terephthalate) [204].

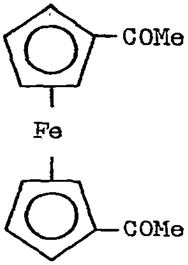
The photoinduced suspension and emulsion polymerizations of methyl methacrylate (MMA) in the presence of ferrocene and carbon tetrachloride as the initiator were investigated. In the suspension photopolymerization the water layer became blue which showed that the ferricinium ion was formed. Addition of ascorbic acid reduced the ferricinium ion to ferrocene and there was an increase in the rate of polymerization of the MMA. The addition of sodium lauryl sulphate as an emulsifier increased the rate of polymerization whilst the addition of cetyltrimethylammonium bromide decreased the rate. It was suggested that the transfer of the ferricinium ion from the monomer layer to the water layer was affected by the charge of the emulsifier [205].

n-Type silicon was shown to behave as a stable photoanode in a cell for the conversion of light to electricity. The other components in the cell were a platinum cathode and an electrolyte consisting of an ethanol solution of tetra(n-butyl)ammonium perchlorate together with the ferricinium-ferrocene couple. It was found that ferrocene was oxidized to the ferricinium ion at a silicon photoanode with approximately 100% efficiency. Prolonged irradiation of the silicon in a one-compartment cell gave a constant photocurrent. In the absence of the ferrocene-ferricinium couple a lower photocurrent was obtained which dropped by more than 90% in less than ten minutes [206].

(ii) Ferrocene stabilizers and improvers

The use of ferrocene derivatives as inhibitors of polyethylene ageing was investigated [207]. Ferrocene behaved as a dehydrogenation catalyst when it was added to friction materials containing organic binders and fillers. These materials were used in the formulation of railway brake shoes and the presence of ferrocene helped to prevent brake fade [208].

A storage-stable anaerobic composition capable of hardening on cadmium surfaces was prepared from oligocarbonate acrylates, benzoyl peroxide and ferrocene [209]. The diacetylferrocene (11.2) has been used as a dye for poly(ethylene terephthalate) [210]. The 2-ferrocenylbenzoquinoline (11.3) has been claimed as a dye for polyester and polyamide materials [211].



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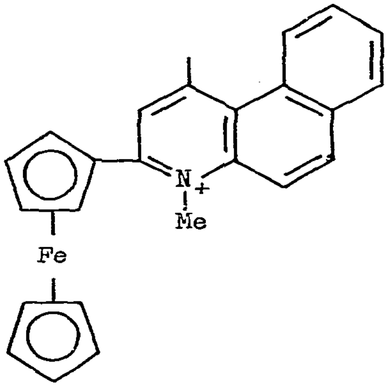


11.3

(iii) Ferrocene in analysis

Ferrocene in ethanol has been used as a reagent for the amperometric titration of vanadium(IV) and iron(III) in metallurgical slags. An acetic-sulphuric acid medium was used in each case and phosphoric acid was added in the determination of vanadium [212].

The kinetics of the reactions of ferrocene with vanadium(V) and vanadium(IV) in acid aqueous-organic media were investigated so that the optimum conditions for the titrimetric determination of vanadium could be selected. The amperometric titration of vanadium(V) by ferrocene was carried out in a mixture of sulphuric acid and acetic acid. It was found that vanadium(V) and vanadium(IV) could be determined in the presence of each other by amperometric titration with ferrocene [213].

Solomatin and co-workers have devised a method for the determination of molybdenum in steels and alloys using ferrocene [214]. Iron(III), molybdenum(VI) and rhenium(VII) were determined indirectly by reaction with ferrocene to give the ferricinium ion and the concentration of this latter ion was estimated spectrophotometrically at 615 nm. Molybdenum(VI) and copper(II) behaved as interfering ions in this estimation whilst manganese(II), iron(II), cobalt, nickel, cadmium, zinc, alkali and alkaline earth metals did not interfere [215].

