

FERROCENE

ANNUAL SURVEY COVERING THE YEAR 1980**

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CONTENTS

1. Reviews	374
2. Structural determinations	374
3. Theoretical studies	375
4. Spectroscopic and physico-chemical studies	376
5. Electrochemistry and photosensitive electrodes	382
6. Preparations of ferrocenes	387
7. Reactions of ferrocene	389
8. Intercalation compounds containing ferrocene	390
9. Ferrocenium salts	392
10. Ferrocenyl carbenium ions	393
11. Ferrocene chemistry	395
(i) Photochemistry	395
(ii) Derivatives containing other metals (metalloids)	396
(iii) Complexes of ferrocene-containing ligands	400
(iv) General chemistry	404
12. Biferrocenes, ferrocenophanes and annelated ferrocenes	410
13. Ferrocene-containing polymers	421
14. Applications of ferrocenes	422
(i) Ferrocene catalysts and photosensitizers	422
(ii) Ferrocene stabilizers and improvers	424
(iii) Ferrocene in analysis	425
(iv) Combustion control	425
(v) Biochemical and biological applications	427
15. References	430

* Ferrocene, Annual Survey Covering the Year 1979, see
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1. REVIEWS

A short review on high resolution heat capacity measurements and phase transition phenomena has been prepared and ferrocene was included [1].

Solomatin has reviewed the use of ferrocene in the analysis of steels and alloys [2].

2. STRUCTURAL DETERMINATIONS

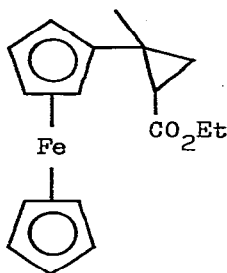
Powder X-ray diffraction and differential scanning calorimetry has been used to characterize a new low-temperature phase of ferrocene, stable below 250°K. The phase was orthorhombic and its molecular arrangement was isomorphous to ruthenocene with an eclipsed conformation [3].

Kaluski has surveyed the conformational state and the deformation of the ferrocene group in ferrocene and biferoecenyl derivatives [4].

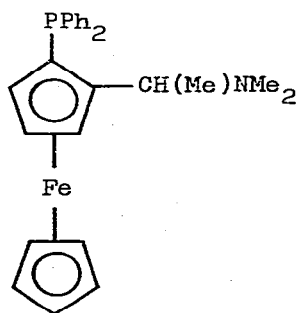
The crystal structure of 2-nitro-3-ferrocenylacrylic acid ethyl ester has been determined by X-ray analysis. The conjugated double bond system $\eta^5\text{-C}_5\text{H}_4\text{-C=C-C=O}$ was not planar. The $\eta^5\text{-cyclopentadienyl}$ rings in the ferrocenyl group were 1.7° from parallel and twisted 5° from an eclipsed conformation [5].

The crystal and molecular structure of the ferrocenylcyclopropane (2.1) has been determined by X-ray diffraction and the *cis*-configuration confirmed [6].

The molecular structure and absolute configuration of the (+)-isomer of the 1,2-disubstituted ferrocene (2.2) were



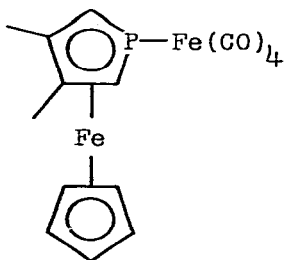
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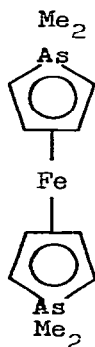
2.2

determined by X-ray analysis. The absolute configuration was $\{(1S)-[(2R)\text{-diphenylphosphinoferrrocenyl}]ethyl\}$ dimethylamine [7].

The crystal and molecular structure of the tetracarbonyl-iron complex of 3,4-dimethylphosphaferrocene (2.3) has been determined by X-ray crystallography. The Fe-P distance was short, 2.211 Å, suggesting that the bond was strong and that phosphaferrocene was a good ligand despite the IR evidence that suggested it was a weak donor [8].



2.3



2.4

The crystal structure of the diarsa-ferrocene (2.4) has been determined by X-ray analysis. The π -bonded rings were eclipsed but neither of them were strictly planar and they were not parallel. The arsenic atoms were situated out of the plane of the four carbon atoms by 0.086 and 0.059 Å and the dihedral angle between the planes of the carbon atoms was 6.2° [9].

3. THEORETICAL STUDIES

The use of general concepts, independent of the method, in the parametrization for the extended Hückel MO theory has been examined. A population analysis was developed using an orthogonal basis and applied to ferrocene to give a set of results more consistent than those obtained in the Mulliken analysis [10].

Ab-initio molecular orbital-self consistent field calculations were carried out for ferrocene on the minimal basis

level and with a double-zeta basis. The metal-ring distance was calculated as 1.9 Å in both cases, in contrast to the experimentally determined value of 1.65 Å [11].

It was shown by calculation that the eclipsed forms of ferrocene and ruthenocene were more stable than the staggered forms. The main contribution to the energy difference between the two forms was the induction energy of the metal in the potential field of the rings. Direct ring-ring electrostatic energy also favoured the eclipsed forms. The calculated net stabilization energy for the eclipsed forms of ferrocene was in good agreement with an experimental estimate from electron diffraction [12].

An oscillator model was used to calculate an energy level scheme for ferrocene [13].

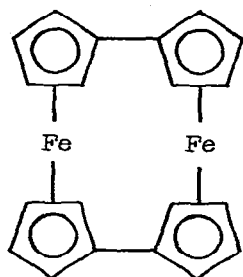
Pauling's bond distance-bond order relationship was used to derive the bond orders of the C-C bonds and the number of π -electrons in the metal-ligand bonds for a series of metallocenes (ferrocene, ruthenocene, nickelocene, vanadocene and manganocene). The values obtained were correlated with observed dissociation energies, these energies were used to predict the metal-ligand distances. A good agreement was obtained between the calculated and the observed metal-ligand distances [14].

4. SPECTROSCOPIC AND PHYSICO-CHEMICAL STUDIES

The He(I) and He(II) photoelectron spectra of ferrocene, decamethylferrocene and several other metallocenes have been measured. Intensity changes between the He(I) and He(II) spectra provided a useful guide to band assignment. Comparisons between the metallocenes were made [15].

The He(I) photoelectron spectra of biferrocene and biferrocenylene (4.1) were recorded and interpreted. On the basis of calculations it was concluded that in these molecules the highest occupied molecular orbitals were levels with dominant ligand character. However, the most stable cation was generated by removing an electron from a 3d level. This conclusion was consistent with the photoelectron spectra [16].

A low temperature Moessbauer investigation was carried out on the solid glassy phase of a liquid crystal obtained by cooling cholesteryl oleyl carbonate containing 3% by weight of 1,1'-diacetylferrocene. A small Moessbauer absorption was



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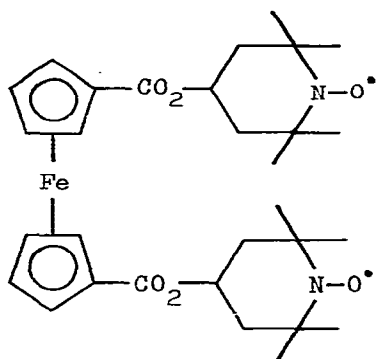
obtained at 95° K and this was enhanced ($>200\%$) upon orientation in a magnetic field [17].

Moessbauer spectra were recorded for ^{57}Fe in ferrocene dissolved in *o*-terphenyl in order to investigate the dynamics of the system in the glass and liquid phases. The glass transition temperature of 273° K for *o*-terphenyl was in agreement with that determined by other means [18].

Diethylferrocene, prepared by cooling the liquid in liquid nitrogen, showed a discontinuous temperature dependence of the Moessbauer spectrum. This was ascribed to transitions from the glassy state to the supercooled liquid state followed by crystallization. Crystalline diethylferrocene showed a similar temperature dependence to that observed for ethylferrocene [19].

The chemical effects of neutron capture in crystalline ferrocene were investigated. The initial retentions of ^{55}Fe and ^{59}Fe recoil atoms were determined, slight differences in retention between the recoil atoms were found. The retention values obtained by irradiation at reactor temperature were much higher than those obtained by irradiation at -78.5° C [20].

ESR spectroscopy has been used to identify two frozen solution conformations of (2,2,6,6-tetramethyl-4-piperidinyl-1-oxyl)ferrocene-1,1'-dicarboxylic ester (4.2) which arose through solvent induced effects. One form had eclipsed cyclopentadienyl rings while the other form showed a staggered arrangement [21].



4.2

The optical properties of the two solid phases of 1:1 decamethylferrocenium tetracyanoquinodimethanide (TCNQ) have been measured in the range 0.1 to 10 eV. One phase was found to contain isolated paramagnetic TCNQ anion monomers while the second phase contained isolated diamagnetic TCNQ dimers. A strong localized exciton was observed in the monomeric phase while the dimeric phase showed charge-transfer in addition to a shifted local exciton. The IR spectrum of the dimeric phase showed an unexpected activity of the symmetrical phonon modes arising through interaction with the radical electron. Normally IR active phonons only were observed in the spectrum of the monomer [22].

The mass spectrometric fragmentation of nineteen 3-ferrocenyl-, 5-ferrocenyl- and 3,5-diferrocenyl-pyrazolines has been investigated. Various processes of heterocyclic nucleus destruction and substituent elimination were observed in addition to fragmentation of the ferrocene nucleus [23].

Mass spectrometry has been used for the quantitative determination of the total deuterium content in (N,N-dimethylaminomethyl)ferrocene, (N,N-dimethylaminoethyl)ferrocene and the corresponding methiodides. The distribution of the label between the side chain and the substituted and unsubstituted rings has also been determined [24].

Ion-molecule reactions of ferrocene and ferrocene derivatives under mass spectrometric conditions have given bimetallic ions.

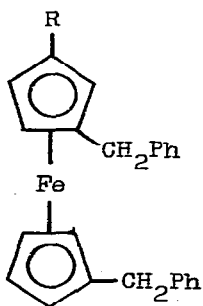
The intensities of these fragments depend on the square of the molecular ion intensity. Typical of the ions characterized were the following: $[(C_5H_5)(RC_5H_4)_2Fe_2]^+$, $[(RC_5H_4)(C_5H_5)_2Fe_2]^+$, $[(R^1C_5H_4)(R^2C_5H_4)_2Fe_2]^+$ [25].

The mass spectra of several π -complexes including benchtorene cymantrene and ferrocene have been obtained by simultaneous evaporation with organic compounds, such as triphenylphosphine, water and iodine, when protonated molecular and fragment ions were obtained. The ions were formed by ion-molecule reactions in the ionization chamber of the mass spectrometer as well as by the interactions of neutral molecules [26].

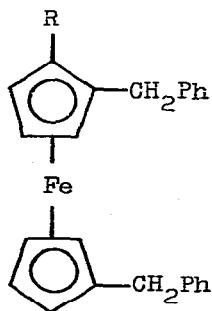
Ferrocene and nickelocene have been excited in the spectral range 3750-5200 Å to achieve collision-free multiphoton dissociation (MPD). A bare metal atom was formed and was detected by 3-photon ionization. The intensity dependence of the MPD process was examined in order to elucidate the mechanism [27].

The multiphoton ionization spectrum of ferrocene showed atomic Fe lines indicating that dissociation, preceding ionization, takes place under conditions of moderate laser excitation [28].

Enthalpies of complexation have been determined for the interaction of metallocenes with hydrogen chloride in liquid xenon. Values obtained for ferrocene, dimethyl-, hexamethyl- and decamethyl-ferrocene were 1.1, 2.1, 3.1 and 3.9 kcal mol⁻¹ respectively. The IR spectrum of the ferrocene-hydrogen chloride complex indicated that the π -electrons of the metallocene took part in complex formation [29].



4.3



4.4

The Raman and infrared spectra of ferrocene and nickelocene were recorded between $4000-5\text{ cm}^{-1}$ at $40-400\text{ }^\circ\text{K}$ to study the mechanism of the phase transitions. Ferrocene and nickelocene exhibited the same disorder at room temperature. The long-range order was shorter for nickelocene than for ferrocene [30].

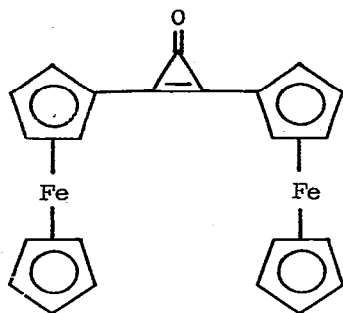
^1H NMR spectra of the chiral trisubstituted ferrocenes [4.3 and 4.4; $\text{R} = \text{COMe}, \text{COPh}, \text{CH}_2\text{Ph}, \text{CHMe}(\text{OH}), \text{CHMe}^+$] were recorded. The 2,5 and 3,4 protons in the monosubstituted rings exhibited magnetic nonequivalence. The methylene protons of the benzyl substituent in the 1,2-disubstituted ring of the ferrocenes (4.4; $\text{R} = \text{COMe}, \text{COPh}$) exhibited magnetic nonequivalence [31].

Rates and activation parameters for hydrogen exchange in ferrocene and in ferrocenyl-bromide, cyanide and carboxylic acid have been determined by ^1H NMR spectroscopy. The interannular transmission effect was estimated and was suggested to operate primarily through an inductive mechanism. Exchange appeared to involve the initial formation of a π -complex between the electrophile and the cyclopentadienyl ring [32].

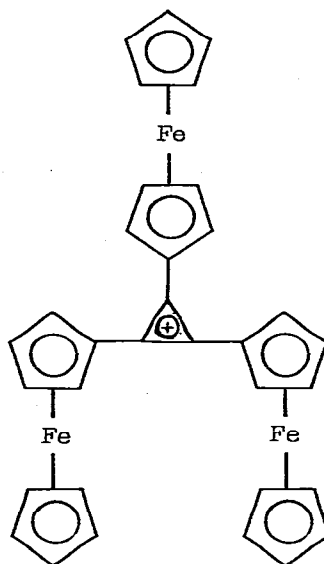
Electron exchange between ferrocene and several substituted ferrocenes and the corresponding ferrocenium ions has been measured in a number of solvents by NMR line broadening in the temperature range $0-30\text{ }^\circ\text{C}$. The rates of exchange did not depend on the dielectric properties of the solvent as predicted by Marcus theory. Substituents exerted only small effects on the rate, thus a ~ 10 -fold increase was observed for decamethylferrocene and a ~ 5 -fold decrease in the presence of a N,N -dimethylaminomethyl group [33].

The stabilization of the cyclopropenium and cyclopropenone ring systems by the ferrocenyl group was investigated. The ^{13}C NMR spectra of the ferrocenyl derivatives (4.5, 4.6 and 4.7) were analysed and the results indicated, for the latter two compounds, that there was significant delocalization of the positive charge into the unsubstituted η -cyclopentadienyl rings. It was suggested that the role of the iron atom in these molecules was to provide a conduit for transmission of the positive charge [34].

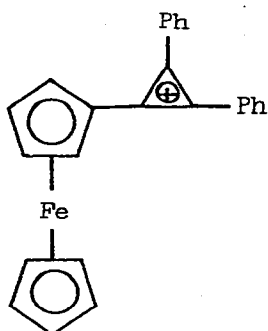
The ^{13}C NMR spectrum of 1,1'-bisdeuterioferrocene was recorded as part of an investigation into fluxional systems containing monohapto and pentahapto cyclopentadienyl rings.



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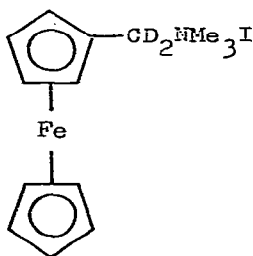
4.7

As expected, the spectrum was temperature independent as there was no degenerate equilibrium to be perturbed [35].

⁵⁷Fe NMR spectra of thirty-five organoiron complexes, mainly of the type $[\text{Fe}(\text{CO})_3(\text{diene})]$ but including ferrocene and some of its derivatives, were measured by direct detection at 2.9 MHz and at natural abundance (2.2%). A large shielding effect was observed on going from ferrocene to the cations $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{CH}_2)]^+$ and $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4\text{CHMe})]^+$. This was thought to be due to the transformation of one cyclopentadienyl ring into a fulvene-type ligand with a concomitant increase in the bending of the carbenium carbon atom towards the iron [36].

The enthalpies of fusion and sublimation for ferrocene were determined accurately by differential scanning calorimetry [37].

The α -deuterium kinetic isotope effect was measured in aqueous solution for the solvolysis of ferrocenyl-1,1-dideuteriomethyltrimethylammonium iodide (4.8). The isotope effect, k_H/k_D , was 1.06 and this small isotope effect was taken as support for a transition state model involving participation of the electrons localized on the iron atom [38].



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5. ELECTROCHEMISTRY AND PHOTSENSITIVE ELECTRODES

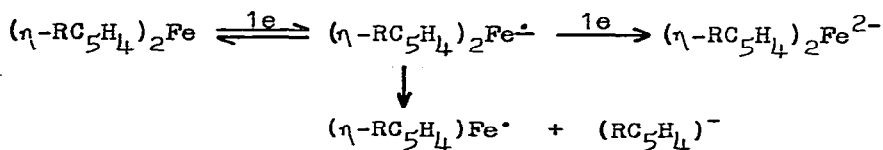
Cyclic voltammetry and current reversal chronopotentiometry have been used to investigate the electrolytic oxidation of ferrocene to the ferrocenium ion in polar aprotic solvents. The process was shown to be very sensitive to trace amounts of oxygen [39].

Ferrocene oxidation has been studied on rotating disc platinum electrodes coated with poly(2-hydroxymethyl-1,4-phenylene)oxide, poly(2,6-dimethyl-1,4-phenylene)oxide and poly[4-(2-aminoethyl)-1,2-phenylene]oxide films. The ferrocene-ferrocenium ion systems were not reversible and when the polymer film was thin or when the speed of rotation of the disc was slow the current densities were similar to those observed with uncoated platinum [40].

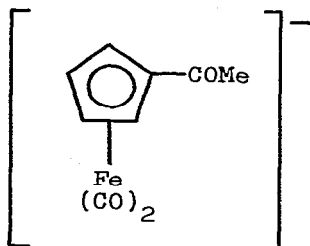
The electrochemical oxidation of ferrocene in propylene carbonate has been investigated by cyclic voltammetry. The

compound was only weakly solvated and the process was polarographically reversible. Various parameters were reported [41].

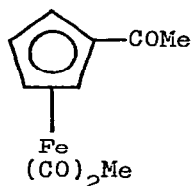
Electrochemical reduction of substituted ferrocenes takes place in two mono-electronic steps to give successively the corresponding ferrocene radical anions and the ferrocene dianions. The radical anions may breakdown to form substituted cyclopentadienyliron radicals as follows:



Thus acetylferrocene in the presence of carbon monoxide gave the (η -acetylcyclopentadienyl)iron dicarbonyl anion (5.1) which was characterized as the methyl adduct (5.2) on the addition of methyl iodide [42].



5.1



5.2

The half-wave potential of ferrocene-ferrocenium ion couple has been determined by cyclic voltammetry in water and in methanol. The standard potential independent of solvent was obtained [43].

Ferrocene and methylferrocene in dimethylformamide exhibited a well characterized one electron reversible polarographic wave at low temperatures (approximately -30°C). At higher temperatures, a two electron reductive cleavage of the molecules occurred [44].

The electrochemical behaviour of ferrocene and other complexes in 2,2'-thiodiethanol has been examined by polarography and voltammetry. The solvent behaved as a "hard" donor with properties intermediate between those of methanol and trimethyl-phosphate [45].

The actual potentials of the ferrocene-ferrocenium redox couple have been determined and the dependence of formal potential and oxidative potential on acidity and on the nature of the organic solvent concentration in a ternary acidic aqueous-organic medium have been measured. Changes of potential observed over a broad range of concentrations arose from ferrocene-ferrocenium association [46].

The ferrocene-ferrocenium couple has been used as a model system to investigate two-phase electrolyte electrolysis with mixtures of an aqueous electrolyte and an organic depolarizer in an organic solvent. Important parameters identified were: conductivity provided for the organic phase by the salts produced at the anode; surface tension differences at the electrode-organic phase and electrode-aqueous phase interfaces and the potential difference at the interface of the aqueous and organic phases [47].

Ferrocene has been proposed as an internal standard for electrochemical measurements especially in non-aqueous solvents. The use of such a standard avoids the problem of relating results to a reference electrode system with an unknown liquid junction potential. The technique was exemplified by the determination of the reduction potential for tris(acetyl-acetonato)ruthenium(III) in acetonitrile. The use of ferrocene as an internal standard was found to be convenient, reproducible and it allowed quantitative comparisons between different solvents [48].

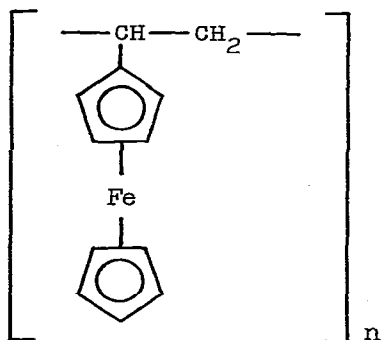
The electroactivity ranges for water-phosphoric acid mixtures containing the ferrocene-ferrocenium couple and using polished platinum, vitreous carbon and mercury electrodes have been determined [49].

The ferrocene-ferrocenium ion couple was used in an electrochemical study of some mixed valence copper complexes [50].

The kinetics of electron transfer between a platinum electrode and ferrocene either in solution or chemically bound to the surface of the electrode have been determined by a

linear and cyclic potential sweep technique. The rate constants obtained showed typical Arrhenius temperature dependence in each case but with different activation energies. Ferrocene in solution behaved kinetically in accordance with Marcus theory. However, the surface reaction was best explained on the basis of elastic electron tunnelling through a surface layer [51].

The properties and structure of electrodeposited poly-(vinylferrocene) (5.3) films on platinum electrodes were studied by electron microscopy and various electrochemical techniques.



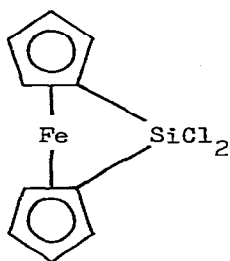
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The results indicated that the polymer films were permeable to dissolved reactants which diffused through the polymer films and reacted at the platinum surface [52].

The application of poly(vinylferrocene) (5.3) coated platinum electrodes as reference electrodes in methyl cyanide was investigated. The reference electrode was prepared by electrodeposition of poly(vinylferrocene) as poly(vinylferrocenium) perchlorate on to a platinum disc electrode which was surrounded by a cylinder of platinum foil as the counter electrode. The coated electrode was stable and exhibited rapid and reversible redox behaviour in methyl cyanide [53].

Monomolecular and multimolecular layers of ferrocene derivatives have been deposited on, or bonded to, electrodes and examined by photoelectron spectroscopy. In many cases the modified surface contained ferrocenium ions [54].

n-Type Si was derivatized with (1,1'-ferrocenediyl)-dichlorosilane (5.4) to give a photoanode suitable for use in aqueous solutions. The derivatized electrode exhibited chemically reversible oxidation of the anchored ferrocene groups when the electrode was irradiated with a He-Ne laser emitting 5.6 mW at 632.8 nm. Uphill oxidation of 3I^- to I_3^- and $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ was effected by illumination of the photoanode but the overall efficiency was low (~1%) [55]. Evidence for Fermi level pinning by p-type Si electrodes was presented and the effect of derivatization on these systems was discussed [56].



5.4

Surface-confined ferrocenium ions were generated on a n-type silicon semiconductor electrode by illumination of the electrode at a potential more anodic than -0.2 V vs. standard calomel electrode. The response of the derivatized photoelectrode to light and potential was utilized to measure, by voltammetry, the time dependence of ferrocenium reduction. Iodide ion, ferrocene and ferrocene derivatives were used as reducing agents. When iodide was the reducing agent the rate of reduction was proportional to the surface ferrocenium concentration and the iodide concentration. The process was relevant to the use of derivatized photoelectrodes in energy conversion applications [57].

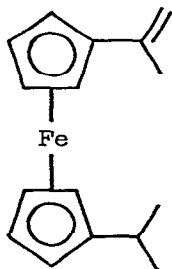
A stable photocurrent was obtained using n-type CdTe in propylene carbonate and methyl nitrate containing ferrocene. Photocorrosion was slow and the system was evaluated as a

semiconductor-electrolyte junction solar cell [58].

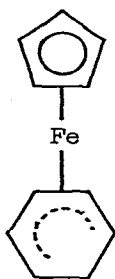
The photoelectrochemical behaviour of hydrogenated amorphous silicon in the ferrocene-ferrocenium system was found to be superior to that of crystalline silicon. This electrolyte system fell short of ideal behaviour on the basis of stability and efficiency considerations [59].

6. PREPARATIONS OF FERROCENES

Cocondensation of 6,6-dimethylfulvene with iron atoms at liquid nitrogen temperatures gave 1-isopropenyl-1'-isopropylferrocene (6.1) in 40% yield as the only product. Isotopic labelling experiments confirmed that the nature of the substituents was determined by intramolecular hydrogen transfer within a preformed iron complex [60]. These results contrast with those reported previously when [2]ferrocenophane and 1,1'-diisopropylferrocene were isolated under similar conditions [61].



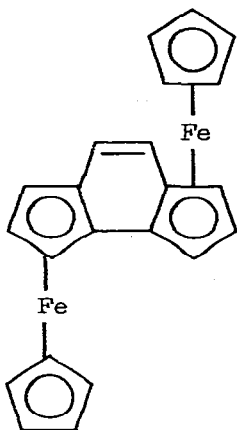
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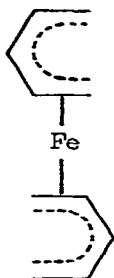
6.2

The cocondensation of iron atoms and benzene on a liquid nitrogen cooled surface gave a reactive intermediate which combined with cyclopentadiene to give a mixture of (η -cyclohexadienyl)(η -cyclopentadienyl)iron (6.2) and ferrocene [62].

Several deuterated metallocenes, (η -C₅D₅)₂M where M = V, Cr, Mn, Fe, Co, Ni were obtained by treatment of C₅D₅Na with the appropriate metal chloride. The metallocenes contained 97.7-98.7% deuterium [63].



6.3



6.4

Treatment of a mixture of lithium cyclopentadienide and dilithium as-indacene with iron(II) chloride gave the ferrocene derivative (6.3) in low yield [64].

The β -ferrocenyl-substituted tetracarbon carborane, 4- $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_4)]$ -2,3,7,8- $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_7$, has been obtained by treatment of $(\text{CH}_3)_4\text{C}_4\text{B}_8\text{H}_8$ with sodium naphthalenide, iron(II) chloride and sodium cyclopentadienide in THF. The crystal and molecular structure of the carborane has been determined by X-ray crystallography. It was found that while the polyhedron was unaffected by the ferrocenyl substituent, the substituted cyclopentadienyl ring in the latter was significantly perturbed at the carbon atom bonded to the polyhedron [65].

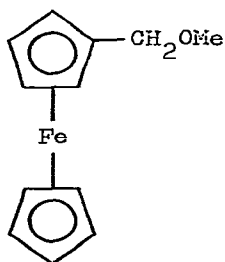
Analogies between the symmetry and orientation of the molecular orbitals for the cyclopentadienyl and pentadienyl ligands have stimulated the synthesis of bis(η^5 -pentadienyl)-iron (6.4) and mono- and di-methyl derivatives of this complex which was termed "open ferrocene". The pentadienide anion and its methyl derivatives were treated with iron(II) chloride in THF at -78°C to give orange-red complexes, such as the parent (6.4). The methylated complexes were in many respects similar to ferrocene being hydrocarbon soluble, sublimable, stable at

and above room temperature and air stable for several hours. The crystal and molecular structure of one complex was confirmed by X-ray crystallography [66].

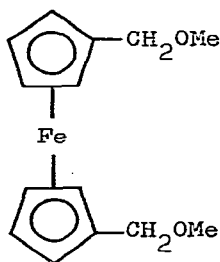
7. REACTIONS OF FERROCENE

The formation of charge-transfer complexes by ferrocene and ferrocene derivatives with tetrabromomethane has been investigated by uv spectroscopy. Ferrocene formed 1:3 complexes in benzene solution, alkylferrocenes formed 1:2 complexes and polysubstituted ferrocenes formed 1:1 complexes [67].