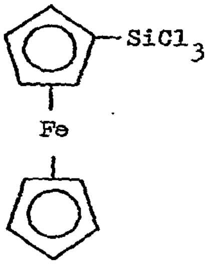
The amperometric titration of mercury(I) and mercury(II) with ferrocene in acetic acid-perchloric acid mixtures was investigated. The best medium for the titrations was 50% acetic acid containing 3M perchloric acid. Under these conditions thallium(I), tellurium(IV), selenium(IV), lead(II), zinc(II), nitrate ion and phosphate ion did not interfere but copper(II), iron(II) and silver(I) did interfere [216].

A study was made of the conditions required for the amperometric titration of lead(IV) by ferrocene in aqueous-organic solutions. The optimum conditions were 2M sulphuric acid in a 1:1 acetic acid-water mixture. The alkaline earth and alkali metals did not interfere but iron(III), thallium(III), silver, mercury and chromium(VI) did interfere [217].

The conditions necessary for the amperometric titration of selenium(IV) with ferrocene have been the subject of a kinetic investigation. A ferrocene concentration of 0.025M was used with 6M hydrochloric acid as the supporting electrolyte in 50% aqueous acetic acid. The reaction was found to be second order and the redox potentials of the selenium(IV)/selenium(0) and the ferricinium/ferrocene couples were determined in aqueous acetic acid, aqueous dimethyl sulphoxide and aqueous propanol at a range of hydrochloric acid concentrations. The detection limit was 10 μg Se/20 mL and interference by metal cations was examined [218].

A series of ferrocenes was determined by coulometric titration, by the use of Cu^{2+}/Cu^{+} as an auxillary redox system in methyl cyanide and a potential difference of 20-50 mV between platinum indicator electrodes. The ferrocenes were oxidized by copper(II) tetrafluoroborate [219].

The properties of n-type germanium semiconductors with surface-bound ferrocene residues have been investigated. The germanium crystal was pretreated by anodization in 6M sulphuric acid and immersed in an iso-octane solution of either trichlorosilylferrocene (11.4) or 1,1'-bis(dichlorosilyl)ferrocene (11.5). Cyclic voltammetry of the derivatized surface in ethanol or



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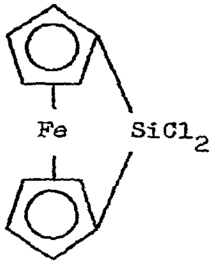

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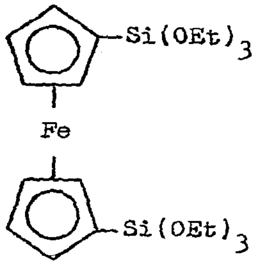
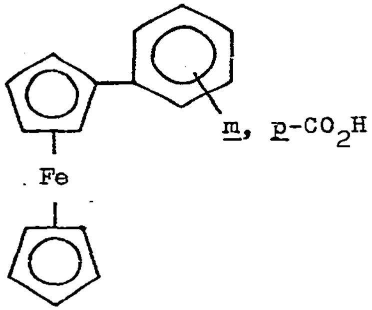


11.6

acetonitrile solutions of tetrabutylammonium perchlorate confirmed that the ferrocene groups were firmly bound to the surface. Illumination of the electrode caused the anodic current peak to be moved by up to ∼200 mV to more negative values which was consistent with the anticipated photoeffects for an n-type semiconductor. Comparisons between the derivatized electrode and a naked n-type germanium photoelectrode in electrolytes containing ferrocene indicated that the interface energetics and kinetics were unaffected by derivatization [220].

Platinum and gold electrode surfaces have also been derivatized with the silylferrocenes (11.4, 11.5 and 11.6). The ferrocene groups appeared to be bound to the metal by Si—O—M linkages where M = Pt, Au. The derivatized electrodes gave persistent cyclic voltammetric waves at a potential expected for an electroactive ferrocene derivative and the parameters accorded with a reversible, one-electron system. Greater than monolayer coverage of the surface was found in each case [221].