Treatment of ferrocene with methyl(chloromethyl)ether in the presence of aluminium chloride gave a mixture of the monosubstituted (7.1) and disubstituted products (7.2). These ethers were converted to methyl- and 1,1'-dimethyl-ferrocene respectively [68].



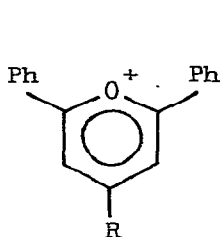
7.1



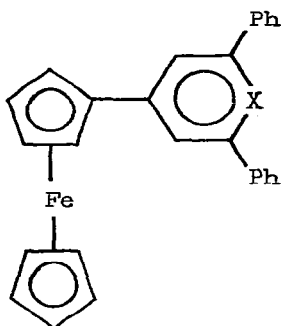
7.2

The effect of temperature on the acylation of ferrocene has been evaluated by reverse-phase high-performance liquid chromatography and used as a convenient laboratory experiment [69].

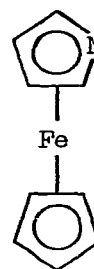
Ferrocene was attacked by the pyrylium cation (7.3; R = H) in acetic anhydride to form the derivative (7.4; X = O⁺) and this was converted to the pyridylferrocene (7.4; X = N) with ammonia. A similar synthesis was achieved with the cation (7.3; R = CH=CHOEt) and ferrocene [70].



7.3



7.4



7.5

Comparisons between the chemistry of ferrocene and azaferrocene (7.5) indicated that the pyrrolyl ring of the latter confers inherent lability on the compound permitting π to σ rearrangements to occur [71].

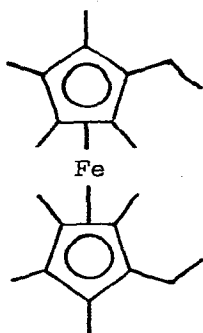
Labelled ruthenocenes have been prepared by transmetalation of ferrocenes with $^{103}\text{RuCl}_3$, thus *o*-chlorobenzoylferrocene was treated successively with $^{103}\text{RuCl}_3$, potassium *t*-butoxide and phosphorus(III) chloride to form ruthenocenecarbonylchloride- ^{103}Ru and this was converted to a labelled estratriene with estradiol [72].

The reaction of methyl-, hydroxymethyl-, formyl-ferrocene and other substituted ferrocenes with $^{103}\text{RuCl}_3$ has been used to prepare ^{103}Ru labelled ruthenocenes. The ruthenocenes were evaluated as radiopharmaceuticals [73].

8. INTERCALATION COMPOUNDS CONTAINING FERROCENE

Several metallocenes including ferrocene have been treated with FeOCl in glyme at temperatures of up to 110°C to form the intercalation complexes $(\eta\text{-C}_5\text{H}_5)_2\text{M}\cdot\text{FeOCl}$, where $\text{M} = \text{Cr}, \text{Fe}, \text{Co}$ and Ni [74].

The intercalation of the alkyl-ferrocene (8.1) into the iron oxide chloride layer structure gave $\text{FeOCl}[(\eta\text{-C}_5\text{Me}_4\text{Et})_2\text{Fe}]_{0.16}$. ^{57}Fe Moessbauer spectroscopy and magnetic susceptibility studies indicated that electron transfer from the metallocene to the host occurred on intercalation [75].



8.1

X-ray diffraction methods have been used to determine the structure of the decamethylferrocene-iron oxide chloride intercalation compound and to show that the FeOCl-FeOCl interlayer distance was expanded by 0.71 nm to 1.50 nm to accommodate the metallocene. The stoichiometry of the complex, 1:13.4, $(\eta\text{-C}_5\text{Me}_5)_2\text{Fe}^+:\text{FeOCl}^-$, indicated that the decamethylferrocene layers were not packed tightly [76].

Mossbauer spectroscopy was used to study the intercalation phases of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+[6\text{FeOCl}]\cdot\text{e}^-$. When prepared at room temperature the intercalated compound was a single phase with a paramagnetic and an antiferromagnetic component. However, when the compound was prepared at higher temperatures two magnetically ordered systems were found both of which differed in their magnetic and quadrupole data as compared with the phase prepared at room temperature [77].

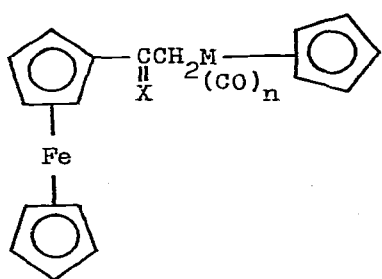
The nature of ferrocene in the thiourea- d_4 -ferrocene inclusion compound has been studied by ^1H NMR spectroscopy at several temperatures. It was found that the five-fold axes of the metallocene molecules were held in a number of non-equivalent orientations at low temperatures. The start of reorientational motion of these axes was linked with a phase transition at 162 °K [78].

9. FERROCENIUM SALTS

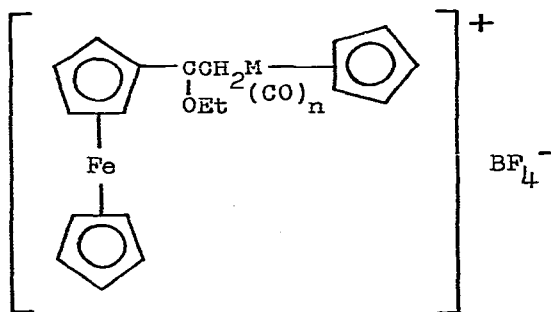
Treatment of ferrocene with sulphuric acid, water and acetic acid (Minisci conditions) gave the ferrocenium ion which underwent homolytic substitution with MeCHO, PhCHO, MeCOCO₂Me to form methylferrocene, phenylferrocene and acetylferrocene [79].

Oxidation of decamethylferrocene by constant potential coulometry at -0.1 V in a 1.5:1 aluminium chloride:1-butylpyridinium chloride melt gave a deep brown solution containing the decamethylferrocenium dication [80].

The ferrocenylketones (9.1; X = O, M = Fe, n = 2, M = Mo, W, n = 3) have been treated with [Et₃O]⁺[BF₄]⁻ to form the salts (9.2; M = Fe, n = 2, M = Mo, W, n = 3) which combined with CH₂(CN)₂ and NH₂OH to form the derivatives [9.1; X = C(CN)₂, NOH, M = Fe, n = 2, M = Mo, W, n = 3] [81].

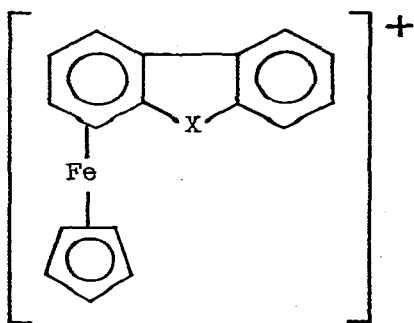


9.1

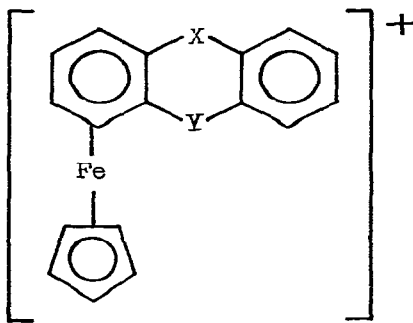


9.2

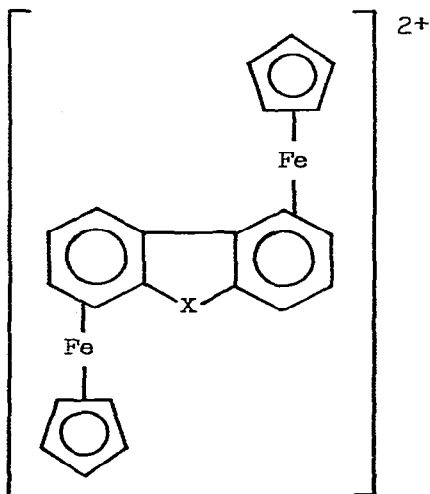
Equimolar quantities of dibenzofuran, dibenzothiophene, xanthene, thioxanthene or phenothiazine, ferrocene and aluminium powder were heated with excess aluminium chloride in decalin. Hydrolysis gave the monocations (9.3; X = O, S) (9.4; X = CH₂, Y = O, S; X = NH, Y = S) respectively which were isolated as the hexafluorophosphate salts. Dicationic species (9.5; X = O, S, NH) and (9.6; X = CH₂, Y = O, S, NH; X = NH, Y = S; X = Y = NH) were similarly prepared. The ¹H and ¹³C NMR spectra of the complexes were recorded and discussed [82].



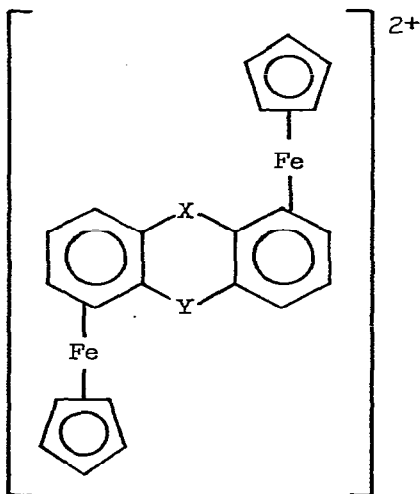
9.3



9.4



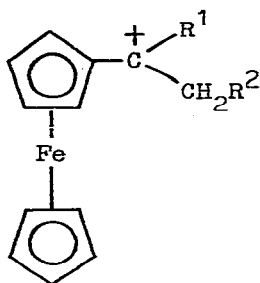
9.5



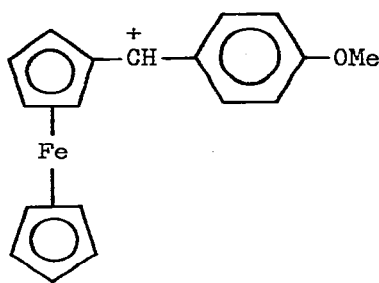
9.6

10. FERROCENYL CARBENIUM IONS

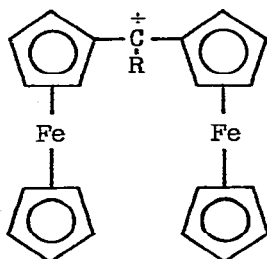
A kinetic investigation of the concomitant addition of water and elimination of a proton from the ferrocenylcarbenium ions (10.1; $R^1 = \text{ferrocenyl}$, $R^2 = \text{H, Me, Ph}$; $R^1 = \text{Ph}$, $R^2 = \text{CMe}_3$) has demonstrated extensive ion pair formation in aqueous acetonitrile solutions of sodium chloride and sodium perchlorate. Alkene formation from $[\text{carbenium}]^+\text{Cl}^-$ ion pairs was faster than from $[\text{carbenium}]^+\text{ClO}_4^-$ ion pairs. This result was interpreted in terms of hindrance to proton loss by the bulky perchlorate



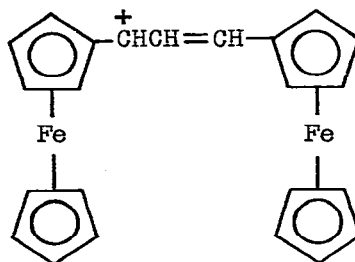
10.1



10.2



10.3

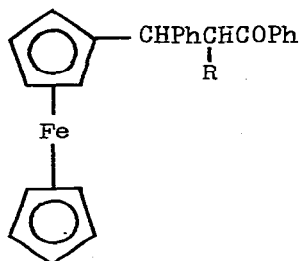


10.4

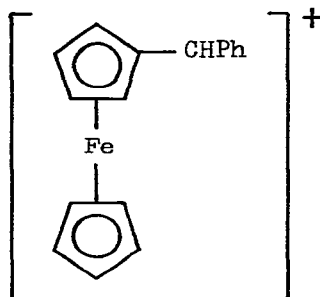
anion which prevented the approach of water molecules [83].

The reactions of the ferrocenylalkyl cations (10.2; 10.3; R = H, Ph; 10.4) with nucleophiles in water and water-acetonitrile were studied. The rate constants from these reactions were approximately correlated with the N_+ scale (N_+ is dependent on the identity of the nucleophile and on the solvent). The results suggested that the N_+ values estimated from the reactivities of triarylmethylcations did not accurately reflect nucleophilicities of bulky amines towards less hindered electrophiles [84].

The secondary ferrocenylcarbenium ion (10.6) has been obtained by the attack of trifluoroacetic acid on the ferrocenylketones (10.5; R = H, COPh) and related ferrocenes [85].



10.5



10.6

Rates of reaction and equilibrium constants were obtained for the reactions of a series of ferrocenylalkyl cations with water in the presence and absence of mineral acid. The rates of addition of water to the cations were sensitive to structural, steric and conformational effects. It was concluded that there was a close mechanistic similarity between nucleophilic addition reactions of triarylmethyl and ferrocenylalkyl cations [86].

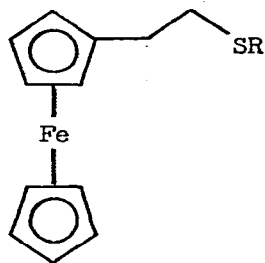
The design and synthesis of polyferrocenyl carbenium and silicenium ions was investigated [87].

11. FERROCENE CHEMISTRY

(i) Photochemistry

The mechanism for the photochemical reaction of ferrocene with iodine in benzene has been shown to occur in three stages; (i) initial photodissociation of I_2 to iodine atoms, (ii) oxidation of ferrocene to ferrocenium iodide by an iodine atom or an iodine-benzene charge transfer complex and (iii) attack of I_2 on ferrocenium iodide to form ferrocenium triiodide. The rate constants for the last two stages were near to the diffusion controlled limit [88].

Photolysis of thioacetic acid and vinylferrocene in the presence of AIBN gave the thioester (11.1; $R = Ac$) and this was hydrolyzed to the thiol (11.1; $R = H$) which has found application as a non-migrating burning-rate modifier for unsaturated



11.1

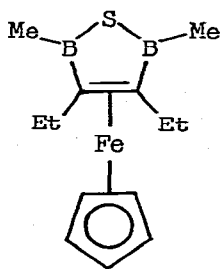
rubber-based propellants [89].

In a flash photolysis-kinetic spectrophotometry investigation of the mechanism of quenching of 2-10 μ M triplet methylene blue substitution inert iron(II) complexes, ferrocene was used as one of the complexes [90].

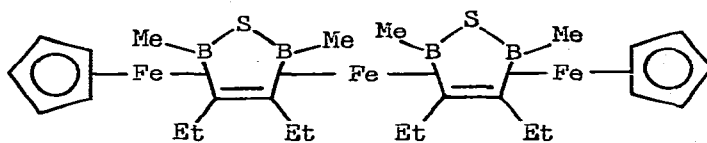
(ii) Derivatives containing other metals (metalloids)

The thiodiborolene sandwich complex (11.2) has been treated with iron(II) chloride to give the four-decker complex (11.3) in 53% yield. The analogous cobalt complex was prepared in the same way [91].

Reaction of the ferrocenyl-silanes (11.4; $R^1 = H, SiHMePh$) with the acetylenes $R^2C\equiv CH$ ($R^2 = \text{ferrocenyl, Ph, Et}_3\text{Si, Ph}_3\text{Si}$)



11.2



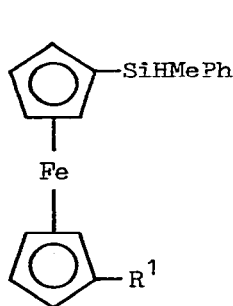
11.3

in the presence of Speier's catalyst, gave the corresponding α - (11.5) and β - adducts (11.6) [92].

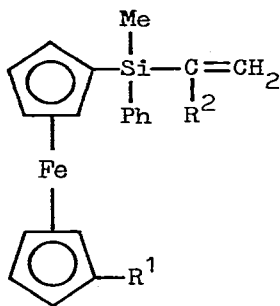
Trivinyltinferrocenoate and triphenyltinferrocenoate were prepared and the polymeric structure of the former compound was established by X-ray analysis. In this compound the tin atoms were five coordinate trigonal bipyramidal with the vinyl groups equatorial and with two apical oxygen atoms from bridging carboxylato groups [93].

The reaction of ferrocenyldiphenylphosphine with styrene oxide gave ferrocenyl(phenyl)(1,2-diphenylethyl)phosphine oxide. The mechanism of this reaction was discussed [94].

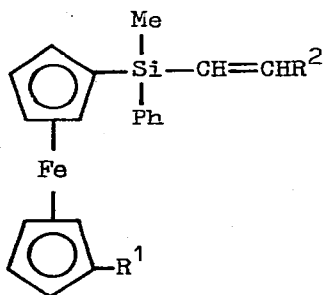
Several 2-substituted chiral ferrocenylphosphines have been prepared from optically resolved, 2-lithiated N,N-dimethyl-



11.4



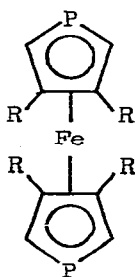
11.5



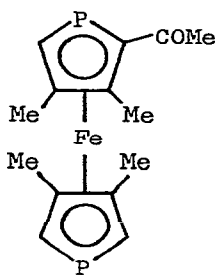
11.6

1-ferrocenylethylamine. The dimethylaminoethyl group was converted, in stereospecific substitutions, into 1-hydroxy-, 1-methoxy-, 1-diphenylphosphino- and various 1-(dialkylamino)-ethyl groups. Circular dichroism results from the chiral ferrocenylphosphines were interpreted in terms of the configuration of the chirality. The complexes were explored as chiral ligands for asymmetric reactions catalyzed by transition metal complexes [95].

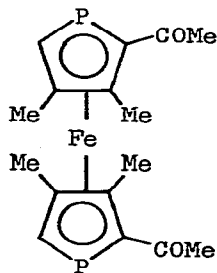
The 1,1'-diphosphaferrocenes (11.7; R = H, Me, Ph) were prepared by treatment of the appropriate 1H-phosphol-1-yl anions with anhydrous iron(II) chloride. The phosphoferrocene (11.7; R = Me) readily underwent Friedel-Crafts acylation to give either the monosubstituted (11.8) or disubstituted



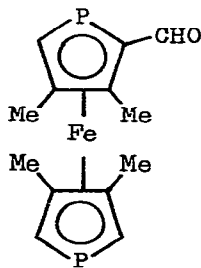
11.7



11.8



11.9



11.10

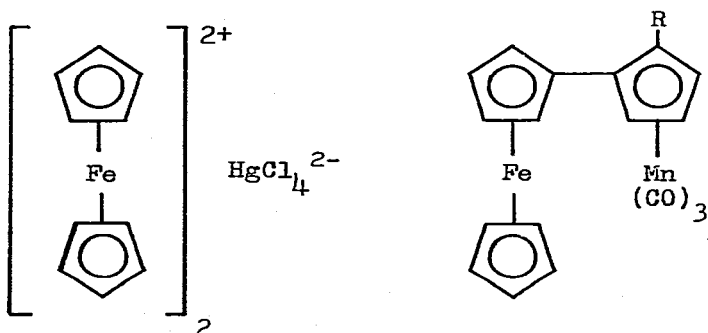
products (11.9). The aldehyde (11.10) was prepared by Vilsmeier formylation. The crystal structure of the phosphoferrocene (11.7; R = Me) was determined by X-ray analysis and this confirmed that the iron atom was sandwiched between the two π -bonded phosphol-1-yl groups [96].

Diferrocenylselenide was oxidized by iodine in dichloromethane to give a mixed valence compound diferrocenylselenium iodine triiodide hemi(methylene chloride). The structure of this latter compound was determined by X-ray analysis. It was composed of discrete mixed valence $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4)]_2\text{Se}^+$ cations and an anion structure consisting of zigzag chains of triiodide ions with iodine molecules present. The two $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{H}_4)$ moieties were structurally different, one was a ferrocenyl group and the other a ferrocenium group. The localized nature of the charge in the mixed valence cation was substantiated by ^{57}Fe Moessbauer spectroscopy [97].

Ferrocenyllithium has been treated with $\text{AgNO}_3 \cdot 3\text{PPh}_3$ to form ferrocenylsilver in 67% yield. In a typical reaction ferrocenylsilver combined with mercury(II) chloride to give ferrocenylmercurichloride [98].

Reaction of ferrocene with excess mercury(II) chloride gave the ferrocenium derivative (11.11) and mercury(I) chloride. Equimolar quantities of ferrocene and mercury(II) chloride gave $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}]_x$ and mercury(I) chloride [99].

The mercuriation of ethyl- and 1,1'-diethylferrocenium trichloroacetate in methanol and acetic acid was studied.



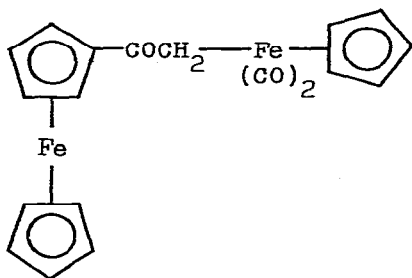
11.11

11.12

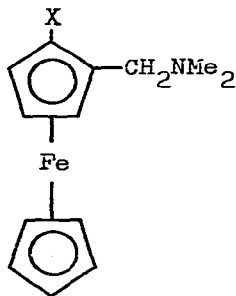
The reaction followed second order kinetics [100].

The mixed cymantrenylferrocene compounds (11.12; R = H, CH₂NMe₂, Cl) were formed by treatment of the appropriate cymantrenyllithium with ferrocenyllithium and copper(II) chloride. 2-[(Dimethylamino)methyl]diferrocenyl was also prepared in the same way [101].

Treatment of the dicarbonyliron complex (11.13) with iodine gave the complex 4(11.13).5I₂. The structure of this complex was determined by X-ray analysis [102].



11.13



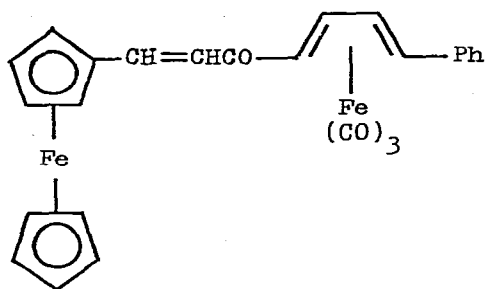
11.14

Enantiomeric 1-diphenylphosphino-2-dimethylaminomethylferrocene (11.14; X = PPh₂) may be prepared conveniently from the optically active organopalladium complex (11.14; X = PdCl) by treatment with LiPPh₂ in THF. The absolute configuration and maximum optical rotation of the product (11.14; X = PPh₂) have been determined [103].

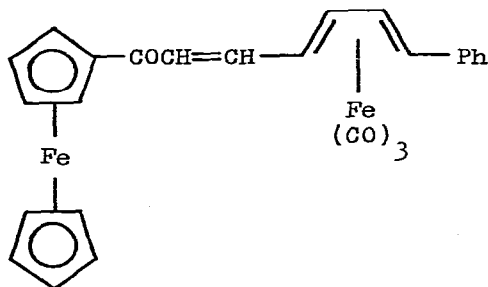
(iii) Complexes of ferrocene-containing ligands

The 1,1'-diacetylferrocene complexes of titanium(IV) chloride, tin(IV) chloride, antimony(V) chloride and vanadium oxychloride were prepared by treating the metal halide with the ligand in dry benzene or toluene. The infrared spectra of the complexes were recorded and discussed [104].

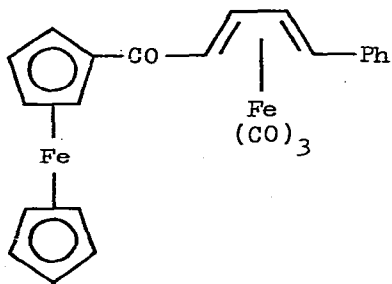
The diiron hexacarbonyl complex of acetylferrocene azine, $[\eta\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}(\text{Me})=\text{N}]_2\text{Fe}_2(\text{CO})_6$, when treated with a series of thiols, RSH (R = Ph, C₁₂H₂₅), gave the complexes $[\eta\text{-C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}(\text{Me})=\text{N}](\text{SR})\text{Fe}_2(\text{CO})_6$ [105].



11.15



11.16

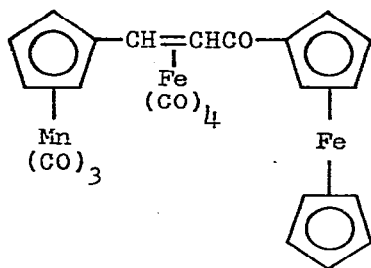


11.17

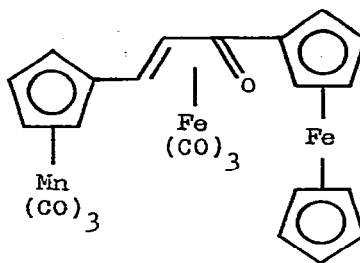
The tricarbonyliron complexes (11.15, 11.16 and 11.17) were prepared by reaction of the corresponding ketones with dodecacarbonyltriiron [106].

A mixture of the η^2 - and η^4 -enone complexes (11.18 and 11.19) was obtained by treatment of the free ligand with enneacarbonyldiiron. However, when dodecacarbonyltriiron was used as the reagent only the complex (11.19) was obtained [107].

(S,R)- and (R,S)- α -(2-Diphenylphosphinoferrocenyl)ethyl-dimethylamine [(+)- and (-)-PPFA] (11.20) were used to prepare the cationic rhodium(I) complexes [(+)- or (-)-(PPFA)Rh(diene)]⁺X⁻ (diene = norbornadiene or cyclooctadiene; X = ClO₄⁻, PF₆⁻, BPh₄⁻, BF₄⁻). The crystal structure of [(PPFA)Rh(η -norbornadiene)]⁺PF₆⁻



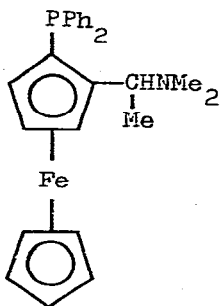
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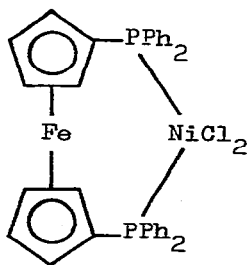
11.19

was determined by X-ray analysis. The PPFA was coordinated to the rhodium atom through the nitrogen and phosphorus atoms with the rhodium atom in a square-planar environment (that is, assuming each norboradiene C=C bond fills a single coordination site). The rhodium(I) complexes catalyzed the asymmetric hydrogenation of acylaminocinnamic acid and acylaminoacrylic acid. The cinnamic acid derivative was hydrogenated in high chemical (approximately 90%) and optical yield (approximately 80%) [108].

The ferrocenylphosphine nickel complex (11.21) has been used as a catalyst for the cross coupling of *t*-butylmagnesium chloride with β -bromostyrene to give the β -substituted styrene, $\text{PhCH}=\text{CHCMe}_3$ [109].



11.20

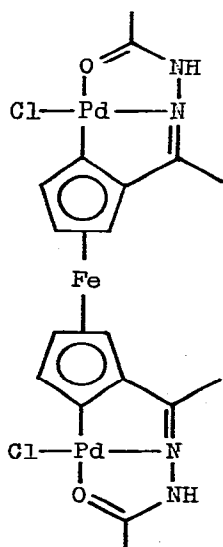


11.21

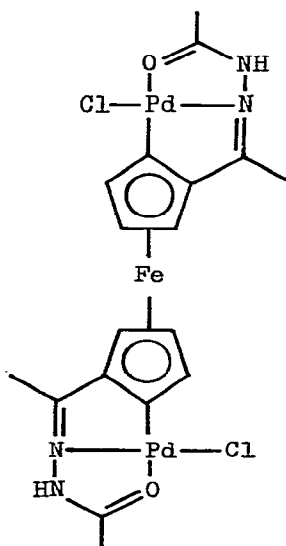
Dichloro[1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) was shown to catalyze the cross-coupling reactions of allylic alcohols with the secondary Grignard reagents, 2-octylmagnesium chloride and 1-phenylethylmagnesium chloride. For example, 2-methyl-4-phenyl-1-pentene was obtained in high yield (80%) from the reaction of 2-methyl-2-propen-1-ol with 1-phenylethylmagnesium chloride [110].