Several ferrocenecarboxylic acids including ferrocenylcarboxylic acid, 1,1'-ferrocenedicarboxylic acid and the carboxylic acids (11.7 and 11.8) were immobilized on a platinum oxide electrode surface through a 3-(2-aminoethylamino)propyltrimethoxysilane residue. The mode of binding is idealized for ferrocenylcarboxylic acid in the amide (11.9). X-ray photoelectron spectra were obtained and were used to support the structural assignments of the bound metallocenes. Cyclic voltammetry was used to investigate the electrochemical properties of the modified electrodes and the



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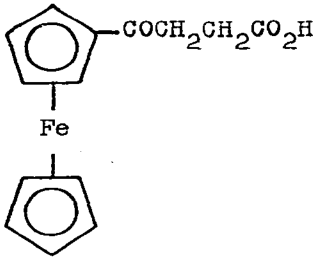

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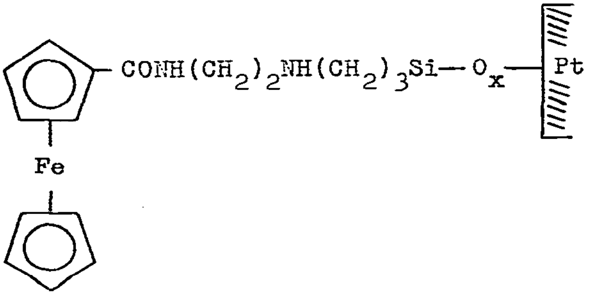


11.9

second-order ferricinium decay kinetics were described. In the case of ferrocenylcarboxylic acid the non-ideal surface activity parameters were smaller and ferricinium stability was enhanced for immobilized multilayers over monolayers [222].

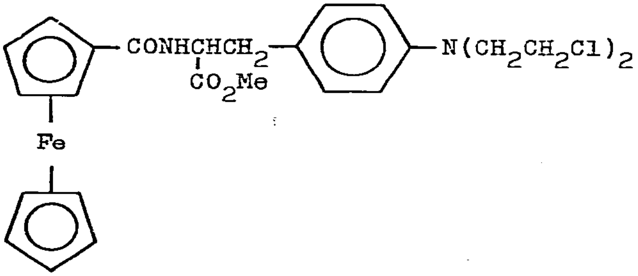
(iv) Combustion control

Ferrocene mixed with mineral oils, non-basic ester solvents and the condensation product of polyethanolamine and fatty acids was added to gasoline. It gave a reduction in the emission of pollutants, protection against corrosion and carburettor cleansing [223]. The treatment of coal with iron compounds, such as ferrocene and substituted ferrocenes, and hydrogen, nitrogen or carbon monoxide at 250° increased the magnetic susceptibility of impurities such as pyrites, and enabled these to be separated by magnetic methods. Clean coal was obtained in 98% yield by this method [224].

(v) Biochemical and biological applications

Rats were given oral doses of ferrocene in sesame oil and the urine from these animals was collected. Two metabolites A and B (approximately 26% of the administered dose) in which the ferrocene nucleus remained intact were isolated. Metabolite A, which was only present in small quantities, was thought to be a sulphate ester of hydroxyferrocene and metabolite B was shown to be ferrocenyl glucuronide. In vitro, the metabolism of ferrocene was shown to require viable liver microsomes, NADPH cofactor and molecular oxygen. Ferrocenyl glucuronide was formed in vitro if uridine-5'-diphosphoglucuronate (UDPGA) was added to the incubations but, in its absence hydroxyferrocene was not observed [225].

The ferrocenyl-amide (11.10) and related compounds were prepared and their antineoplastic activity in mice against sarcoma was studied [226].



11.10

A number of substituted ferrocenes were shown to behave as synergists for known insecticides and acaricides. For example, the deposit left after evaporating a mixture of 1% α-propionylferrocene and 2-isopropyloxyphenyl-N-methylcarbonate was lethal to Musca domestica whereas the components themselves were ineffective [227].

Ferrocenylcholine and ferrocenylmethyltrimethylammonium iodide were shown to inhibit the _in vitro_ hydrolysis of butyrylcholine by the enzyme horse serum butyrylcholinesterase [228].

Ferrocene derivatives have been claimed as iron-containing agricultural fertilizers. Ferrocene was treated with trimethylacetic acid and phosphoric acid at 100° C to form trimethylacetylferrocene. The compound was used after dilution and mixing with a surfactant [229].

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