Chiral rhodium(I) complexes containing the ligand (S)-N,N-dimethyl-1-[(R)-1',2-bis(diphenylphosphino)ferrocenyl]ethylamine have been used as catalysts for the asymmetric homogeneous hydrogenation of prochiral olefins. The ferrocenylphosphine ligand was modified in order to determine the steric effect of substituents at the asymmetric centre on the efficiency of the catalyst [111].

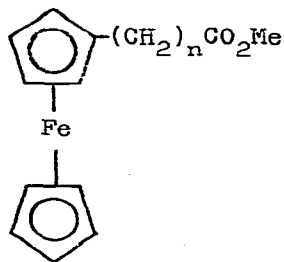
1,1'-Diacetylferrocene bis(acetylhydrazone) underwent double cyclopalladation to give the isomers (11.22 and 11.23). The reactions of the isomers (11.22 and 11.23) with triphenylphosphine were investigated [112].



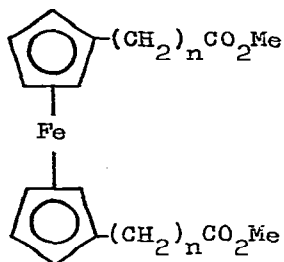
11.22



11.23

(iv) General chemistry

11.24

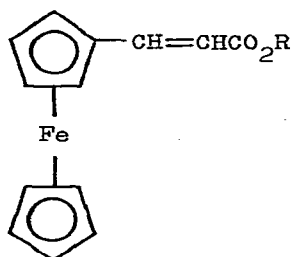


11.25

Reaction of ferrocene with the chlorocarboxylic acid esters, $\text{Cl}(\text{CH}_2)_n\text{CO}_2\text{Me}$ ($n = 2, 3, 5$) in the presence of aluminium chloride and aluminium powder gave a mixture of the corresponding alkylated ferrocenes (11.24 and 11.25). Treatment of ferrocene with acrylonitrile in the presence of aluminium powder gave 2-cyanoethylferrocene in low yield [113].

The oxidative decomposition of ferrocenium derivatives and substituted ferrocenes containing electron withdrawing groups was studied. The effect of media acidity and the salt and substituent effects were investigated [114].

Formylferrocene was treated with $(\text{EtO})_2\text{POCH}_2\text{CO}_2\text{R}$ in the presence of tetrabutylammonium iodide in a two phase system of

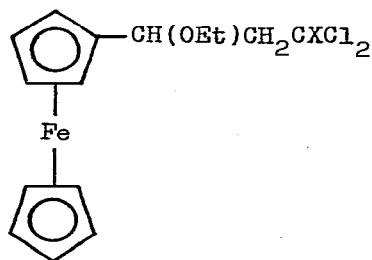


11.26

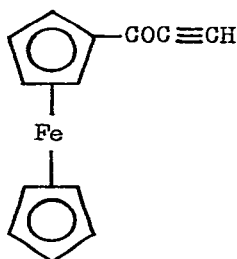
dichloromethane and aqueous sodium hydroxide to give the corresponding olefins (11.26; R = Et, Pr, Bu) in good yields. A similar route was used to prepare $\text{FcCH}=\text{CH}_2$ and $\text{FcCH}=\text{CHPh}$ [115].

The ferrocenylchloropropanes (11.27; X = H, Cl) have been converted to the acetylene (11.28) and the α, β -unsaturated aldehyde (11.29) respectively on treatment with ethanolic potassium hydroxide and then sulphuric acid. The reactions of the analogous ruthenocene derivatives were examined [116].

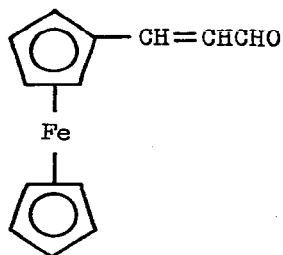
Ferrocenylphenylmethyldibenzoylmethane (11.30) was attacked by phenylmagnesium bromide to give a mixture of products with ferrocenyldiphenylmethane (60%) as the dominant component. Reactions with other nucleophiles including lithiopiperidene, phenyllithium, potassium ethoxide and methylmagnesium iodide were investigated [117].



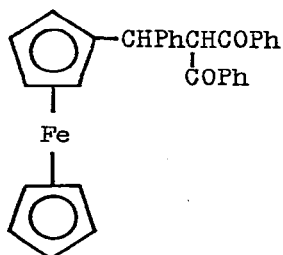
11.27



11.28

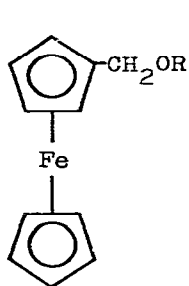


11.29

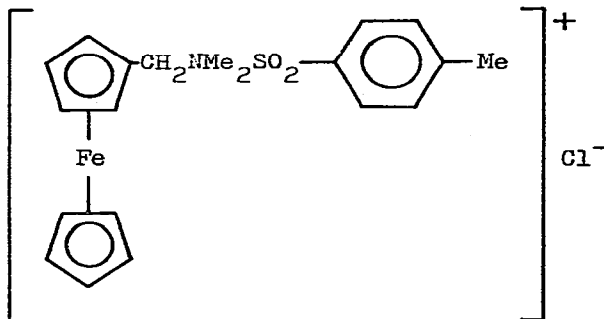


11.30

Deuterium exchange in cyano-, acetyl-, formyl- and benzoyl-ferrocene occurred in the presence of pyridine and involved only the substituted cyclopentadienyl ring in a non-statistical pattern to give principally the [$^2\text{H}_4$]-substituted ferrocene. The exchange was explained on the basis of a $\eta^5 \rightarrow \eta^1$ rearrangement [118].



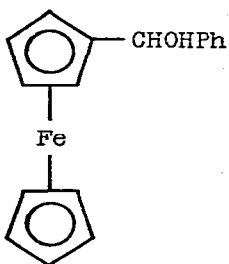
11.31



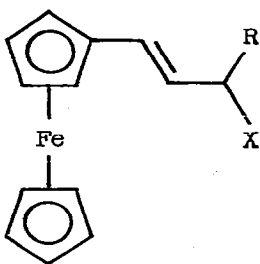
11.32

A series of ferrocenylmethyl-ethers (11.31; R = Et, Bu, octyl, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{OH}$, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) was prepared by treatment of the ferrocenylmethyl-ammonium salt (11.32) with the corresponding alcohol in the presence of sodium hydroxide [119].

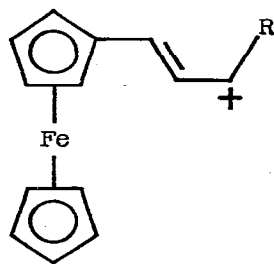
Deoxygenation of α -phenylferrocenylmethanol (11.33) with pentacarbonyliron in toluene gave a mixture of benzylferrocene 67% and 1,2-diferrocenyl-1,2-diphenylethane 19%. The reaction



11.33



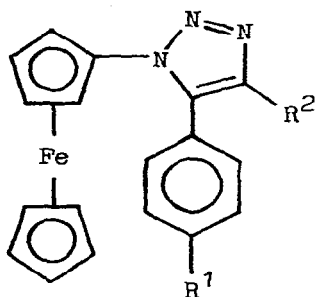
11.34



11.35

appeared to be general for alcohols that formed relatively stable carbanions and the mechanism was discussed [120].

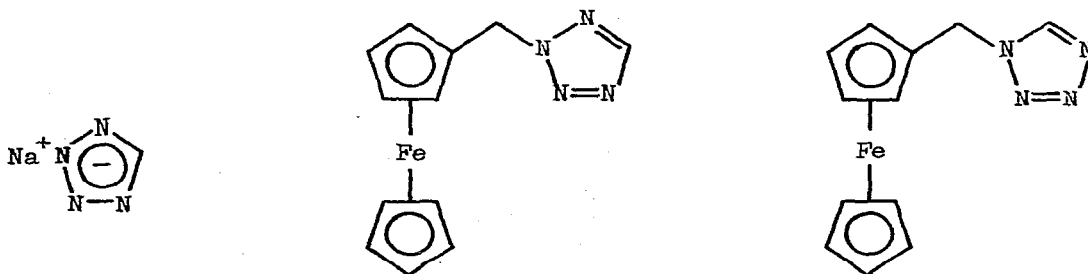
The allyl alcohols (11.34; R = H, Me; X = OH) have been converted to the allyl cations (11.35; R = H, Me) with trifluoroacetic acid and then to the derivatives (11.34; R = H, Me; X = OH, OMe, $SC_6H_4CO_2H$) by treatment with the appropriate anions. Attack took place exclusively on the α -allyl carbon atom [121].



11.36

Cyclization of $(\eta-C_5H_5)Fe(\eta-C_5H_4.SO_2N_3)$ with phosphoranes $Ph_3P=CR^2COR^1$ gave the ferrocenyl-1,2,3-triazoles (11.36; $R^1 = H, Me, MeO, Cl, Br, NO_2, R^2 = H; R^1 = H, R^2 = Me$). The ferrocenyl group was removed by treatment of the triazoles with ethanol [122].

The anions of substituted tetrazoles and 1,2,4-triazoles were alkylated by chloromethylferrocene and 1,1'-di(chloromethyl)-



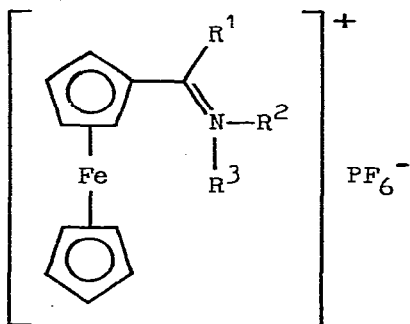
11.37

11.38

11.39

ferrocene. For example, the reaction of chloromethylferrocene with the sodium salt (11.37) gave a 1:1 mixture of the ferrocenylmethyl derivatives (11.38 and 11.39) [123].

Several ferrocenyliminium salts [11.40; $R^1 = H, Me, Ph$; $R^2 = H, R^3 = Me, Pr^i, Bu^t$; $R^1 = H, Ph, R^2, R^3 = Me, Et, Pr^i, R^2R^3 = (CH_2)_5$] have been obtained from ferrocenylketones and primary or secondary amines. Those obtained from primary amines were deprotonated to the corresponding ferrocenylimines [124].



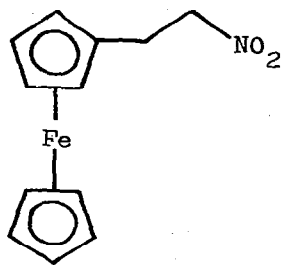
11.40

The nitroalkylferrocene (11.41) has been converted to the nitrile N-oxide (11.42) with $PhNCO$ and Et_3N which then underwent dimerization to form the binuclear product (11.43) or 1,3-dipolar cycloaddition of acrylonitrile, styrene, 1-heptene and trimethylvinylsilane to give the derivatives (11.44; $R = CN, Ph, C_5H_{11}, SiMe_3$) respectively [125].

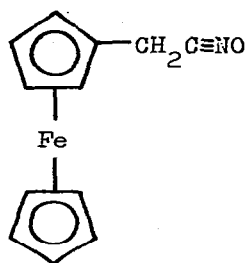
l-Cis-piperitol has been treated with cobaltacetylacetonate and 1,1'-bis(diphenylphosphino)ferrocene in THF at $-38^\circ C$ to give d-isomenthane [126].

The ferrocenylmethyl-sulphides [11.45; $R = o-C_6H_4CO_2R^1$ ($R^1 = H, Me$), $CH_2CH_2NHR^2$ ($R^2 = H, Ac$), $o-C_6H_4NHR^3$ ($R^3 = H, Ac$), CH_2COR^4 ($R^4 = Me, Et$)] were prepared by the treatment of (ferrocenylmethyl)trimethylammonium iodide with the corresponding thiol [127].

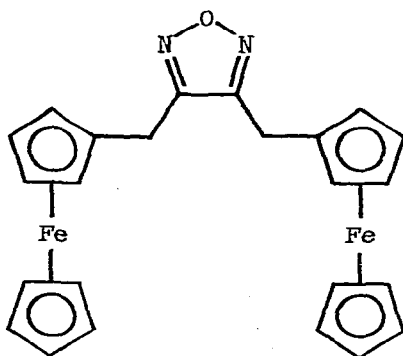
The treatment of α -ferrocenylcarbinols with sodium hydride followed by carbon disulphide and then an alkyl halide gave a ferrocenyltrithiocarbonate. Thus the trithiocarbonate (11.47; $R = Me$) was formed from the carbinol (11.46) by intramolecular



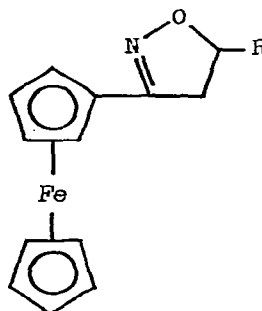
11.41



11.42



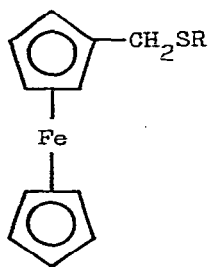
11.43



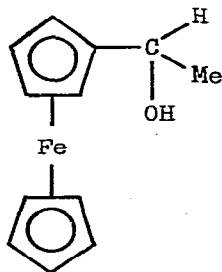
11.44

nucleophilic displacement of oxygen with sulphur. The displacement occurred with retention of configuration [128].

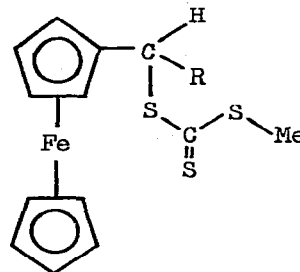
The trithiocarbonate (11.47; R = Me) combined with enneacarbonyldiiron in acetone to form the dibridged hexacarbonyldiiron complex (11.48; R = Me). The structure of this complex was confirmed by X-ray crystallography. Under the same conditions the trithiocarbonate (11.47; R = H) gave two products, each with a dibridged hexacarbonyldiiron group (11.48; R = H and 11.49). The mechanism of the reaction was discussed [129].



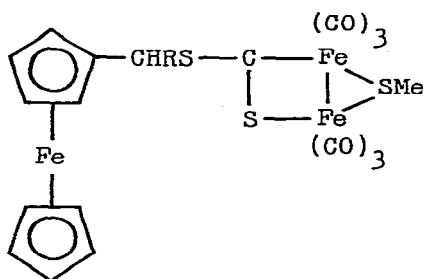
11.45



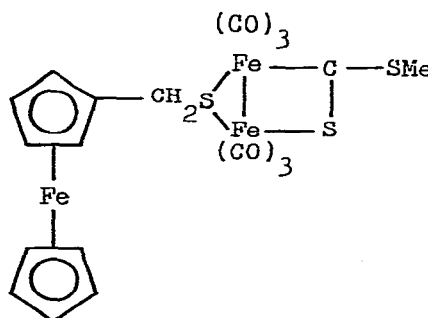
11.46



11.47



11.48

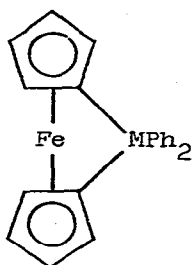


11.49

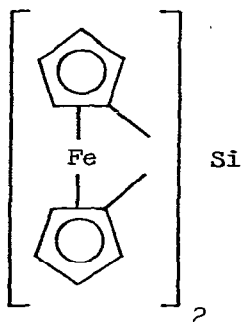
12. BIFERROCENES, FERROCENOPHANES AND ANNELATED FERROCENES

Lithioferrocene and 1,1'-dilithioferrocene were coupled in the presence of tetrakis[iodo(tributylphosphine)copper(I)] to give biferrocene and bis(η -fulvalene)diiron respectively. When a 2:3 mixture of the lithio-ferrocenes was used, terferrocene and quaterferrocene were isolated also [130].

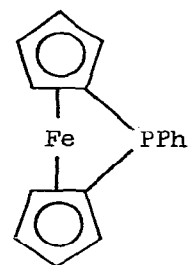
The reaction of 1,1'-dilithioferrocenebis(tetramethylethylenediamine) with dichlorodiphenylsilane, dichlorodiphenylgermane, tetrachlorosilane and dichlorophenylphosphine gave the [1]ferrocenophanes (12.1; M = Si, Ge, 12.2 and 12.3) respectively. Similar reactions with dichlorodiphenyltin and dichlorodimethyltin



12.1



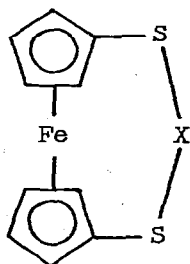
12.2



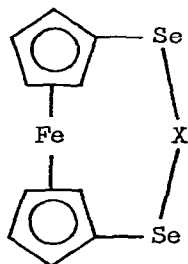
12.3

gave polymeric products. The spectroscopic properties of the [1]ferrocenophanes were consistent with ring tilted structures with the angle between the two cyclopentadienyl rings varying between 19.2° in the silane (12.1; $M = \text{Si}$) to 26.7° in the phosphine (12.3). [131].

The crystal and molecular structures of the diphenylgermane (12.1; $M = \text{Ge}$) and the phenylphosphine (12.3) have been confirmed by X-ray crystallographic methods. The cyclopentadienyl rings in the germane (12.1; $M = \text{Ge}$) are inclined at an angle of 16.6° while the same angle in the phosphine (12.3) was 26.7° . The character and origins of the structural distortions were discussed [132].

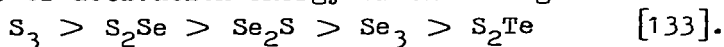


12.4

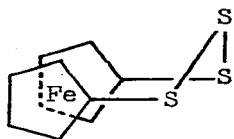


12.5

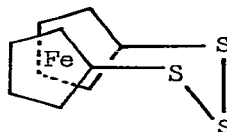
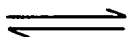
Several [3]-ferrocenophanes with Group VI bridging elements have been prepared and investigated. The sodium salt of 1,1'-ferrocenedithiol was treated with selenium and tellurium(IV) chloride to give the ferrocenophanes (12.4; X = Se, Te) respectively, while 1,1'-dilithioferrocene combined with selenium in boiling hexane to form the complex (12.5; X = Se). The diselenium sulphur complex (12.5; X = S) was obtained from 1,1'-ferrocene-diselenol and sulphur dichloride. The complexes (12.4 and 12.5) were fluxional in solution and the ^1H NMR spectra indicated an order of activation energy of the bridges as :



An accurate analysis of the variable temperature ^1H NMR spectrum of 1,2,3-trithia-[3]-ferrocenophane (12.6) was carried out. The energy barrier of the bridge reversal process (12.6A \rightleftharpoons 12.6B) was calculated as $\Delta G^\ddagger(298\text{K}) = 80.6 (\pm 1.3) \text{ kJ mol}^{-1}$ [134].

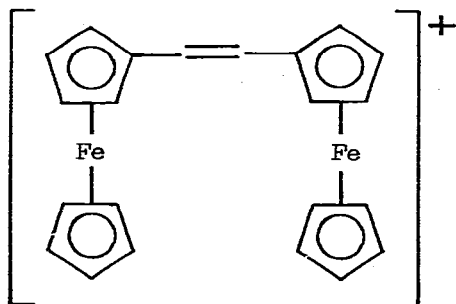


12.6A



12.6B

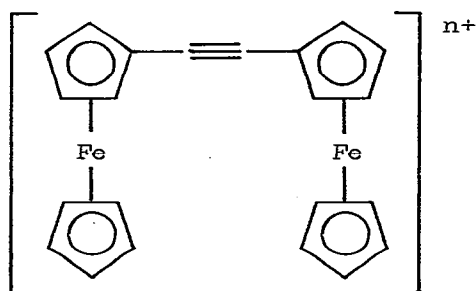
Electron transfer in mixed valence ferrocenes such as azo-ferrocene, 1,2-diferrocenylethene (12.7) and 1,1-diferrocenyl-



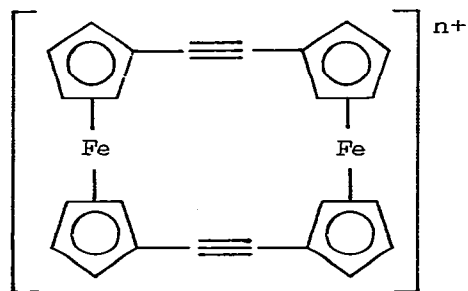
12.7

ethene mono-cations has been investigated. Electron transfer was shown to be independent of interaction between ferrocene moieties in the ground state and in some complexes took place through space rather than through the bridge linking the two metallocene groups [135].

Electron transfer in the mixed-valence and dioxidized diferrocenylacetylene (12.8; $n = 1, 2$) and [2.2]ferrocenophane-1,13-diyne (12.9; $n = 1, 2$) cations has been investigated by Moessbauer, EPR and IR spectroscopy. Iron-57 Moessbauer results demonstrated that the mixed-valence cation (12.8; $n = 1$) was localized while the mixed-valence cation (12.9; $n = 1$) was delocalized. EPR spectroscopy confirmed the latter result. The cation (12.8; $n = 2$) as the triiodide salt showed antiferromagnetic behaviour where $\mu_{\text{eff}}/\text{Fe}$ decreased to $1.39 \mu_{\text{B}}$ at 4.2°K . The correlation between g -tensor anisotropy and the value of quadrupole splitting was used to provide information on mixed-valence effects in fused ferrocenes [136].



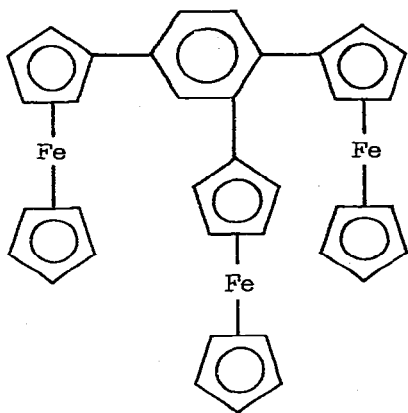
12.8



12.9

Several mixed valence benzene and ketone bridged ferrocenes have been prepared and studied. 1,2,4-Triferrocenylbenzene (12.10) showed mixed valence behaviour in solution on oxidation with iodine while triferrocenyldiketone and diferrocenylketone showed anomalous Moessbauer behaviour as the oxidized solids. The characteristics of the mixed-valence ferrocenes were used as models for electron transfer in biological systems [137].

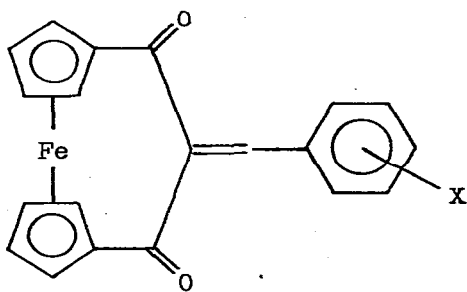
Condensation of [3]ferrocenophane-1,3-dione with benzaldehydes, $\text{XC}_6\text{H}_4\text{CHO}$, in the presence of triethylamine gave the



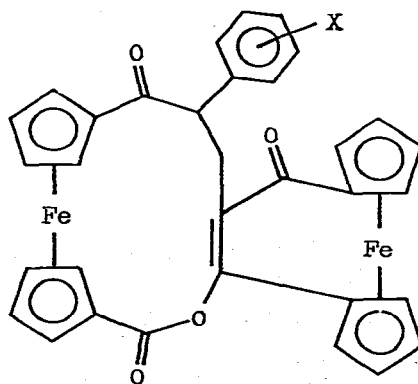
12.10

2-benzylidene [3]ferrocenophane-1,3-diones (12.11; X = H, 3-, 4-Cl, 3-, 4-Br, 4-Me, 4-MeO, 4-Me₂N, 4-NO₂, 4-CN) and in some cases the binuclear ferrocenophanes (12.12; X = 3-Cl, 4-NO₂, 4-CN) as minor products [138].

Oxidation of [4]ferrocenophan-7-one with barium permanganate gave [4]ferrocenophane-6,7-dione and reduction with LiAlH₄-AlCl₃



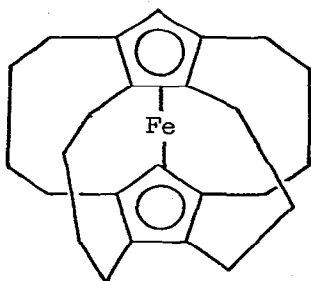
12.11



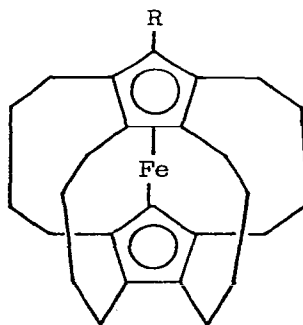
12.12

in ether-benzene mixtures gave [4]ferrocenophane. Reduction with the same reagents in dimethoxyethane gave [4]ferrocenophan-7-ol [139].

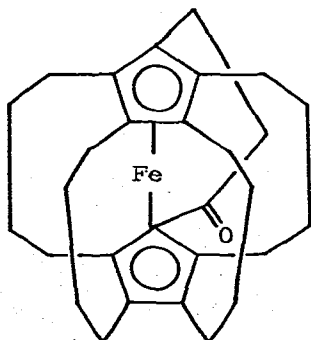
The crystal and molecular structure of [4][4][4][3]ferrocenophane (12.13) has been determined by X-ray crystallography. Considerable distortions of the bond lengths and angles were present in the methylene bridges. Oxo[4][4][4][3]ferrocenophane underwent bridge enlargement and reduction with $\text{LiAlH}_4\text{-AlCl}_3$ to form [4][4][4][4]ferrocenophane (12.14; R = H) the crystal and molecular structure of which was confirmed by X-ray methods. The ferrocenophane (12.14; R = CHO) was condensed with $\text{BrCH}_2\text{CO}_2\text{Et}$



12.13



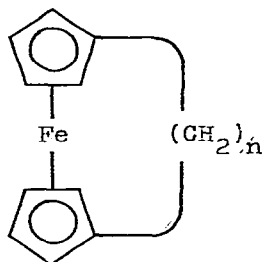
12.14



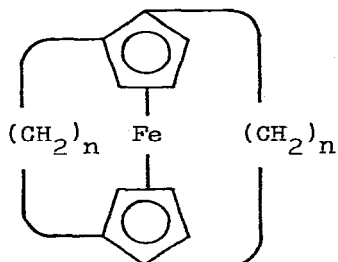
12.15

and subjected to catalytic reduction then hydrolysis to form the carboxylic acid (12.14; $R = \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$). Intramolecular cyclization of this intermediate gave the penta-bridged ferrocene (12.15) [140].

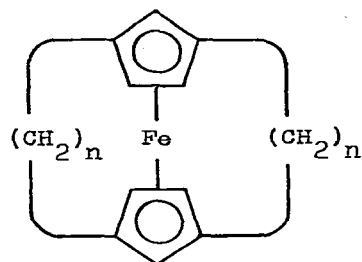
The hydrogenation of singly-bridged (12.16; $n = 3, 4$ and 5), doubly-bridged (12.17; $n = 3, 4$ and 12.18; $n = 3, 4$) and triply-bridged (12.19; $n = 3, 4$) ferrocenes has been investigated. The



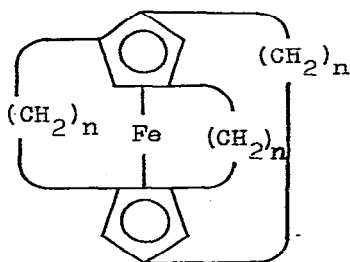
12.16



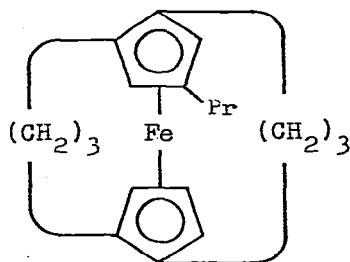
12.17



12.18

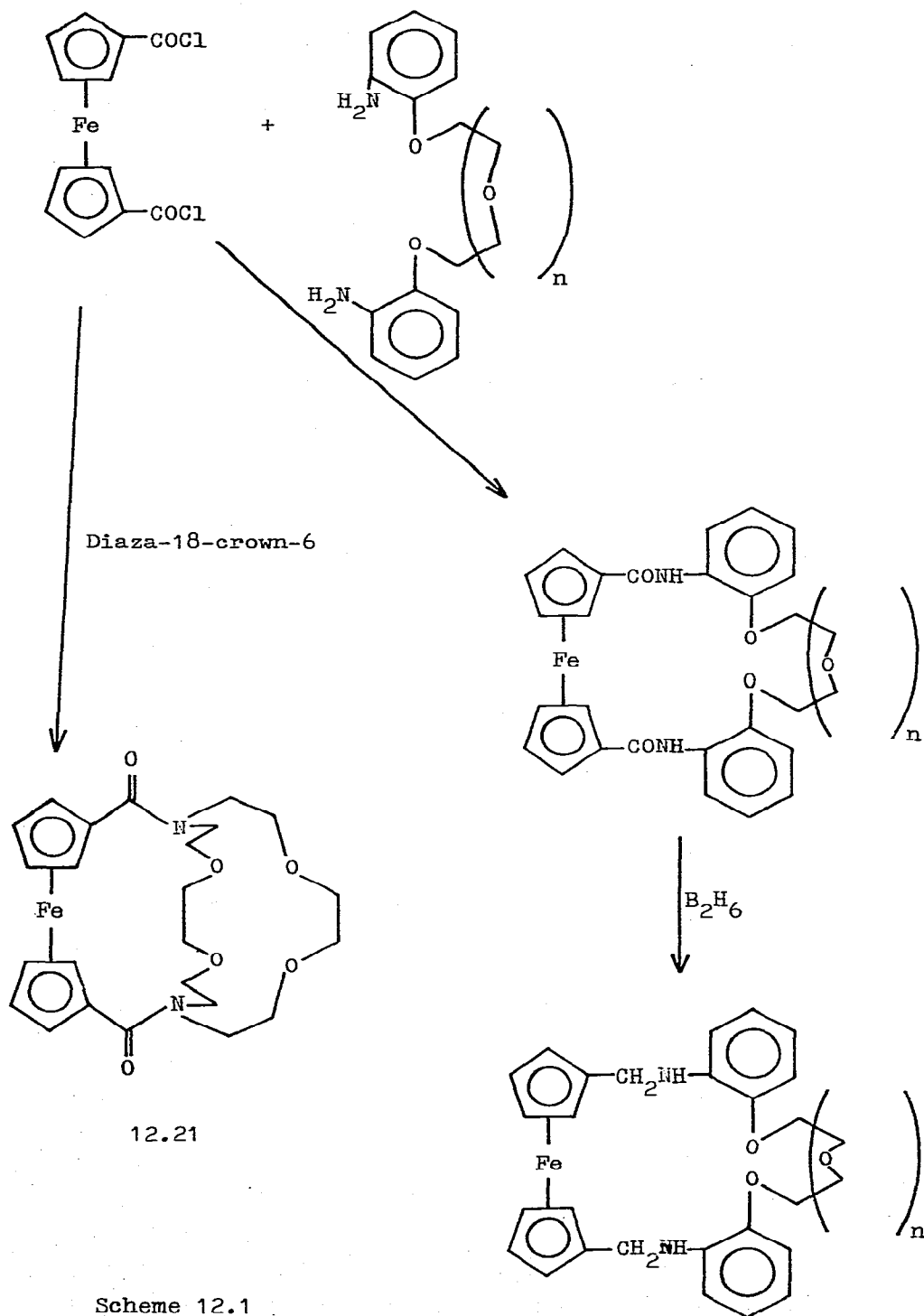


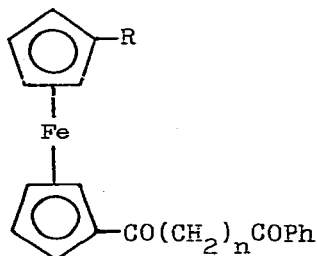
12.19



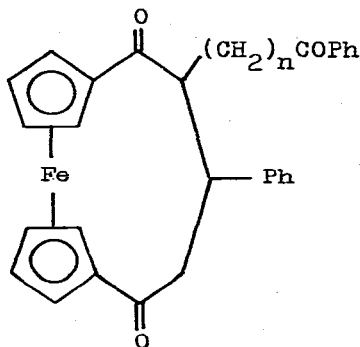
12.20

singly- and doubly-bridged ferrocenes were hydrogenated to the corresponding polycyclic hydrocarbons and the mechanism appeared to involve initial protonation of the iron atom. The triply-bridged compound with trimethylene bridges (12.19; $n = 3$) underwent bridge opening to the propylferrocene (12.20) while the tetramethylene bridged compound (12.19; $n = 4$) was inert under





12.22



12.23

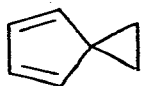
the conditions used. The order of ease of hydrogenation for the singly- and doubly-bridged ferrocenes was:

Ferrocene > (12.16; n = 3) > (12.16; n = 5) > (12.17; n = 4) > (12.18; n = 4) > (12.17; n = 3) > (12.18; n = 3) [141].

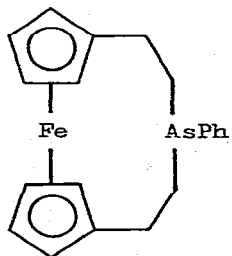
A series of macrocyclic compounds containing the ferrocene unit was prepared (Scheme 12.1). Preliminary studies indicated that the cryptand (12.21) extracted metal picrates from aqueous solution into methylene chloride with a high degree of specificity which followed the order:

$\text{Ca}^{2+} \gg \text{Li}^+ > \text{Mg}^{2+} \approx \text{Na}^+ \gg \text{K}^+$ [142].

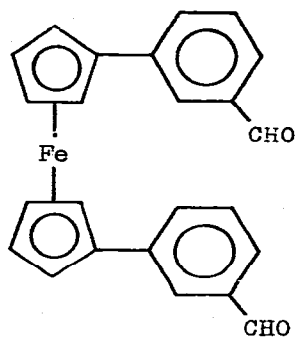
Acylation of the ferrocenylketones (12.22; R = H, n = 5 - 8) with $\text{PhCH}=\text{CHCOCl}$ gave the corresponding diketones (12.22;



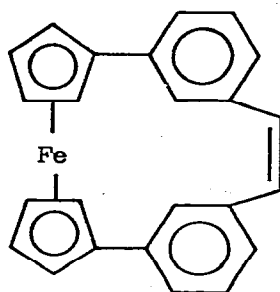
12.24



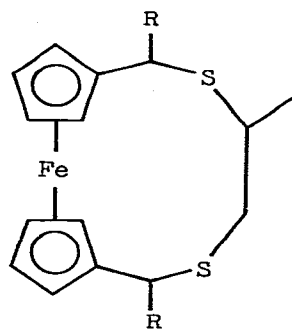
12.25



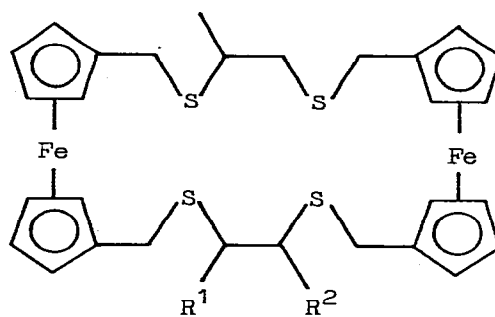
12.26



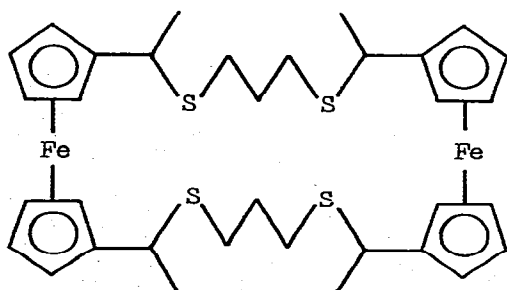
12.27



12.28



12.29



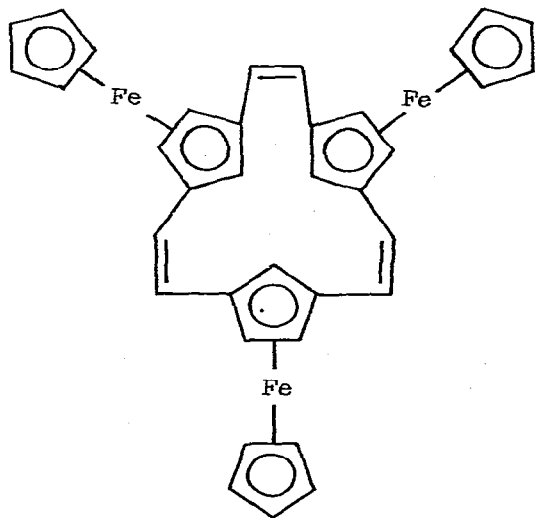
12.30

$R = \text{COCH=CHPh}$, $n = 5 - 8$) which cyclized on treatment with sodium hydroxide to give the ferrocenophanes (12.23; $n = 4 - 7$) [143].

Several reactions of the spirocyclopentadiene (12.24) have been reported including its conversion to ferrocenophane (12.25) by treatment with PhAsLi_2 and then iron(II) chloride [144].

Substitution of ferrocene with two molecules of the diazonium cation $[\text{m-HO}_2\text{C.C}_6\text{H}_4.\text{N}_2]^+$ followed by esterification, reduction with lithium aluminium hydride and oxidation with manganese dioxide afforded the dialdehyde (12.26) which was subjected to reductive coupling with $\text{TiCl}_4\text{-Zn}$ to form the metacycloferrocenophane (12.27) [145].

Several thiaferrocenophanes have been prepared by treatment of hydroxymethylferrocenes with 1,2- and 1,3-dimercaptopropanes. Thus 1,1'-bis(hydroxymethyl)ferrocene combined with $\text{HSCHMeCH}_2\text{SH}$ to form the dithiaferrocenophane (12.28; $R = \text{H}$) and a mixture of two isomeric binuclear ferrocenophanes (12.29; $R^1 = \text{H}$, $R^2 = \text{Me}$; $R^1 = \text{Me}$, $R^2 = \text{H}$). 1,1'-Bis(hydroxyethyl)ferrocene combined with the same reagent to give a mixture of three stereoisomers of the dithiaferrocenophane (12.28; $R = \text{Me}$) and with $\text{HS(CH}_2)_3\text{SH}$ to



12.31

give five stereoisomers of the thiaferrocenophane (12.30) [146].

Oxidation of 1,3-bis(hydroxymethyl)ferrocene with benzene-selenic anhydride afforded 1,3-diformylferrocene in high yield. Reductive coupling of the dialdehyde using TiCl_4 - LiAlH_4 in THF gave di-, tri- and tetra-nuclear ferrocenophanes. It was suggested that the cyclic trinuclear species (12.31) existed as two isomers [147].

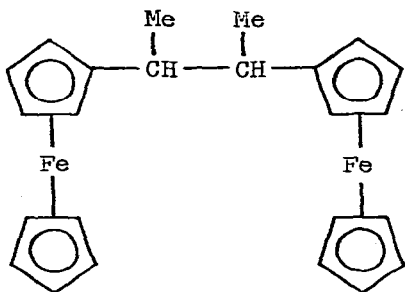
13. FERROCENE-CONTAINING POLYMERS

Ultrathin films of plasma polymerized vinylferrocene on platinum electrodes underwent rapid exchange of electrons with the electrode at room temperature when immersed in butyronitrile containing tetrabutylammonium perchlorate. However, at temperatures of -50°C and -85°C the transport of electrochemical charge through the film was diffusion controlled by Fick's law under infinite and finite boundary conditions which were time and temperature dependent. The activation energy and entropy for the process were determined as $3.7 \text{ kcal mol}^{-1}$ and $-32 \text{ cal mol}^{-1} \text{ deg}^{-1}$. The mechanism of charge diffusion was controlled by the cooperative movements of polymer chains necessary for site-site collisions and counter ion transport [148].

Plasma polymerization of vinylferrocene has been used to produce a stable coating of an electroactive polymer on pyrolytic graphite electrode surfaces. The electrochemical properties of the polymer film were investigated by cyclic voltammetry and the film was found to be electrocatalytically active in the oxidation of ascorbic acid in aqueous acid solution [149].

Vinylferrocene was polymerized in a radiofrequency argon plasma to give thin adherent films of polymer on glass, carbon and platinum electrodes. The electrochemistry of the modified electrodes was investigated. The thin films of polymer exhibited a nonlimiting transport of electrochemical charge while with thicker films the response was diffusion-controlled [150].

Acylation, reduction and dehydration of 2,3-diferrocenylbutane (13.1) afforded 2-ferrocenyl-3-(vinylferrocenyl)butane which was polymerized in the presence of borontrifluoride etherate and copolymerized with methyl methacrylate to give a copolymer of molecular weight 7700. The polymerization of the diacetate of 1,1'-bis(α -hydroxyethyl)ferrocene and 1-(1'-acryloyl-1-ethylferrocenyl)-2-(1-ethylferrocenyl)ethane has also been



13.1

investigated [151].

Copolymers containing the s-triazine ring were formed in low yield by an interfacial technique from cyanuric chloride and ferrocenedicarboxylic acid sodium salt. The copolymers were semiconductors, showed moderate thermal stability, were active against selected bacteria and were insoluble. The parameters affecting the efficiency of copolymerization were examined [152].

Heat treatment of acetylferrocene-furfural resins gave ultra-fine iron particles dispersed in a glass-like carbon matrix. The properties of the iron particles were investigated by magnetic susceptibility, saturation magnetization, ESR and the Moessbauer effect. Body-centred cubic (bcc) iron, expanded bcc iron, hexagonal close-packed iron and cluster iron were all present. The presence of Fe(I) was also confirmed [153].

14. APPLICATIONS OF FERROCENES

(i) Ferrocene catalysts and photosensitizers

The 1:3 ferrocene-carbon tetrabromide charge transfer complex in a polymeric matrix has been used as the light sensitive layer in a perspective photoimaging material. Imaging was achieved by irradiation and thermal fixing at 70-75 °C. The image did not have a grain structure and showed a resolution of 400 lines/mm with a line width of 30 m [154].

A photosensitive composition for photographic use has been formulated using ferrocene and ferrocene derivatives, halogenated hydrocarbons, toner additives and solvent. Resolution during

manufacture was increased by adding a protective colloid such as poly(vinyl acetate) [155].

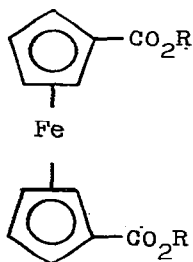
Hydroxyethylferrocene has been used as a sensitizer in photo-degradable polyethylene films. The physicomechanical strength of polymer films was unaffected by the metallocene which was an efficient sensitizer [156].

The effect of biferrocene on the photochemical decomposition of polyethylene was investigated. The addition of 0.15% biferrocene caused photosensitization and this was attributed to the effect of the oxidation products of the cyclopentadiene. When 0.5% biferrocene was present in the polyethylene stabilization occurred as a result of the screening action of iron(III) oxide formed by the decomposition of the biferrocene [157].

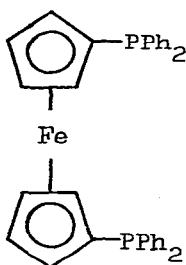
Ferrocene or poly(vinylferrocene) and carbon tetrachloride have been used as initiators for vinyl polymerization. The effect of monomer polarity and solvent polarity on the initiation and rate of polymerization was investigated. An increase in polarity of either solvent or monomer enhanced both processes [158].

The polymerization of *p*-methyl- and *p*-ethyl- α -chloro- β -formylstyrene has been initiated by poly(α -chloro- β -formyl-*p*-ferrocenylstyrene) and poly[*p*-ferrocenylphenylacetylene] which behave as redox initiators. Higher yields were obtained by redox polymerization than by thermal polymerization [159].

The rate of polyesterification during the final stages of unsaturated polyester formation was increased by the addition of 1,1'-ferrocenedicarboxylic acid (14.1; R = H) or the dimethyl,



14.1



14.2

(14.1; R = Me) diethyl (14.1; R = Et) or diallyl (14.1; R = CH₂CH=CH₂) esters. Thus polymerization of fumaric acid with diethylene glycol at 200 °C in an inert atmosphere in the presence of dimethyl-1,1'-ferrocenedicarboxylate gave the polyester in 38% yield. Transesterification of the ferrocene esters occurred during the reaction and ferrocene residues were incorporated into the polymer chain [160].

The rhodium complex (PPh₃)₃Rh(CO)H, in the presence of a bidentate ligand such as 1,1'-bis(diphenylphosphino)ferrocene (14.2) and a monodentate ligand such as dimethylphenylphosphine, was an effective catalyst for the hydroformylation of 1-hexene [161].

(ii) Ferrocene stabilizers and improvers

16-Ferrocenylhexadecanoic acid was prepared and its properties as a surfactant were investigated. The surfactant was incorporated into monolayer films and assemblies, micelles and vesicles. The reactivity of the ferrocenyl-surfactant towards oxidizing agents and complexing agents was investigated. It was concluded that the ferrocene moiety was not rigidly orientated in the hydrophobic core of the vesicles or micelles and that it was available for oxidation by polar reagents [162].

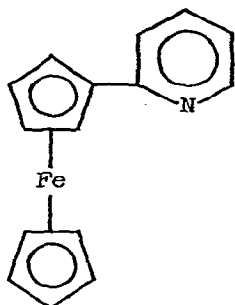
Ferrocenes, such as 1-(hydroxybenzoylferrocene), 1-(methoxybenzoyl)ferrocene and dimethylferrocene-1,1'-dicarboxylate have been added to polypropylene as light stabilizers [163].

The modification of poly(ethylene terephthalate) by the addition of ferrocene gave fibres with improved fatigue properties and low shrinkage. Physico-chemical studies indicated an increase in structural ordering and crystallinity of the ferrocene-modified polymer during fibre formation [164].

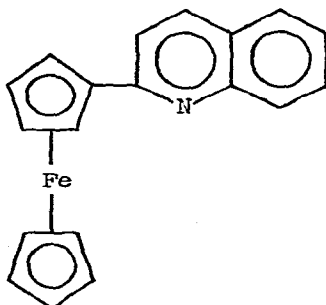
The addition of 0.085-0.40% acetylferrocenehydrazone to a 19-21% cellulose triacetate spinning solution gave acetate fibres with good light resistance, good heat and wear resistance and resistance to double flexure [165].

The corrosion resistance of a polyester-aluminium laminate was enhanced by the incorporation of 0.1-0.5 wt. % 1,1'-diacetylferrocene into the poly(ethylene terephthalate) layer [166].

The corrosion of steel in the presence of α -pyridyl- (14.3) and α -quinolyl-ferrocene (14.4) has been studied. The ferrocenes were effective corrosion inhibitors in the presence of non-oxidizing acids but when nitric acid was present they were not



14.3

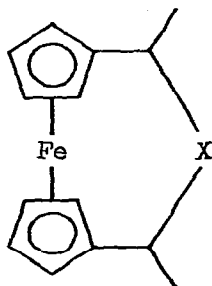


14.4

effective [167].

6,8-Dimethyl-7-thia[3]ferrocenophane (14.5; $x = S$)
 6,8-dimethyl-7-oxa[3]-ferrocenophane (14.5; $X = O$) α -hydroxyethyl-ferrocene and diferrocenyldisulphide were tested as antiwear additives in oil. The last two derivatives were particularly effective at high loads [168].

Ferrocene at a level of 5% inhibits tree growth in solid extruded cable insulation and increases the needle-plane breakdown voltage by 100%. The effectiveness of ferrocene was ascribed to the low ionization potential rather than to its electron scavenging effect or to an increase in dielectric strength. The compound was however, oxidized in air and by dicumylperoxide [169].



14.5

p- $\{N-[4-(4\text{-Octyloxybenzoyloxy})\text{benzylidene}] \text{amino}\}$ phenyl ferrocenecarboxylate (10% by weight) was added to a nematic liquid crystal composition. The composition exhibited good stability after prolonged ultra-violet irradiation and after heating at 80 °C [170].

Treatment of a molybdenite ore with ferrocene (16 kg per ton of ore) at 400 °C and subsequent magnetic separation allowed the ore to be separated more efficiently from weakly-magnetic gangue [171].

Polymeric compositions imitating mother-of-pearl were prepared from polystyrene and acrylic resin. It was found that the addition of ferrocene or acetylferrocene improved the mother-of-pearl effect and the impact toughness of the polymer [172].

Ferrocene derivatives were among the additives used in the preparation of concrete with good insulating properties [173].

(iii) Ferrocene in analysis

Ferrocenecarboxaldehyde has been used as a model aldehyde analyte to demonstrate a technique for the selective determination of aldehydes and ketones at a chemically modified platinum electrode. The ferrocenecarboxaldehyde underwent selective preconcentration by chemical reaction with allylamine adsorbed on the electrode and was then determined by differential pulse voltammetry. The detection limit was 10^{-7} M ferrocenecarboxaldehyde [174].

The specificity of an ion selective electrode, used for the tetraphenylborate anion, was increased and the range of measurement extended by employing as the sensing element, a mixture of diethylferrocene and diethylferrocenium tetraphenylborate in nitrobenzene applied to platinum [175].

(iv) Combustion control

Vinylferrocene was heated with thioacetic acid in the presence of 2,2'-azobis(2-methylpropionitrile) to give 1-ferrocenyl-2-thioacetoxylethane which was converted to 2-ferrocenylethanethiol by treatment with sodium ethoxide. The 2-ferrocenylethanethiol was used as a burning rate modifier in solid propellants [176].

The effect of ferrocene as an anti-smoke additive in poly(vinyl chloride) was studied by self-ignition. Self-ignition was monitored visually, thermally and by gas chromatography of the gases around the sample. Ferrocene modified the self-ignition of the polymer by inducing glowing phenomena and smoke formation

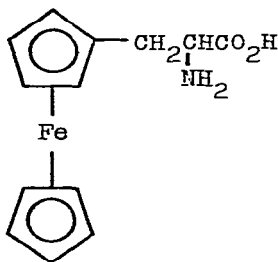
was reduced [177].

Ferrocene has been used as a smoke suppressant in polyurethane foams. The foam was manufactured by treating a polyol with a polyisocyanate in the presence of ferrocene in FeCl_3 . Smoke production by the burning foam was substantially reduced [178].

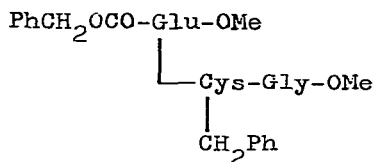
A mixture of ferrocene, benzoic acid, magnesium naphthenate, an anionic surfactant and a glyceride in paraffin oil gives stable emulsions of fuel oil and water [179].

(v) Biochemical and biological applications

A β -ferrocenylalanyl group (Fer), (14.6) has been incorporated into the peptide $[\text{Fer}^4, \text{Leu}^5]$ enkephalin, Tyr-Gly-Gly-Fer-Leu-OH, by a fourteen step coupling sequence [180].



14.6

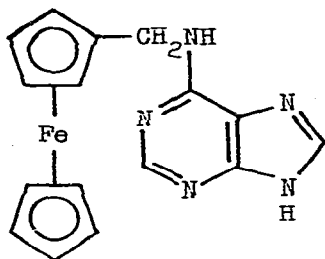


14.7

Resolution of N-formyl-3-ferrocenyl-DL-alanine using the brucine salt gave the D- and L-forms which were deformylated to yield 3-ferrocenyl-L-alanine and the corresponding D- enantiomer. The L-form was converted through a sequence of steps to cyclo-(3-ferrocenyl-L-alanyl-L-propyl) [181].

R-(-)-1-ferrocenyl-2-methylpropylamine underwent a stereoselective four-component condensation with $\text{PhCH}_2\text{SCH}_2\text{CHO}$, $\text{MeOCOCH}_2\text{NC}$, $\text{PhCH}_2\text{OCO-Glu-OMe}$ followed by acidolysis with $\text{CF}_3\text{CO}_2\text{H}$ and $\text{HSCH}_2\text{CO}_2\text{H}$ to yield the isomer-free glutathione derivative (14.7) which subsequently gave glutathione on deprotection with sodium in liquid ammonia [182].

Ferrocenylmethylamine and 6-chloropurine combined together in methoxyethanol to form N^6 -ferrocenyladenine (14.8) and $\text{N}^6, 9$ -bis(ferrocenylmethyl)adenine. The methiodide of (N,N-dimethylaminomethyl)ferrocene was attacked by adenine in boiling

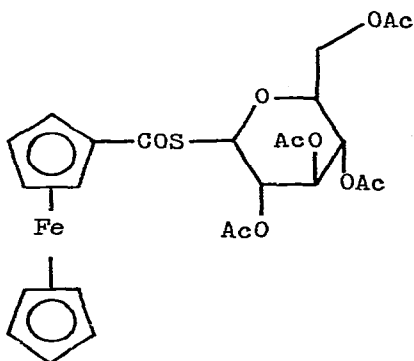


14.8

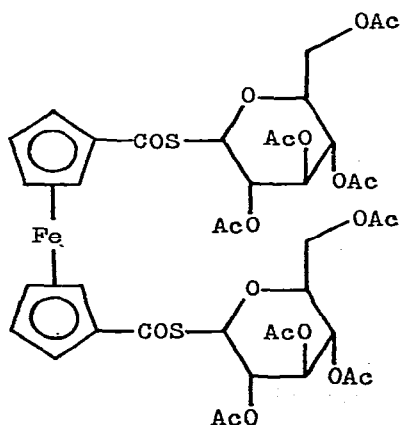
water to give 7- and 9-ferrocenylmethyladenine [183].

The 270 MHz ^1H NMR spectra of the ferrocenyl-sugar derivatives (14.9 and 14.10) were recorded. Proton spin lattice relaxation rates were used to assign the proton resonances in the substituted η -cyclopentadienyl rings. It was concluded that the unsubstituted ring was spinning more rapidly than the substituted η -cyclopentadienyl ring [184].

Ferrocenylmethylaminodextran has been formed by conjugating ferrocenylmethylamine with a 40,000 Dalton dextran and the heavy-metal labelled dextran was used for indirect histochemical demonstration of lectin receptors [185].



14.9



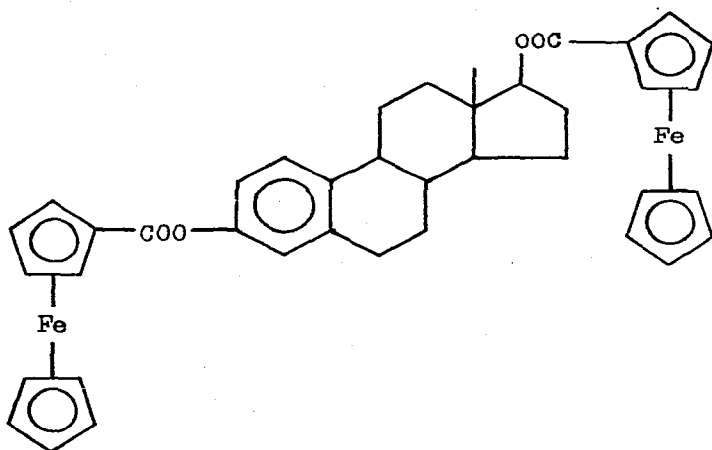
14.10

Administration of ferrocene vapour labelled with ^{59}Fe by inhalation caused 10% to be deposited in the lungs and 25% in the upper respiratory tract. ^{59}Fe was found to be retained tenaciously in the nasal or pulmonary areas. These results suggest that chronic effects may result from the inhalation of ferrocene and that the current threshold limit of 10 mg m^{-3} may be too high [186].

An investigation was carried out on the effect of polycyclic hydrocarbons and ferrocene containing acetylene glycols on the change in the physicochemical properties of cultured chick embryo cells. 1-Ferrocenyl-1-phenyl-4-methyl-1,4-dihydropent-2-yne inhibited growth and it was thought that this was associated with the anticarcinogenic activity of this molecule [187].

The effect on liver regeneration of adding 0.15% by weight of 1,1'-diacetylferrocene, acetylferrocene or ferrocene to the diet of partially hepatectomized rats was investigated. There was an increase in liver regeneration in the presence of 1,1'-diacetylferrocene [188].

Treatment of estradiol with ferrocenylcarbonyl chloride in the presence of 4-dimethylaminopyridine gave the ester (14.11). Testosterone- and cholesteryl-ferrocenylcarboxylates were prepared similarly [189].



14.11

Several methylcarbamates have been prepared from ferrocenyl-ketoximes and aldoximes and evaluated as acetylcholinesterase inhibitors. The relationship between activity and the nature of the substituent on the methylene carbon atom was discussed [190].

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